[E 253] - New Insights From The Jülich Ozone-Sonde Intercomparison Experiments: Calibration Functions Traceable To One Ozone Reference Instrument

QUADRENNIAL OZONE SYMPOSIUM

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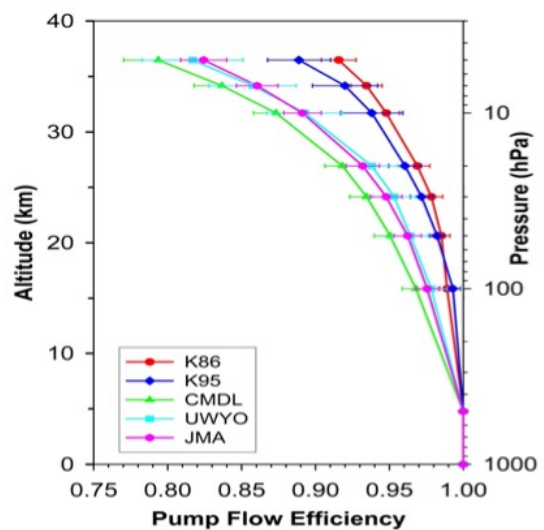
Achievements

1. Much better understanding of the performance of ozonesondes in general, and the underlying processes, including their limitations (i.e. inefficiencies) and the corrections to be applied.

2. JOSIE (incl. BESOS) and related scientific activities such as ASOPOS 1.0 and O3S-DQA have:
   a) Removed inhomogeneities by instrumental or procedural artifacts
   b) Reduced the uncertainties in the global network by more than a factor 2 to an overall uncertainty of about 5-10%.

3. Nowadays through recommendations made by ASOPOS 2.0 (GAW Report No. 268) the QA/QC for ozonesondes has the potential to improve the overal uncertainty to 5 % and to guarantee the long term stability of ozonesonde records.

Remaining Problems

1. Stoichiometry of the overall sensing reaction of KI+O3-> I2, which is dependent of the solution strengths of KI and the phosphate buffer (keep pH=7) in the ECC-sensing (cathode) cell (*Johnson et al.*, JGR, 2002).

2. Applied, but old pump efficiencies (K86 & K95 by Komhyr) are too low compared to newer ones (JMA,CMDL & UWYO) (*Tarasick et al.,* ESS, 2021)

3. Background current dependent on amount of ozone exposure (*Smit et al*, JGR, 2007)

4. ECC ozone signal is composed of a fast and slow time response (*Voemel et al.,* AMT, 2010):
   i. Fast component (90-98% of signal) with 20-25 sec. response time
   ii. Slow component (2-10% of signal) with 20-25 min. response time

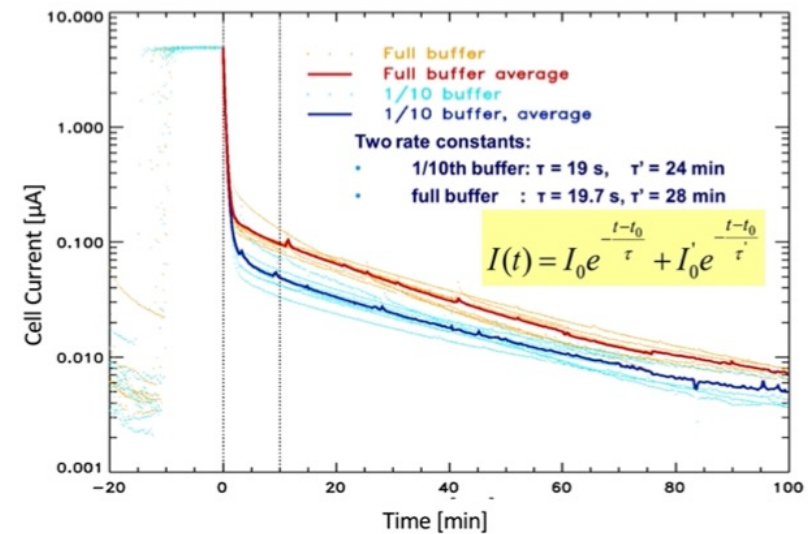Stoichiometry 2KI+O3-> I2 (Johnson et al. JGR, 2002)
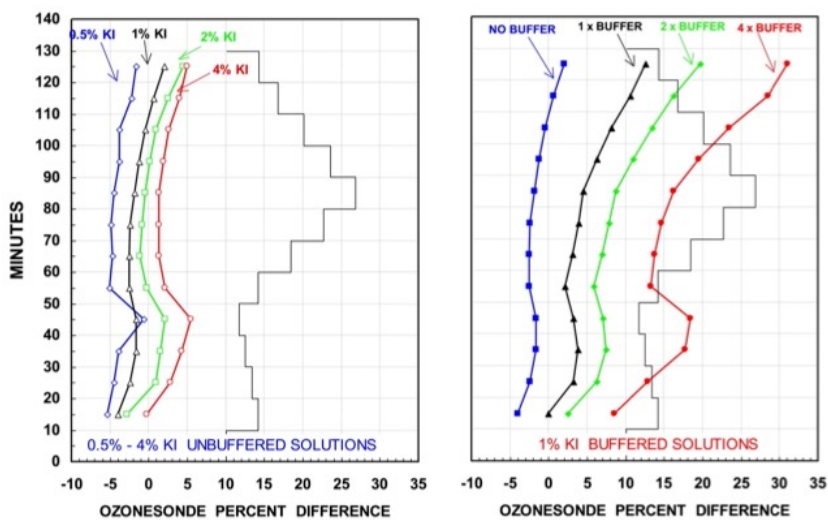
Pump Efficiencies (Tarasick et al., ESS, 2021)

Time Response Voemel et al., AMT, 2010

Two rate constants:
- 1/10th buffer: $\tau = 19$ s, $\tau' = 24$ min
- full buffer : $\tau = 19.7$ s, $\tau' = 28$ min

$$I(t) = I_0 e^{-\frac{t-t_0}{\tau}} + I_0' e^{-\frac{t-t_0}{\tau'}}$$

The Background Current: Physical and Chemical Origin Derived From Measurements Made at RMI/Uccle-Belgium

Method (using zero air filter at RMI/Uccle) during ground check :

I. Before ozone exposure, flushing ECC-cell for 10 min. with zero air: *Record* **IB0**

II. Ozone exposure of the ECC-cell 10 min. with 5 μA ozone equivalent

III. Flushing ECC-cell for 10 min. zero air: *Record* **IB1** *and then stop flushing*

IV. No Flushing until t= 60 min. then flush 5 min. zero air**:** *Record* **IB60** *and then stop flushing*

V. No Flushing until t=120 min. then flush 5 min. zero air : Record **IB120**

Results

➢ Fast response time τ_{Fast}=25 sec.

➢ Slow response time τ_{Slow}=25 min.

➢ Fast and slow response times are consistent with *Voemel et al.,* AMT, 2010)

➢ Slow response is independent of flushing: chemical origin

➢ *IB0* is independent of ozone exposure and constant: ECC-Cell property

➢ *IB1 – IB0* is the ozone exposure dependent part of the background current, which has a chemical origin
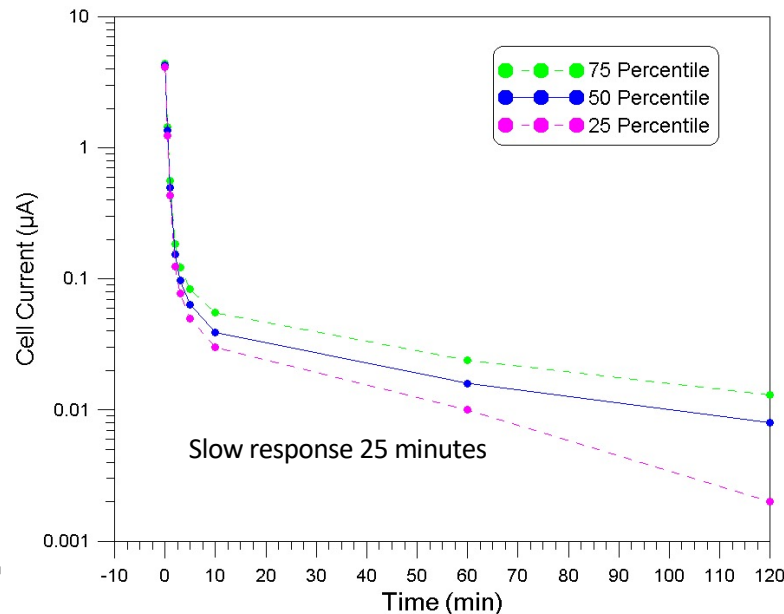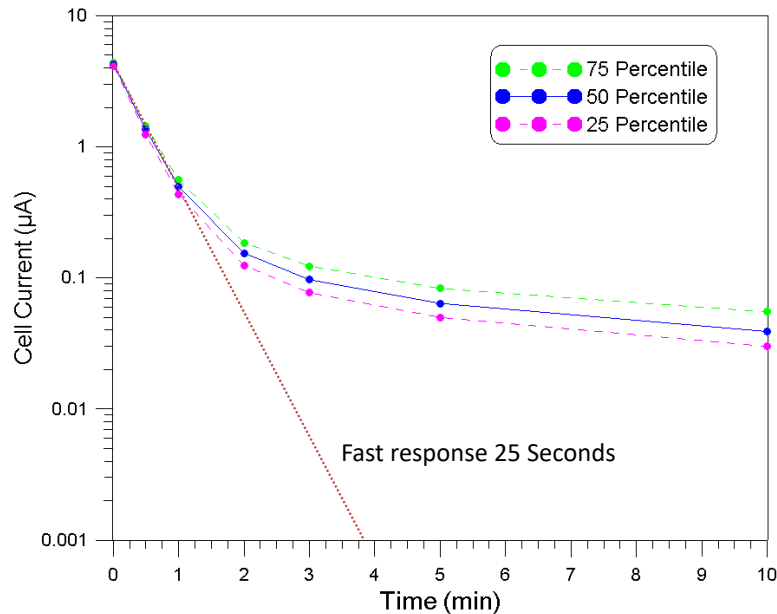
IB0 = 0.010 ± 0.010 μA (N=608)
IB1 = 0.045 ± 0.039 μA (N=602)

IB60 = 0.017 ± 0.013 μA (N=360)
IB120 = 0.009 ± 0.010 μA (N=257)

Conclusions:

➢ Background current consists of a <u>constant</u> *IB0* component …

➢ … plus an ozone-exposure dependent background component with a chemical relaxation time that is similar to the observed slow response time τ_{Slow}

➢ This ozone-exposure dependent background is the result of a slow secondary reaction pathway, whereby the phosphate buffer plays a crucial role

The overall measured signal $I_M(t)$ is assumed to be the linear superposition of a fast contribution $I_{Fast}(t)$ and a slow contribution $I_{Slow}(t)$:

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

a) Fast part (I_{Fast} with $\tau_{Fast} \approx$ 20-25 sec.): conversion factor α is the fast fraction, i.e. stoichiometry S_{Fast} of the fast reaction path way converting Ozone into Iodine (I_2), which is close to 1.0.

b) Slow part (I_{Slow} with $\tau_{Slow} \approx$ 20-25 min.): conversion factor β is small fraction, i.e. stoichiometry S_{Slow} of the secondary, slow reaction pathway producing additional Iodine (I_2), which is of the order of 0.0 to 0.10.

c) Because $\beta \ll \alpha$ and $\tau_{Slow} \gg \tau_{Fast}$, I_{Slow} acts as that part of the background current that is ozone-exposure dependent and can be determined by convolution of $I_M(t) - I_{B0}$ with τ_S=20-25 minutes

d) I_{Fast} can be de-convoluted 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:

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

The overall, total efficiency η_T is: η_A = Absorption efficiency , η_P = Pump efficiency, and η_C = Conversion efficiency

The conversion efficiency can be dependent of sonde type and sensing solution type.

The conversion efficiency is directly related to the stoichiometry of the conversion of O_3 into I_2 from the fast reaction pathway. It can be determined from comparison with the reference UV-ozone photometer at the WCCOS (e.g. JOSIE), such that the inverse of η_C is then the calibration function of the ECC sonde determined as function of altitude (i.e. pressure)

First order response of a sensor (here ECC: I_{ECC}) that is approximately exponentially to a change in I_{ECC}, is described by the common "growth law equation":

$$\frac{dU_m}{dt} = k * (U_a - U_m) \qquad\qquad (Eq.3)$$

Where U_m is the instantaneous measured O_3 cell current, U_a is the ambient ("true") O_3 cell current that is driving the change in U_m, and k is a constant.

The solution of Eq.3 over a small time step $\Delta t_k = t_{k-1} - t_k$ gives the measured signal (O_3 cell current) as a function of time:

$$U_m(t_k) = U_a(t_k) - \{U_a(t_k) - U_m(t_{k-1})\} * Exp\left(-\frac{\Delta t_k}{\tau}\right) \qquad\qquad (Eq.4)$$

Assumption: time step Δt_k (=t_k-t_{k-1}) is relatively small to the response time τ (=1/k). Further it is assumed that the "true" (ambient) signal U_a is **quasi-stationair** during time step Δt_k such that $U_a(t_k) = U_a(t_{k-1})$

Case 1: Convolution of the signal ($I_{Slow}(t)$)

Equation Eq.4 can be re-written into:

$$U_m(t_k) = U_a(t_k) - \{U_a(t_k) - U_m(t_k - 1)\} * X \qquad (Eq.5)$$

whereby response function X as :

$$X = Exp\left(-\frac{\Delta t_k}{\tau}\right) \qquad (Eq.6)$$

Case 2: De-convolution of the signal ($I_{Fast}(t)$)

Equation Eq.4 can be re-written into:

$$U_a(t_k) = \frac{U_m(t_k) - U_m(t_{k-1})*X}{(1-X)} \qquad (Eq.7)$$

whereby response function X as :

$$X = Exp\left(-\frac{\Delta t_k}{\tau}\right) \qquad (Eq.6)$$

Note: Δt_k (=t_k-t_{k-1}) is relatively small to the response time τ, such that response function X is close to one, which indicates that factor (1-X) in denominator of Eq.7 is close to zero, such that the de-convoluted signal will become noisy (as expected)!!

Slow ECC Current: Determination Stoichiometry S_{Slow} = β-Factor

2009 JOSIE
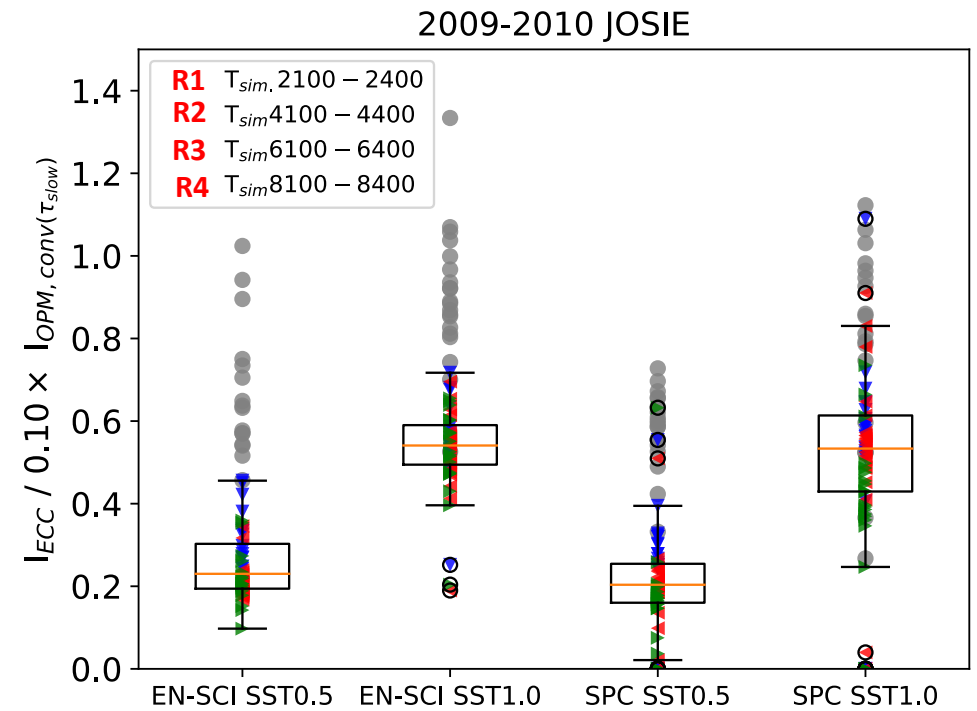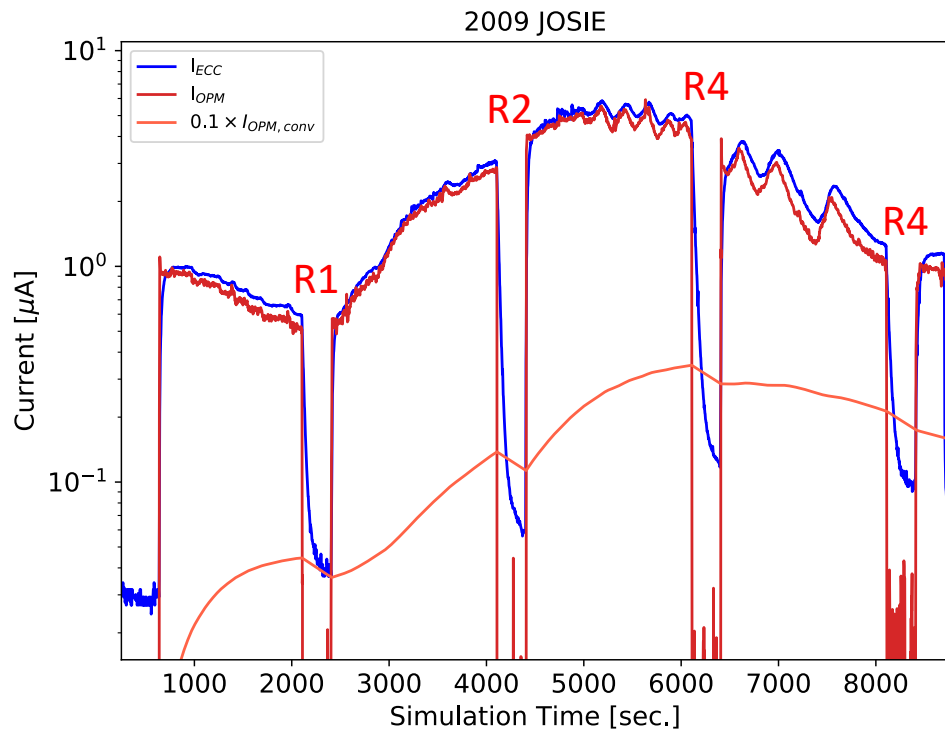
2009-2010 JOSIE

1. Using JOSIE 2009/2010 $I_{ECC}(t)$-IB0 and $I_{OPM}(t)$ (OPM = Ozone PhotoMeter as JOSIE reference at WCCOS)

2. $I_{OPM}(t)$ is derived from $P_{O3}(t)$ of OPM using Eq.2 with $T_P(t)$ and new pump efficiency of JMA (Nakano, priv.com., 2016) while η_A=1.0 and η_C= 1.0.

3. Convolution of $I_{OPM}(t)$ (in graph 0.1* $I_{OPM}(t)$)

4. After 5 minutes of each downward response (R1, R2, R3, and R4) the remaining $I_{ECC}(t)$-IB0 signal is the slow part of the measured ECC signal, then the Ratio of ECC slow signal and the convolution of OPM signal is the **Stoichiometry S_{Slow} = β-Factor** .

➢ Clearly no difference between SPC and EN-SCI when using same SST

➢ Stoichiometry factor S_{Slow} of slow reaction pathway is for:
   • 1.0%KI + 1.0 Buffer: 0.055+/-0.005
   • 0.5%KI + 0.5 Buffer: 0.025+/-0.005

➢ It is obvious that the difference between SPC and EN-SCI when using same SST has its origin in the fast part of the conversion of O_3 into I_2, and not in the slow part

Determination I_Fast(t) through De-convolution: Importance of Proper Smoothing and Adjustment I_Slow at Launch

Proper Smoothing
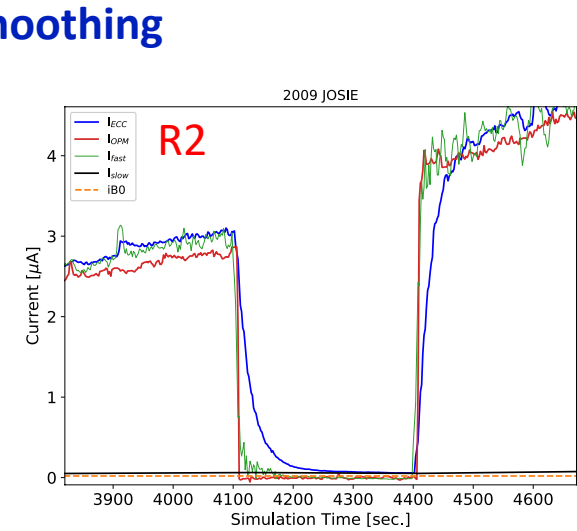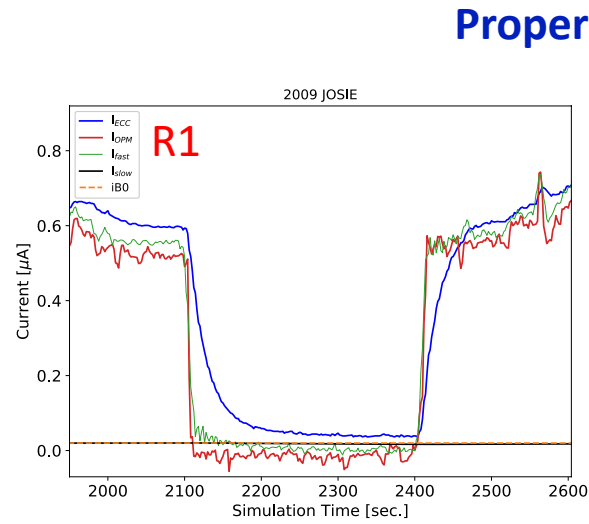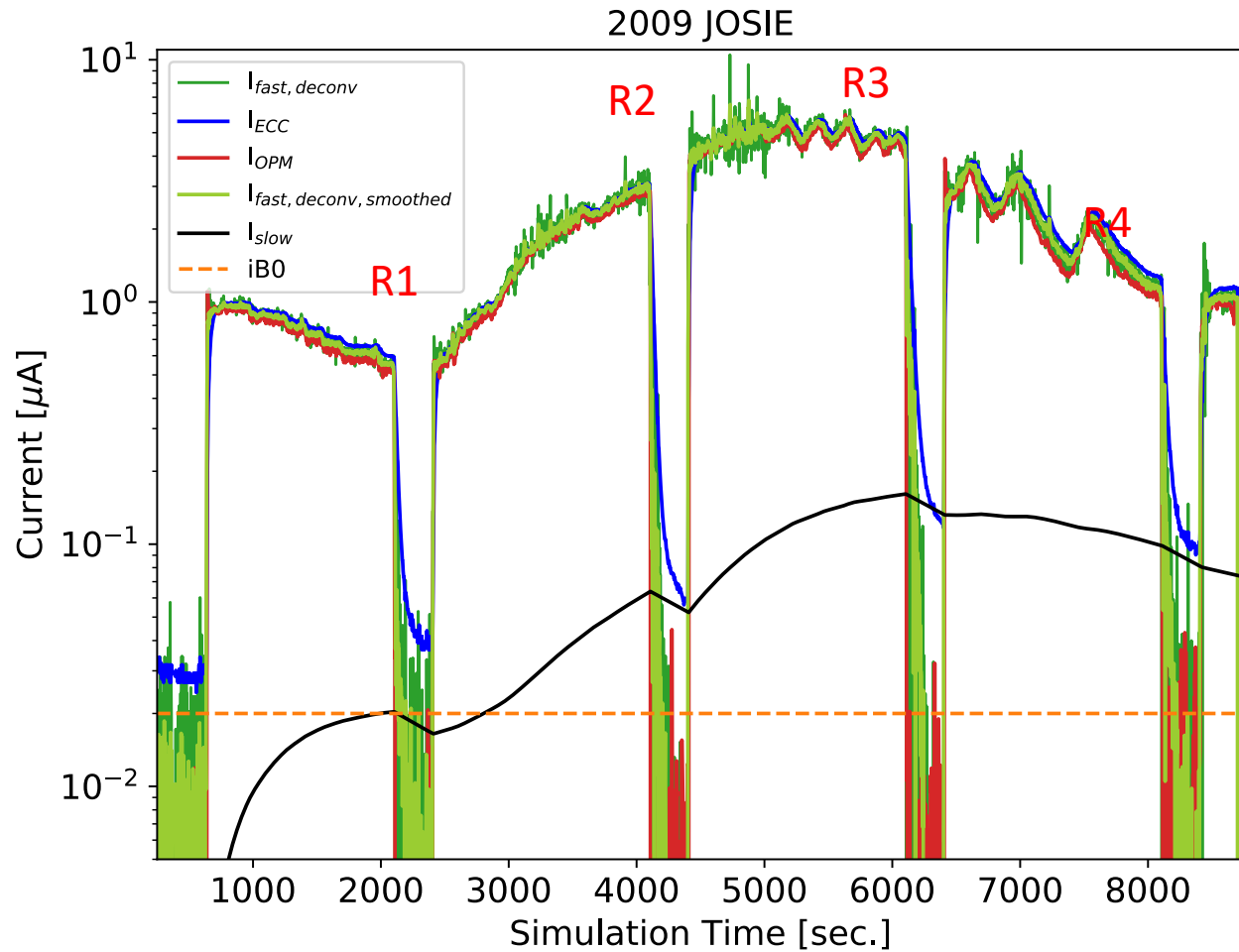
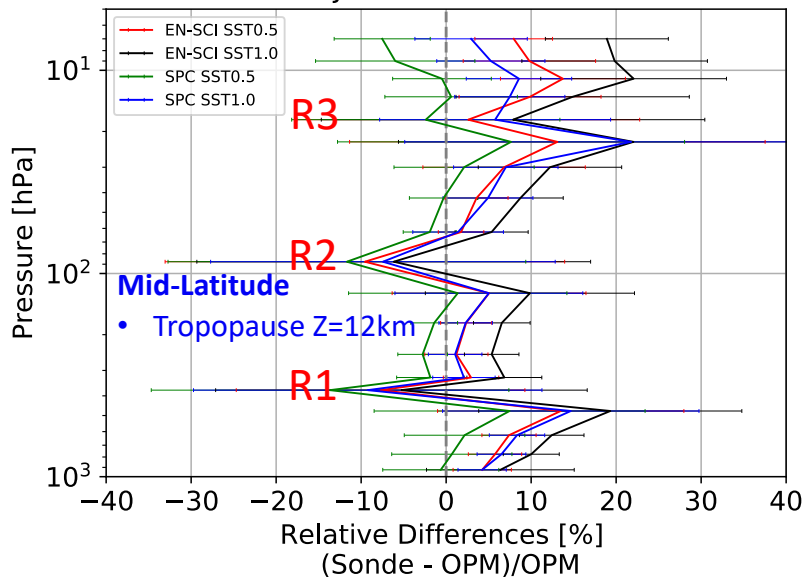**Adjustment I_Slow at Launch**
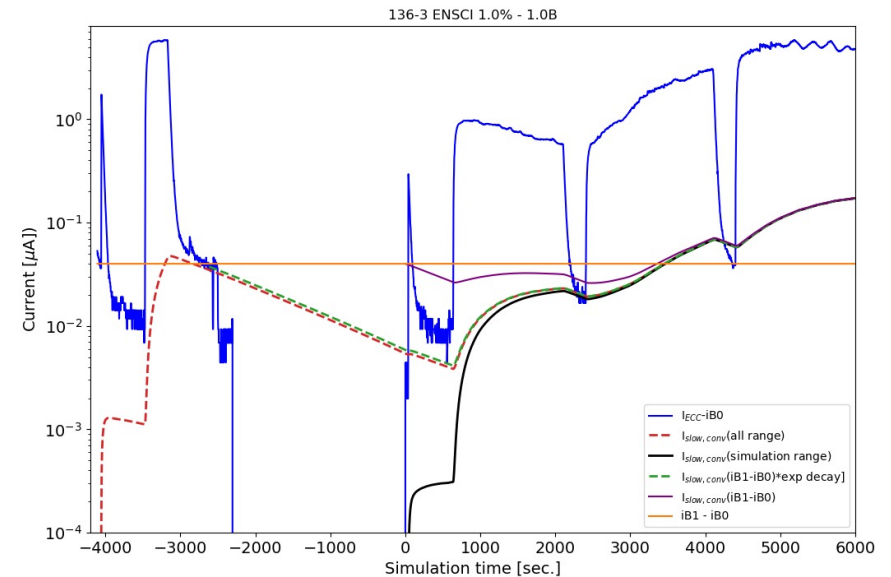
Best adjustment *I_slow* at Launch is:

a. Time stamp of IB1 recorded at ground check: t_{IB1}

b. $(I_{B1} - I_{B0})$ can be assumed as I_{Slow} at recording I_{B1}

c. Time stamp of Launch: t_{Launch}

d. Best approximation for I_{Slow} at launch is to calculate

$$(I_{B1} - I_{BO}) \times Exp\left[-(t_{IB1} - t_{Launch}) / \tau_{Slow} \right]$$

Comparison Conventional Method Versus New Time Response Resolving Methodology
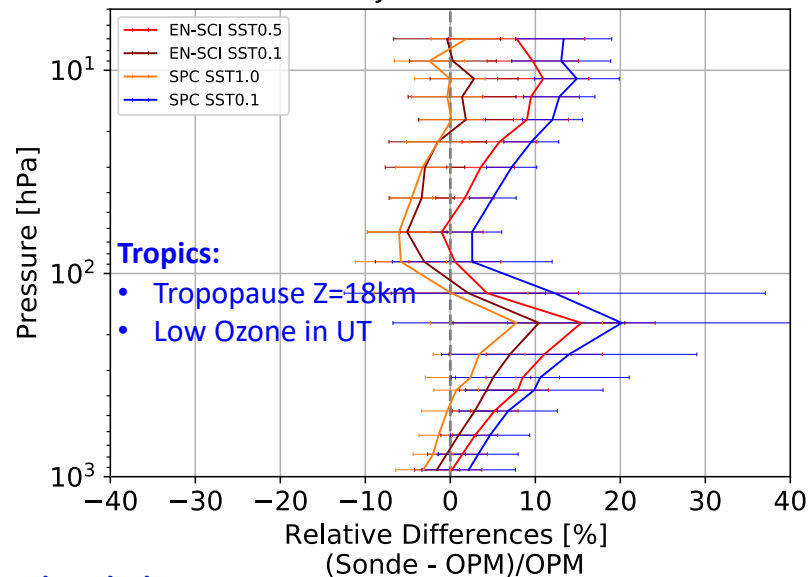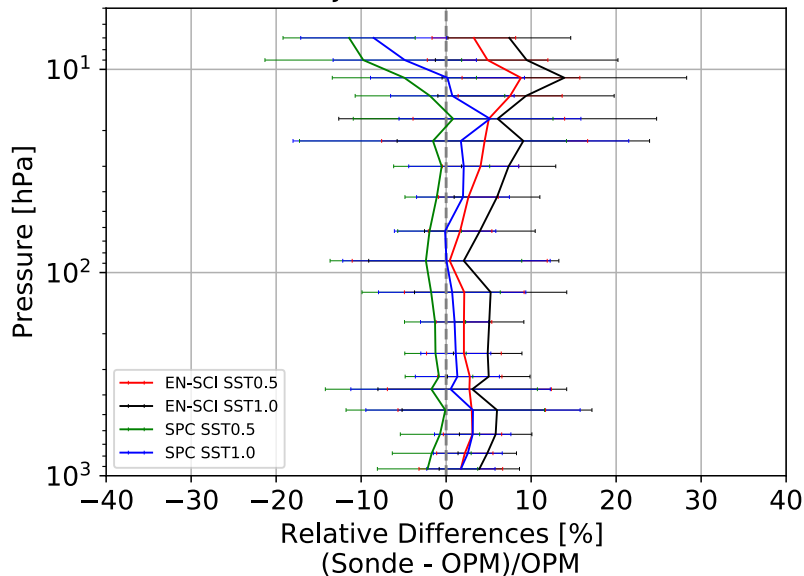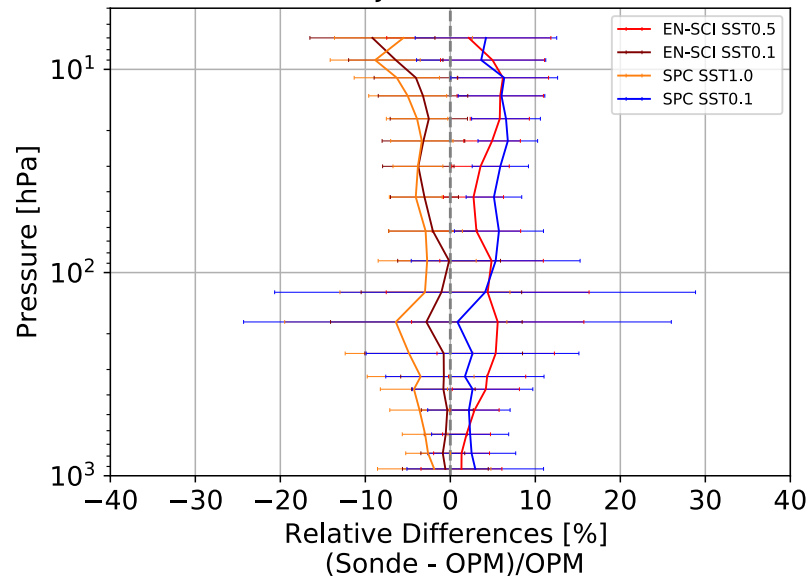
Conventional Method of using:

I. Pump Efficiencies of Komhyr:
   - K86 for SPC, and K95 for ENSCI
II. Constant Background I_{B1} Correction
III. Conversion efficiency of 1.00

➔ **No calibration functions can be derived from comparison with OPM, because they are dependent of the ozone profile**

New Methodology of using:

I. New Pump Efficiencies of JMA
II. Constant Background I_{B0} Correction
III. Derive $I_{Slow}(t)$ as ozone-exposure dependent background current through convolution (20-25 min.) of $I_M(t)-I_{BO}$ applying empirical derived stoichiometry factor of slow component
IV. Determine $I_{Fast}(t)$ through de-convolution (20-25 sec.) from $I_M(t)$ after substraction of I_{B0} and $I_{Slow}(t)$

➔ **Calibration functions can be derived, now independent of the ozone profile**

Conclusions and Outlook

1. The new concept of using realistic pump efficiencies (here JMA-Nakano 2016) together with resolving the slow (20-25 min response) and fast (20-25 seconds) components of the ECC current signal through use of convolution and deconvolution techniques is very promising and has been also reported recently by *Voemel et al.,* AMT, 2020 and *Tarasick et al.,* ESS, 2021.

2. Through the new methodology we have solved three inconsistencies in the conventional method of data processing: improper pump efficiencies (K86 and K95), improper background correction and time delaying effects through two different time responses (20-25 sec and 20-25 min)

3. The stoichiometry factors of the slow reaction pathway and the conversion efficiencies of the different sonde types and sensing solutions have been derived from JOSIE 2009/2010 and are thus referenced to the common OPM as reference instrument. In other words the conversion efficiencies are traceable.

4. 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.

5. The algorithms to be applied (incl. the low-pass filtering) are straight forward and relative easy to implement in the data processing software.

6. The new concept has the potential to introduce calibration functions (inverse conversion efficiency) traceable to the OPM of WCCOS (JOSIE).

Next Step: Publication in QOS 2021 Special Issue!!

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Abstract

Ozone sounding records constitute the longest time series of the vertical ozone distribution between the surface and 30-35 km altitude. Vertical ozonesonde profiles provide the single data source with sufficient vertical resolution to resolve the vertical ozone gradients, particularly at the tropopause region. Ozonesondes also constitute a backbone for calibrating ozone measuring satellites calibrated and maintaining the long-term stability of the global ozone record. However, ozonesonde instruments of various types have discrepancies and bias with one another, even when the modern electrochemical concentration cell (ECC) sonde, currently the standard device in the global ozonesonde networks (GAW-NDACC-SHADOZ), is used [1, 2, 3].

To resolve these inhomogenities the O3S-DQA (Ozone Sonde Data Quality Assessment) started in 2012 has shown that the overall uncertainty of ozonesonde measurements can be improved from about 10-20% down to 5-10% [4, 5, 6, 7, 8, 9, 10]. JOSIE 2017-SHADOZ [11] has demonstrated that to achieve an uncertainty better than 5%, then (i) SOP's (Standard Operating Procedures) have to be more unified; (ii) data processing has to be improved through a better correction of the pumpflow rate at low pressures in conjunction with a better correction of the ozone exposure dependent stoichiometry of the O3+KI reaction in the electrochemical cell of the ECC-sonde. To overcome both shortcomings, unified SOP's have been provided by the new ASOPOS (Assessment of Standard Operating Procedures for Ozone-Sondes) report and in addition, a new methodology of data processing has been developed. The latter through the use of better pump corrections combined with resolving the time delays of the slow ($\cong$20-25 min) and fast ($\cong$20-25 sec) components of the ECC-ozone current. Through this new methodology (i) the ozone exposure dependent background current and (ii) the time response of the fast ECC-O3 current in the electrochemical cell, can be resolved such that the ozonesonde profile can be improved by ±5% or even more [12, 13].

In this study we have used the JOSIE 2009/2010 and JOSIE 2017-SHADOZ results to investigate this new methodology of data processing and we have quantified the stoichiometry factors and their uncertainties of the fast as well as the slow reaction pathways for the different sensing solution types used in the global ozonesonde network. In the new methodology of data processing we introduce calibration functions for the ECC-ozonesonde that will allow us to get the global ozonesonde records traceable to one common standard, the ozone reference UV-photometer (OPM) used in JOSIE. We will present and discuss the results of this study, with inclusion of a full uncertainty budget when applying the new methodology of data processing. Further, we will discuss the proposed reaction mechanisms for the fast and slow reaction pathways, in conjunction with the ozone exposure varying background signal.

Backup Slides

KI+O$_3$ Chemistry in Aqueous Solution in Presence of Phosphate-Buffer (after Saltzmann & Gilbert, 1959)

➢ **Slow reactions increase with phosphate buffer concentration**

➢ **Buffered solutions with no KI show no evidence of O$_3$ reactions, thus additional reactions with O$_3$ are secondary reactions after the initial O$_3$+ KI reaction.**

Primary reaction pathway:

(R1) $2KI + H_2O + O_3 \rightarrow 2KOH + I_2 + O_2$

In ion-notation:

(R2) $O_3 + 2H^+ + 2I^- \rightarrow O_2 + I_2 + H_2O$

    Or in detail (postulated after Saltzmann & Gilbert) :

    (R3) $O3 + I^- \rightarrow IO^- + O_2^*$ (fast)

    (R4) $IO^- + I^- + \mathbf{2H^+} \rightarrow I_2 + H_2O$ (fast, neutral/acid)

    (R5) $O_2^*. + M \rightarrow O_2 + M.$ (fast)

    Losses of IO-, i.e. I$_2$:

    (R6) $IO^- + IO^- \rightarrow 2I^- + O_2$ (slow)

- If all O$_3$ would be absorbed and react with KI then this **primary reaction pathway** it would be expected that the stoichiometry for O$_3$/IO- i.e. O$_3$/I$_2$ in neutral/acid solution to be one.

- However, self reaction of IO$^-$ (R6) can be a loss mechanism competing with formation of I$_2$ (R4).

- In general, loss mechanisms of IO$^-$ might compete with R4 and then the stoichiometry of primary reaction pathway is less than one.

- ECC shows for 1% KI and no buffer a stoichiometry less than one (*Johnson et al.*, JGR, 2002).

Secondary Reaction Pathway: Impact of Phosphate Buffer

(R7) $O_2^* + I^- + H_2PO_4^- \rightarrow IO^- + H_2PO_5^-$ (fast)

(R8) $H_2PO_5^- + I^- \rightarrow H_2PO_4^- + IO^-$ (slow)

(R4) $IO^- + I^- + 2H^+ \rightarrow I_2 + H_2O$. (fast)

But also losses of I$_2$ iodine (via IO$^-$ losses):

(R9) $H_2PO_5^- + IO^- \rightarrow H_2PO_4^- + I^- + O_2$ (slow)

(R6) $IO^- + IO^- \rightarrow 2I^- + O_2$. (slow)

- R7 is the key reaction to form extra IO$^-$ that can react via R4 into I$_2$ and is contributing in addition to the **fast reaction pathway and thus adding to the stoichiometry causing the fast ECC signal.**

- **H2PO5$^-$ can be seen as the interim reactant that is formed fast but via R8 decaying slowly** to form extra IO$^-$ that can produce in addition extra I$_2$ which is causing the slow part of the ECC current.

- It is known that H$_2$O$_2$ reacts similar as **H$_2$PO$_5^-$** to form IO$^-$, i.e. I$_2$ with typical time constant of 20-25 minutes: this fits to the slow, secondary response time of ECC of typical 20-25 minutes.

- The extra stoichiometry caused by the buffer is 50% into fast signal (R7) and 50% into slow signal (R8).

- The stoichiometry of the fast reaction mechanism is dependent of the strengths of KI and buffer in the cathode solution: The assumption that the stoichiometry is one, is not exactly true.

Composition of Measured ECC-Ozone Signal Fast and Slow Component

The measured ECC current ($I_{M,ECC}$) is the superposition of:

$$I_{M,ECC} = I_{Prim,Fast} + I_{Sec,Fast} + I_{Sec,Slow} + I_{B0} = I_{Fast} + I_{Slow} + I_{B0}$$

$I_{Prim,Fast}$ = Current caused from <u>fast primary reaction path</u>

$I_{Sec,Fast}$ = Current caused from <u>fast part of secondary reaction pathway</u>

$I_{Sec,Slow}$ = Current caused from <u>slow part of secondary reaction pathway</u>

I_{B0} = Background current independent of ozone exposure, which is of instrumental origin and is assumed to be constant: measured at ground check before ozone exposure!

$I_{Prim,Fast} + I_{Sec,Fast} = I_{fast}$ = Fast Cell Current with 20-25 seconds time response, which is determined by I_2 mass transfer towards the cathode.

$I_{sec,Slow} = I_{Slow}$ = Slow Cell Current with 20-25 minutes time response, which is determined by IO^-, i.e. I_2 production most likely from slow reaction R8:

$$H_2PO_5^- + I^- \rightarrow H_2PO_4^- + IO^- \quad \textbf{(slow)}$$

I. The overall stoichiometry S_{All} of the chemical conversion of O_3 into I_2 is the sum of the stoichiometry factors S_{Fast} and S_{Slow} of the fast and slow reaction pathways, respectively.

II. From the response tests (fast decay from 5µA down to 0.1-0.5µA within less than 1 minute) it can be concluded that S_{Fast} is close to one (0.9-1.1) and at least a factor 10 larger than S_{slow}, which is small (0.01-0.10)

$$Basic\ ECC-Formula:\ P_{O_3} = \frac{R}{2 \cdot F} * \frac{T_P}{(\eta_T * \Phi_P)} * I_{Fast}\ , whereby\ \frac{R}{2 \cdot F} = 0.043085\ and\ I_{Fast} = I_{M,ECC} - I_{Slow} - I_{B0}$$