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. These results are all based on using the standard buffers for SST1.0 and half that buffer for SST0.5.

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.

Table 5: *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%.*

Y dependent =	Ratio	X independent	Pressure	Ozone sonde or SST
SST 0.5%	0.96	SST 1.0%	P ≥ 30 hPa	Both SPC & ENSCI
SST 0.5%	$0.90+0.041*\log_{10}(p)$	SST 1.0%	P < 30 hPa	Both SPC & ENSCI
SPC	0.96	ENSCI	P ≥ 30 hPa	0.5% & 1.0%
SPC	$0.764+0.133*\log_{10}(p)$	ENSCI	P < 30 hPa	0.5% & 1.0%

SPC-1.0%	1.01	ENSCI-0.5%	P > 0	

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. The graph at the end of this document displays the relationships in Table 5 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).

Recommendations:

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.*

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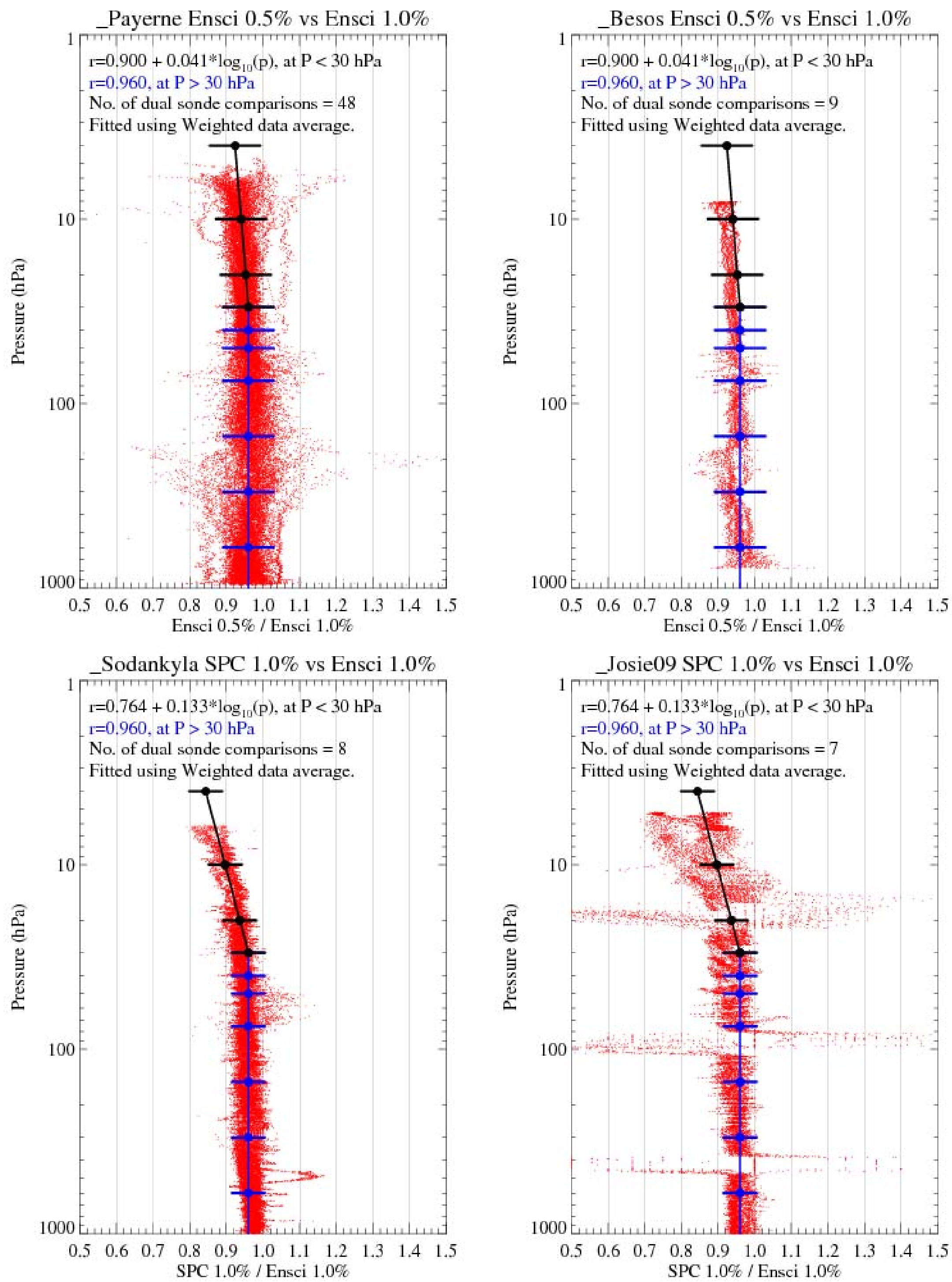
_Payerne Ensci 0.5% vs Ensci 1.0%
r=0.900 + 0.041*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 48
Fitted using Weighted data average.
Pressure (hPa)
Ensci 0.5% / Ensci 1.0%
_Besos Ensci 0.5% vs Ensci 1.0%
r=0.900 + 0.041*log10(p), at P < 30 hPa
r=0.960, at P > 30 hPa
No. of dual sonde comparisons = 9
Fitted using Weighted data average.
Pressure (hPa)
Ensci 0.5% / 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 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%