SI2N/O3S-DQA Activity:

Guide Lines for Homogenization of Ozone Sonde Data

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Prepared
by
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Activity as part of

SPARC-IGACO-IOC Assessment

(SI2N)

"Past Changes in the Vertical Distribution of Ozone"

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1. Introduction

Within the new SPARC-IGACO-IOC Initiative on "Past Changes in the Vertical Distribution of Ozone" (SI2N) (SPARC-News Article by Neil Harris, Johannes Staehelin and Richard Stolarski, Sept 2010: http://igaco-o3.fmi.fi/VDO/files/Harris_ozone_trends_initiative.pdf) an "Ozone Sonde Data Quality Assessment (O3S-DQA)" activity has been initiated with the following two major objectives:

1. Homogenization of selected ozone sonde data sets to be used for this ozone assessment: Goal reduce uncertainty from 10-20% down to 5-10% (focus on transfer functions)
2. Documentation of the homogenization process and the quality of ozonesonde measurements generally to allow the recent record to be linked to the older records.

In the context of the O3S-DQA activity we have had two meetings; one at NOAA/GMD-Boulder CO (USA) and the other at NASA/GSFC-Greenbelt MD (USA) where we selected the O3-sounding stations to be involved in the homogenization process and formulated the guidelines for re-processing sonde data (including the use of transfer functions). In this document we give the guidelines for the homogenisation of long term ozone sonde data in the scope of the SI2N initiative.
These guidelines includes the strategy to be followed and how to deal/correct for :

- Different sensing solutions and sonde type: Transfer functions
- Background current corrections (Ib0, Ib1, Ib2)
- Pump flow rate: humidity correction
- Pump flow efficiency correction at lower pressures
- Pump temperature (internal-, external-, box-)
- Total ozone normalization factor
- Determination of residual ozone
- Different radiosondes

An Essential aspect of this homogenization will be the estimation of expected uncertainties and the detailed documentation of the reprocessing of the long term ozone sonde records of the participating sounding stations (Annex-1). The reprocessing will be coached by an ozonde sonde expert of the O3S-DQA panel (Annex-1 & 2)

2 Metrological Terminology: Uncertainty, Precision, Bias and Accuray

What is precision and accuracy?
So, if you are playing soccer and you always hit the left goal post instead of scoring, then you are **not** accurate, but you **are** precise!

Low Accuracy
High Precision

High Accuracy
Low Precision

High Accuracy
High Precision

Preamble on precision, accuracy

1. *Precision and Accuracy are qualitative concepts and should be avoided in quantitative expressions.*
2. *Accuracy cannot be expressed as a numerical value.*
3. *The term 'accuracy of measurement' should not be used for trueness of measurement and the term 'measurement precision' should not be used for 'accuracy of measurement'.*
4. *Accuracy is inversely related to the combination of systematic error (bias) and random error (uncertainty) that occur in a single measurement result (Figure 1)*
5. *Accuracy is concerned with the difference between a single measurement result and a true (or the conventional true) value*

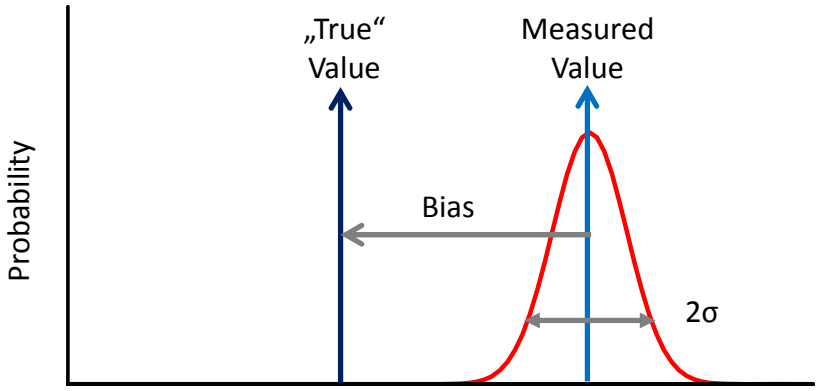


Figure 1: *If a distribution of measured values follows a symmetric (normal) propability distribution around an arithmetic average then a one σ- standard deviation is the standard uncertainty, or precision of the measurement, whereas accuracy is how close the measurement is to the "true" value.*

Excerpts of WMO/GAW Glossary of QA/QC-Related Terminology
(Source: http://www.wmo.int/pages/prog/gcos/documents/gruanmanuals/GAW/QC-Related%20Terminology.pdf)

Conventional true value (of a quantity)=Assigned value

- value **attributed to a particular quantity**
- *accepted as having an uncertainty appropriate for a given purpose*

Precision

- **degree of internal agreement among independent measurements made under specific conditions**
- *precision is expressed numerically by e.g. standard deviation or variation coefficient.*
- *it is a measure of the dispersion of values.*

Random error

- **result of a measurement minus the mean that would result from an infinite number of measurements of the same measurand carried out under repeatability conditions**
- *random error is equal to error minus systematic error.*
- *because only a finite number of measurements can be made, it is possible to determine only an estimate of random error.*

Repeatability (of results of measurements)

- **closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement**
- *repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.*
- *for the dispersion characteristics, information on the level of confidence should be provided, e.g. '±1 standard deviation'*

Measurand = particular quantity subject to measurement

Measurement = set of operations having the object of determining a value of a quantity.

Standard uncertainty (of a measurement)

- **uncertainty of the result of a measurement expressed as a standard deviation**

True value (of a quantity)

- **value consistent with the definition of a given particular quantity**
- *this is a value that would be obtained by a perfect measurement.*
- *true values are by nature indeterminate*

Uncertainty of a measurement

- To express the degree to which a measured result is unknown
- **standard uncertainty** to express the uncertainty in terms of 1 standard deviation),
- **combined standard uncertainty** as the positive square root of the sum of a number of terms contributing to the uncertainty)

3. The Electrochemical Ozone Sonde: Principle of Operation and Overall Uncertainty

Introduction

The instrumental lay out of electrochemical ozone sondes and their performances are described in detail by Smit and the ASOPOS panel in GAW report Nr.201 "Quality Assurance and Quality Control for Ozonesonde Measurements in GAW",. WMO Global Atmosphere Watch report series, No. 201, World Meteorological Organization, Geneva, 2011.
http://www.wmo.int/pages/prog/arep/gaw/documents/GAW_201_30_Sept.pdf)].

In this section only the basics of the operation of an ozone sonde together with the concept of an uncertainty analysis are given to quantify the contributions of the uncertainties of the different instrumental parameters to the overall uncertainty of the ozone partial pressure measured by the sondes. In this guidelines document we will focus on the quantification of the contributions of the different uncertainties to be expected from the homogenization (i.e. reprocessing) of long term ozone sonde records of each sounding station that participates in the O3S-DQA-activity.

Principle of Operation

The electrochemical ozone sonde is based on the titration of ozone in a potassium iodide (KI) sensing solution according to the redox reaction:

[R-1] $2\,KI + O_3 + H_2O \longrightarrow I_2 + O_2 + 2\,KOH$

The amount of generated „free" iodine (I_2) is measured in electrochemical reaction cell(s). Continuous operation is achieved by a small electrically driven gas sampling pump which bubbles ambient air through the sensing solution of the electrochemical cell. Transported by the stirring action of the air bubbles, the iodine makes contact with a platinum cathode and is reduced back to iodide ions by the uptake of 2 electrons per molecule of iodine.

[R-2] $I_2 + 2e \xrightarrow{Pt} 2\,I^-$ [cathode reaction]

An electrical current I_M [µA] generated in the external circuit of the electrochemical cell is, after correction for a background current I_B [µA], directly related to the uptake rate of ozone in the sensing solution. By knowing the gas volume flow rate Φ_P [cm^3s^{-1}] of the air sampling pump, its temperature T_P [K] and the conversion efficiency of the ozone sensor η_C, the measured partial pressure of ozone P_{O3} [mPa] is determined from Faraday's first law of electrolysis and the idea gas law and given by the relation:

[Eq.1] $$P_{O3} = \frac{R}{2 \cdot F} \frac{T_P}{(\eta_C \cdot \Phi_P)} \cdot (I_M - I_B) \text{ with } \frac{R}{2 \cdot F} = 0.043085$$

whereby R is the universal gas constant and F is Faraday's constant. The number 2 originates from the fact that each molecule of Iodine (I_2) formed from the reaction of KI+O3 will be converted back into 2 Iodide (I^-)ions and deliver thereby 2 electrons in the external electrical current circuit to contribute to the measured electrical current I_M.

Overall Uncertainty: A Gaussian Approach

From Eq.E-1 the partial pressure of ozone measured by the electrochemical sensor is a function of the measured sensor current (I_M), the background current (I_B), the conversion efficiency (η_C), the temperature of the gas sampling pump (T_P) and the volumetric flow rate (Φ_P):

[Eq.2] $$P_{O_3} = P_{O_3}\left(I_{M,}, I_B, \eta_C, \Phi_P, T_P \right)$$

The instrumental uncertainty of the electrochemical ozone sensor for the measurement of ozone is a composite of the contributions of the individual uncertainties of the different instrumental parameters listed above. Some of the contributions depend on air pressure, such that the overall uncertainty of the ozone measurement will be a function of pressure i.e. altitude.

The basic idea of the O3S-homogenization process is to remove all known systematic bias effect(s) from the measured instrumental parameters used in Eq. E-1 to determine the partial pressure of ozone during a vertical balloon sounding. It is assumed that for all measured parameters, after removal of their biases, the remaining uncertainties will be random and follow Gaussian statistics, such that applying the Gaussian law of error propagation [e.g. *Bevington and Robinson,* 1992] to Eq. E-2 the overall relative uncertainty of P_{O3} is expressed as :

[Eq.3] $$\frac{\Delta \mathbf{P_{O3}}}{\mathbf{P_{O3}}} = \sqrt{\frac{(\Delta \mathbf{I_M})^2 + (\Delta \mathbf{I_B})^2}{(\mathbf{I_M} - \mathbf{I_B})^2} + \left(\frac{\Delta \eta_C}{\eta_C}\right)^2 + \left(\frac{\Delta \Phi_P}{\Phi_P}\right)^2 + \left(\frac{\Delta \mathbf{T_P}}{\mathbf{T_P}}\right)^2}$$

From Eq.E-3 it is seen that the contribution of the conversion efficiency (η_C), pump flow rate (Φ_P), pump temperature (T_P) is the sum of the squares of their relative uncertainties. The contributions of the measured sensor current (I_M) and the background current (I_B) are more complicated. The square of the difference of both parameters in the denominator in equation Eq.E-3 indicates the sensitivity of the overall relative uncertainty of the ozone pressure to these two parameters. In cases of low ozone, when I_M and I_B are of the same order of magnitude, they contribute equally to the overall uncertainty in the measurement.

The contributions of the individual uncertainties of the different instrumental parameters are given in more detail in Chapter 8.

4. Strategy O3S-Homogenization Process

I. In Time (O3-trends @ individual stations)

Each station will homogenizehis/her O3S-record individually

- Following guidelines prescribed by O3SDQA
- Using transfer functions based on dual soundings
- Coaching by O3S-DQA-experts.

II. In Space (Validation: e.g. satellites)

- All individual O3S station records using JOSIE 2009 based transfer functions to refer the homogenized O3S data to one standard (UV-Photometer@WCCOS-JOSIE)

III. Testing for Consistency

- Comparison with other O3 profiling instrument @ O3S-site (e.g. NDACC)
- Troposphere-UTLS: MOZAIC-O3
- Stratosphere: MATCH-approach
- Satellites

Figure 1 shows the scheme of the homogenization process. Essential for the activity is that during the entire homogenisation process, each station will be coached by an O3S-DQA panel expert, for consultation and for recommendations to the station PI in the spirit of the guide lines as formulated by the O3S-DQA panel.

Coaching Team (See Annex-1):

- Sam Oltmans: Southern Hemisphere (incl. SHADOZ)
- Terry Deshler: Polar region
- Herman Smit: European (incl 3xBM) + JMA + MATCH
- Bryan Johnson/Sam Oltmans: NOAA stations
- David Tarasick/Jonathan Davies: Environmental Canada (EC)
- Frank Schmidlin NASA stations
- Rene Stuebi Payerne, Nairobi, La Reunion

Storage of reprocessed O3S-data:

1. At ftp-site at WCCOS-Data Server: Details coming up soon
2. Data format: As far as possible in station's existing format, but add at least three or four extra columns for the reprocessed new PO3 by sonde, its overall relative uncertainty after correction, the corrected pump temperature, and if possible raw cell current (μA)
3. It is important that after reprocessing each station provides good documentation of the reprocessing (incl. decisions, compromises made).

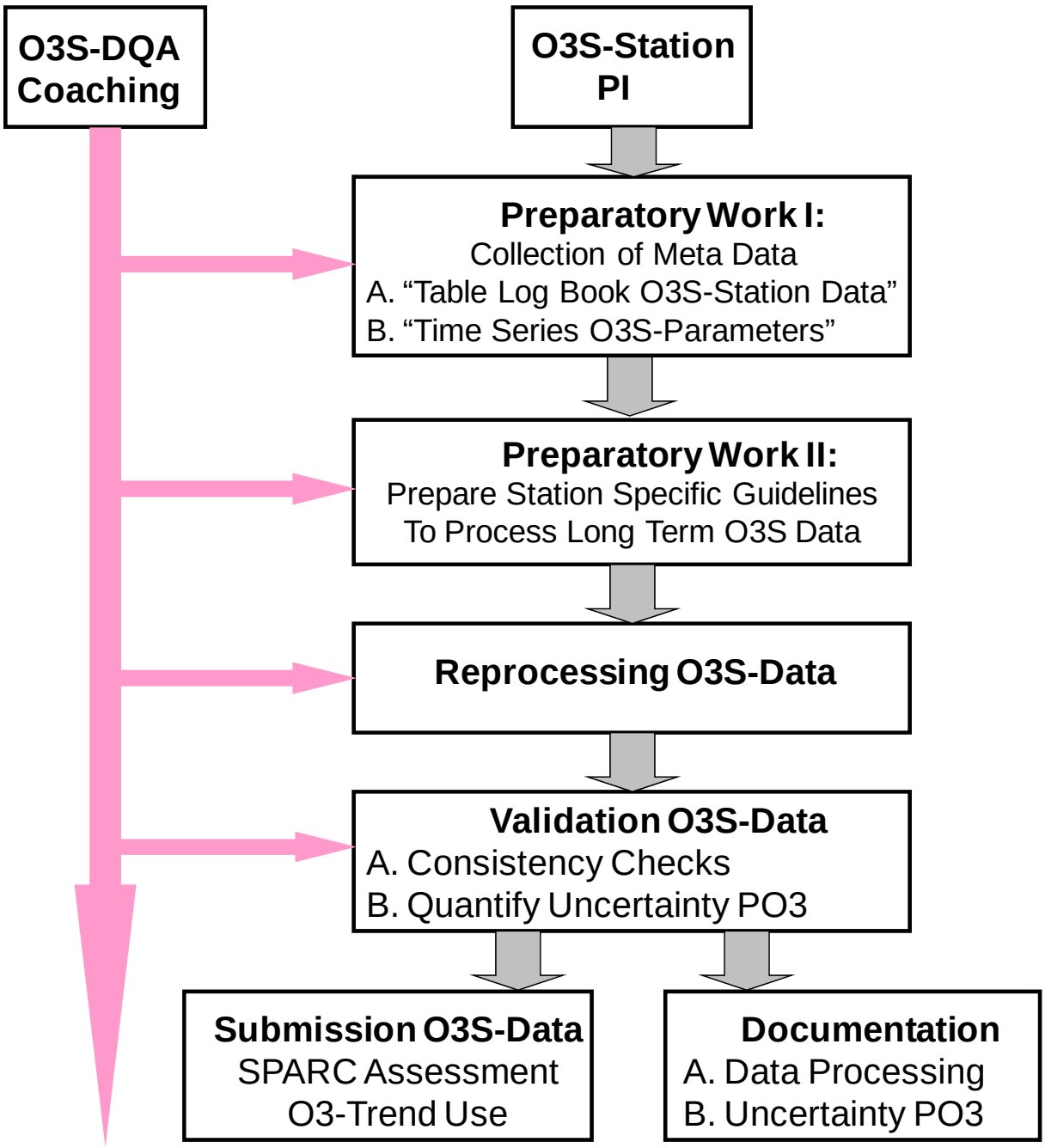


Figure 2: *Scheme of Homogenization Process of Long Term O3S-Data Per Station*

5. Preparatory Work On O3S Data Homogenization

Preparatory Work Phase I:
In a first step in advance of starting the re-processing of the long term O3S-records each O3S-Station should do "Preparatory Work I":

a) **"Table Log Book O3S-Station Data"** (See Table 1 template below) with the major specifications of the O3S-Station with time flags in orde to track when changes have been made during long term operation
b) **"Time Series O3S-Parameters"** (in electronic form) of:
   1. Total ozone normalization factor ($N_F(t)$)
   2. Total ozone column by spectroscopic instrument (e.g. Dobson, Brewer or ..) (TOC(t))
   3. Residual ozone column above burst altitude (ROC(t))
   4. Background current (ib0(t) , ib1(t), ib2(t)) determined on the flight day
   5. Pump flow rate ($\Phi_P(t)$) obtained from flight preparation
   6. Pump temperature in flight ($T_P(t)$ at launch and at P_{Air}= 400 , 200 , 100, 50 , 25 hPa)

Preparatory Work Phase II:
Based on information collected each station should consult his/her O3S-DQA-coach (to be assigned by the O3S-DQA panel) in order to compile the general guidelines for homogenization into guidelines specific for that individual station.

6. Reprocessing of O3S Data

After completing these station specific guidelines the actual re-processing of the data can be started. In the re-processing and eventual revision of data the philosophy to be followed would be to use the data processing prescribed in the SOPs (GAW-Report #201) as closely as possible. In the case of a deviation from the prescribed SOPs, the uncertainty contribution to the overall uncertainty should be estimated to the extent possible.
Realistically it is expected that for each station not all the recommended re-processing tasks can be fulfilled. Even in these non-fulfilled cases, there should always be an estimate of the specific instrumental/procedural contribution to the overall uncertainty. The overall uncertainty will be included as an extra column in the reprocessed data. Further, a crucial aspect of the homogenization process is the documentation (i.e. log book) of the procedures that have been followed.

7. Validation of O3S Data

After the O3S-Data have been reprocessed quality checks have to be done for internal consistency but also for external consistency through comparison with other ozone profiling platforms, which should be achieved through collaborations with other investigators. A final outcome of this validation process should be a detailed documentation of the re-processing. Thus it is essential that throughout the entire homogenisation process eventual error sources and their contribution to the overall uncertainty of the PO3-ozone sonde profile data should be watched for, quantified and documented. A large part of the task of the coach is to keep track of these error sources. An important challenge will be to quantify the overall uncertainty of the measured ozone partial pressure as part of the long term vertical ozone sonde profile data (entered as an additional column).

Table 1: *Template of* ***"Table Log Book O3S-Station Data"*** *with major specifications of the O3S-Station including time flags when changes have been done during long term operation*

Item	**Remarks**	
Sensing Solution Type (SST)	For ECC-sonde types: SST1%, SST0.5%, SST2.0% or any other SST ***(See Table 2)***	
Ozone Sonde Type	Model Type and Manufacturer Do you have ozonesonde indentification information: e.g. serial number-flightnumber	
Radio Sonde Type	Model Type and Manufacturer Do you have radiosonde indentification information e.g. serial number-flightnumber	
Data Interface Type	Electronic board interfacing ozone sonde and radiosondes Model Type and Manufacturer Do you have interface indentification information e.g. serial number-flightnumber	
Background Current	• Which background current(s) have been recorded and are available and which was used • Typical background currents (see Smit and ASOPOS panel, 2011) o Ib0: Before exposure to ozone @ laboratory o Ib1: After exposure to ozone @ laboratory o Ib2: @ launch site • Or in case of any other background current please describe briefly how this had been determined.	
Total Ozone Normalization Factor	Factor available? How determined? Applied to measured vertical ozone sonde profile?	
Total Ozone Measurement	Type of spectroscopic device measuring total ozone column during soundings	
Residual Ozone Column (above balloone bursting altitude)	Method of determing residual ozone CMR: Constant Mixing Ratio SRC: Residual from Satellite Climatology (e.g SBUV or another one)	
Temperature Pump Location	Pump temperature measured ? 1. If Yes: location? a. Int = Internal: in Teflon block of pump b. Ext = Externally attached to pump or its tubings (taped or epoxied) c. Box = Location inside the Styrofoam box of O3 2. If No: What pump temperature has been assumed/estimated ?	
Pumpflow Measurement	Bubble flow meter or other type In case bubble flowmeter: Any corrections done for "wetting effect" (See Smit and ASOPOS panel, 2011)?	
Source of Zero Ozone	• What kind of ozone removal techniques have been used to produce ozone free air to record background	

	current(s) • If Ozone destruction/absorption filter has been used: Can you describe the type of filter used	
Laboratory Air Conditions (PTU): Pressure (P) Temperature (T) Relative Humidity (U)	Ambient PTU conditions at location of preparation room when measuring pump flow rate. Have they been recorded? 1. If Yes: P, T & U data available? 2. If No: Can you give typical range of ambient air P,T and U in O3S preparation room: Approximate average plus/minus one standard deviation.	
Data Reduction Method	Using standard formula (E1)? If not, describe deviations. What kind of corrections applied: 1. Pumpflow efficiency as function of pressure: Komhyr 1986, Komhyr 1995 or any other table? 2. Background correction: which background current I_b has been used (incl. pressure dependent or constant). 3. Total ozone normalization applied (Yes/No) 4. Any other correction(s)	
Software Data Reduction	Using commercial software package (e.g. Vaisala): Is there a record of version number?	
Ozone cell current signal	Original (raw) ozone cell current available. Yes/No	
O3S-Preparation Unit	Manufacturer and Type	
Any other issues		

Table 2 *Most common sensing solution types and their chemical composition in aqueous solution for cathode cells of ECC-ozone sondes. For the anode sensing solution, usually a KI saturated cathode solution is employed.*

Sensing Solution Type (SST)	KI [g/L]	P_H-Buffer		KBr [g/L]
		$NaH_2PO_4.H_2O$ [g/L]	$Na_2HPO_4.12H_2O$ [g/L]	
SST1.0: 1.0% KI & full buffer [(a)]	10	1.250	5.0	25
SST0.5: 0.5% KI & half buffer [(b)]	5	0.625	2.5	12.5
SST2.0: 2.0% KI & no buffer [(c)]	20	0	0	0
SST1.0&0.1: 1.0% KI & 0.1buffer [(d)]	10	0.125	0.5	25

(a) Komhyr [1986] , SPC-6A instruction manual [Science Pump Corporation, 1996].
(b) ENSCI-Z instruction manual [EN-SCI Corporation, 1996].
(c) Johnson et al. [2002].
(d) Bryan Johnson [private communication 2012]

8. General Guidelines for Homogenisation of O3S-Data

Based on the information collected in preparatory phase I (i.e. "Table Log Book O3S-Station Data"+ "Time Series O3S-Parameters") the Station PI together with his O3S-DQA Coach will compile the general guidelines for homogenization into guidelines specific for each station individually. The general guidelines addressing different instrumental/procedural aspects are described in this chapter.

8.1 Conversion Efficiency η_C

The conversion efficiency η_C includes both, the absorption (i.e. capture) efficiency of O_3 (α_{O3}) from the gaseous into the liquid phase of the sensing solution and the stoichiometry of the conversion of O_3 into I_2 ($S_{O3/I2}$):

[Eq.4] $$\eta_C = \alpha_{O3} \bullet S_{O3/I2}$$

Normally, for pH = 7 buffered KI sensing cathode solutions $S_{O3/I2}$ has been assumed to be 1.00 with an uncertainty of about ±0.03 [*Dietz et al*., 1973], while α_{O3} will be one for the initial operation. Thus during normal operation η_C is assumed to be one. If, however, in the course of a sounding the uncertainties of the sensor cell characteristics change, the overall uncertainty can be expressed by

[Eq.5] $$\frac{\Delta \eta_{C,}}{\eta_C} = \sqrt{\left(\frac{\Delta \alpha_{O3}}{\alpha_{O3}}\right)^2 + \left(\frac{\Delta S_{O3/I2}}{S_{O3/I2}}\right)^2}$$

8.1.1 Absorption efficiency of O_3 (α_{O3}): Limitations for 2.5 cm^3 cathode sensing solution

Since laboratory and field investigations have shown that α_{O3} is gas-phase diffusion limited in the lower troposphere [Davies et al., 2003] and the sensing solution evaporates at a rate dependent on the temperature of the cell and the ambient pressure during the sounding, α_{O3} may possibly change during a flight. This, however, is not the case. Although, evaporation lowers the amount of liquid for uptake of gaseous ozone, α_{O3} is not significantly affected [e.g. *Komhyr,* 1971, *Davies et al.*, 2003]. At higher altitudes this uptake is getting very efficient due to much faster mass transfer (i.e.faster diffusion) at lower pressures. Thus α_{O3} stays at 1.00, with an uncertainty of less than 2 % throughout the entire profile. This is indeed the case for sonde sensors which are charged with 3.0 cm^3 of cathode sensing solution. The only exception is for ECC-sensors which have been charged with 2.5 cm^3**.** In this case only ~96% of the ozone is captured by the sensing solution at 1000 hPa ground pressure [Davies et al., 2003]. Davies also showed that at lower pressures the 4% deficit vanishishes rapidly (faster gas-diffusion) such that at pressures below 100 hPa α_{O3} equals to 1.00 (Figure 3).

Recommendations:

1.) *For 2.5 cm^3 cathode sensing solution the absorption efficiency should be processed by :*

[Eq.6A] $\alpha_{O3}(P_{Air}) = 1.0044 - 4.4x10^{-5} P_{Air}$ *at 100 hPa <P_{Air} < 1050 hPa*

[Eq.6B] $\alpha_{O3}(P_{Air}) = 1.00$ *at $P_{Air} \leq 100$ hPa*

2.) *For 3.0 cm^3 cathode sensing solution absorption efficiency is one for all pressures:*

[Eq.6C] $\alpha_{O3}(P_{Air}) = 1.00$ *at all* $P_{Air} < 1050$ *hPa*

3.) The uncertainty of α_{O3} *is estimated to be approximately ±0.01 throughout the entire profile for both volumes of cathode sensing solution used.*

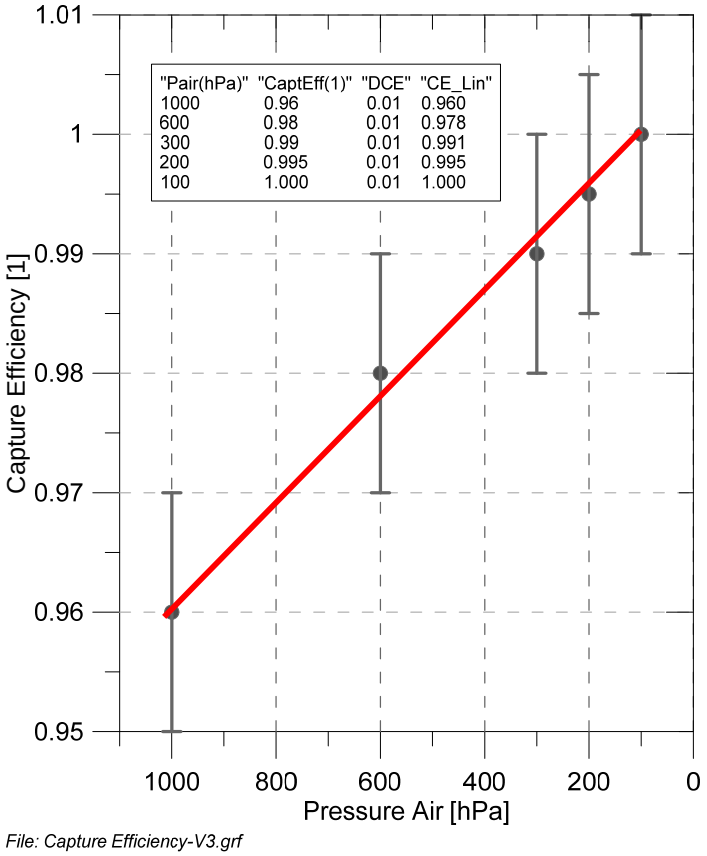


Figure 3: *Absorption efficiency (Gaseous into Liquid) of ozone for ECC O3 Sonde for* V_{ECC}*=2.5 cm*^{3} *compared to* V_{ECC}*=3.0 cm*^{3} *cathode sensing solution (after Davies et al. 2003)*

8.1.2 Stoichiometry of the conversion of O_3 into I_2 ($S_{O3/I2}$) : Impact of different sensing solution types→ Transfer functions for SPC6A-ENSCI-SST1% and SST0.5%

Different compositions of sensing solutions (e.g. ECC-sonde: SST1.0 or STT0.5) in cathode cell or different ozone sensor types (e.g. ECC-sonde: SPC-6A or ENSCI-Z) can have stoichiometry factors slightly different from one. These deviations from 1 may also increase through a sounding due to evaporation of water from the sensing solution, causing an increase of solution strength. For this O3S-DQA activity these deviations of the stoichiometry factor from one at different SST's and/or ECC-sonde types will be corrected by the use of so called transfer functions.

Transfer functions for SPC6A-ENSCI-SST1% and SST0.5%

Rationale:
One of the goals of earlier ozone sonde inter comparisons was to compare ozone sensitivity of the two types of ozonesondes, Science Pump Corporation (SPC) and ENSCI, and the two KI solution strengths in wide use, 1.0% and 0.5%. This was done in the laboratory with the JOSIE experiments (Smit et al., 2007), field experiments using dual sonde and multiple ozonesonde payloads (Kivi et al., 2007) and in the BESOS multi-sonde photometer inter comparison flight (Deshler et al., 2008). To account for differences in solution strength and sonde type, Kivi et al. proposed altitude dependent transfer functions based on dual sonde flights, while Deshler et al. proposed pressure dependent transfer functions from the BESOS multi-sonde flight. Since the BESOS flight there have been additional laboratory comparisons and dual flight measurements by several investigators (Stuebi et al., 2008; Mercer et al., 2008), with consequent alternate suggestions of transfer functions. With this subsequent work it is clear that there have been enough dual ozone sonde comparisons to formulate reasonable transfer functions which can apply across all these comparisons.

This final analysis of the dual ozone sonde data focused on the two primary WMO SOP recommendations of SPC 1.0% or ENSCI 0.5%. Comparison sonde profiles used in the analysis are from the laboratory (JOSIE 2009), mid latidue multi-sonde flights (BESOS and NOAA), mid latitude dual-sonde (Payerne and Wallops Island) and polar dual-sonde (Sodankyla and McMurdo Station). The data were compared using scatter plots, with a simple ratio fit to measurements at pressures > 30 hPa and ozone > 0.5 mPa. Including ozone less than 0.5 mPa increased the uncertainty of the comparisons considerably, the usual result of comparing small numbers, but does not change the average ratios substantially. At pressures < 30 hPa the relationship has some pressure dependence, but can be reasonably approximated by a linear equation in $\log_{10}$(pressure, in hPa). The results from all data sets are reasonably consistent across the different platforms, sensing solutions, and locations. The relationships are summarized in the following table. The standard deviation of these ratios is ± 0.05, if the very low ozone values at low altitudes are removed.

The results are that the dependent sonde measurements, the measurements desired, can be obtained from the independent sonde measurements by a simple multiplication, using the Ratio. Thus ozone partial pressure for the sonde type and SST desired = Ratio(p) • partial pressure measurements from the sonde type and SST used. Figure 4 displays the relationships in Table 3 and their comparison with the Payerne and BESOS flights for the ratio ENSCI0.5% to ENSCI1.0%, and with Josie 2009 and Sodankyla data for SPC1.0% to ENSCI1.0%.

This analysis will be soon be extended by a scientific paper, being led by Rene Stübi and Terry Deshler. For the interested reader detailed graphs of different comparisons are documented in Annex I (not included here).

Table 3: *Recommended relationships for conversion from SST1% to SST0.5% for both SPC6A and ENSCI and to convert from ENSCI to SPC6A for both SST1% and SST0.5%.*

Equation	***Y dependent =***	***Ratio***	***X independent***	***Pressure***	***Ozone sonde or SST***
Eq.7A	SST 0.5%	0.96	SST 1.0%	P ≥ 30 hPa	Both SPC & ENSCI
Eq.7B	SST 0.5%	$0.90+0.041*\log_{10}(p)$	SST 1.0%	P < 30 hPa	Both SPC & ENSCI
Eq.7C	SPC	0.96	ENSCI	P ≥ 50 hPa	0.5% & 1.0%
Eq.7D	SPC	$0.764+0.133*\log_{10}(p)$	ENSCI	P < 50 hPa	0.5% & 1.0%
Eq.7E	SPC-1.0%	1.01	ENSCI-0.5%	P??	

<u>Recommendations:</u>

1) *Stations should reprocess their O3S-data corresponding to the WMO SOP guide lines on use of either SPC 1.0% or ENSCI 0.5%.*
2) *If the only change in a data record is from one of the WMO SOP recommendations to the other, then no transfer function needs be applied. The ratio of SPC 1.0% to ENSCI 0.5% is 1.0 to within 1.0%.*
3) *If there were changes for a period of time using either ENSCI 1.0% or SPC 0.5% sondes, then the long term record should be corrected to one of the two WMO standards, using the ratios provided in the table above. Typically, if a station switched from SPC to ENSCI they may have used ENSCI 1.0% for a period of time before the 0.5% SST was recommended. They then have the option of modifying their data to ENSCI 0.5% or SPC 1.0% using the table above.*
4) *For the sonde homogenization program, the recommendation is to use the simplest approach to homogenize the data to one of the two standards. For example, if measurements are made using ENSCI, 1.0% KI, then modify the measurements to ENSCI 0.5% by multiplying the ozone partial pressure measurements by m=0.96 for p > 30 hPa, and by $m=0.90 + 0.041*\log_{10}(p)$, for p < 30 hPa; or to SPC 1.0% using m=0.96 for p > 30 hPa, and by $m=0.764 + 0.1332*\log_{10}(p)$, for p < 30 hPa.*
5) *When the partial pressure measurements are modified an additional uncertainty of 0.05 that corresponds to $\Delta S_{O3/I2}$, the uncertainty of the stoichiometry $S_{O3/I2}$ in equation Eq.5. and must be added to the formula describing the uncertainty of the measurements, to account for the uncertainty in the dual sonde comparisons.*
6) *Stations which used SSTs outside of 0.5% and 1.0%, should develop and document their own transfer functions to provide a sonde and solution strength independent record for the long term stations.*

References

Deshler, T., J. M. Mercer, H. G.J. Smit, R. Stuebi, G. Levrat, B. J. Johnson, S. J. Oltmans, R. Kivi, A. M. Thompson, J. Witte, J. Davies, F. J. Schmidlin, G. Brothers, T. Sasaki, Atmospheric comparison of electrochemical cell ozonesondes from different manufacturers, and with different cathode solution strengths: The Balloon Experiment on Standards for Ozonesondes, *J. Geophys. Res.*, *113*, D04307, doi:10.1029/2007JD008975, 2008.

Kivi, R., E. Kyrö, T. Turunen, N. R. P. Harris, P. von der Gathen, M. Rex, S. B. Andersen, and I. Wohltmann (2007), Ozonesonde observations in the Arctic during 1989–2003: Ozone variability and trends in the lower stratosphere and free troposphere, J. Geophys. Res., 112, D08306, doi:10.1029/2006JD007271.

Mercer J., et al., Atmospheric comparisons of electrochemical cell ozonesondes with different cathode solution strengths and from different manufacturers: A method to homogenize 0.5% and 1.0% KI measurements, *European Geophysical Union*, Vienna, Austria, April, 2008.

Smit, H.G.J., W. Straeter, B. Johnson, S. Oltmans, J. Davies, D.W. Tarasick, B. Hoegger, R. Stubi, F. Schmidlin, T. Northam, A. Thompson, J. Witte, I. Boyd, F. Posny (2007),, Assessment of the performance of ECCozonesondes under quasi-flight conditions in the environmental simulation chamber: Insights from the Juelich Ozone Sonde Intercomparison Experiment (JOSIE), J. Geophys. Res., 112, D19306, doi:10.1029/2006JD007308.

Stuebi R., Levrat G.. Mercer J., Deshler T., Davis J., Johnson B., Oltmans S., Kivi R., Kiro E., Schmidlin F., Analysis of ECC dual flights at various sites: transfer functions for correcting KI concentrations and sonde manufacturers influences, *Quadrenniel Ozone Symposium*, Tromso, Norway, July 2008.

Deshler, T., J. M. Mercer, H. G.J. Smit, R. Stuebi, G. Levrat, B. J. Johnson, S. J. Oltmans, R. Kivi, A. M. Thompson, J. Witte, J. Davies, F. J. Schmidlin, G. Brothers, T. Sasaki, Atmospheric comparison of electrochemical cell ozonesondes from different manufacturers, and with different cathode solution strengths: The Balloon Experiment on Standards for Ozonesondes, *J. Geophys. Res.*, *113*, D04307, doi:10.1029/2007JD008975, 2008.

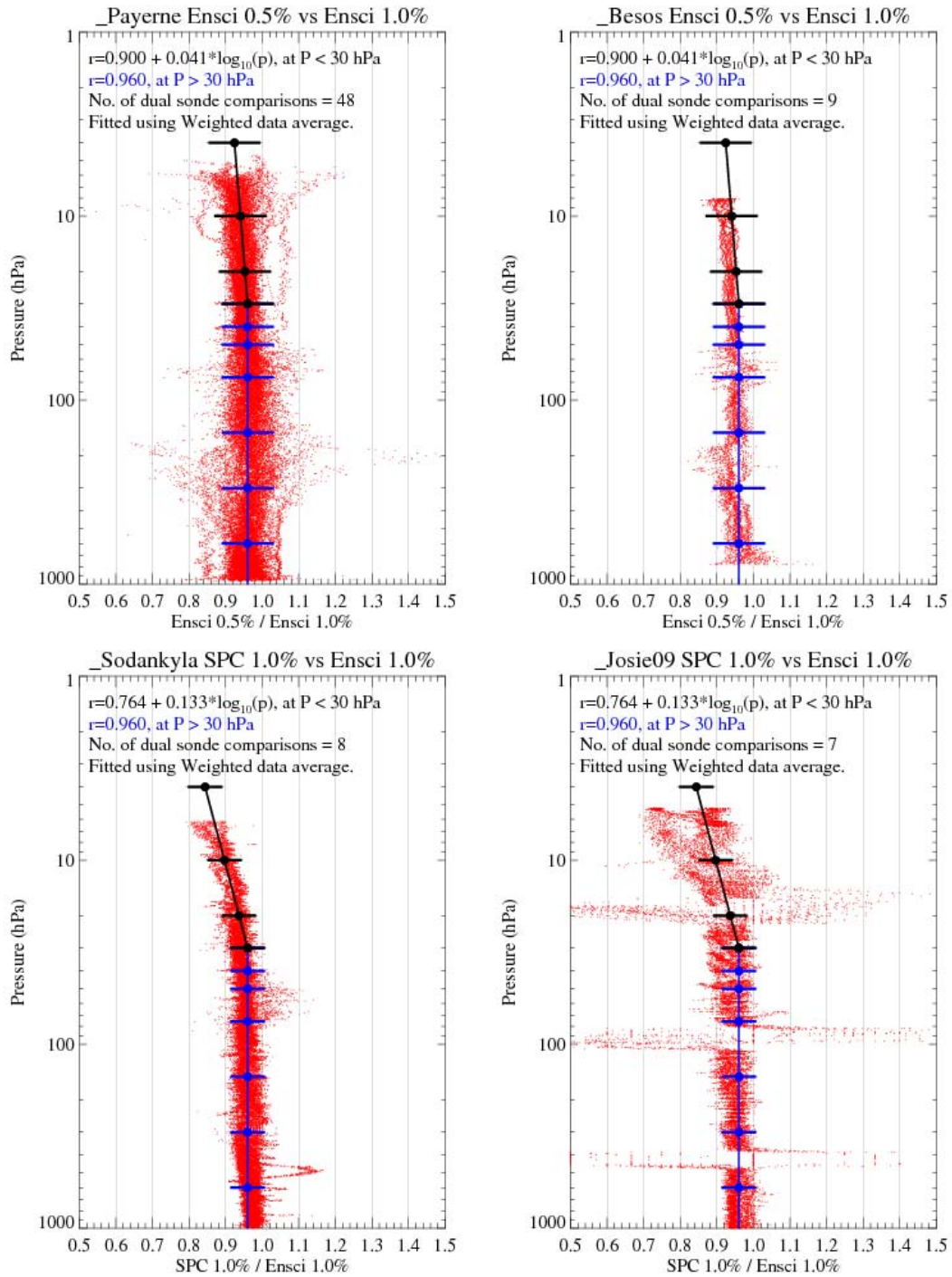


Figure 4: *Graphical display of the relationships in Table 3 and their comparison with the Payerne and BESOS flights for the ratio ENSCI0.5% to ENSCI1.0%, and with Josie 2009 and Sodankyla data for SPC1.0% to ENSCI1.0%*

8.2. Corrections of the Background Current

Rationale:
The origin of the background current of the ECC-sonde is not well understood [*Voemel and Diaz*, 2010]. In literature several sources are mentioned. *Komhyr* [1969, 1986] assumed the background current if primarily caused by oxygen and thus would decline with ambient air (i.e. oxygen) pressure and thus be pressure dependent; however, *Thornton and Niazy* [1982] and other investigators have shown that the background current is independent of oxygen. Since the mid 1970' the electrode in the cathode cell has been preconditioned by the manufacturer in such a way that oxygen interferences can be excluded. *Thornton and Niazy* [1982, 1983] suggested that the source of the background current is the reduction of tri-iodide normally present in the cathode solution. They explained time variations in the background current by the slow rates of solution mass transport and of heterogeneous electron transfer for tr-iodide. *Thornton and Niazy* [1983] found a pressure dependent factor in the background current below 30 hPa but its impact on the O3S measurements in the middle stratosphere is rather small.

At tropical (and perhaps other locations with high atmospheric moisture) background measurements using the standard ozone destruction filter to produce ozone free air may give very unrepresentative results (high backgrounds). It is postulated that moisture deactivates the ozone destroying sites in the "charcoal based – Hopcolite?" filter. In the period ~1980-1990 measured backgrounds at tropical sites fall in the range 0.1-0.7 microamperes at sites such as Hilo and Samoa. After 1990 backgrounds are systematically lower but still may have been improperly measured when using the standard ozone destruction filter. In background current measurements made at Juelich with purified zero air, a definite change in the background current characteristics of the SPC 5A were noted beginning in 1990. Earlier results gave background currents after exposure to ozone generally in the range 0.15-0.25 microamperes. Measurements made in 1990 and later gave values generally in the range 0.06-0.10 microamperes. Properly measured background currents measured since the mid 1990s from both Ensci and SPC are generally very low less than 0.05 microamperes. (See also *Tables 4 & 5 and Figures 5 & 6).*

The treatment of background current and its changes with time will have an impact particularly on tropospheric ozone amounts. This could be a particular problem in the tropics where tropospheric ozone levels are often lower, and problems with the standard ozone filter (also used in various test units) are largest.

Impacts on ozone in the stratosphere may arise from assuming an oxygen dependent background as done by some standard commercial processing routines. Until relatively recently many of the ozone processing routines used a "pressure declining background" formulation that essentially reduced the background to zero in the stratosphere.

ECC-Sonde Type		ENSCI-Z		SPC-6A	
JOSIE	Sensing Solution Type	Background Current Before O_3-Exposure [µA]	Background Current After O_3-Exposure [µA]	Background Current Before O_3-Exposure [µA]	Background Current After O_3-Exposure [µA]
1996	SST1.0	0.05±0.01	0.07±0.02	0.02±0.01	0.07±0.01
1998	SST1.0	0.05±0.02	0.11±0.03	0.03±0.02	0.11±0.01
2000	SST1.0	0.02±0.03	0.06±0.05	0.02±0.01	0.05±0.02
2000	SST0.5	0.02±0.02	0.05±0.02	0.00±0.01	0.03±0.02
2000	SST2.0	0.02±0.02	0.06±0.03	0.02±0.01	0.05±0.03
BESOS 2004	SST1.0	0.00-0.02	0.05-0.06	0.00-0.01	0.04-0.07
BESOS 2004	SST0.5	0.00-0.01	0.02-0.03	-0.02-0.02	0.01-0.02
2009	SST1.0	0.02±0.01	0.05±0.01	0.01±0.01	0.04±0.01
2009	SST0.5	0.02±0.01	0.04±0.01	0.01±0.01	0.03±0.01
2010	SST1.0	0.02±0.01	0.04±0.02	0.00±0.02	0.04±0.01
2010	SST0.5	0.01±0.01	0.02±0.01	0.00±0.03	0.03±0.01

Table 4 *Survey of average background current (±1σ) before and after exposure of ozone obtained during pre-flight preparations of ECC-sondes "flown" during JOSIE 1996, 1998 and 2000 [Smit et al., 2007], BESOS 2004 [Deshler et al., 2008], JOSIE 2009 & 2010.. The background currents were recorded before and after pumping for 10 minutes air with ozone (150-200 ppbv) through the sensor whereby each time before the background current was measured the sensor was flushed for ten minutes with ozone free air (purified air).*

Sation/Year(s)	ECC-Type/SST1	Background Current Before O_3-Exposure [µA]	Background Current After O_3-Exposure [µA]
FZJ/1987	SPC5A/SST1.0 Simple Filter/Dry Lab@20C	0.07±0.03	0.09±0.03
FZJ/1988	SPC5A/SST1.0 Purified Air	0.06±0.02	0.09±0.02
FZJ/1989	SPC5A/SST1.0 Purified Air		0.09±0.05
FZJ/1990	SPC5A/SST1.0 Purified Air		0.09±0.02
FZJ/1991	SPC5A/SST1.0 Purified Air		0.04±0.03
Nairobi/1997-2011	ENSCI-Z/ SST1.0&SST0.5 Purified Air		0.05±0.02

Table 5 *Survey of average background current (±1σ) before and after exposure of ozone obtained during pre-flight preparations of ECC-sondes launched at different stations.*
Note: In 1991 a sudden decrease of the back ground currents had been identified. In the 1990's a similar decrease had been observed at other stations and since 2000 even small negative values between 0 and about -0.03µA have been observed.

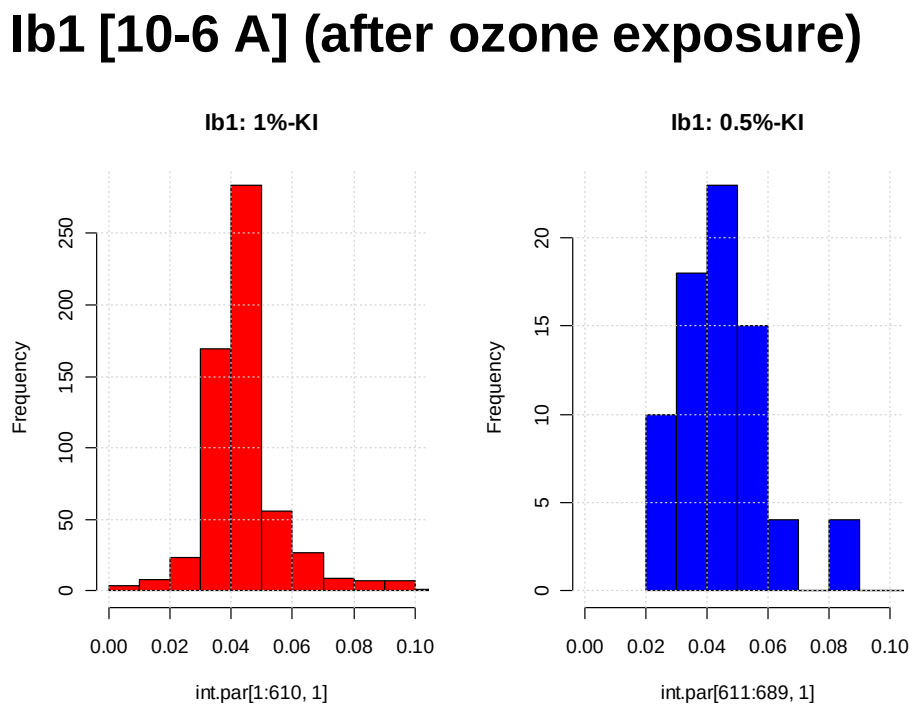


Figure 5: *Background current distributions for ENSCI-Z at SST1.0% and SST0.5% obtained between 1997 and 2011 using purified air.*

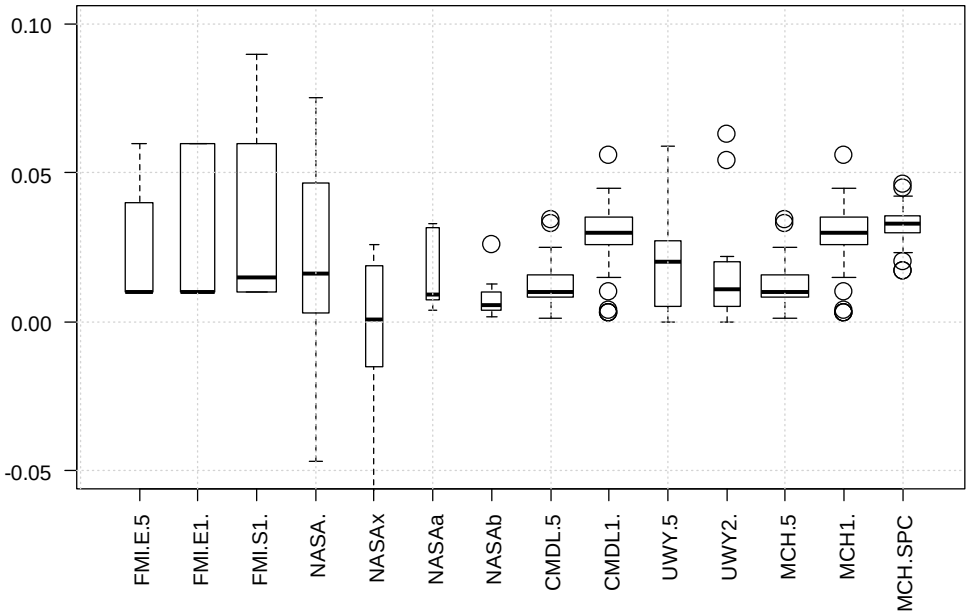


Figure 6*: Background currents at different sites obtained during dual soundings (not clear puerified or filtered air). Source: Rene Stuebi.*
(Presentation made at O3S-DQA/Boulder-USA in October 2011.

Recommendation:

1. *With properly measured backgrounds, the current standard operating procedure of subtracting the full background current from the measured ozone current should be followed. For all ECC-sondes flown, at least since 1975, there is no oxygen (i.e. pressure) dependence of the background current such that a constant background current correction throughout the entire vertical O3S-profile should be applied.*
2. *Unrealistic high background currents may be caused by a small leackage of anode cell solution through the ion bridge. However, from stations using purified air it has been clearly shown that this only happens very incidentally (<1-2 times per year). Impurities of chemicals or distilled water may also cause larger background currents but then in most cases the sonde would also show a bad time response, Usually those sondes would not have passed the time response test of the pre-filght preparation.*
3. *Where "unrealistic" backgrounds were measured during a portion of the record, an average correction should be applied for reprocessing the data. This average correction can be determined by inspecting measured backgrounds and determining a lower envelope of the measurements. Or if more representative background measurements have been made during a portion of the record this may suggest an average background to be used in reprocessing the periods to be corrected. The background ranges suggested in the discussion above can be used as a guideline for determining the corrected background current.*

   General guidelines to obtain proper backround current $\boldsymbol{I_B}$ *for unrealistic values:*

   A. *Stations using purified air:* $\boldsymbol{I_B}$*-climatology delivers a range of representative* $\boldsymbol{I_{B,Mean} \pm \sigma_{IB}}$
   B. *Stations using simple ozone destruction filters: If station* I_B *exceed* $\boldsymbol{I_{B,Mean} + 2\sigma IB}$ *then* $\boldsymbol{I_B}$ *should be replaced by the more representative climatological value of* $\boldsymbol{I_{B,Mean}}$ *, however with larger uncertainty* $\boldsymbol{2\sigma_{IB}}$
4. *It is important that the contribution of the selected background correction to the overall uncertainty of the measured ozone concentration be estimated based on experimental evidence*

References

Reid S.J., G. Vaughan, A.R. Marsh, and H.G.J. Smit (1996), Intercomparison of ozone measurements by ECC sondes and BENDIX chemiluminescent analyser, J. Atm. Chem., 25, 215-226.

Smit, H.G.J., W. Sträter, D. Kley, and M.H. Profitt (1994), The evaluation of ECC-ozonesondes under quasi flight conditions in the environmental simulation chamber at Jülich, in *Proceedings of Eurotrac symposium 1994,* edited by P.M. Borell et al., SPB Academic Publishing bv, The Hague, The Netherlands, 349-353.

Thornton, D.C., and N. Niazy (1982), Sources of background current in the ECC-ozonesonde: Implication for total ozone measurements, J. Geophys. Res., 87, 8943-8950.

Thornton, D.C. and N. Niazy (1983), Effects of solution mass transport on the ECC ozonesonde background current, Geophys.Res.Lett. 10, 148-151.

Voemel, H., K. Diaz (2010) Ozone sonde cell current measurements and implications for observations of near-zero ozone concentrations in the tropical upper troposphere, Atmos.Meas.Tech., 3, 495-505, doi:10.5194/amt-3-495-2010, http://www.atmos-meas-tech.net/3/495/2010/,

8.3 Pump Temperature Measurement

Rationale:

The measurement of pump temperature is required to properly account for the amount of air passing through the pump into the ECC sensor cell. The "truest" pump temperature (applied in formula Eq.1) should be inside the volume of the cylindrical housing of the moving piston of the pump. However, for technical reasons the pump temperatures have been measured at other locations: inside the pump base, outside at the surface of the pump base or as close as possible to the pump base. During more then four decades of ozone soundings the locations of the pump temperature measurements have been changed several times, introducing inhomogenities in the ozone sounding record. Basically 5 different cases of pump temperature measurements have been identified and characterized.

Case I: Box temperature measurements by thermal rod in analog sounding systems:

In the 1960s to the end of the 1980s, in the initial configuration of the ECC ozonesonde, flown with analog radiosonde and paper chart recording system, the box temperature ($T_{P,Box}$) was measured in lieu of the pump base temperature ($T_{P,Base}$). This was a standardized system with the rod thermistor mounted at the bottom of the electronics circuit board near the base of the ozonesonde housing. This arrangement, which has been used for ECC-2A, ECC-3A and ECC-4A sonde types, appears to have produced a consistent relationship between the "box" temperature ($T_{P,Box}$) and the pump base (body) temperature ($T_{P,Base}$) [Komhyr and Harris, 1971] as shown in Figure 7.

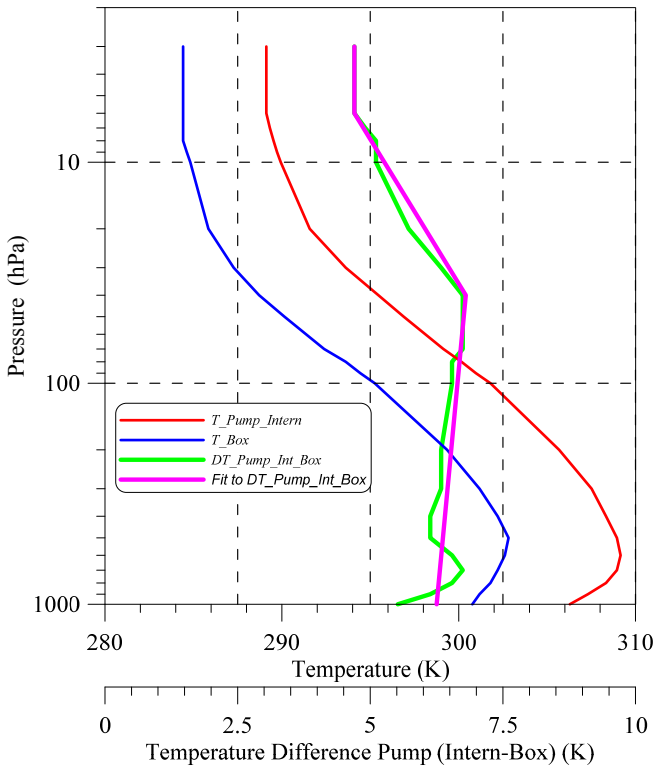


Figure 7: *Relation box temperature ($T_{P,Box}$) and internal pump temperature ($T_{P,Base}$) of ECC-2A, ECC-3A, and ECC-4A ozone sonde types manufactured in 1970's and 1980's. [Source: Komhyr and Harris, 1971]*

The difference between $T_{P,Box}$ and $T_{P,Base}$ can be approximated as a function of ambient air pressure by:

[Eq.8A] $T_{P,Base} - T_{P,Box} = \Delta T_{PBB}(P_{Air}) = 7.43 - 0.393 Log_{10}(P_{Air})$ *at* $P_{Air} \geq$ *40 hPa*

[Eq.8B] $T_{P,Base} - T_{P,Box} = \Delta T_{PBB}(P_{Air}) = 2.7 + 2.6 Log_{10}(P_{Air})$ $6 < P_{Air} <$ *40 hPa*

[Eq.8C] $T_{P,Base} - T_{P,Box} = \Delta T_{PBB}(P_{Air}) = 4.5$ *at* $P_{Air} \leq$ *6 hPa*

Th uncertainty of this approximation is assumed to be ±1 K

Case II: Box temperature measurements by thermistor in digital sounding systems:

Beginning with the use of digital ozonesonde electronics in ~1990, the capability of measuring the temperature of the pump directly, and thus the temperature of the air flowing through the pump, was possible. In some of the early implementations of digital ozonesondes, the measurement of "box" temperature was continued based on adopting portions of the procedures in the instructions for analog ozonesondes. In this configuration the thermistor was suspended in the ozonesonde Styrofoam box in the vicinity of the pump (See Vaisala preparation guidelines recommended between 1988 and 1996). If Vaisala (or Science Pump Corporation) guidelines have been strictly followed then the relation of box temperature and internal pump temperature is approximately very similar to Case III (see below) of a taped thermistor at the pump base- However, incidentally the placement of the thermistor has not always been positioned consistently at the same location near the pump base such that the relationship between this "box" temperature and the internal pump temperature could be variable and here the coaches have to find the best compromise.

Case III: External pump (taped thermistors) temperature measurements in digital sounding systems:

Experiments done during JOSIE-2000 demonstrate that for a thermistor mounted on or within the pump base, good thermal contact is required. A thermistor taped at the surface of the pump body measuring the external pump temperature ($T_{P,Ext}$) deviates significantly from a thermistor mounted within the pump base that measures the internal pump temperature ($T_{P,Int}$). Figure 8 shows the typical evolution of the internal and external (taped) pump temperature as a function of pressure [Smit et al., 2007]. Because of frictional heating of the moving piston of the pump the internal temperature within the pump base is higher than the external pump temperature. At the start of the simulations the differences were between 0.5 and 2 Kelvin, increasing to ~7-10 K at 50 hPa pressure and then slightly decreasing towards lower pressures. Similar observations of internal and external pump temperatures have been made by O'Connor et al. [1998] during a series of ozone soundings in the field. In Sodankylä (Finland) a series of multi-thermistor flights were made. The flights showed that under Arctic wintertime conditions large differences can be observed depending on the placement of the thermistor. [Kivi et al, 2007]. The results (incl. pressure behaviour) and are very similar to the JOSIE 2000 results [Smit et al., 2007].

Based on the JOSIE 2000 results the relation of the difference between internal and external pump temperature has been fitted as a function of pressure:

[Eq.9A] $T_{P,Int} - T_{P,Ext} = \Delta T_{PIE}(P_{Air}) = 20.6 - 6.7 Log_{10}(P_{Air})$ *at* $P_{Air} >$ *70 hPa*

[Eq.9B] $T_{P,Int} - T_{P,Ext} = \Delta T_{PIE}(P_{Air}) = 8.25$ *at* $15 \leq P_{Air} \leq$ *70 hPa*

[Eq.9C] $T_{P,Int} - T_{P,Ext} = \Delta T_{PIE}(P_{Air}) = 3.25 - 4.25 Log_{10}(P_{Air})$ *at* $5 \leq P_{Air} <$ *15hPa*

The corresponding uncertainty of ΔT_{IE} is expressed as:

[Eq.10A] $\delta_{\Delta T_{PIE}}(P_{Air}) = 3.9 - 1.13 Log_{10}(P_{Air})$ *at* $P_{Air} >$ *70 hPa*

[Eq.10B] $\delta_{\Delta T_{PIE}}(P_{Air}) = 0.3 + 1.13 Log_{10}(P_{Air})$ *at* $P_{Air} \leq$ *70 hPa*

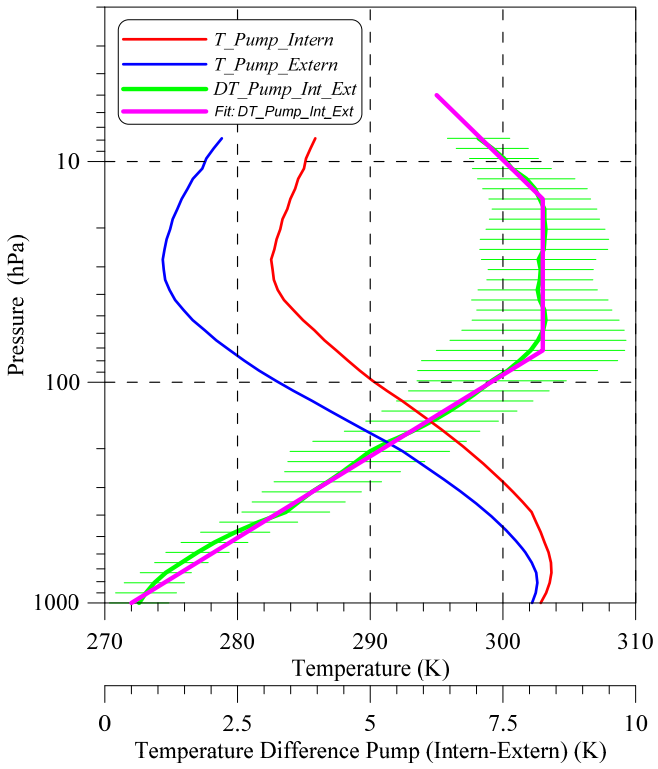


Figure 8: *Internal and external (taped) pump temperature and their relative differences as a function of pressure obtained from combined internal and external temperature measurements over an ensemble of 8 ECC sondes (3 ENSCI-Z and 5 SPC-6A) tested during JOSIE 2000 [Smit et al., 2007].*

Case IV: External pump (epoxied/glued thermistors) temperature measurements in digital sounding systems:

In the 1990's at several ozonesonde sites the thermistor was expoxied (glued) at the surface of the pump base. This configuration was used for example at NOAA for a limited period of time. Pump temperatures during the period when this configuration was used were compared to the current configuration as well as with the analog box temperature measurement. The expoxied thermistors appear to perform more like the box temperature in the analog ozonesondes. This configuration does not seem to be a direct measurement of the pump temperature as is the case when the thermistor is mounted within the block. Evidently the thermal contact with block for the expoxied thermistor is not that good and the thermistor is measuring something closer to the box temperature albeit in a consistent way. The behaviour of the temperature difference between the internal pump base and the thermistor glued on the surface of the pump base have been investigated as a function of pressure in the ozone sonde simulation chamber at WCCOS (Juelich, Germany). Results are shown in Figure 9 for three ozone sonde simulation experiments (2x tropical and 1x mid latitude ambient air pressure and temperature profiles).

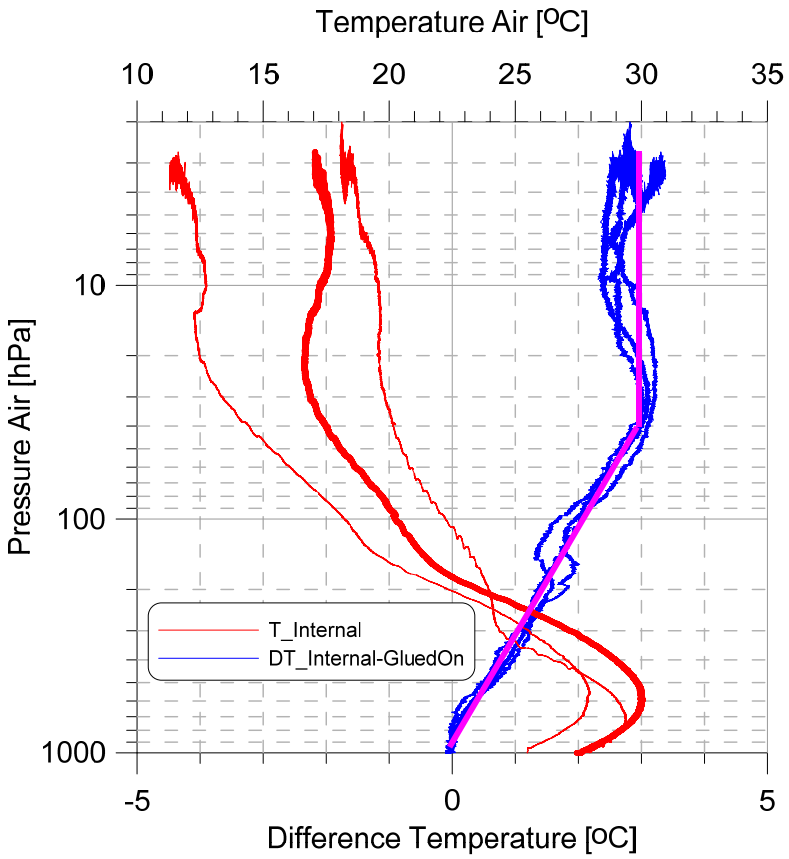


Figure 9: *Temperature measurements made at different locations of the ECC-pump: Internal pump base temperature ($T_{P,Int}$), temperature difference between internal pump base ($T_{P,Int}$) and the thermistor epoxied (glued) on the surface of the pump base. Measurements were made in the simulation chamber at WCCOS during three ozone sonde simulation experiments (2x tropical and 1x mid-latitude pressure and temperature profiles)*

The pressure dependence of the temperature difference between the internal pump base and the epoxied thermistor can be approximated by:

[Eq.11A] $$T_{P,Int} - T_{P,Glued} = \Delta T_{PIG}(P_{Air}) = 6.4 - 2.14 Log_{10}(P_{Air}) \qquad at\ P_{Air} > 40\ hPa$$

[Eq.11B] $$T_{P,Int} - T_{P,Glued} = \Delta T_{PIG}(P_{Air}) = 3.0 \qquad at\ 3 \le P_{Air} \le 40\ hPa$$

The uncertainty of this parametrization is estimated to be ±0.5 K.

Case V: Internal pump (thermistors inside pump base) temperature measurements in digital sounding systems:

Beginning with the introduction of the Ensci Z sonde in 1995 a thermistor was mounted in a hole drilled in the pump body. This was a year later in 1996 adopted by SPC in the 6A model of the sonde. Currently all implementations of the ozonesonde measure the pump temperature.

Truest pump temperature

As mentioned before the best, "truest", pump temperature that should be applied in formula Eq.1 is the actual temperature inside the cylindrical housing of the moving piston of the pump. Laboratory measurements made in the simulation chamber at WCCOS have shown that the so called piston temperature is about 1-3 K larger than the internal pump base temperature depending on the pressure (See Figure 10). This means that to obtain the "best" pump temperature the internal pump base temperature have to be corrected by this temperature difference ΔT_{PI} as a function of ambient air pressure by:

$$[Eq.12] \qquad T_{P,Piston} - T_{P,Int} = \Delta T_{PPI}(P_{Air}) = 3.90 - 0.80 Log_{10}(P_{Air}) \qquad at\ P_{Air} > 3\ hPa$$

Uncertainty of this correction is estimated to be about ±0.5 K

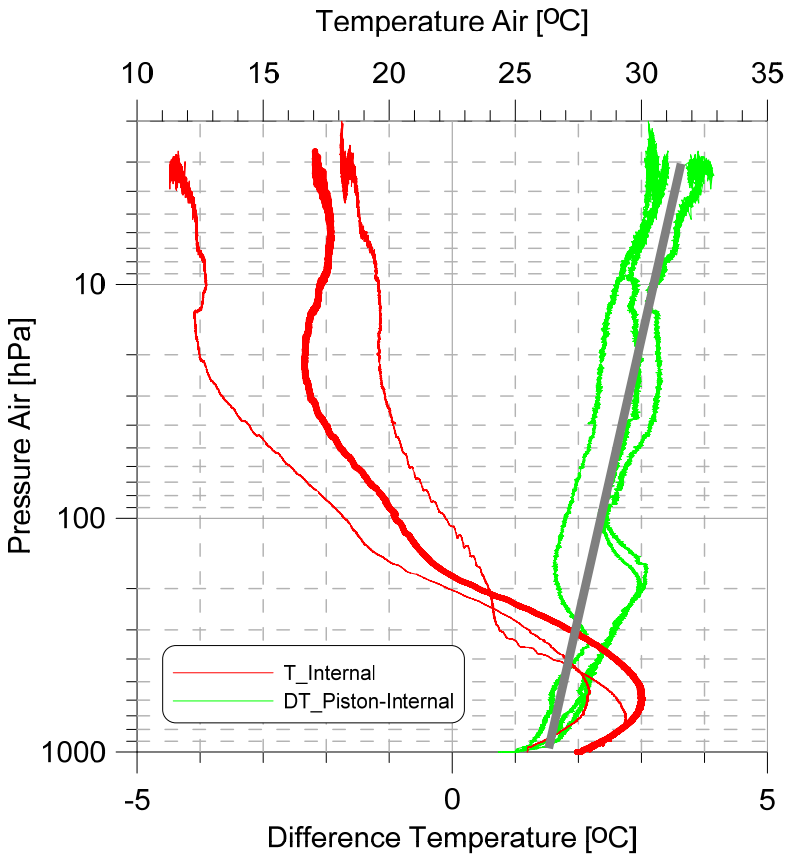


Figure 10: *Temperature measurements made at different locations of the ECC-pump: Internal pump base temperature ($T_{P,Int}$), and difference of the temperature inside the cylindrical chamber of the moving piston (TP,Piston) with the internal pump base temperature ($T_{P,Int}$). Measurements were made in the simulation chamber at WCCOS during three three ozone sonde simulation experiments (2x tropical and 1x mid-latitude pressure and temperature profiles)*

Recommendations:

The "truest" pump temperature T_P to be applied in formula Eq.1 is described as:

[Eq.13] $$T_P = T_{P,Truest} = T_{P,Measured} + \Delta T_{PC}(P_{Air}) + \Delta T_{PPI}(P_{Air})$$

Whereby the uncertainty of "truest" pump temperature T_P is composed as follows:

[Eq.14] $$\left(\frac{\Delta \mathbf{T_P}}{\mathbf{T_P}}\right)^2 = \left(\frac{\Delta \mathbf{T_{P,Measured}}}{\mathbf{T_{P,Measured}}}\right)^2 + \left(\frac{\delta(\Delta \mathbf{T_{PC}})}{\mathbf{T_{P,Measured}}}\right)^2 + \left(\frac{\delta(\Delta \mathbf{T_{PPI}})}{\mathbf{T_{P,Measured}}}\right)^2$$

A.) $T_{P,Measured}$ is the temperature as measured (recorded) by the sounding system. The uncertainty of this measurement depends on the type of temperature sensor and sounding system used. In general, it is assumed that for the "analog" sounding systems (Case I) the uncertainty is ~±1.0 K, while for the modern (digital) sounding systems (Cases II-V) the uncertainty is ~±0.5 K.

B.) $\Delta T_C(P_{Air})$ is the correction to obtain the internal pump base temperature from the measured temperature as characterized by the five cases I-V as described before.

Case I *Box temperature in analog sounding systems*:

$\Delta T_C(P_{Air}) = \Delta T_{PBB}(P_{Air})$ [see Eq.8]

Uncertainty $\delta(\Delta T_{PBB}) = \pm 1.0$K

Case II & III: *Box or taped temperature measurements by thermistor in digital sounding systems*

$\Delta T_C(P_{Air}) = \Delta T_{PIE}(P_{Air})$ [seeEq.9]

Uncertainty $\delta(\Delta T_{PIE})$ described by [see Eq.10]

Case IV: *External pump (epoxied/glued thermistors) temperature measurements in digital sounding systems:*

$\Delta T_C(P_{Air}) = \Delta T_{PIG}(P_{Air})$ [see Eq.11]

Uncertainty $\delta(\Delta T_{PIG}) = \pm 0.5$K

Case V: *Internal pump (thermistors inside pump base) temperature measurements in digital sounding systems*

No correction: $\Delta T_C = 0$ K & Uncertainty $\delta(\Delta T_C) = 0$ K

C.) $\Delta T_{PPI}(P_{Air})$ is the correction to obtain the "truest" pump piston housing temperature from the internal pump base temperature as given by [Eq.12], whereby uncertainty contribution $\delta(\Delta T_{PPI}) = \pm 0.5$K.

With a correction or no correction, in both cases the contribution to the overall uncertainty should be quantified by a realistic estimate.

References

Kivi, R., E. Kyro, T. Turunen, N. R. P. Harris, P. von der Gathen, M. Rex, S. B. Andersen, and I. Wohltmann (2007), Ozonesonde observations in the Arctic during 1989–2003: Ozone variability and trends in the lower stratosphere and free troposphere, J. Geophys. Res. 112, D08306, doi:10.1029/2006JD007271.

Komhyr, W.D., and T.B. Harris (1971), Development of an ECC-Ozonesonde, NOAA Techn. Rep. ERL 200-APCL 18ARL-149.

O'Connor, F.M., G. Vaughan, Murphy, G. (1998), Box and pump temperature measurements and the possible bias between Science Pump Corporation and ENSCI-type sondes, Polar stratospheric ozone 1997, EC Air Pollution Report 66, 712-15.

Smit, H.G.J., W. Straeter, B. Johnson, S. Oltmans, J. Davies, D.W. Tarasick, B. Hoegger, R. Stubi, F. Schmidlin, T. Northam, A. Thompson, J. Witte, I. Boyd, F. Posny (2007),, Assessment of the performance of ECC ozonesondes under quasi-flight conditions in the environmental simulation chamber: Insights from the Juelich Ozone Sonde Intercomparison Experiment (JOSIE), J. Geophys. Res., 112, D19306, doi:10.1029/2006JD007308.

8.4 Pump Flow Rate at Ground: Corrections for "Humidification Effect" & "Piston Temperature"

Rationale:

The ozonesonde sensor current is directly proportional to the amount of ozone gas bubbled into the cathode sensor solution. An accurate volumetric flow rate from the ozonesonde Teflon pump is thus required to calculate ambient ozone concentration. The ozonesonde pump flow rate is usually measured by a soap film flowmeter. a common direct method to measure gas flow rate in the laboratory. A typical flowmeter consists of a 100 ml graduated cylinder. soap solution and stopwatch. Accuracy and precision depends on a good eye and human response using the stopwatch when tracking the single film bubble moving past the start and stop marks as air is pumped through the calibrated tube. The flow is reported as ml/min or T100 seconds (the time it takes to displace 100 ml of air through the Teflon pump).

The ECC standard operating procedure calls for an average of 5 measurements of flow rate using the soap film flowmeter. after the pump has been running for at least 10 minutes. Precision will usually be better than 1%. The accuracy will also be very good since it is a direct. simple measurement. However. the technique is susceptible to an offset due to the evaporation of the sensor solution or soap bubble solution during the measurement. this is called the 'humidification effect". Laboratory measurements have shown that dry air passing through the cathode cell or the bubble flow meter get very close to saturation (RH=98-100%) [Johnson, private communication].

The SOP [Smit and ASOPOS-panel, GAW-Report#201] gives a correction method for this effect based on relative humidity and air temperature. For example. under typical laboratory conditions with the source air at 25 C and ambient pressure of 960 hPa the humidification correction to flow (ml/min) would range from 0.967 (3.3%) at 0% RH (maximum evaporation) and linearly reach unity (no evaporation) at 100% RH.

It is not clear how many present stations routinely apply this correction. but it is almost certainly not applied to the historical data. which raises the question. Should any corrections be used on ozonesonde data targeted for homogenization? If not corrected this would introduce a bias in the ozone record which should be avoided as much as achievable. However, applying these corrections would require accurate records or good estimates of the temperature and RH during the flow rate measurement. Room temperature and RH are often recorded as part of the SOP, but may not represent the condition of the filtered air sampled by the ozonesonde. Thus ex post facto corrections may introduce new artifacts if not accurately applied or a wrong T and RH are recorded. The exception to this is for sites that have used a zero-dry air source, where RH is known to be near 0%. Then the correction would be based on recorded temperature alone and would be near the maximum of 4% if room temperature is higher than 25C. Therefore it would be helpful to know what air source was used at the sites when measuring the flow rate.

Further, a pump airflow rate measurement bias not generally taken into account stems from a difference in the sonde pump (piston) temperature and the temperature of the room in which the air flowrate mearement instrument is located. At ground for an optimally operating pump the equilibrium pump temperature is about 2K higher than the ambient temperature [*Komhyr et al.*, 1995]. This effect of ~2K has been confirmed by laboratory measurements made at WCCOS at Juelich (Germany). This means that at an ambient room temperature of 290-300 K, the airflow rate through the pump is greater than that measured at room temperature by a factor of approximately 297/295 = 1.007. This means that this would introduce a negative relative bias of about -0.7% in the ozone sonde readings.

Recommendations:

1. It is assumed that the pumpflow rate ($\Phi_{P,Measured}$) at ground can be measured with a relative uncertainty ($\Delta\Phi_{P,Measured}/\Phi_{P,Measured}$) better than ±2%.
2. The corrected pump flowrate ($\Phi_{P,Ground}$) determined at ground is expressed as:

   [Eq.15] $\Phi_{Pump,Ground} = \left[1 + C_{PL} - C_{PH}\right] \bullet \Phi_{P,Measured}$

   whereby the measured pump flowrate should be corrected for:

   a.) The temperature difference between internal pump base temperature (T_{Pump}) and the ambient room temperature (T_{Lab}) of the flowrate measurement (ΔT-effect = 2K): Correction factor C_{PL}, whereby:

   [Eq.16] $C_{PL} = \dfrac{T_{Pump} - T_{Lab}}{T_{Lab}}$, usually ($T_{Pump}$- T_{Lab}) is ~ +2 K with an uncertainty of about ±0.5 K

   b.) The humidification effect: Correction factor C_{PH} expressed as:

   [Eq.17] $C_{PH} = \left[1 - \dfrac{RH_{In}}{100}\right] \bullet \dfrac{P_{H_2O,Sat}(T_{Lab})}{P_{Lab}}$

   whereby RH_{In} is the relative humidity of the sampled air entering the cathode cell, while P_{Lab} and T_{Lab} are the ambient air pressure and temperature in the vicinity of the bubble flow meter, i.e. laboratory or preparation room (P, T, RH) conditions. $P_{H2O,Sat}(T_{Lab})$ is the saturated water vapor pressure at T_{Lab} [K] or t_{Lab} [°C] and there are several empirical formulas, such as by Magnus-Teten [*Murray*, 1967]:

   [Eq.18] $Log_{10}\left(P_{H2O,Sat}\right) = \dfrac{\left(7.5 \bullet t_{Lab}\right)}{\left(t_{Lab} + 237.3\right)} + 0.7858$ *(Note: t_{Lab} in degrees Celsius!!!)*

   See also *Figure 11*

   In case of using dry air then RH_{In}=0 , while in most all other cases when using ozone destroying air filters RH_{In} will be approximately the same as the ambient RH in the laboratory or preparation room, RH_{Lab}. For all remaining cases in which the laboratory (preparation room) conditions of temperature and relative humidity are not well known it should be attempted to determine for both, T_{Lab} and RH_{Lab}, the range of realistic values and determine the range of C_{PH} values and derive/estimate from these values a reasonable average C_{PH} and its uncertainty ΔC_{PH}. The most simple approach could be:

   [Eq.19] $C_{PH,Average} = (C_{PH,High}+C_{PH,Low})/2$ and $\Delta C_{PH} = \pm(C_{PH,High}-C_{PH,Low})/2$
3. The use of uncorrected flow rates increases the overal uncertainty of the O3S-measurement; The potential contribution of the humidification effect to the overall uncertainty of the ozone sonde performance should be quantified by a realistic estimate.
4. To obtain the uncertainty of the corrected pump flowrate determined at ground Consequently the propagation of individual uncertainty contributions can be expressed as:

   [Eq.20] $\dfrac{\Delta\Phi_{P,Ground}}{\Phi_{P,Ground}} = \sqrt{\left(\dfrac{\Delta\Phi_{P,Measured}}{\Phi_{P,Measured}}\right)^2 + \left(\dfrac{\Delta C_{PL}}{1 + C_{PL} - C_{PH}}\right)^2 + \left(\dfrac{\Delta C_{PH}}{1 + C_{PL} - C_{PH}}\right)^2}$

   $C_{PL} << 1$ and $C_{PH} << 1$ such that this simplies into:

$$[Eq.21] \quad \frac{\Delta \Phi_{P,Ground}}{\Phi_{P,Ground}} = \sqrt{\left(\frac{\Delta \Phi_{P,Measured}}{\Phi_{P,Measured}}\right)^2 + (\Delta C_{PL})^2 + (\Delta C_{PH})^2}$$

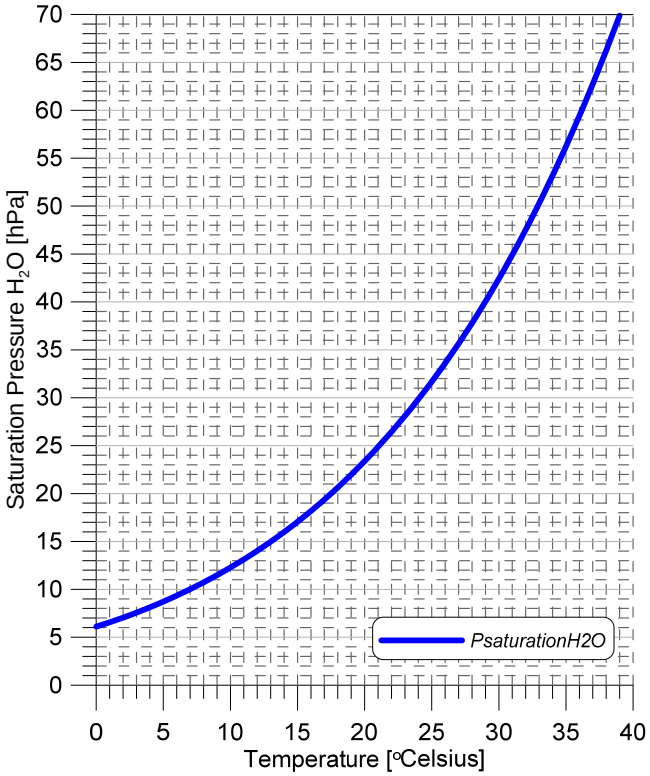


Figure 11: *Saturation pressure of water vapor as function of temperature after the empirical formula by Magnus-Teten [Murray, 1967]*

References

Smit, H.G.J., and ASOPOS-panel, Quality Assurance and Quality Control for Ozonesonde Measurements in GAW,. WMO Global Atmosphere Watch report series, No. 201, World Meteorological Organization, Geneva, 2011. (http://www.wmo.int/pages/prog/arep/gaw/documents/GAW_201_30_Sept.pdf)

8.5 Pump Flow Efficiency at Low Pressures.

Rationale:

At ambient air pressures below 100 hPa the efficiency of the gas sampling pump degrades due to pump leakage, dead volume in the piston of the pump, and the back pressure exerted on the pump by the cell solution [*Komhyr*, 1967, *Steinbrecht et al*., 1998]. This decrease in pump efficiency at reduced pressures is accounted for by applying a pump correction factor C_{PF}, (=1/Pump efficiency) which is a function of ambient air pressure specific for each sonde type:

[Eq.22] $$\Phi_P(P_{Air}) = \frac{\Phi_{P,\,Ground}}{C_{PF}(P_{Air})}$$

Pump flow rates of ECC-sondes, measured at the ground, range between 190 and 230 ml/min. Typical correction factors C_{PF} as a function of ambient pressure for each ozonesonde type are listed in *Table 6*

The correction tables are based on empirical averages obtained from pump flow efficiency measurements made at different air pressures in the laboratory [*SPARC-IOC-GAW,* 1998]. The uncertainty of the correction factors presented increases substantially at pressures below about 20 hPa which can contribute significantly to the overall uncertainty of the sonde performance above 25-30 km altitude. The uncertainty of the pumpflow efficiency is one of the most prominent contributions to the overall uncertainty of the sonde measurements above 25 km altitude.

Pressure [hPa]	ECC *Komhyr,* 1986	ECC *Komhyr et al.,*1995	ECC *Johnson et al.,*2002	BM *Steinbrecht et al.,*1998	KC96 *Kobayashi et al.,*1966
1000<>200	1	1	1	1	1
100	1.007 ± 0.005	1.007 ± 0.005	1.035 ± 0.011	1.027 ± 0.004	1.02
50	1.018 ± 0.006	1.018 ± 0.005	1.052 ± 0.012	1.075 ± 0.006	1.04
30	1.022 ± 0.008	1.029 ± 0.008	1.072 ± 0.015	1.108 ± 0.007	1.07
20	1.032 ± 0.009	1.041 ± 0.012	1.088 ± 0.018	1.150 ± 0.011	1.11
10	1.055 ± 0.010	1.066 ± 0.023	1.145 ± 0.020	1.280 ± 0.020	1.25
7	1.070 ± 0.012	1.087 ± 0.024	1.200 ± 0.025	1.5 ± 0.1	1.40
5	1.092 ± 0.014	1.124 ± 0.024	1.260 ± 0.030	1.8 ± 0.2	1.66
3	1.124 ± 0.025	1.241 ± 0.043	---	---	---

Table 6: *Pump flow correction factors (C_{PF}) as a function of air pressure for (i) ECC-ozone sondes reported by Komhyr. 1986. Komhyr et al.. 1995. and Johnson et al. 2002; (ii) Brewer Mast ozone sonde reported by Steinbrecht et al.. 1998; (iii) Carbon iodine (KC96) ozone sonde [Kobayashi and Toyama. 1966].*

Recommendations:

1. The SOPs (GAW-Report #201) recommends the Komhyr 1986 correction (solution volume 3.0 ml) for Science Pump (SPC6A) sondes. and the Komhyr 1995 curve (solution volume not explicitly defined, most likely also 3.0 ml) for ENSCI (now DMT=Droplet Measurement Technologies) sondes. The two curves differ by about 1% at 10 hPa and 3% at 5 hPa.

2. For SPC-2A&3A&4A&5A) sondes it is recommended Komhyr 1986 also be used. The most recent correction table is actually based on pump flow experiments performed in the mid 1960's (Reference) and most likely the best table to apply.
3. A few stations (e.g. NOAA) in the network are using their own experimentally derived correction table (e.g. Johnson et al.. 2002). For other stations using their own pump correction table. the impact on the homogenization has to be explored by the station PI and the O3S-DQA coach before starting the actual data processing for homogenization.
4. The O3S-DQA process should estimate for each correction table used the contribution to the overall uncertainty as a function of pressure.
5. To obtain C_{PF} values between different pressure levels this should be on Log(P) scale through either linear interpolation or use of polynomials as listed in *Table 7).*
6. *Consequently the propagation of individual uncertainty contributions can be expressed as:*

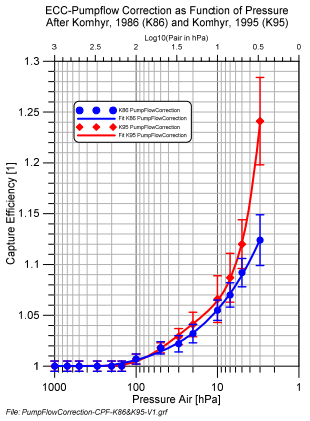
$$[Eq.23]\ \frac{\Delta \Phi_P}{\Phi_P} = \sqrt{\left(\frac{\Delta \Phi_{P,Ground}}{\Phi_{P,Ground}}\right)^2 + \left(\frac{\Delta C_{PF}}{C_{PF}}\right)^2}$$

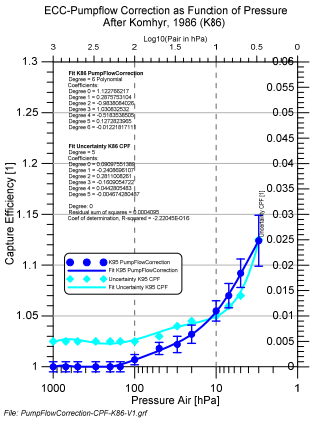
Table 7: Overview panel to support the processing of pumpflow correction factors (C_{PF}) for K86 (Komhyr 1986) and K95 (Komhyr et al., 1995) as function of ambient pressure (P_{Air}) (Graphs with better resolution in Annex 2)

Pressure(hPa)	Log10Pair	CPF_K86	D_CPF_K86	CPF_K95	D_CPF_K95
1000	3	1	0.005	1	0.005
700	2.84509804	1	0.005	1	0.005
500	2.698970004	1	0.005	1	0.005
300	2.477121255	1	0.005	1	0.005
200	2.301029996	1	0.005	1	0.005
150	2.176091259	1	0.005	1	0.005
100	2	1.007	0.005	1.007	0.005
50	1.698970004	1.018	0.006	1.018	0.005
30	1.477121255	1.022	0.008	1.029	0.008
20	1.301029996	1.032	0.009	1.041	0.012
10	1	1.055	0.01	1.066	0.023
7	0.84509804	1.07	0.012	1.087	0.024
5	0.698970004	1.092	0.014	1.12	0.024
3	0.477121255	1.124	0.025	1.241	0.043

Komhyr, W.D. (1986), Operations handbook - Ozone measurements to 40 km altitude with model 4A-ECC-ozone sondes, *NOAA Techn. Memorandum ERL-ARL-149.*

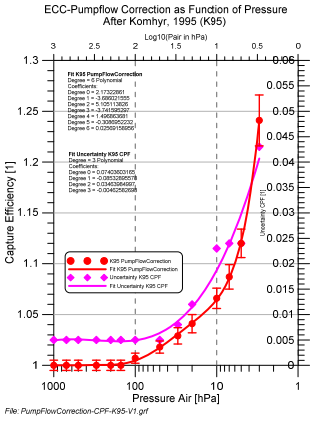
Komhyr, W.D., R.A. Barnes, G.B. Brothers, J.A. Lathrop, and D.P. Opperman (1995), Electrochemical concentration cell ozonesonde performance evaluation during STOIC 1989, *J. Geophys. Res., 100,* 9231-9244.





Fit K86 PumpFlowCorrection
Degree = 6 Polynomial
Coefficients:
Degree 0 = 1.122766217
Degree 1 = 0.2875753104
Degree 2 = -0.9838084026
Degree 3 = 1.030832532
Degree 4 = -0.5183538505
Degree 5 = 0.1272823965
Degree 6 = -0.01221817111

Fit Uncertainty K86 CPF
Degree = 5
Coefficients:
Degree 0 = 0.09097551389
Degree 1 = -0.2408696107
Degree 2 = 0.2811008261
Degree 3 = -0.1609054722
Degree 4 = 0.0442805483
Degree 5 = -0.004674280487



Fit K95 PumpFlowCorrection
Degree = 6 Polynomial
Coefficients:
Degree 0 = 2.17322861
Degree 1 = -3.686021555
Degree 2 = 5.105113826
Degree 3 = -3.741595297
Degree 4 = 1.496863681
Degree 5 = -0.3086952232
Degree 6 = 0.02569158956

Fit Uncertainty K95 CPF
Degree = 3 Polynomial
Coefficients:
Degree 0 = 0.07403603165
Degree 1 = -0.08532895578
Degree 2 = 0.03463984997
Degree 3 = -0.00462582698

References

Johnson. B.J.. S.J. Oltmans. H. Voemel. H.G.J. Smit. T. Deshler. and C. Kroeger (2002). ECC Ozonesonde pump efficiency measurements and tests on the sensitivity to ozone of buffered and unbuffered ECC sensor cathode solutions. J. Geophys. Res.. 107. D19 doi: 10.1029/2001JD000557.

Komhyr. W.D. (1967). Nonreactive gas sampling pump. Rev. Sci. Inst.. 38. 981-983.

Komhyr. W.D. (1986). Operations handbook - Ozone measurements to 40 km altitude with model 4A-ECC-ozone sondes. NOAA Techn. Memorandum ERL-ARL-149.

Komhyr. W.D.. R.A. Barnes. G.B. Brothers. J.A. Lathrop. and D.P. Opperman (1995). Electrochemical concentration cell ozonesonde performance evaluation during STOIC 1989. J. Geophys. Res.. 100. 9231-9244.

Steinbrecht W.. R. Schwartz. and H. Claude (1998). New pump correction for the Brewer Mast ozone sonde: Determination from experiment and instrument intercomparisons. J. Atmos. & Ocean. Technol.. 15. 144-156.

Torres. A.L. (1981). ECC ozonesonde performance at high altitude: pump efficiency. NASA Technical Memorandum 73290. 10 pp.. NASA Wallops Flight Center. Wallops Island. USA.

8.6 Total Ozone Normalization

Rationale:

Although the sonde measurement is in principle absolute, in practice ECC ozonesondes have a precision of 3-5% and an absolute accuracy of about 10% [*Smit et al.,* 2007; *Kerr et al*, 1994; *Deshler et al.,* 2008; *Liu, G., et al.,* 2009]. The primary reason for the common practice of normalizing, or "correcting" ozone soundings by scaling linearly to a total ozone measurement is undoubtedly historical: the older Brewer-Mast sonde, when prepared according to the manufacturer's instructions, had a typical response equivalent to about 80% of the actual ozone amount, and so needed to be scaled to give a more accurate result. Although the ECC sonde response is much closer to 100%, the practice continues because it demonstrably reduces uncertainties in ozonesonde data [e.g., *Kerr et al.,* 1994; *Smit et al.,* 1996; *Beekman et al.,* 1994, 1995]. Uncertainties are 7–10% for non-corrected data and 5–7% for corrected data [*Fioletov et al.,* 2007]. This improvement is because of the greater accuracy of total ozone measurements: for well-calibrated total ozone instruments the standard uncertainty of direct sun measurements is less than 3% [*Basher,* 1982].

However, the process introduces a degree of uncertainty because the amount of ozone above the balloon burst height can only be estimated. Several methods for doing this are in use, including the use of a climatological estimate (McPeters and Labow, 2012), or extrapolating the profile assuming a constant mixing ratio above the balloon burst altitude. It is also not clear that a scaling factor that is constant with altitude is appropriate in all cases. This is of particular concern for the tropospheric part of the profile. If a normalization is used it will be necessarily weighted to the larger stratospheric part of the profile and the ozone profile record will no longer be independent of the total ozone record. This is an important issue for trend studies (although to some extent alleviated if there is no trend in correction factors), and will introduce errors if the total ozone calibration is in error.

The normalization or correction factor is unquestionably of value as a data quality control indicator. Since the scaling is linear in measured ozone, it can be applied (and as easily removed) in post-processing or by the data user.

Recommendations:

1. Ozone Column Sonde (OCS), the integrated vertical ozone sonde profile from surface until bursting point, should be calculated after all other corrections have been applied.
2. How the residual (ROC) has been calculated, either by constant mixing ratio or satellite climatologies and the contribution to the uncertainty of the normalization factor, should be documented. The recommended residual method is to use satellite climatology by McPeters and Labow, 2012. If the residual is derived using the constant mixing ratio method then the amount of the residual should be documented.
3. Total Ozone Column Sonde = TCS= OCS + ROC
4. The parameters of the independent total ozone column measurement (TOC) by Dobson, Brewer or any other device (incl. WLcode, ObsType, Instrument, Number) should also be reported.
5. Total Ozone Normalization Factor = N_F = TOC/TCS
6. ECC ozonesonde records should **NOT** be scaled to a total ozone measurement, but that the scaling factor (correction factor) should be calculated and reported, according to the WOUDC and NDACC convention, as a negative value indicating that it has not been applied.

References:

Basher, R. E. (1982), Review of the Dobson spectrophotometer and its accuracy, *WMO Ozone Rep. 13,* World Meteorol. Org., Geneva.

Beekman, M., G. Ancellet, G. Mégie, H. G. J. Smit, and D. Kley (1994), Intercomparison campaign of vertical ozone profiles including electrochemical sondes of ECC and Brewer-Mast type and a ground-based UV-differential absorption lidar, *J. Atmos. Chem*, *19*, 259-288.

Deshler, T., et al. (2008), Atmospheric comparison of electrochemical cell ozonesondes from different manufactures, and with different cathode solution strengths: The balloon experiment on standards for ozonesondes (BESOS), *J. Geophys. Res., 113*, D04307, doi:10.1029/2007JD008975.

Fioletov, V. E., D. W. Tarasick, and I. Petropavlovskikh (2006), Estimating ozone variability and instrument uncertainties from SBUV(/2), ozonesonde, Umkehr, and SAGE II measurements: Short-term variations, *J. Geophys. Res.*, *111*, d02305, doi: 10.1029/2005JD006340.

Kerr, J.B., H. Fast, C.T. McElroy, S.J. Oltmans, J.A. Lathrop, E. Kyro, A. Paukkunen, H. Claude, U. Köhler, C.R. Sreedharan, T. Takao and Y. Tsukagoshi (1994), The 1991 WMO international ozonesonde intercomparison at Vanscoy, Canada,. *Atmosphere-Ocean, 32*, 685-716.

Liu, G., D. W. Tarasick, V. E. Fioletov, C. E. Sioris, and Y. J. Rochon (2009), Ozone correlation lengths and measurement uncertainties from analysis of historical ozonesonde data in North America and Europe, *J. Geophys. Res., 114*, D04112, doi:10.1029/2008JD010576

McPeters, R. D., G. J. Labow, B. J. Johnson, A satellite-derived ozone climatology for balloonsonde estimation of total column ozone, J. Geophys. Res., 102, 8875-8886, 10.1029/96JD02977, 1997.

McPeters R. D., G. J. Labow, J. A. Logan (2007), Ozone climatological profiles for satellite retrieval algorithms, J. Geophys. Res., 112, D05308, doi:10.1029/2005JD006823.

McPeters, R. D., and G. J. Labow (2012), Climatology 2011: An MLS and sonde derived ozone climatology for satellite retrieval algorithms, *J. Geophys. Res.*, 117, D10303, doi:10.1029/2011JD017006.

Smit, H.G.J., W. Sträter, M. Helten, D. Kley, D. Ciupa, H.J. Claude, U. Köhler, B. Hoegger, G. Levrat, B. Johnson, S.J. Oltmans, J.B. Kerr, D.W. Tarasick, J. Davies, M. Shitamichi, S.K. Srivastav and C. Vialle [1996] JOSIE: The 1996 WMO international intercomparison of ozonesondes under quasi-flight conditions in the environmental chamber at Jülich, in *Atmospheric Ozone: Proceedings of the Quadrennial O_3 Symposium, l'Aquila, Italy*, edited by R. D. Bojkov and G. Visconti, pp. 971-974, Parco Sci. e Tecnol. d'Abruzzo, Italy, 1996.

Smit, H.G.J., W. Straeter, B. Johnson, S. Oltmans, J. Davies, D.W. Tarasick, B. Hoegger, R. Stubi, F. Schmidlin, T. Northam, A. Thompson, J. Witte, I. Boyd and F. Posny (2007) Assessment of the performance of ECC-ozonesondes under quasi-flight conditions in the environmental simulation chamber: Insights from the Juelich Ozone Sonde Intercomparison Experiment (JOSIE), *J. Geoph Res., 112,* D19306, doi:10.1029/2006JD007308.

8.7 RadioSonde Changes

Rationale

Errors in radiosonde pressure or temperature will imply corresponding errors in calculated geopotential heights, causing measured ozone concentrations to be assigned to incorrect altitudes and pressures. This is potentially an important issue for the derivation of trends, as radiosonde changes may therefore introduce vertical shifts in the ozone profile, and apparent changes in ozone concentration at a given height. A number of different radiosonde designs, from several manufacturers, have been used in the global observing network over the last four decades. This history will in general vary by country, agency or even by station, and so will need to be documented for each station individually.

Temperature differences between the VIZ sonde, used widely in the 1980's and early 1990's, and the Vaisala RS-80 sonde, adopted subsequently by several agencies, including NOAA and Envoronment Canada, are well documented. The VIZ sonde showed a warm bias in the daytime by as much as 2C (*Richter and Philips*, 1981; *Luers and Eskridge*, 1995; *Wang and Young*, 2005). From simultaneous measurements made during a WMO intercomparison in 1985, *Schmidlin* (1988) estimates that this bias contributed 17m at 50hPa and 71m at 10hPa to the difference in geopotential height estimates from the two sondes. This corresponds to a shift of ~1% at 10hPa (31km), but less than 0.1% at 50hPa (21km). Nevertheless, statistical comparisons show that the switch from VIZ to Vaisala RS-80 at U.S. stations introduced a shift of as much as 120m at 50hPa in the daytime (*Elliot et al.,* 2002).

Pressure errors appear to have a much larger effect (e.g. *Morris et al.,* 2012): comparisons with radar measurements of height showed the VIZ to be high. relative to the radar (and the Vaisala). in daytime by ~150m at 20hPa and up to 500m at 10hPa (*Schmidlin*, 1988; *Nash and Schmidlin*, 1987), while at night both VIZ and Vaisala RS80 calculated geopotentials were low by ~100m at 20hPa, and ~150m at 10hPa. These daytime differences correspond to ozone differences of ~2% and ~7% at 20 hPa and 10hPa respectively. The effect of pressure errors is most significant at higher altitudes: a 1hPa offset will introduce a geopotential height error of 63m at 100hPa, 120m at 50hPa, and over 300m at 20hPa; these correspond to ozone differences of 0.25%, 0.5% and ~4% respectively.

Pressure errors also seem more variable, as well: local noon flights during the same intercomparison show much smaller height differences between the VIZ and Vaisala, and a separate investigation at Uccle (*De Muer and De Backer*, 1992) found that VIZ sondes launched between 1985 and 1989 calculate altitude too *low* relative to a radar: up to 1410m at 30km and up to 870m at 15km. They estimate a corresponding ozone error of 14% at 30km. At 15km, 870m corresponds to an ozone error of ~4%, but implies a rather surprising average pressure error of 17hPa.

The Vaisala RS-92 is currently in wide use, and has replaced the RS-80. Comparison flights with GPS tracking show that it gives more accurate heights than the RS80; differences from the GPS are small except for sondes produced before July, 2004 (*Steinbrecht et al.,* 2008; *Nash et al.,* 2006). RS80 sondes, however, were found to be low by ~20m in the troposphere, and high by 100m at 10hPa (*Steinbrecht et al.,* 2008; also *da Silveira et al.,* 2006).

Unfortunately intercomparison experiments do not tell the whole story, as not all manufacturing changes are advertised by a change in model number. For example, *Steinbrecht et al.* note systematic differences between batches of RS-92 sondes produced before July, 2004. It is therefore recommended that stations document, in as much detail as possible, changes in radiosonde type, and the expected systematic differences in the ozone profile. These are probably small below 50hPa. At higher altitudes it may be possible to correct offsets in the ozone record by statistical methods

Recommendations:

No corrections but good documentation of radiosonde type(s) deployed (incl. time flags) is required to estimate/quantify the contribution of the radio sonde type to the overall uncertainty of the ozone sonde performance. Also, recommended a detailed documentation (incl. references) of eventual known bias effects in pressure and/or temperature readings of the radiosonde at different pressure levels.

References:

da Silveira, R. B., et al., (2006), WMO intercomparison of GPS radiosondes, Alcantara, Brazil, 20 May–10 June 2001. WMO/TD–No. 1314, 65 pp. [Available online at http://www.wmo.int/pages/prog/www/IMOP/publications/IOM-90_RSO-Brazil/IOM-90_RSO_EMA_Alcantara2001.pdf.]

De Muer, D., and H. De Backer (1992), The discrepancy between stratospheric ozone profiles and from other techniques: A possible explanation, in *Proceedings of the 17th Quadriennal Ozone Symposium*, NASA Conf. Publ. 3266, 815-818, 1992.

Elliott, W. P., R. J. Ross, and W. H. Blackmore (2002), Recent changes in NWS upper-air observations with emphasis on changes from VIZ to Vaisala radiosondes. *Bull. Amer. Meteor. Soc.*, **83**, 1003-1017.

Luers, J. K., and R. Eskridge (1995), Temperature corrections for the VIZ and Vaisala radiosondes, *J. Appl. Meteor., 34*, 1241–1253.

Morris, G., D Martins, A.M. Thompson, A. Reed, E. Joseph and E. Thompson (2012), The impact of radiosonde pressure sensor errors on ozone profiles and columns as reported by ozonesondes, *22nd Quadriennal Ozone Symposium*, Toronto, Canada, August 27-31, 2012.

Nash, J., and F. J. Schmidlin (1987), WMO international radiosonde comparison (U.K. 1984, U.S.A. 1985). WMO/TD–No. 195, 103 pp.

Nash, J., R. Smout, T. Oakley, B. Pathack, and S. Kurnosenko (2006). WMO intercomparison of high quality radiosonde systems, Mauritius, February 2005. WMO/TD–No. 1303, 115 pp. [Available online at http://www.wmo.int/pages/prog/www/IMPO/publications/IOM-83_RSO-Mauritius/IOM-83_Radiosondes_Vacoas2005.pdf.]

Richner, H., and P. D. Phillips (1981), Reproducibility of VIZ radiosonde data and some sources of error, *J. Appl. Meteor.,* 954-962.

Schmidlin, F. J., (1988), WMO international radiosonde intercomparison. Phase II: Wallops Island, Virginia, USA, 1985. WMO/TD–No. 312, 113 pp.

Steinbrecht, W, H. Claude, F. Schönenborn, U. Leiterer, H. Dier, E. Lanzinger (2008), Pressure and Temperature Differences between Vaisala RS80 and RS92 Radiosonde Systems. *J. Atmos. Oceanic Technol.*, **25**, 909–927.

Wang, J., and K. Young (2005), Comparisons of 7-year radiosonde data from two neighboring stations and estimation of random error variances for four types of radiosondes, *13th Symposium on Meteorological Observations and Instrumentation*, Savannah, GA, USA 19-23 June 2005.

Annex-1: List of Participating Stations

Region	Location	Organization	Principal Investigator	E-Mail	Participate	Coaching
Arctic	Canada-Resolute	EC-(Environmental Canada)	David Tarasick	david.tarasick@ec.gc.ca	Yes	Tarasick/Davies
Arctic	Canada-Alert	EC-(Environmental Canada)	David Tarasick	david.tarasick@ec.gc.ca	Yes	Tarasick/Davies
Arctic	Canada-Eureka	EC-(Environmental Canada)	David Tarasick	david.tarasick@ec.gc.ca	Yes	Tarasick/Davies
Arctic	Finland-Sondankyla	FMI	Rigel Kivi	rigel.kivi@fmi.fi	Yes	Terry Deshler
Arctic	Spitzbergen –Ny Alesund	AWI	Peter von der Gathen	peter.von.der.gathen@awi.de	Yes	Terry Deshler
Arctic	Greenland-Scoresbysund	DMI	Niels Larsen	nl@dmi.dk	Yes	Terry Deshler
Arctic	Greenland-Summit	NOAA	Bryan Johnson	bryan.johnson@noaa.gov	Yes	Johnson&Oltmans
Europe	Germany-Hohenpeissenberg	DWD	Hans Claude	hans.claude@dwd.de	Yes	Herman Smit
Europe	Germany-Lindenberg	DWD	Holger Voemel	holger.voemel@dwd.de	Yes	Herman Smit
Europe	Switzerland–Payerne	MeteoSuisse	Rene Stuebi	rene.stubi@meteoswiss.ch	Yes	Rene Stuebi
Europe	Belgium – Uccle	KMI	Hugo Debacker	hugo.debacker@meteo.be	Yes	Herman Smit
Europe	Netherlands – De Bilt	KNMI	Marc Allaart	marc.allaart@knmi.nl	Yes	Herman Smit
Europe	France – ObsHauteProvence	CNRS	Gerard Ancellet	gerard.ancellet@latmos.ipsl.fr	Yes	Herman Smit
Europe	UK-Lerwick	UKMO	David Moore	david.moore@metoffice.gov.uk	Yes	Herman Smit
Europe	Iceland-Keflavik	INTA	M.Gil	gilm@inta.es	Yes	Terry Deshler
Europe	Spain–Izana(Canary Islands)	IMN	Alberto Redondas	aredondasm@aemet.es	Yes	Herman Smit
North America	Canada-Churchill	EC-(Environmental Canada)	David Tarasick	david.tarasick@ec.gc.ca	Yes	Tarasick/Davies
North America	Canada-Edmonton	EC-(Environmental Canada)	David Tarasick	david.tarasick@ec.gc.ca	Yes	Tarasick/Davies
North America	Canada-Goose Bay	EC-(Environmental Canada)	David Tarasick	david.tarasick@ec.gc.ca	Yes	Tarasick/Davies
North America	Canada-Kelowna	EC-(Environmental Canada)	David Tarasick	david.tarasick@ec.gc.ca	Yes	Tarasick/Davies
North America	Canada-Bratts Lake	EC-(Environmental Canada)	David Tarasick	david.tarasick@ec.gc.ca	Yes	Tarasick/Davies
North America	Canada-Egbert	EC-(Environmental Canada)	David Tarasick	david.tarasick@ec.gc.ca	Yes	Tarasick/Davies
North America	Canada-Yarmouth	EC-(Environmental Canada)	David Tarasick	david.tarasick@ec.gc.ca	Yes	Tarasick/Davies
North America	USA-Wallops Island	NASA	Frank Schmidlin	francis.j.schmidlin@nasa.gov	Yes	Frank Schmidlin
North America	USA-Narragansett, RI	NOAA	Bryan Johnson	bryan.johnson@noaa.gov	Yes	Johnson&Oltmans
North America	USA-Huntsville, AL	NOAA	Bryan Johnson	bryan.johnson@noaa.gov	Yes	Johnson&Oltmans
North America	USA-Boulder, CO	NOAA	Bryan Johnson	bryan.johnson@noaa.gov	Yes	Johnson&Oltmans
North America	USA-Trinidad, CA	NOAA	Bryan Johnson	bryan.johnson@noaa.gov	Yes	Johnson&Oltmans
Central Pacific	Hawaii–Hilo	NOAA	Bryan Johnson	bryan.johnson@noaa.gov	Yes	Johnson&Oltmans
Japan	Japan-Sapporo	JMA	Hiroaki Naoe	hnaoe@met.kishou.go.jp	Yes	Herman Smit
Japan	Japan-Tsukuba/Tateno	JMA	Hiroaki Naoe	hnaoe@met.kishou.go.jp	Yes	Herman Smit
Japan	Japan-Naha	JMA	Hiroaki Naoe	hnaoe@met.kishou.go.jp	Yes	Herman Smit
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South America	Suriname-Paramaribo	KNMI	Rinus Scheele	rinus.scheele@knmi.nl	Yes	Herman Smit
South America	Brazil-Natal	NASA	Frank Schmidlin	francis.j.schmidlin@nasa.gov	Yes	Frank Schmidlin
South America	Ecuador-Galapagos Islands	NOAA	Bryan Johnson	bryan.johnson@noaa.gov	Yes	Johnson&Oltmans
South Pacific	AmericanSamoa-Pago Pago,	NOAA	Bryan Johnson	bryan.johnson@noaa.gov	Yes	Johnson&Oltmans
South Pacific	Fiji-Suva	NOAA	Bryan Johnson	bryan.johnson@noaa.gov	Yes	Johnson&Oltmans
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Australia	Australia-Macquarie Island	BOM	Matt Tully	m.tully@bom.gov.au	Yes	Sam Oltmans
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Antarctica	Marambio	FMI	Rigel Kivi	Rigel.Kivi@fmi.fi	Yes	Terry Deshler
Antarctica	Neumayer	AWI	Gert Koenig-Langlo	gert.koenig-langlo@awi.de	Yes	Terry Deshler
Antarctica	McMurdo	UWYO (University Wyoming)	Terry Deshler	deshler@uwyo.edu	Yes	Terry Deshler
Antarctica	South Pole	NOAA	Bryan Johnson	bryan.johnson@noaa.gov	Yes	Johnson&Oltmans

Annex-2: O3S-DQA Panel & Associates

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Deshler	Terry	University Wyoming, USA	deshler@uwyo.edu
Schmidlin	Frank	NASA, USA	francis.j.schmidlin@nasa.gov
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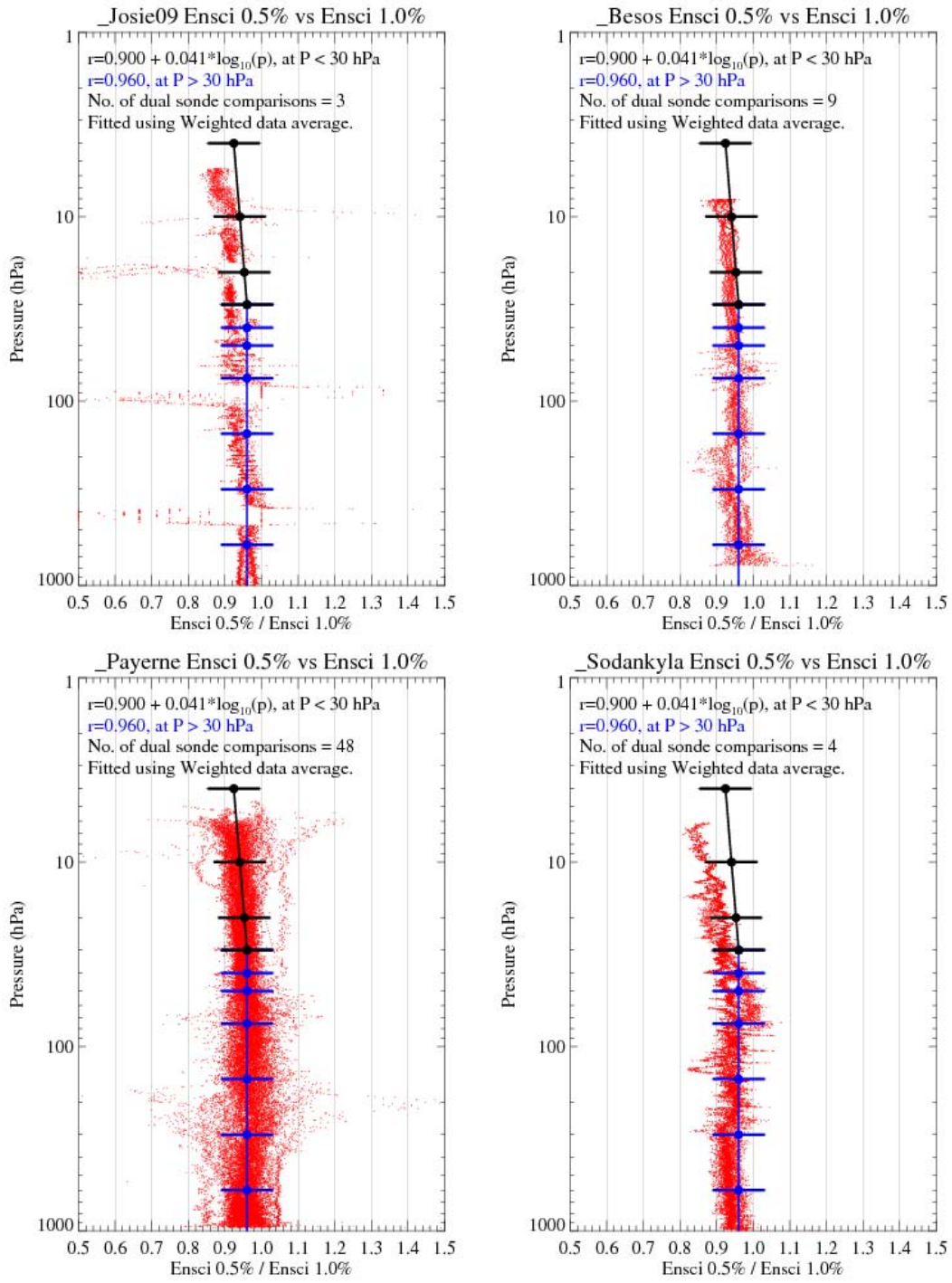
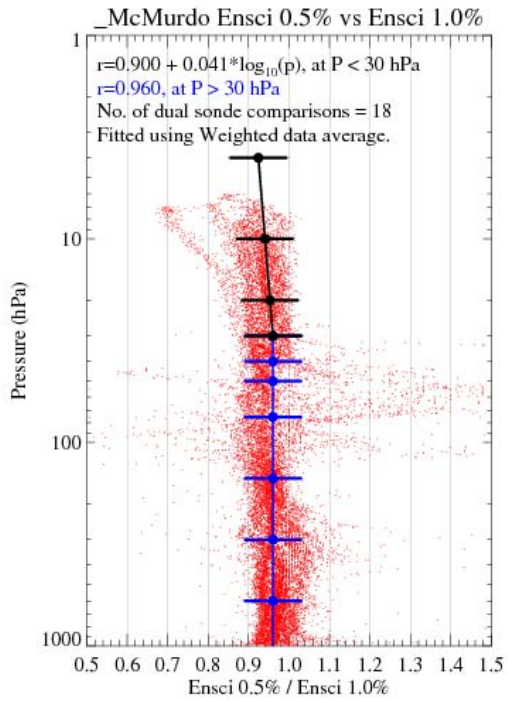
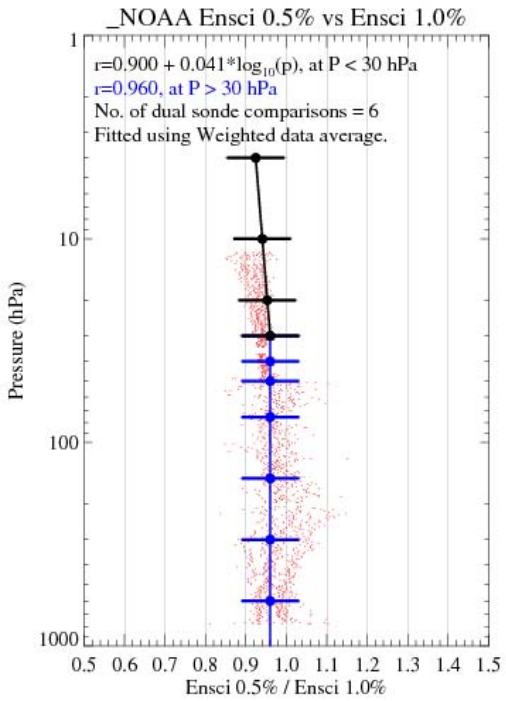
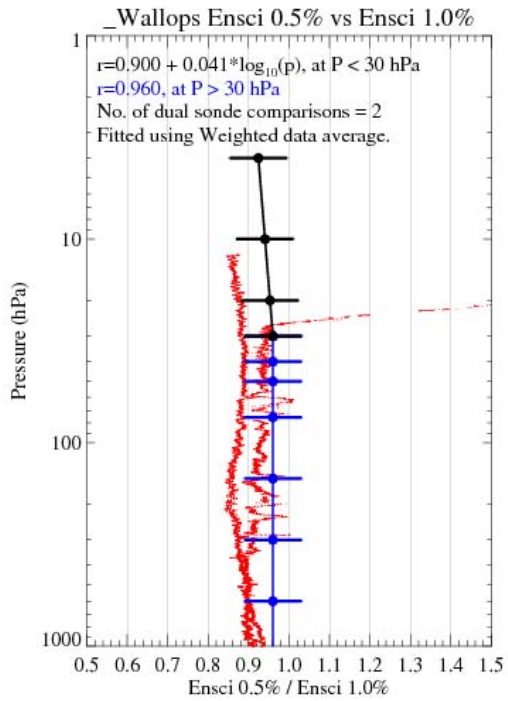
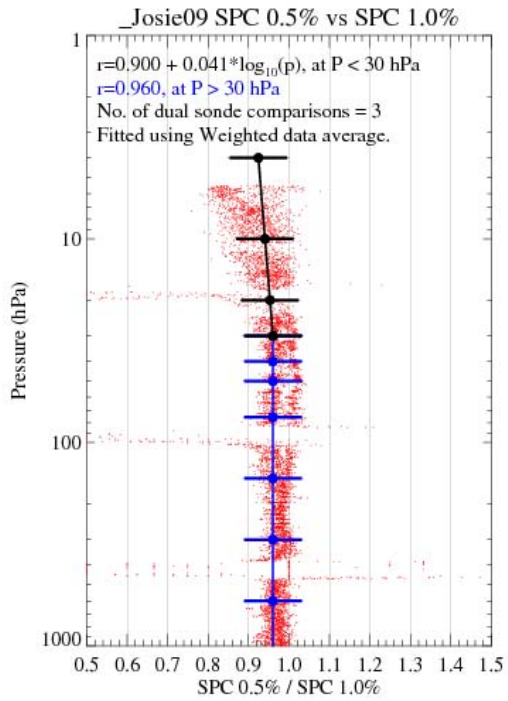
Annex-3: Graphs on Comparisons to Derive Transfer Functions (by Rene Stuebi and Terry Deshler)

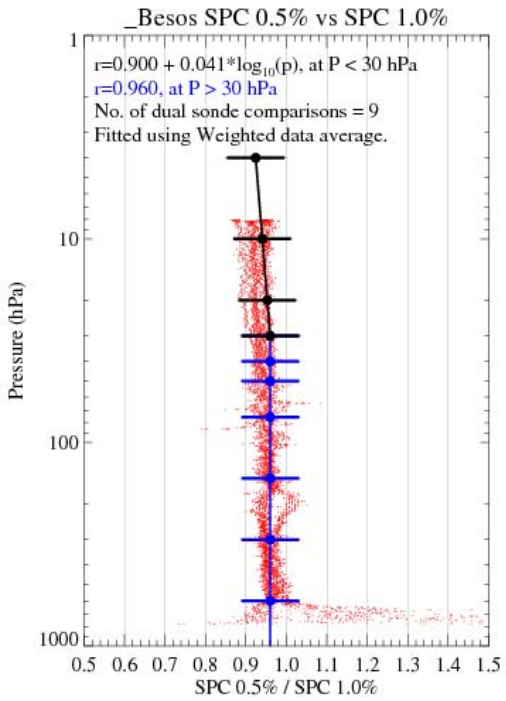


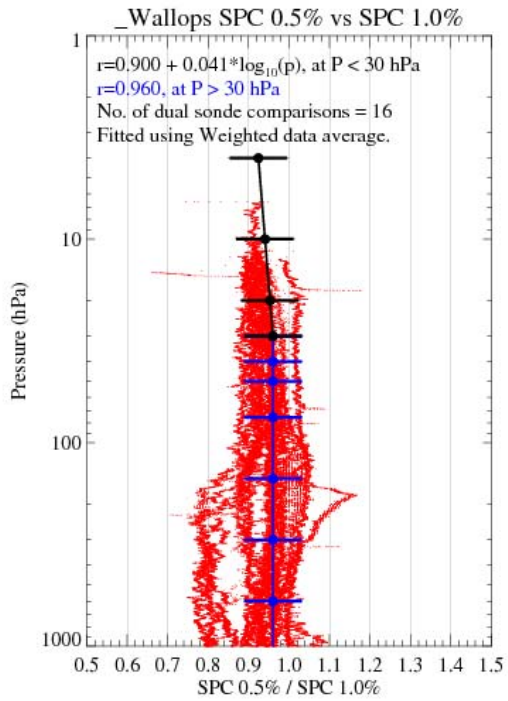

_McMurdo Ensci 0.5% vs Ensci 1.0%
r=0.900 + 0.041*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 18
Fitted using Weighted data average.
Pressure (hPa)
1
10
100
1000
0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5
Ensci 0.5% / Ensci 1.0%

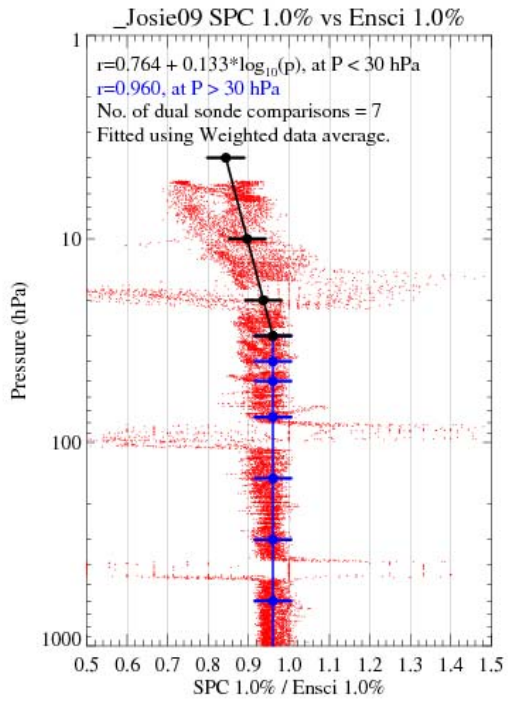

_NOAA Ensci 0.5% vs Ensci 1.0%
r=0.900 + 0.041*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 6
Fitted using Weighted data average.
Pressure (hPa)
1
10
100
1000
0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5
Ensci 0.5% / Ensci 1.0%

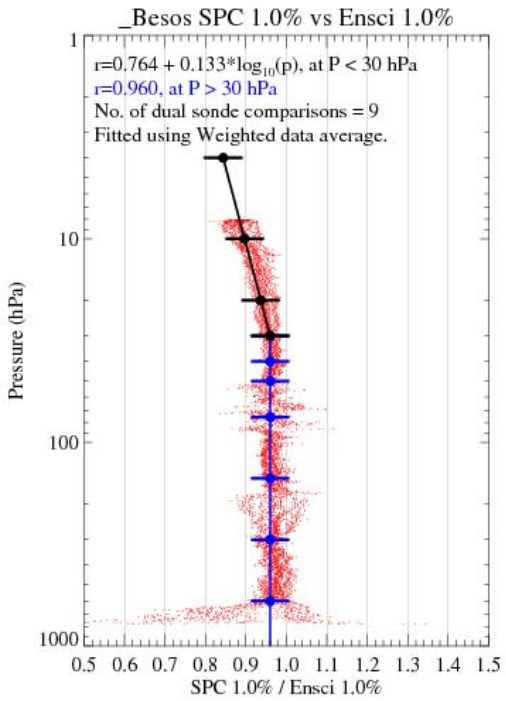

_Wallops Ensci 0.5% vs Ensci 1.0%
r=0.900 + 0.041*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 2
Fitted using Weighted data average.
Pressure (hPa)
1
10
100
1000
0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5
Ensci 0.5% / Ensci 1.0%

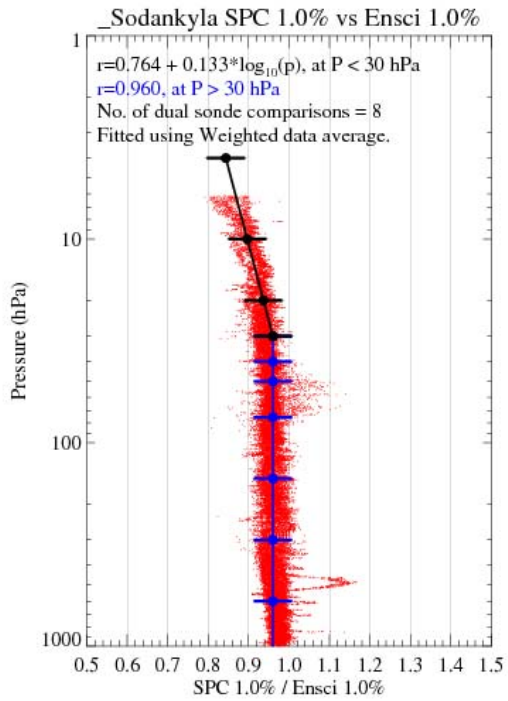

_Josie09 SPC 0.5% vs SPC 1.0%
r=0.900 + 0.041*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 3
Fitted using Weighted data average.
Pressure (hPa)
SPC 0.5% / SPC 1.0%

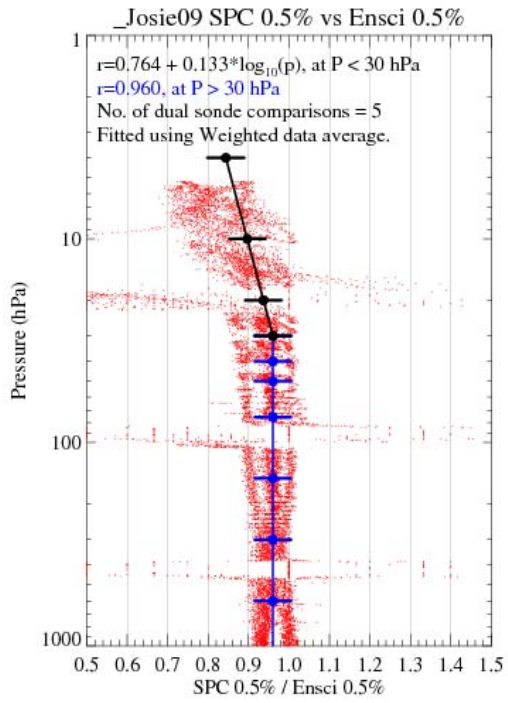

_Besos SPC 0.5% vs SPC 1.0%
r=0.900 + 0.041*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 9
Fitted using Weighted data average.
Pressure (hPa)
SPC 0.5% / SPC 1.0%

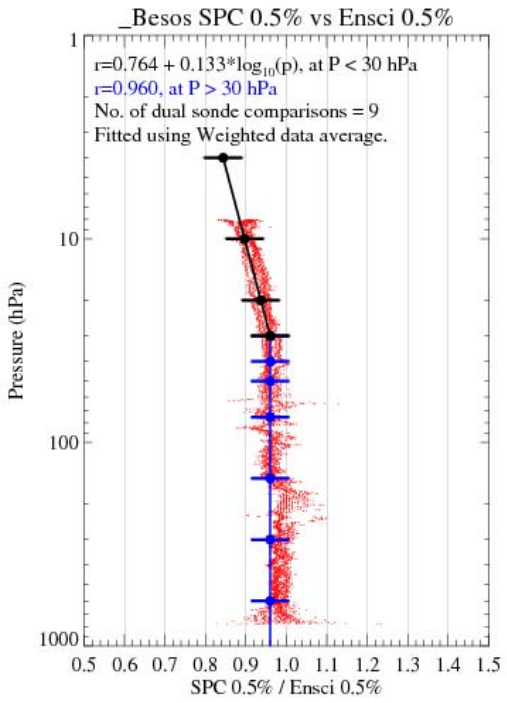

_Wallops SPC 0.5% vs SPC 1.0%
r=0.900 + 0.041*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 16
Fitted using Weighted data average.
Pressure (hPa)
SPC 0.5% / SPC 1.0%

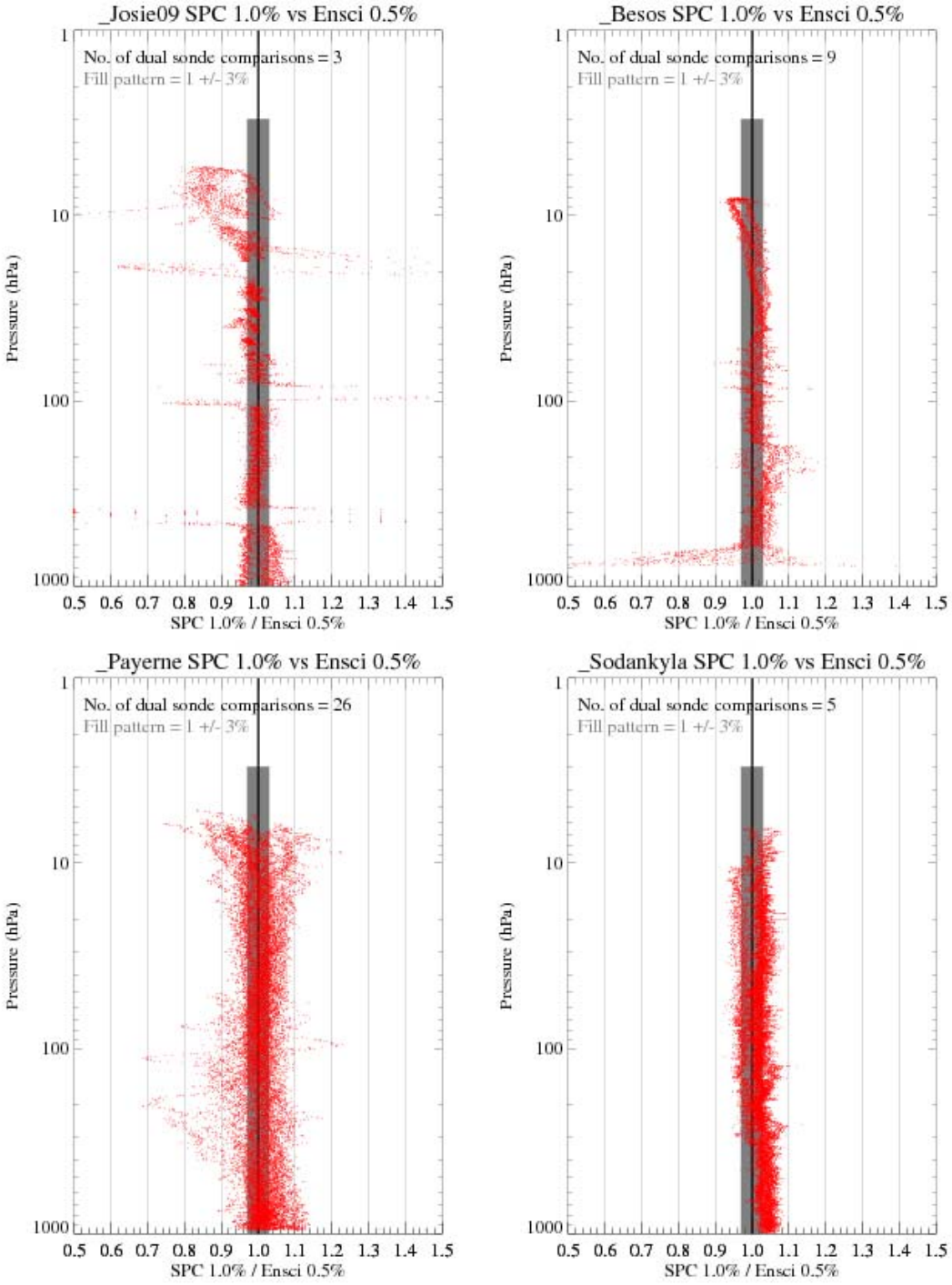

_Josie09 SPC 1.0% vs Ensci 1.0%
r=0.764 + 0.133*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 7
Fitted using Weighted data average.
Pressure (hPa)
SPC 1.0% / Ensci 1.0%


_Besos SPC 1.0% vs Ensci 1.0%
r=0.764 + 0.133*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 9
Fitted using Weighted data average.
Pressure (hPa)
SPC 1.0% / Ensci 1.0%


_Sodankyla SPC 1.0% vs Ensci 1.0%
r=0.764 + 0.133*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 8
Fitted using Weighted data average.
Pressure (hPa)
SPC 1.0% / Ensci 1.0%


_Josie09 SPC 0.5% vs Ensci 0.5%
r=0.764 + 0.133*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 5
Fitted using Weighted data average.
Pressure (hPa)
1
10
100
1000
0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5
SPC 0.5% / Ensci 0.5%


_Besos SPC 0.5% vs Ensci 0.5%
r=0.764 + 0.133*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 9
Fitted using Weighted data average.
Pressure (hPa)
1
10
100
1000
0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5
SPC 0.5% / Ensci 0.5%


_Josie09 SPC 1.0% vs Ensci 0.5%
No. of dual sonde comparisons = 3
Fill pattern = 1 +/- 3%
_Besos SPC 1.0% vs Ensci 0.5%
No. of dual sonde comparisons = 9
Fill pattern = 1 +/- 3%
_Payerne SPC 1.0% vs Ensci 0.5%
No. of dual sonde comparisons = 26
Fill pattern = 1 +/- 3%
_Sodankyla SPC 1.0% vs Ensci 0.5%
No. of dual sonde comparisons = 5
Fill pattern = 1 +/- 3%
Pressure (hPa)
1
10
100
1000
0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5
SPC 1.0% / Ensci 0.5%