New Insights From The Jülich Ozone-Sonde Intercomparison Experiments (JOSIE): Calibration Functions Traceable To One Ozone Reference Instrument

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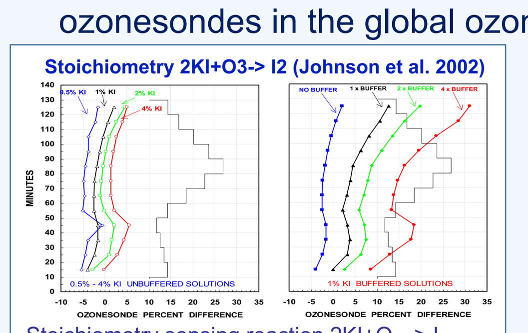
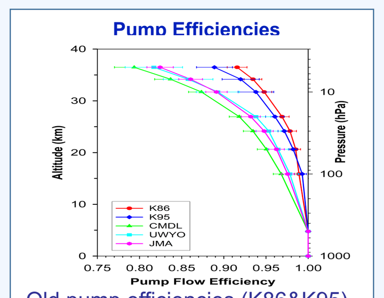
Time Response Correction (TRC): Introduction

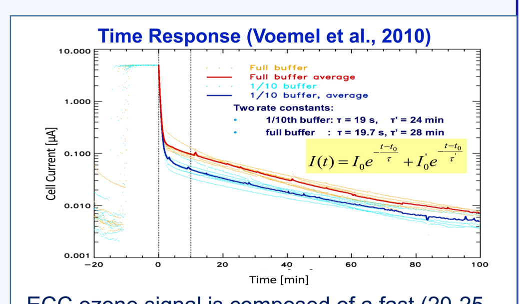
1. ASOPOS (Assessment of Standard Operating Procedures for Ozone-Sondes) 2.0 (***GAW Report No. 268, 2021***) formulated three outstanding problems in the performance of ECC-ozonesondes in the global ozonesonde network:



Stoichiometry sensing reaction 2KI+O_3 -> I_2
- Dependent of KI and pH-Buffer strength
- Not well understood and quantified.



Old pump efficiencies (K86&K95) are too low compared to newer ones (CMDL, UWYO, JMA).

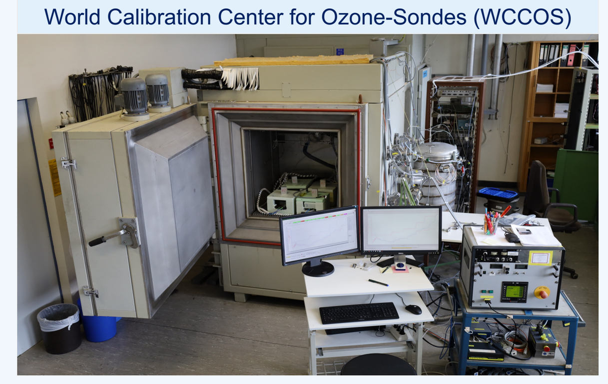


ECC ozone signal is composed of a fast (20-25 sec.) and slow (20-25 min.)time response, which is still not corrected for.

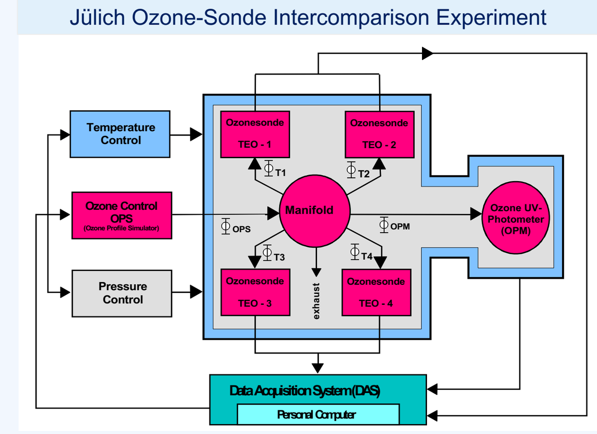
2. Within ASOPOS 2.0 a new concept of using better pump efficiencies (***JMA: Nakano et al.***, AMT, 2023) and resolving the slow and fast signal components was developed (***Tarasick et al.***, ESS, 2021 & ***Vömel et al.***, AMT, 2020).
3. In this study this concept has been further investigated and developed by using the JOSIE 2009/2010 and JOSIE 2017-SHADOZ data and comparing to the reference ozone photometer (OPM at WCCOS) (***Smit et al.***, in press AMT, 2023) to achieve:
   - **Time Responses Correction (TRC)** through convolution and deconvolution of the measured ECC ozone current and proper treatment of background current.
   - **Calibration functions** to quantify the unknown stoichiometry.
   - **Ozonesonde data traceable to one common standard**: the OPM of JOSIE.

TRC-Development: JOSIE 2009/2009 Data

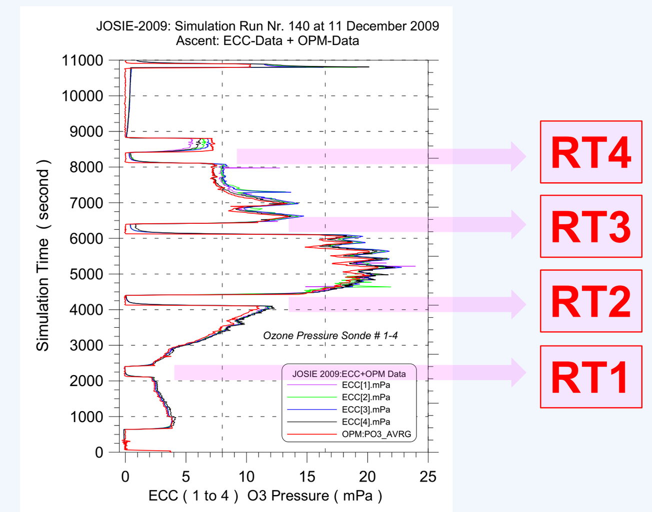
Environmental Simualtion Chamber at Jülich
World Calibration Center for Ozone-Sondes (WCCOS)



JOSIE
Jülich Ozone-Sonde Intercomparison Experiment



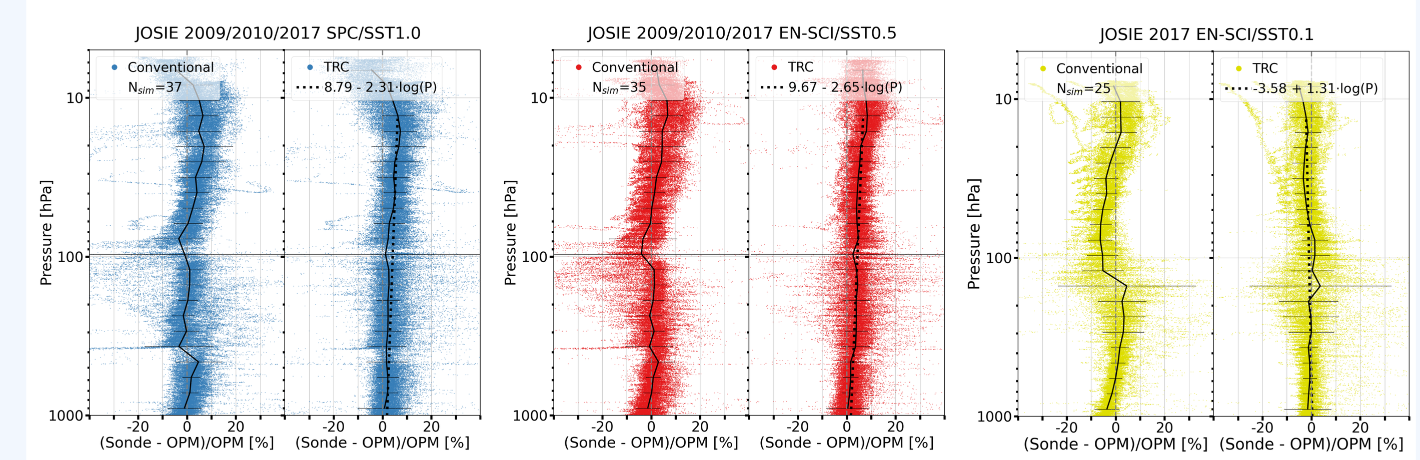
JOSIE 2009/2010 Design:
- Two manufacturers (18 x SPC & 18 x EN-SCI)
- Two standard Sensing Solution Types (SST):
  - i. SST1.0 = 1.0%KI/1.0 Buffer
  - ii. SST0.5 = 0.5%KI/0.5 Buffer
- Simulation of mid-latitude vertical profiles
- JOSIE 2009: New sondes (N=36)
- JOSIE 2010: Refurbished sondes (N=36)
- Downward step time response tests (4 x 5 min.)



Conversion Efficiency TRC: Calibration Functions $\eta_C(P)$

JOSIE 2009/2010 & 2017
- Linearly increasing bias with decreasing Log_{10}(pressure) very similar for mid-latitude and tropical ozone profiles: Lumped JOSIE 2009/2010 and 2017 together.

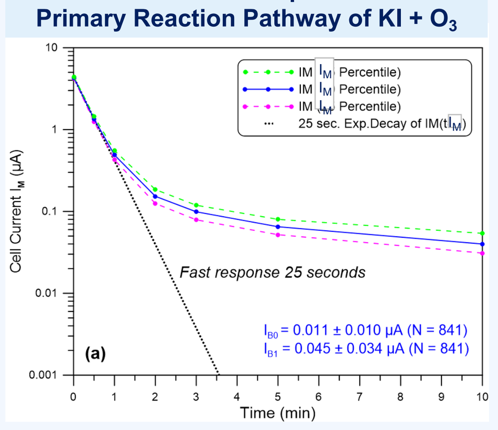
JOSIE 2017 SST 1% KI & 0.1 Buffer
- S_{slow} determined from laboratory time response tests at RMI
- Slightly linearly decreasing bias with decreasing Log_{10}(pressure)



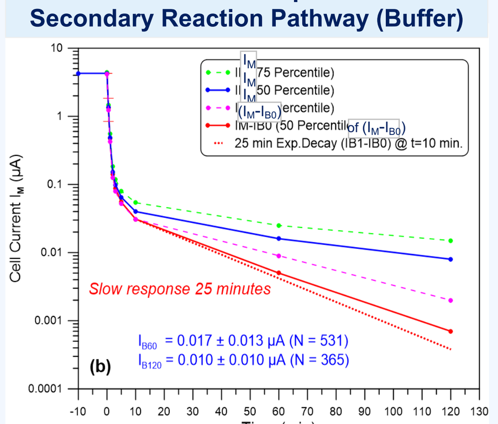
- Linear regression of rel. differences of sonde to OPM of TRC method is the correction term of the overal conversion efficiency η_C when deviating from one *(dotted straight line)*.
- Calibration function is overal $\eta_C(P)$ calibrated to OPM: $\eta_C(P) = 1 + a + b \cdot Log_{10}(P)$
- The **calibration coefficients *a* and *b*** are determined for each pair of sonde (SPC or EN-SCI) and sensing solution type (Table 4 in ***Smit et al.*** 2023, AMTD in press) **TRCC = TRC + Calibration**

Background Current: Physical and Chemical Origin

Fast Time Response: Primary Reaction Pathway of KI + O_3



Slow Time Response: Secondary Reaction Pathway (Buffer)

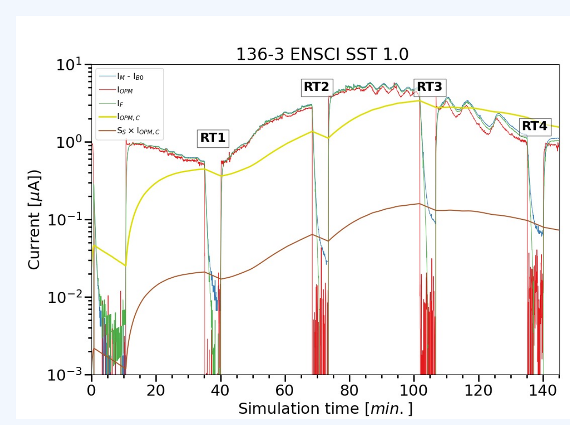


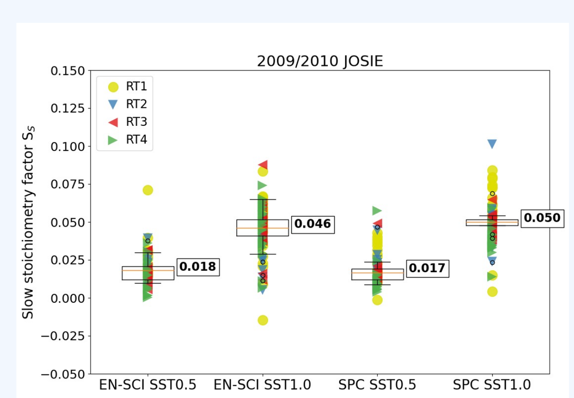
Response tests during pre-flight preparation:

a. Before O_3 exposure, flushing ECC-cell for 10 min. with zero air: I_{B0}
b. O_3 exposure of cell: 10 min. with 5 µA O_3.
c. Flushing cell for 10 min. zero air: I_{B1}, *stop flushing*
d. No flushing until t = 60 min. & flush 5 min. zero air: I_{B60} *& stop flushing*
e. No flushing until t =120 min & flush 5 min. zero air: I_{B120}

Results:
- Time responses: τ_{Fast}= 25 sec. & τ_{Slow}= 25 min.
- Slow response is independent of flushing.
- At t = 60 & 120 min remaining current approaches I_{B0}
- I_{B0} is independent of past O_3 exposure, i.e. ECC-cell property: I_{B0} **is constant**.
- $(I_{B1} - I_{B0})$ is the past ozone exposure dependent part of the background current with a chemical origin.
- $(I_{B1} - I_{B0})$ is the result of a slow secondary chemical reaction pathway, which is directly related to the phosphate buffer strength.

Slow Current I_{Slow}: Slow Stoichiometry Factor S_{Slow}



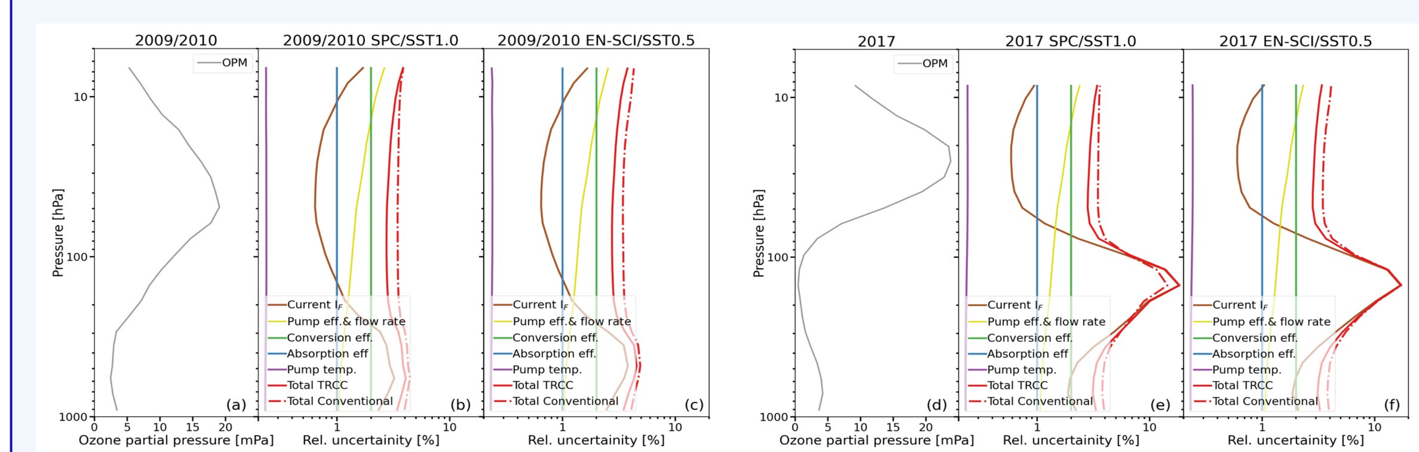


Determination S_{slow} Factor:

a. Using JOSIE 2009/2010 $I_{ECC}(t)$-IB0 and $I_{OPM}(t)$ (OPM = Ozone PhotoMeter as JOSIE reference at WCCOS)
b. $I_{OPM}(t)$ is derived from $P_{O3}(t)$ of OPM (**Eq.2**) with $T_P(t)$ and new pump efficiency of JMA (***Nakano et al., 2023***), while η_A= ***1.0 and*** η_C= ***1.0.***
c. Convolution of $I_{OPM}(t)$
d. At end of each response test (RT1, RT2, RT3, and R4):
   - i. Remaining $(I_{ECC}(t)$-$I_{B0})$ signal is the slow part of $I_M(t)$
   - ii. Ratio of slow signal and corresponding **convolved** $I_{OPM}(t)$ signal is the ***slow stoichiometry factor*** S_{Slow}

Results S_{slow} Factor:
- No difference between SPC and EN-SCI using same SST
- Stoichiometry factor S_{Slow} of slow reaction pathway between 0.017 and 0.050 (uncertainty ≈ 20-30%)
- Larger S_{Slow} for larger KI and buffer strength
- Different behaviour between SPC and EN-SCI using same SST has its origin in the primary, fast part of the conversion of O_3 into I_2, and **not** in the slow part

ECC-Sonde Uncertainty Budget TRC + Calibration



- Background current (I_{B0} + $I_{Slow}(t)$) in the troposphere and conversion efficiency in the stratosphere are the dominant uncertainty sources

ECC-Current: Resolving Fast & Slow Component

The overall measured cell current $I_M(t)$ is:

$$I_M(t) = I_{Fast}(t) + I_{Slow}(t) + I_{B0} \quad or \quad I_{Fast}(t) = I_M(t) - I_{Slow}(t) - I_{B0} \quad (Eq.\ 1)$$

a. Fast current component (I_{Fast} with τ_{Fast} ≈ 20-25 sec.) with stoichiometry S_{Fast} of the fast reaction pathway converting O_3 into I_2, which is close to 1.0.
b. Slow current component (I_{Slow} with τ_{Slow} ≈ 20-25 min.) with small stoichiometry S_{Slow} of the secondary pathway in presence of phosphate buffer producing additional Iodine (I_2), which is of the order of 0.0 to 0.10.
c. I_{Slow} acts as that part of the background current that is past ozone-exposure dependent.
d. Because S_{Slow} << S_{Fast} and τ_{Slow} >> τ_{Fast} , I_{Slow} can be determined by **convolution of** $I_M(t)$-I_{B0} with τ_S= 20-25 minutes, and **treated as a time varying background current**.
a. $I_{Fast}(t)$ **can be de-convolved to resolve any delay effects** in the profile caused by the 20-25 sec. time response, such that finally the ozone partial pressure measured by the ECC-sonde is:

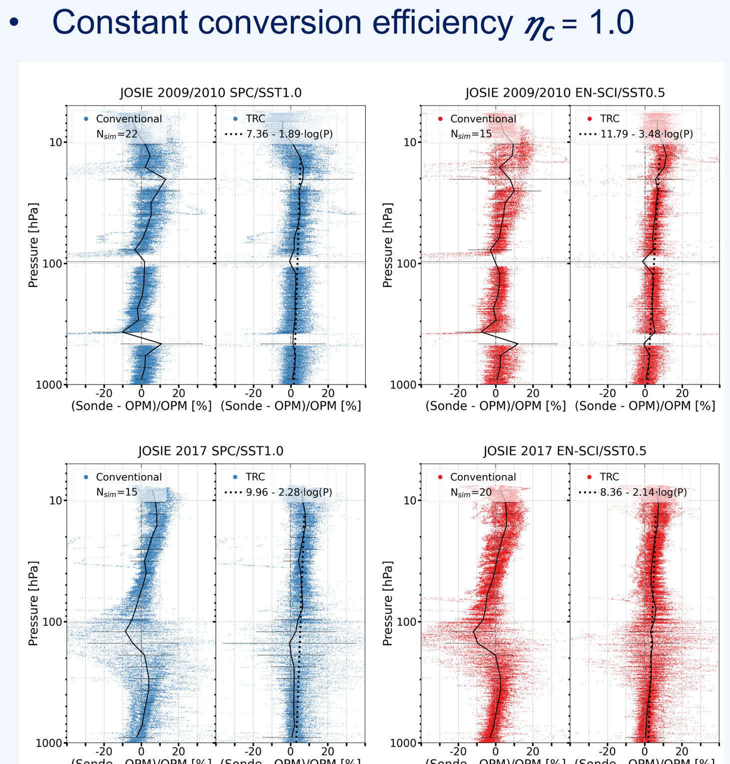
$$P_{O_3} = \frac{R}{2 \cdot F} * \frac{T_P}{(\eta_T * \Phi_P)} * I_{Fast}, whereby\ \frac{R}{2 \cdot F} = 0.043085 \ and \ \eta_T = \eta_A * \eta_P * \eta_C \quad (Eq.\ 2)$$

f. Total efficiency η_T is: η_A = Absorption efficiency , η_P = Pump efficiency, and η_C = Conversion efficiency (initially set to 1.00)
f. The conversion efficiency is finally determined from comparison with the JOSIE-reference ozone photometer (OPM): **Introduction of calibration functions**

JOSIE: Conventional Versus TRC Method

Conventional (GAW No.268)
- Improper Komhyr pumpefficiency (K86/K95)
- Constant background current I_{B1} correction
- Constant conversion efficiency η_C = 1.0

Time Responses Correction (TRC)
- Correct pumpefficiency (Nakano, 2023)
- Constant background current I_{B0} correction
- Resolving $I_{slow}(t)$ and $I_{Fast}(t)$



JOSIE 2009/2010 (TRC): Mid-latitude
- Large reduction of relative differences around response time (RT1..4) intervals
- Independent of past ozone exposure
- Slightly linearly increasing bias with decreasing Log_{10}(pressure) *(dotted line)*

JOSIE 2017 (TRC): Tropics
- Large reduction of relative differences in tropopause region (100-150 hPa)
- Independent of past ozone exposure
- Slightly linearly increasing bias with decreasing Log_{10}(pressure) *(dotted line)*

Conclusions and Recommendations

1. The new concept of using realistic pump efficiencies (here JMA-Nakano et al., AMT, 2023) together with resolving the slow and fast components of the ECC signal through use of convolution and de-convolution is very promising, and is an in-depth study of recently work reported by Voemel et al. (AMT, 2020) and Tarasick et al. (ESS, 2021).
2. The new methodology solves three inconsistencies in the conventional method of data processing: (i) improper pump efficiencies (K86 and K95); (ii) improper background correction and (iii) time delaying effects through two different time responses
3. The stoichiometry factors of the slow reaction pathway and the conversion efficiencies of of pairs of different types of sonde and sensing solutions have been derived from JOSIE 2009/2010 and are thus traceable to the common OPM as reference instrument.
4. The conversion efficiencies are represented by linear Log_{10}(P) calibration functions
5. Through the introduction of simple calibration functions data of the global ozonesonde network can be made traceable to one reference standard, i.e. the OPM of WCCOS (JOSIE).
6. The new concept is not affecting the quality of the performance of the ECC-sonde, but it is a new methodology of post-flight data processing.
7. The algorithms to be applied (incl. the low-pass filtering) are straightforward and relatively easy to implement in existing data processing software.
8. Unsolved is the underlying chemistry of the redox reaction of O3 + KI in detail, this includes the different performances between EN-SCI and SPC sondes when operated with same sensing solutions.
9. Use of high quality zero air filters during sonde preparation (SOP's) is required a-priori.
10. Regular pump efficiency calibrations at low pressures are essential for proper QA/QC
11. Follow strictly the Standard Operating Procedures formulated by ASOPOS (GAW Report No. 268, 2021: *https://library.wmo.int/idurl/4/57720*).

The present study in detail and all references are in *Smit et al.*, AMTD, 2023 (in press): *https://doi.org/10.5194/egusphere-2023-1466*