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)

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Received 16 March 2006; revised 19 March 2007; accepted 22 June 2007; published 11 October 2007.

[1] Since 1996, quality assurance experiments of electrochemical concentration cell (ECC) ozonesondes of two different model types (SPC-6A and ENSCI-Z) have been conducted in the environmental simulation facility at the Research Centre Juelich within the framework of the Juelich Ozone Sonde Intercomparison Experiment (JOSIE). The experiments have shown that the performance characteristics of the two ECC-sonde types can be significantly different, even when operated under the same conditions. Particularly above 20 km the ENSCI-Z sonde tends to measure 5–10% more ozone than the SPC-6A sonde. Below 20 km the differences are 5% or less, but appear to show some differences with year of manufacture. There is a significant difference in the ozone readings when sondes of the same type are operated with different cathode sensing solutions. Testing the most commonly used sensing solutions showed that for each ECC-manufacturer type the use of 1.0% KI and full buffer gives 5% larger ozone values compared with the use of 0.5% KI and half buffer, and as much as 10% larger values compared with 2.0% KI and no buffer. For ozone sounding stations performing long term measurements this means that changing the sensing solution type or ECC-sonde type can easily introduce a change of ±5% or more in their records, affecting determination of ozone trends. Standardization of operating procedures for ECC-sondes yields a precision better than ±(3–5)% and an accuracy of about ±(5–10)% up to 30 km altitude.

Citation: Smit, H. G. J., et al. (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.

1. Introduction

[2] A widely used method to measure in-situ ozone up to altitudes of 30–35 km is through the use of compact balloon borne sondes [e.g., *SPARC-IOC-GAW*, 1998]. Ozone soundings provide the longest (30–40 years) records of the vertical ozone distribution between the surface and 30–35 km altitude compared to other ozone profiling techniques (e.g., satellites, lidar). Up to an altitude of about 20 km ozonesondes constitute the most important data source with long term coverage for the derivation of ozone trends, particularly in the region around the tropopause [e.g., *Logan*, 1994; *SPARC-IOC-GAW*, 1998; *World Meteorological Organization*, 2003, 2007]. Ozone soundings are crucially important in validation and evaluation of satellite measurements, particularly for their long term stability [e.g., *SPARC-IOC-GAW*, 1998]. Ozonesondes are used in research programs such as South Hemispheric ADditional OZonesondes (SHADOZ) in the tropics [e.g., *Thompson et al.*, 2003], IONS (INTEX Ozonesonde Network Study) in

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0148-0227/07/2006JD007308

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mid-latitudes [*Thompson et al.*, 2007b] and MATCH in the polar regions [e.g., *Rex et al.*, 1998].

[3] The ozonesonde consists of an ozone sensing device, which is flown on a latex balloon and is interfaced to a standard meteorological radiosonde for data transmission to a ground station [e.g., *Smit*, 2002]. In an electrochemical cell, the reaction of ozone with potassium iodide in aqueous solution is used to measure continuously the ozone concentration. Three major different types of ozonesondes, i.e., Brewer-Mast [*Brewer and Milford*, 1960], electrochemical concentration cell (ECC) after *Komhyr* [1969], and the carbon iodine cell [*Kobayashi and Toyama*, 1966], are presently in use. Each sonde type has a unique design [e.g., *Smit*, 2002].

[4] Each ozone sounding is made with a new or refurbished instrument, which has to be prepared and checked according to well defined procedures prior to flight. To assess the performance of the sondes and to quantify any systematic differences among the various sonde types, several intercomparisons have been carried out since 1970 [e.g., *SPARC-IOC-GAW*, 1998]. The earlier intercomparisons [*Attmannspacher and Dütsch*, 1970, 1981; *Kerr et al.*, 1994], included only ozonesondes, without comparisons to a reference profile measured by a separate technique. Other intercomparisons [e.g., *Hilsenrath et al.*, 1986; *Aimedieu et al.*, 1987; *McDermid et al.*, 1990; *Komhyr et al.*, 1995; *Beekmann et al.*, 1994, 1995] used a reference profile measured by other techniques. Results of these intercomparisons yield better estimates of absolute errors for the sonde measurement as a function of altitude. Most of these studies were based on short-term intercomparison campaigns in the field and were focused on sonde performance in the stratosphere. Since the 1990s investigations have been made to address the performance of ozonesondes in the troposphere [*Beekmann et al.*, 1994, 1995; *Reid et al.*, 1996; *Ancellet and Beekmann*, 1997; *Tarasick et al.*, 1998; *Johnson et al.*, 2002]. However, ozone assessments have shown inconsistencies in trends derived from data gathered from different sounding stations. To ensure more confidence in the observed trends there is a need to improve the homogeneity and quality of ozone sounding data [*SPARC-IOC-GAW*, 1998; *World Meteorological Organization*, 2003, 2007].

[5] To achieve consistent data sets quality assurance (QA) of ozonesonde performance is a pre-requisite. QA is achieved by intercalibration and intercomparison of existing ozonesonde types as well as through standardization of procedures for preparing and data processing of ozonesondes [*WMO/GAW report No. 104*, 1995]. As part of the QA-plan for ozonesondes that are in routine use in the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO), the environmental simulation facility at the Research Centre Juelich [*Smit et al.*, 2000; http://www.fz-juelich.de/icg/icg-2/esf/]) is established as the World Calibration Centre for Ozone Sondes (WCCOS). The facility enables control of pressure, temperature and ozone concentration to simulate flight conditions of ozone soundings up to 35 km. The accurate UV-photometer of *Proffitt and McLaughlin* [1983] serves as a reference. Since 1996 the Juelich Ozone Sonde Intercomparison Experiment (JOSIE) activities [http://www.fz-juelich.de/icg/icg-2/josie/] have been conducted at the simulation facility to assess the performance of ozonesondes of different types and manufacturers [*Smit and Kley*, 1998; *Smit and Straeter*, 2004a, 2004b]. A major goal of the JOSIE experiments conducted between 1996 and 2000 was to investigate under controlled laboratory conditions the precision, accuracy and response of different ozonesonde types as a function of altitude and ozone concentration.

[6] JOSIE has focused on the performance of the ECC-type of ozonesondes which is nowadays most widely used. More than 80% of the world wide WMO/GAW ozone sounding network use ECC-sondes. Although the principle of ECC sonde operation has remained the same [*Komhyr*, 1969], ECC-ozonesondes have gone through several modifications of the instrument and procedures since they were first manufactured in the early 1970s [e.g., *Johnson et al.*, 2002]. These variations and their associated uncertainties can have significant effects on the sonde performance, leading to uncertainties in trend analysis [*SPARC-IOC-GAW*, 1998]. Nowadays, ECC-sondes are manufactured by either Science Pump Corporation (Model type: SPC-5A before 1996 and SPC-6A since 1996) or Environmental Science Corporation (Model type: ENSCI-Z since 1995). A major concern about consistency in ozonesonde data stems from the use of different guidelines in pre-flight preparation [*SPARC-IOC-GAW*, 1998]. The use of different sensing solutions in the ozonesonde cells is another factor that strongly influences the performance of the ECC-sonde as shown by *Boyd et al.*, [1998] and *Johnson et al.* [2002].

[7] This paper reports on the three JOSIE-simulation experiments to assess the performance of the ECC-sonde types compared with an accurate UV-photometer. The objectives are twofold: (1) to guide operators and data handlers who seek objective evaluation of various techniques presently in use; (2) to explain to the larger scientific community using ozonesonde data the origins of systematic variations in ozone profiles taken by different instruments and techniques. To determine precision, accuracy and response of the ozonesondes as a function of sonde type, altitude, and ozone level, the different ozonesonde types were tested under a variety of typical atmospheric conditions.

2. Experimental Details of JOSIE

2.1. Environmental Simulation Facility for Ozone Soundings

[8] The functional diagram of the Jülich facility shown in Figure 1 is described in detail by *Smit et al.* [2000]. Specifications of the environmental chamber's capabilities, control and measurements are summarized in Table 1.

[9] In order to simulate vertical ozone profiles dynamically in time a separate gas mixing system is installed to provide via a manifold up to four ozone sondes plus UV-photometer (OPM) with regulated ozone concentrations. Excess amounts of air are exhausted with additional tube into the test room such that the manifold is kept to test room pressure conditions to prevent over pressure effects over the inlet tubes connected to the sondes and UV-photometer.

[10] The ECC-sondes are coupled with the data acquisition system via an electronic interface that measures cathode cell current (accuracy ±0.01 μA), pump temperature (accuracy ±0.5 K), pump motor current (accuracy ±2 mA)

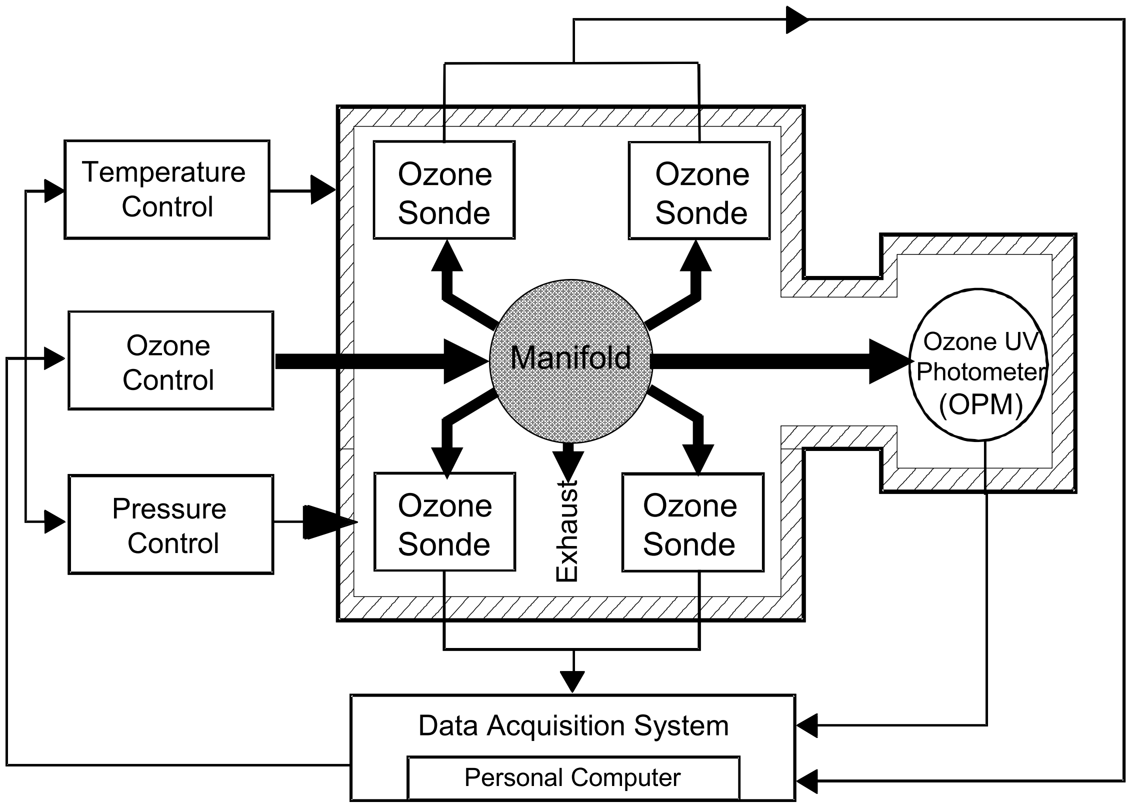

Figure 1. Set up for the simulation of vertical ozone soundings.

supplying the pump motor with 12 V. The air temperature at the inlet tube of each sonde and of the UV-photometer is individually recorded with a Pt100-thermistor (accuracy ±0.5 K). A small adjustable electrical heater (0–10 W) keeps the temperature inside the Styrofoam box of the sonde at values similar to temperatures obtained during normal balloon flights.

[11] In the JOSIE simulations different types of vertical profiles of pressure, temperature and ozone concentrations versus time represent prototype soundings with ascent velocities of about 5 m/s. Two simulation profiles are shown in Figure 2. The first type is a typical mid-latitude profile taken from the *Standard Atmosphere* [1976] for 40–50°N with a tropopause height of 12 km. The second profile simulates tropical conditions with a tropopause at 18 km, low tropopause temperatures and very low ozone values in the middle and upper troposphere [*Kley et al.*, 1996]. From the actual air pressure and temperature measured during a simulation run the corresponding simulated altitude is calculated step by step as the cumulative sum of the height difference between two successive pressure levels using the hypsometric equation [e.g., *Curry and Webster*, 1999].

2.2. Electrochemical Concentration Cell (ECC)

[12] The ECC-sensor developed by *Komhyr* [1969, 1971], based on an electrochemical method, consists of two cells which serve as cathode and anode chamber, respectively. Both cells contain a platinum mesh, serving as electrodes and are immersed in a KI-solution of different concentrations. The two chambers are linked by an ion bridge in order to provide an ion-pathway and to prevent mixing of the cathode and anode electrolytes. The iodometric reaction of ozone with potassium iodide in aqueous solution is used to measure continuously the ozone concentration:

$$2\ \mathrm{KI} + \mathrm{O_3} + \mathrm{H_2O} \longrightarrow \mathrm{I_2} + \mathrm{O_2} + 2\ \mathrm{KOH} \qquad (1)$$

Followed at the platinum-cathode by

$$\mathrm{I_2} + 2\ \mathrm{e} \longrightarrow 2\ \mathrm{I^-} \qquad (2)$$

Table 1. Specifications of Environmental Simulation Facility of World Calibration Centre of Ozone Sondes (WCCOS) at Research Centre Juelich (FZJ), Germany[a]

Test room volume is 500 l (80 × 80 × 80 cm) capable to test 4 sondes simultaneously	
Computer controlled simulation of "real" atmospheric conditions:	
a.) Pressure:	1–1000 hPa
b.) Temperature:	200–300 K
•dynamic:	Rate = ±2 K/min
•static:	Fluctuations <0.1–0.2 K
c.) Ozone:	1–10,000 ppbv (0.1–30 mPa)
Ozone Reference:	
Dual beam ozone UV-photometer (OPM) [*Proffitt and McLaughlin*, 1983]:	
•response: 1 s	
•precision: ±0.025 mPa,	
•accuracy: ±2% (0–25 km), ±3.5% (30–35 km)	

[a]The pressure inside the test chamber was measured with three different capacitive manometers: 1–1000 hPa, 0.1–100 hPa, and 0.01–12.5 hPa with an accuracy better than ±0.5% of its readings. The ozone photometer (OPM) is installed in a separate vacuum vessel which is connected to the simulation chamber such that the instrument has the same pressure conditions as the test chamber.

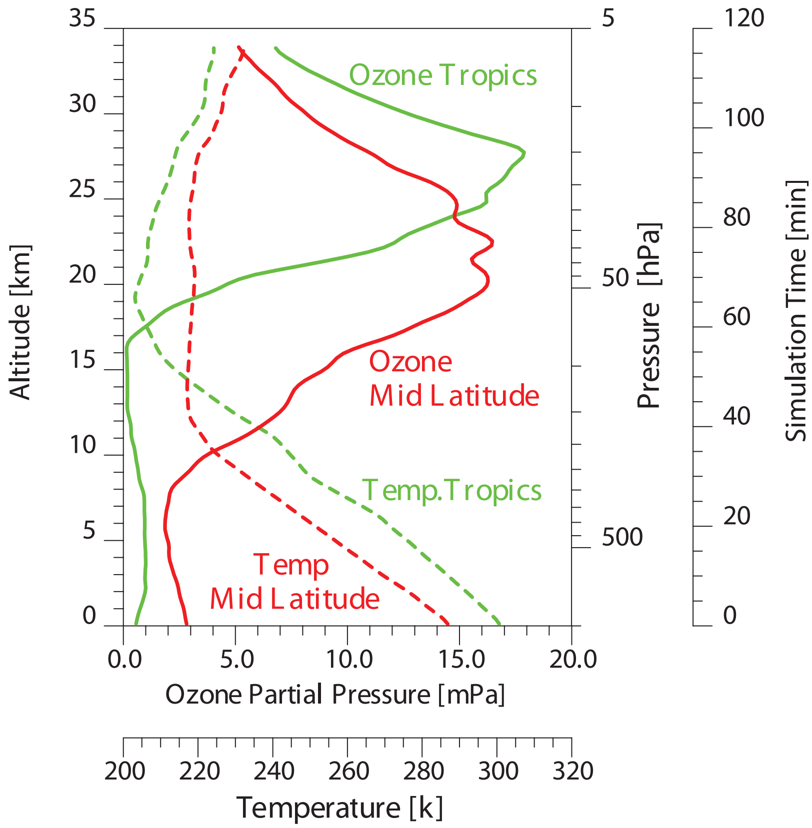

Figure 2. Vertical profiles of the simulation of ozone partial pressure and temperature at mid-latitudinal and tropical conditions.

Thus for each molecule of ozone entering the cathode's solution, a current of two electrons is produced that flows through the external circuit. A small electrically driven gas sampling pump fabricated from Teflon [*Komhyr*, 1967] forces ambient air through the cathode cell containing the sensing solution so that an electrical current is generated which is proportional to the amount of ozone bubbling through the cell. By knowing the gas flow rate Φ_P (cm^3 s^{-1}), its temperature T_P (K) and the conversion efficiency of the ozone sensor η_C, the electrical cell current I_M (μA) after subtraction of a background current I_B (μA) is converted to the ozone partial pressure P_{O3} [*Komhyr*, 1969]:

$$P_{O3} = 0.04308 \cdot \eta_C \cdot \frac{T_P}{\Phi_P} \cdot (I_M - I_B) \quad (3)$$

The constant 0.04307 is determined by the half ratio of gas constant and Faraday constant [*Komhyr*, 1969]. The electrical cell current I_M and pump temperature T_P are measured in situ during the sounding. The background current I_B and volumetric flow rate Φ_P of the gas sampling pump of each sonde are measured in the laboratory at ambient air pressure during pre-flight preparations. The conversion efficiency η_C represents the absorption efficiency of O_3 into the sensing solution and the stoichiometry of the conversion of O_3 into I_2. During normal operation it is assumed that the conversion efficiency η_C is unity at neutral pH [*Komhyr*, 1969, 1986]. Usually a sodium-hydrogen phosphate buffer is added to the cathode sensing KI-solution to keep the pH neutral at 7.0. Further, potassium bromide (KBr) is added. Although, its role is less clear KBr probably stabilizes the conversion of ozone into iodine [*Saltzman and Gilbert*, 1959].

2.3. Data Processing ECC-Ozone Sonde

[13] Unless otherwise mentioned, the sonde data are processed according to equation (3) following the guidelines of *Komhyr* [1986] (Table 2). The temperature T_P of the airflow is measured at the outside of the Teflon block of the pump.

Table 2. Standard Corrections Used for Processing Sonde Data Recommended by *Komhyr* [1986]

Temperature Air Sampling	Pump Flow Efficiency Correction	Background Current Correction	Total Ozone Normalization
Outside of pump	Empirical table, *Komhyr* [1986]	Before exposure to ozone oxygen (pressure) dependent	No

Table 3. Pump Flow Correction Factors (C_{PF}) as Function of Air Pressure for ECC-Ozonesondes Reported by *Komhyr*, 1986, and *Komhyr*, 1995[a]

	Pump Flow Correction Factor C_{PF} for 2.5 cm^3 Cathode Solution		
Pressure, hPa	*Komhyr*, 1986	*Komhyr*, 1995	NOAA, 1996
1000	1	1	1
100	1.007 ± 0.005	1.007 ± 0.005	1.018 ± 0.005
50	1.018 ± 0.006	1.018 ± 0.005	1.035 ± 0.008
30	1.022 ± 0.008	1.029 ± 0.008	1.053 ± 0.013
20	1.032 ± 0.009	1.041 ± 0.012	1.071 ± 0.020
10	1.055 ± 0.010	1.066 ± 0.023	1.120 ± 0.025
7	1.070 ± 0.012	1.087 ± 0.024	1.160 ± 0.030
5	1.092 ± 0.014	1.120 ± 0.024	1.210 ± 0.040
3	1.124 ± 0.025	1.241 ± 0.043	1.350 ± 0.070

[a]Column with NOAA, 1996 are average correction factors obtained from individual pump flow efficiency measurements of the 6 sondes operated by NOAA at JOSIE 1996 (See section 3).

[14] The background current is measured two times during pre-flight preparation: Once before and once after the sonde had been exposed to a sampling flow with about 100 ppbv ozone for about 10 min. Both background measurements were made after flushing the sondes with purified (ozone free) air for 10 min. A pressure dependent background current correction is used that assumes oxygen dependence with a gradual decline that is proportional with decreasing pressure [*Komhyr*, 1986] and is negligible in the upper troposphere and stratosphere. It is thereby assumed that the background current is caused by a small interference of oxygen reacting with KI in the cathode and producing iodide i.e., small additional current.

[15] At reduced air pressures, the pump flow rate declines due to pump leakage, dead volume in the piston of the pump, and the back pressure exerted on the pump by the cathode cell solution [*Komhyr*, 1967; *Steinbrecht et al.*, 1998]. This decrease in pump efficiency at reduced pressures is corrected by multiplying the pump flow rate in equation (3) with a pump correction factor C_{PF} as function of air pressure. Table 3 lists the two most widely applied tables of C_{PF}. These are based on laboratory measurements of the pump efficiency at reduced pressures [*Komhyr*, 1986; *Komhyr et al.*, 1995].

[16] In field operations, ozonesonde data profiles are sometimes normalized, i.e., linearly scaled, to an independently determined ozone column amount [*SPARC-IOC-GAW*, 1998]. To complete the total ozone column derived from the ozonesonde profile a residual ozone column above the burst altitude is determined. The independent measurement, typically from a Dobson or Brewer spectrophotometer, provides a means for evaluating the quality of the profile. In routine operation the normalization factors for ECC-sondes are in the range of 0.9–1.1 [*SPARC-IOC-GAW*, 1998]. In JOSIE the normalization factor N_{TO} is defined as the ratio of the integrated column of ozone obtained from both, the UV-photometer and the sonde. N_{TO} is thereby determined after making all other corrections to the profile.

2.4. Design of JOSIE

[17] JOSIE 1996 addressed primarily the profiling capabilities of three types of ECC ozonesondes (SPC-5A, SPC-6A and ENSCI-Z), where the sondes were tested using different operating procedures [*Smit and Kley*, 1998]. JOSIE 1998 compared the performance of brand new manufactured ECC-sondes (SPC-6A and ENSCI-Z) from the two manufacturers [*Smit and Straeter*, 2004a]. JOSIE 2000 investigated the influence of the use of three different cathode sensing solutions (standard 1.0% potassium iodide (KI) & full buffered, 0.5% KI & half buffered and 2.0% KI & unbuffered, on the performance of both ECC-sonde types [*Smit and Straeter*, 2004b].

3. JOSIE 1996

[18] JOSIE 1996, carried out in February/March 1996, was attended by representatives of eight laboratories involved in the GAW ozonesonde network to assess the performance of the major ozonesonde types (ECC, BM and KC79) in routine use today [*Smit and Kley*, 1998]. The focus was on assessing whether differences in instrument preparation and data analysis from each laboratory would cause significant differences in measurements. Four laboratories tested their operating procedures using the ECC sondes types SPC-5A, SPC-6A and ENSCI-Z (Table 4). In addition, four other laboratories using non-ECC sonde types participated in JOSIE 1996 [*Smit and Kley*, 1998], but these investigations are not subject of this paper.

[19] Each sounding laboratory participated in a total of six simulation experiments: 4 simulation runs with a mid-latitudinal profile and 2 runs using a tropical profile (Figure 2). The preparation of the ECC-sondes in the laboratory, prior to a simulation run, mostly followed the guidelines described by *Komhyr* [1986]. Although, not part of the Komhyr's guidelines, for cleaning purposes CNRS exposed the entire instrument to highly ozonized air for about one day (Table 4). For all sondes the cathode cell was prepared with 1.0% KI & full buffer sensing solution (SST1.0, Table 5) as recommended by the manufacturers of SPC-5A and SPC-6A sondes [*Science Pump Corporation*, 1996] and ENSCI-Z sondes [*EN-SCI Corporation*, 1994]. All sondes were brand new and manufactured after January 1995.

[20] The raw ECC-sonde data of each participating sounding laboratory were processed by WCCOS applying procedures specific for that laboratory (Table 4). All four laboratories measured the temperature T_P of the sample airflow (See also equation (3)) at the outside of the Teflon block of the pump.

[21] Several times during the simulation ozone was temporarily set to zero level to investigate the in-flight time response characteristics. In general, throughout the entire profile the in-flight response time of the ECC-sonde is within 20–30 seconds. For normal operations, with an ascent velocity of 5 m/s, this means an altitude resolution of 100–150 m.

[22] Figure 3 gives an overview of the sonde comparisons with the UV-photometer showing for each participating ECC-laboratory the relative deviations of the sonde from the UV-photometer obtained from six simulations runs. All sondes show throughout the entire profile a relative precision of about ±(2–5)%. In the troposphere (below ~12 km altitude) the sondes show a small average bias varying between −4% and +3%. In the stratosphere (above

Table 4. Survey of JOSIE 1996, 1998 and 2000 With Participating Laboratories With the ECC Sonde Types Used and Their Specific Preparations, Sensing Solution Type (SST, Table 5) and Data Processing Methods (Pump Flow Correction, Background Correction and Total Ozone Normalization) Applied[a]

Participant	Sonde Type	Preparation	Sensing Solution Type (Table 5)	Pump Flow Efficiency correction (Table 3)	Background Current correction	Total Ozone Normalization
			JOSIE 1996			
NOAA	ENSCI-Z	*Komhyr* [1986]	SST1.0	Individual calibration [*Johnson et al.* 2002]	Full	No
FZJ	SPC-6A	*Komhyr* [1986]	SST1.0	Empirical table, *Komhyr* [1986]	Pressure dependent	No
EC	SPC-5A	*Komhyr* [1986]	SST1.0	Empirical table, *Komhyr* [1986]	Pressure dependent	No
CNRS	SPC-5A	*Komhyr* [1986] + Exposure entire instrument to highly ozonized air	SST1.0	Empirical table, *Komhyr* [1986]	Pressure dependent	No
			JOSIE 1998			
FZJ	ENSCI-Z	*Komhyr* [1986]	SST1.0	Empirical table, *Komhyr* [1986]	Pressure dependent	No
FZJ	SPC-6A	*Komhyr* [1986]	SST1.0	Empirical table, *Komhyr* [1986]	Pressure dependent	No
			JOSIE 2000			
NOAA	ENSCI-Z & SPC-6A	*Komhyr* [1986]	SST2.0	Empirical table, *Komhyr* [1986]	Pressure dependent	No
EC	SPC-6A	*Komhyr* [1986]	SST2.0	Empirical table, *Komhyr* [1986]	Pressure dependent	No
NIWA	ENSCI-Z	*Komhyr* [1986]	SST0.5	Empirical table, *Komhyr* [1986]	Pressure dependent	No
FZJ	SPC-6A	*Komhyr* [1986]	SST0.5	Empirical table, *Komhyr* [1986]	Pressure dependent	No
NASA	SPC-6A	*Komhyr* [1986]	SST1.0	Empirical table, *Komhyr* [1986]	Pressure dependent	No
ASP	ENSCI-Z	*Komhyr* [1986]	SST1.0	Empirical table, *Komhyr* [1986]	Pressure dependent	No
URI	ENSCI-Z	*Komhyr* [1986]	SST0.5 & SST2.0	Empirical table, *Komhyr* [1986]	Pressure dependent	No
JMA	KC96	-	-	-	-	-

[a]Full background correction assumes no pressure dependence, i.e., full background subtraction from measured cell current (equation 3), while pressure dependent means linear dependent. Participants JOSIE 1996: National Oceanic and Atmospheric Administration/Climate Monitoring Division (NOAA/GMD), USA; Forschungszentrum Jülich (FZJ), Germany; Environment Canada (EC), Canada; Centre Nationale de la Recherche Scientifique (CNRS), France. JOSIE 1998: All sondes were prepared and processed by the staff of the simulation facility (FZJ). Participants JOSIE 2000: National Oceanic and Atmospheric Administration/Global Monitoring Division (NOAA/GMD), USA; Environment Canada (EC), Canada; National Institute of Water and Atmospheric Research (NIWA); New Zealand, Forschungszentrum Jülich (FZJ), Germany; National Aeronautic Space Agency/Wallops Flight Facility (NASA/WFF), USA; Aerological Station Payerne (ASP, Meteo Swisse), Switzerland; University of Reunion Island (URI), France; Japan Meteorological Agency (JMA) Japan. JMA were deploying the KC96-sonde, a carbon iodine cell type after *Kobayashi and Toyama* [1966].

$\sim$12 km altitude) FZJ- and EC-sondes show only a small average bias (1–5%) while NOAA-sondes exhibit a positive bias of (8–16)% and CNRS -sondes a negative bias of −(7–9)%.

[23] The enhanced ozone values measured by the NOAA -sondes at lower pressures are most likely caused through the use of a larger pump flow efficiency correction than the other ECC-sonde users (Table 4) in conjunction with the increase of sensitivity of the ozone sensor during flight operation. In general, by the time the sonde reaches the lower/middle stratosphere, it has been operating for nearly 60 min and uncertainties in the sensor cell have increased. Some of the sensing solution has evaporated at a rate dependent on the temperature of the cell and ambient pressure. Evaporation causes the concentration of the sensing solution to increase, which can enhance the sensitivity of the sensor to ozone. *Johnson et al.* [2002] showed that the latter impact is significant in presence of the "pH-buffering" phosphate chemicals. Although, all sondes suffer from the same evaporation of sensing solution, increasing sensitivity, it is through the use of larger pump flow correction factors of NOAA that their sonde readings typically overestimate ozone more than other laboratories which use lower pump flow corrections.

[24] Usually the sodium-hydrogen phosphate buffer is added to the cathode sensing KI-solution to keep the pH neutral at 7.0. However, the buffer can also be the cause for the controversy of yielding a stoichiometric factor (I_2/O_3) larger than unity. The reaction mechanism and stoichiometric factor (I_2/O_3) of the net iodometric reaction (1) has been studied by a large number of investigators using a variety of KI-solution [e.g., *Boyd et al.*, 1970] and pH-buffers [e.g., *Dietz et al.*, 1973]. It appeared that depending on the concentrations of KI and the pH-buffer the stoichiometric

Table 5. JOSIE: Sensing Solution Types and Their Chemical Composition in Aqueous Solution for Cathode Cell of ECC-Ozone Sondes[a]

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

[a]For the anode sensing solution, usually a KI saturated cathode solution is employed.
[b]*Komhyr* [1986], SPC-6A instruction manual [*Science Pump Corporation*, 1996].
[c]ENSCI-Z instruction manual [*EN-SCI Corporation*, 1996].
[d]*Johnson et al.* [2002].

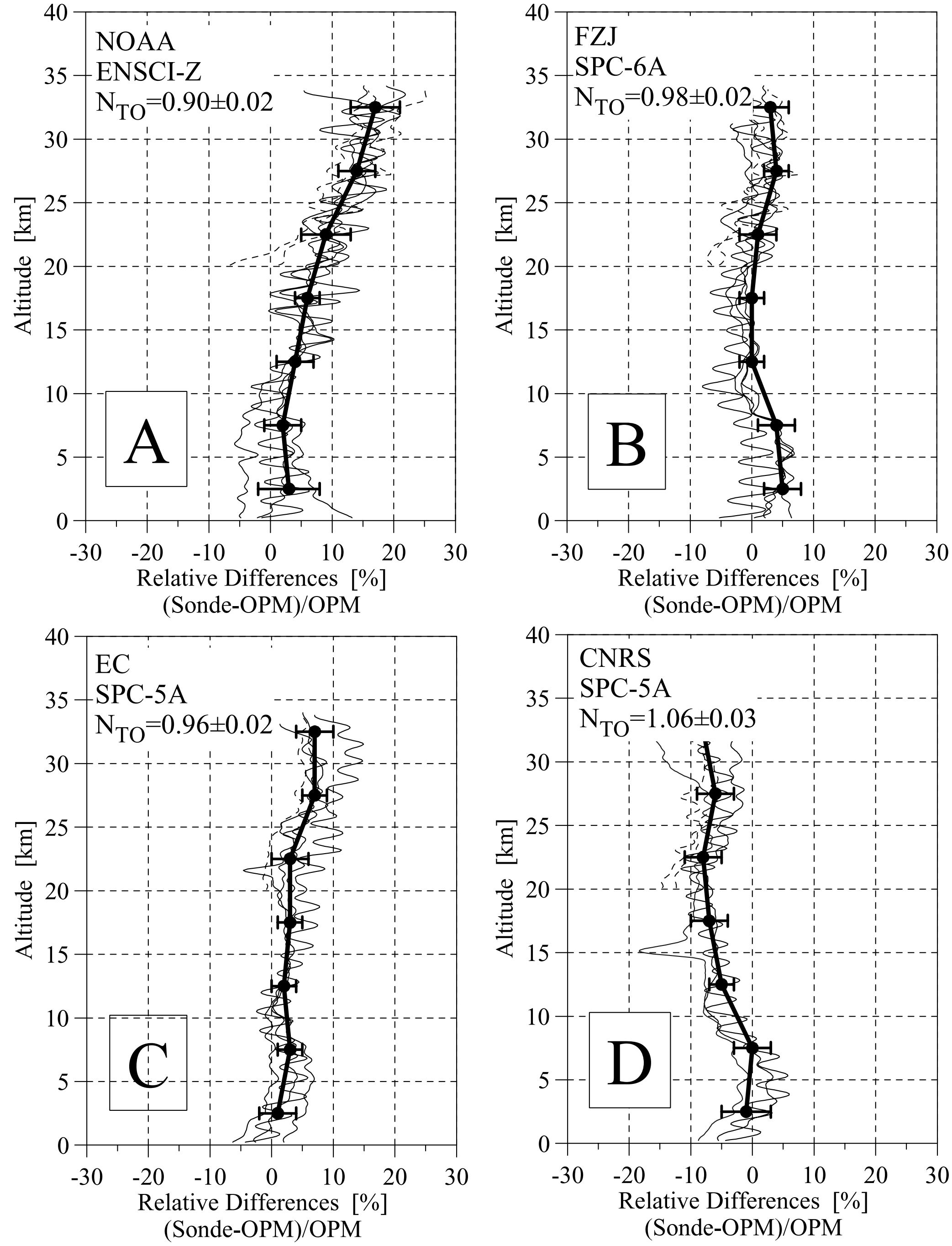

Figure 3. JOSIE 1996: Relative deviations of the individual ECC-sonde readings from the UV-photometer (OPM) for each participating laboratory obtained from six simulation runs of the mid latitudinal (solid lines) and the tropical (broken lines) profiles as a function of altitude. Due to the very low ozone concentrations in the tropospheric part of tropical profiles below 20 km are excluded. Bold line with solid dots represents the relative bias of the sonde to the OPM averaged in 5 km altitude bins. Uncertainty bars represents the relative precision of the sonde. All data were processed following guidelines in Table 4. N_{TO} ($\pm 1\sigma$) represents the average total ozone normalization factor determined for each participant. Two measured profiles (one by EC and one by CNRS) were excluded from further comparisons due to sonde failures [*Smit and Kley*, 1998].

factor can extend to 1.25. *Saltzman and Gilbert* [1959] suggested that side reactions involving the phosphate buffer can lead to additional iodine and thus to an increase of the stoichiometric ratio of iodine to ozone. The influence of different sensing solutions (KI and pH-buffer) on sonde performance is reported in JOSIE 2000 (Chapter 5).

[25] In the troposphere the performance of the ECC-sondes operated by CNRS is consistent with the perfor-

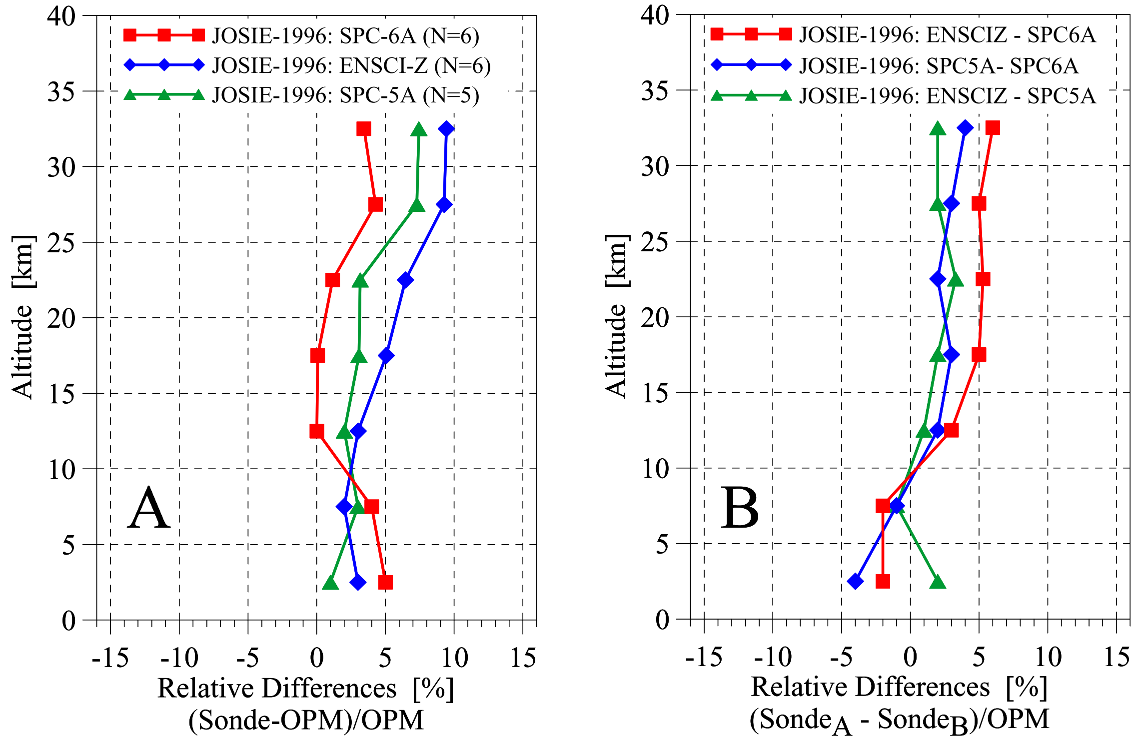

Figure 4. JOSIE 1996: Average relative bias of SPC-5A (N = 5 sondes, EC), SPC-6A (N = 6 sondes, FZJ) and ENSCI-Z (N = 6 sondes, NOAA) sonde type compared to UV-Photometer (OPM) (diagram A) and average relative differences between the three ECC-sonde types compared to OPM (diagram B). All data processed with pump correction from *Komhyr* [1986], pressure dependent background correction and no total ozone normalization (Table 3). The displayed data are averaged over altitude bins of 5 km.

mance of the ECC-sondes operated by NOAA, FZJ and EC. However, in the stratosphere ECC sondes from CNRS showed about 5–7% lower ozone values than the ECC-readings obtained by FZJ- and EC-sondes. Although FZJ, EC and CNRS used similar preparation procedures [*Komhyr*, 1986], CNRS preparations included for cleaning purposes exposure of the entire ECC-sonde (sensor+pump+motor) to highly ozonized air which was generated by a UV-lamp through photolysis of oxygen. This highly ozonized air had a deteriorating effect on the pump motor or pump during the simulation runs. At lower air pressures a strong increase of the electrical current of the pump motor was observed indicating enhanced friction of the pump that is causing too low flow rates and thus too low ozone readings. Therefore the SPC-5A-sondes deployed by CNRS were excluded from further data analysis.

[26] To investigate the performance of the three different types of ECC sondes in more detail the raw sounding data of SPC-5A (EC), SPC-6A (FZJ) and ENSCI-Z (NOAA), were processed following exactly the same *Komhyr* [1986] correction (Table 2) and compared to the UV-photometer (Figure 4). The precision, determined by the standard deviation of the average of the sonde deviations (= bias) relative to the UV-photometer for all three ECC-sonde types, is nearly ±(3–5)%. This together with the bias relative to the UV-photometer (Figure 4a) can be used to determine the accuracy, defined as the sum of bias and precision. Although the differences observed among the three sonde types are smaller than 5% at all altitudes, in the stratosphere the ENSCI-Z ozone readings are systematically ~2% and ~4% larger than SPC-5A and SPC-6A sondes, respectively, and SPC-5A are ~2% larger than SPC-6A. These higher ENSCI-Z ozone readings are most likely due to a higher sensitivity of the ozone sensor to the cathode sensing solution causing a stoichiometric factor (I_2/O_3) larger than unity [*Johnson et al.*, 2002]. Shortly after the JOSIE 1996 campaign *EN-SCI Corporation* [1996] recommended the use of 0.5% KI, half pH-buffered sensing solution type SST0.5 (Table 5) for the ENSCI-Z sondes in order to lower the sensitivity of the sensor to ozone.

[27] JOSIE also demonstrated that even small differences in the preparation and correction procedures can introduce significant differences in the performance of the sonde. Good precisions and accuracies better than ±5% were obtained where the ECC-sondes were operated by the same procedures [e.g., *Komhyr*, 1986] that demonstrate the need for standardization of operating procedures.

4. JOSIE 1998

[28] JOSIE-1998 primarily focused on a quality check of the instrumental performance of newly manufactured ECC-sondes. A total of 26 ECC-sondes, 13 sondes of each model type (SPC-6A and ENSCI-Z) was randomly picked from stocks at different GAW sounding sites. All sondes were brand new, in the original packaging, and the manufacturing date was after 1 January 1997. SPC-5A sondes were excluded from JOSIE 1998 because their production ended in 1996.

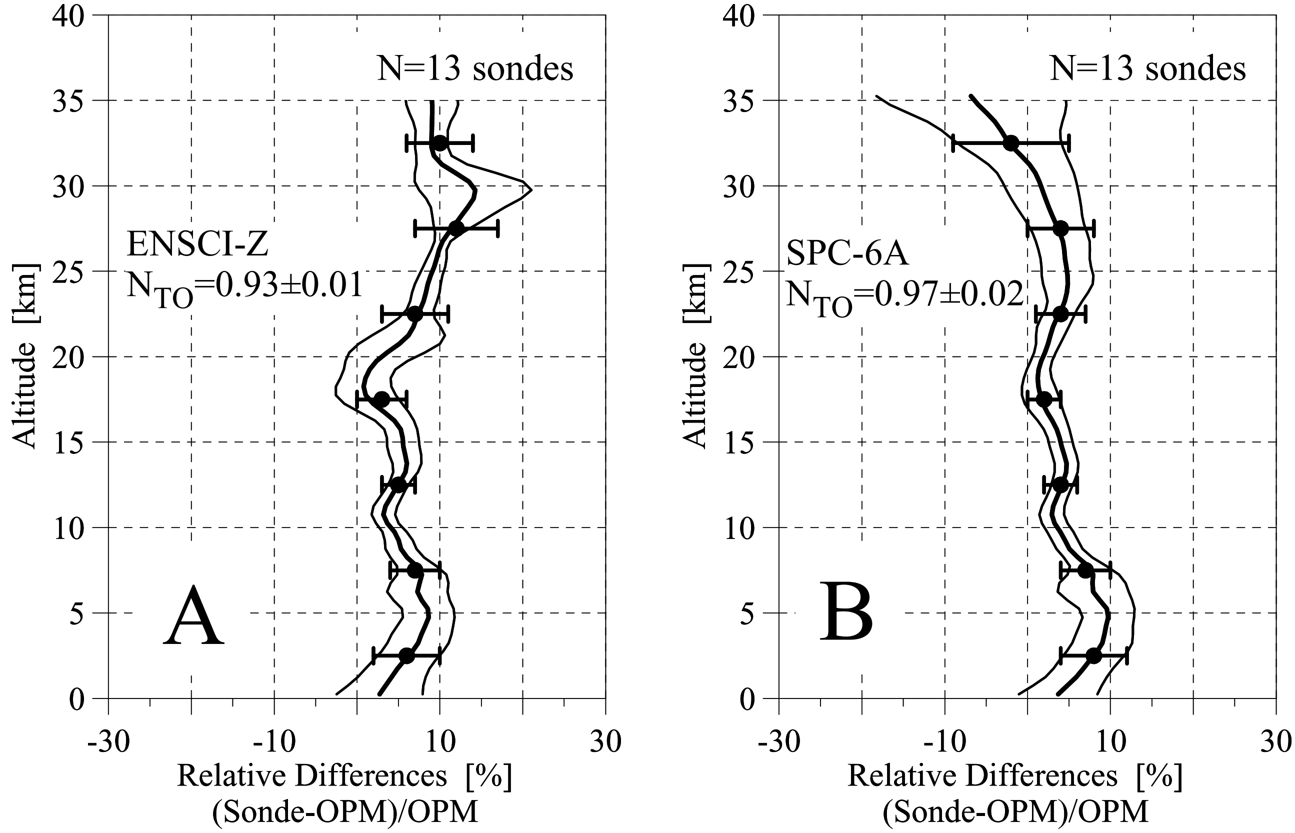

Figure 5. JOSIE 1998: comparison of all (N = 13) tested ENSCI-Z (diagram A) and all (N = 13) tested SPC-6A ozonesondes (diagram B). Results presented as averaged ($\pm 1\sigma$) relative deviations of the individual sonde readings from the UV-photometer (OPM). Solid dots with uncertainty bars represents the average relative bias and precision of the sonde to the OPM after splitting the overall results in 5 km altitude bins. All data were processed with pump correction from *Komhyr* [1986], pressure dependent background correction and no total ozone normalization (Table 2). N_{TO} ($\pm 1\sigma$) represents the average total ozone normalization factor determined for each sonde type.

[29] All sondes were subject to the same operating procedures [*Komhyr*, 1986] with preparation, simulations and data processing carried out by the WCCOS staff. Details of the JOSIE 1998 design and strategy are described by *Smit and Straeter* [2004a]. For both ECC-sonde types the cathode sensing solution SST1.0 (Table 5) was used. Each sonde was tested during a simulation run at typical mid-latitude conditions similar to JOSIE-1996 (Figure 2). In each simulation run four sondes (two SPC-6A and two ENSCI-Z) were tested simultaneously. The data processing methods applied followed *Komhyr* [1986] as summarized in Table 2 and, similar to JOSIE 1996, the pump temperature T_P was measured at the outside of the Teflon block of the pump.

[30] Results of the 26 tested sondes over seven simulation runs are reported in detail by *Smit and Straeter* [2004a]. For each sonde type an overview of the comparison with the UV-photometer is shown in Figure 5. Up to 20 km altitude both sonde types show a similar performance with a precision better than ±(2–4)% and a positive bias of about 5–10% relative to the UV-photometer. However, in the stratosphere (above 20 km) the performance of the two sonde types starts to deviate significantly. The precision of the SPC-6A sonde decreases with altitude to about ±(5–10)% whereas the observed bias changes sign with altitude from about +5% at 25 km into −8% at 35 km. This is in contrast to the ENSCI-Z sonde type, which exhibits a precision of ±(4–5)% and a rather large positive bias of about 10% up to 35 km altitude. These results are similar to JOSIE 1996 (Figure 5). The accuracy (= bias+precision) of the SPC-6A and ENSCI-Z sondes is primarily determined by the bias, which is mostly positive in magnitude.

5. JOSIE 2000

[31] JOSIE 2000 primarily focused on the influence of the chemical composition of the cathode sensing solution (KI and the phosphate buffer) on the performance of the ECC-sonde. On the basis of laboratory and field tests of ECC-sondes *Johnson et al.* [2002] found that depending on the concentrations of the cathode sensing solution, the stoichiometric ratio of the ozone to iodine conversion (equation 1) can increase from 1 up to 1.05–1.2. Johnson showed experimentally that this increase is mostly caused by the phosphate buffer with only a minor contribution from the KI concentration. During JOSIE 2000 the three most commonly used cathode sensing solution types (SST) were tested (Table 5). SST1.0 (1.0% KI & full pH-buffer) is the

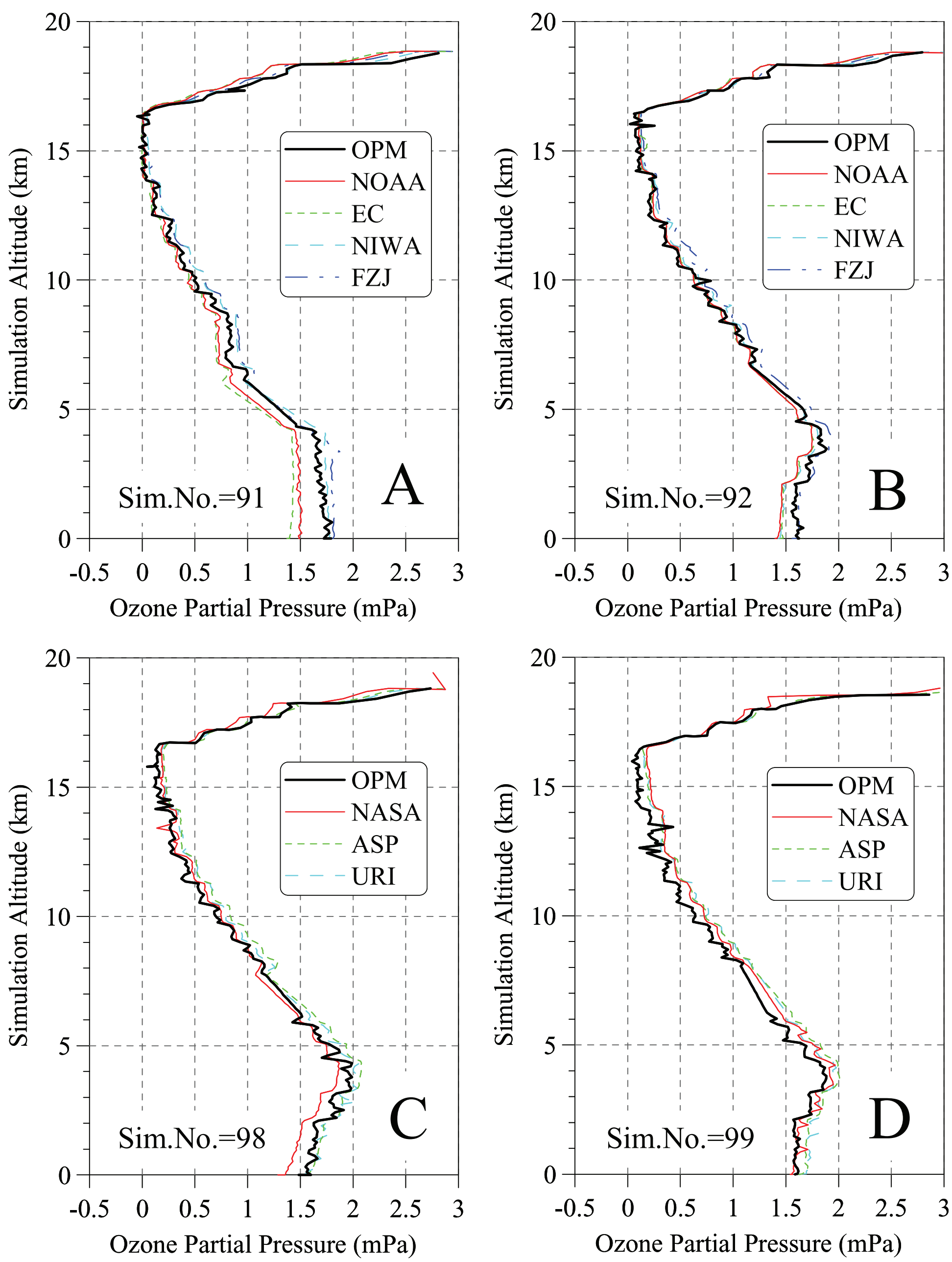

Figure 6. JOSIE 2000: Vertical ozone profiles measured by the different participants using different sonde and sensing solution types (thin lines, Table 6) and the UV-photometer (OPM) (bold line) for the tropospheric parts of the tropical profiles.

conventional sensing solution used in JOSIE 1996 and JOSIE 1998 which is based on the guidelines described by *Komhyr* [1986] and is most widely used for the ozonesonde types SPC-4A, -5A, and -6A manufactured by *Science Pump Corporation* [1996]. SST0.5 (0.5% KI & half pH-buffer) is the sensing solution recommended by *EN-SCI Corporation* [1996] since 1996 as the cathode solution for their sondes. The third sensing solution SST2.0, a non-pH-buffered solution with no KBr, but with 2.0% KI for the cathode cell has been introduced by *Johnson et al.* [2002]. In September/October 2000 JOSIE brought together 7 sounding stations testing ECC-sondes (SPC-6A & ENSCI-Z) with the three different solution types (Table 4). Details of the JOSIE 2000 campaign are reported by *Smit and Straeter* [2004b].

[32] Each sounding laboratory participated in six simulation experiments: (a) two runs using the mid-latitude profile (Figure 2), (b) two runs using the tropical profile (Figure 2) and (c) two runs using a sub-tropical profile as defined in *Standard Atmosphere* [1976]. For each SST a similar number of SPC-6A sondes and ENSCI-Z sondes were tested. The pre-launch procedures of each ozonesonde prior to a run were performed by the field operators of the participating stations using their own ground test equip-

Table 6. JOSIE: Summary of the Average Total Ozone Normalization Factors Obtained for Each Combination of ECC Sonde Type and SST[a]

	Total Ozone Normalization Factor (Correction After *Komhyr*, 1986)			
Campaign	Sensing Solution Type	ENSCI-Z (*N = Number of Sondes*)	SPC-6A (*N = Number of Sondes*)	Difference ENSCI-Z Minus SPC-6A
JOSIE-1996	SST1.0	0.94 ± 0.02 (*N = 6*)	0.98 ± 0.02 (*N = 6*)	−0.04
JOSIE-1998	SST1.0	0.93 ± 0.01 (*N = 13*)	0.97 ± 0.02 (*N = 13*)	−0.04
JOSIE-2000	SST1.0	0.93 ± 0.03 (*N = 8*)	1.00 ± 0.05 (*N = 8*)	−0.07
JOSIE-2000	SST0.5	0.96 ± 0.02 (*N = 8*)	1.03 ± 0.04 (*N = 5*)	−0.07
JOSIE-2000	SST2.0	1.03 ± 0.02 (*N = 6*)	1.09 ± 0.03 (*N = 7*)	−0.06

[a]The factors are calculated for data corrected according to *Komhyr* 1986 (Table 3). Corresponding results from JOSIE- 1996 and JOSIE-1998 are included.

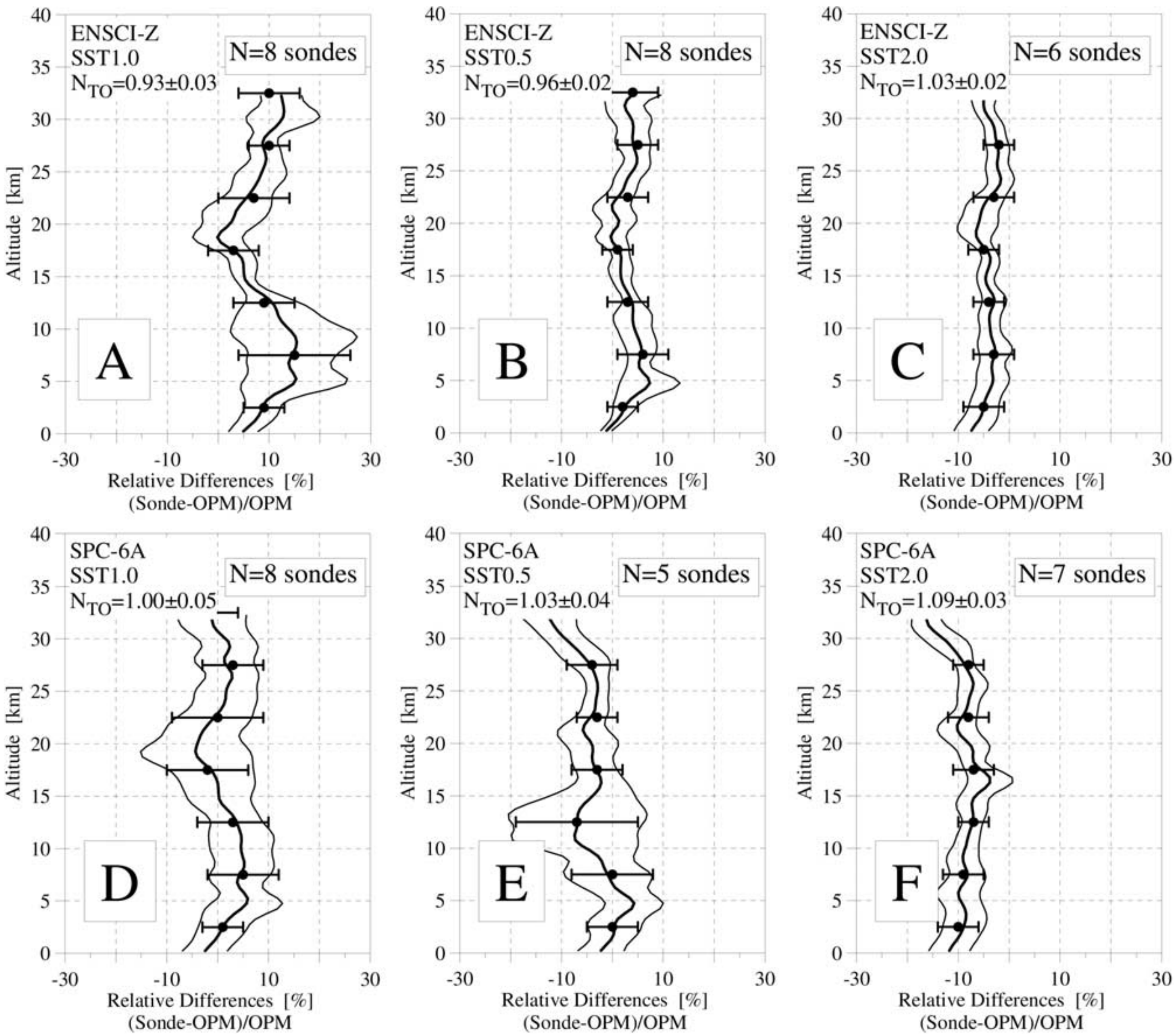

Figure 7. JOSIE 2000 comparison of ENSCI-Z (upper diagrams A, B & C) and SPC-6A (lower diagrams D, E & F) versus UV-photometer (OPM) for SST1.0, SST0.5 and SST2.0, respectively. Displayed are the averages ($\pm 1\sigma$) of the relative deviations of the individual sonde readings from the UV-photometer for each combination of sonde type and SST. The tropospheric parts of the tropical simulations (to 20 km) are not included in the relative deviations. Solid dots with uncertainty bars represents the average relative bias and precision of the sonde to the OPM after splitting the overall results in 5 km altitude bins. All data were processed with pump correction from *Komhyr* [1986], pressure dependent background correction and no total ozone normalization (Table 2). N_{TO} ($\pm 1\sigma$) represents the average total ozone normalization factor determined for each sonde type and SST.

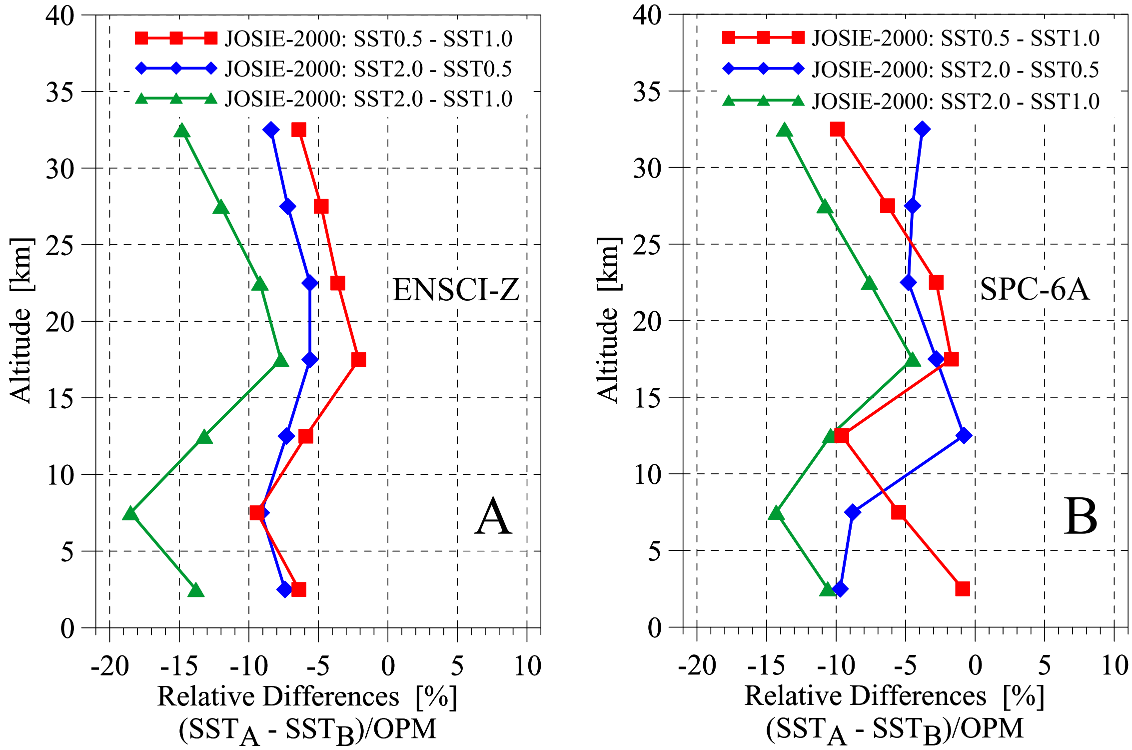

Figure 8. JOSIE 2000: Relative differences among the use of different SST for ENSCI-Z sonde type (diagram A) and SPC-6A sonde type (diagram B) as a function of altitude in bins of 5 km. All data were processed with pump correction from *Komhyr* [1986], pressure dependent background correction and no total ozone normalization (Table 2).

ment. During the simulation the sonde data were stored on-line in the WCCOS data acquisition system. All ECC-sonde data were processed and corrected according to the operating procedures of *Komhyr* [1986] (Table 2).

[33] A total of 49 ECC-sondes (22 SPC-6A and 27 ENSCI-Z) were "flown" in the simulation chamber. The sondes were all brand new with a manufacturer date not older than about one year. The results of the individual profiles show that in general the sondes track the simulated ozone profiles very well. Even for tropical profiles at very low tropospheric ozone partial pressures (0.3–1 mPa) the agreement is still good for both sonde types (Figure 6). These results from JOSIE 2000 are in good agreement with the tropical ozone profiles of JOSIE-1996 and are reassuring in terms of trends deduced from SHADOZ upper tropospheric ozone profiles [*Solomon et al.*, 2005; *Thompson et al.*, 2007a].

[34] Time response tests made during JOSIE 2000, whereby ozone was set to zero for a short period of 3–4 min, show that the response time of SPC-6A or ENSCI-Z sonde, typically 20–30 s, is not dependent on the SST [*Smit and Straeter*, 2004b].

[35] The normalization factors for different combinations of sonde type and SST show a consistent pattern (Table 6). Nearly all factors for the standard corrected data range between 0.93 and 1.09 with a small variability of about ±(0.02–0.05). However, for each sonde type the normalization factors for SST0.5 and SST2.0 are about 3% and 9–10%, respectively, larger than for SST1.0. For each SST the factors for ENSCI-Z are about 6–7% lower than for SPC-6A sondes indicating that ENSCI reports more ozone than SPC-6A. For SST1.0 the observed differences between ENSCI-Z and SPC-6A are about 3 % larger during JOSIE 2000 compared to JOSIE 1996 & 1998 (Table 6) which also showed the same ENSCI-SPC6A offset.

[36] For each combination of sonde type and SST, the overall sonde comparisons with the UV-photometer are displayed as relative deviations from the UV-photometer in Figure 7. Both sonde types show a relative variability, i.e., precision of about ±(3–6)% throughout the entire profile with some outliers up to ~±12%. The origin of these outliers is not really understood. Although the best precision for both sonde types is achieved with SST2.0, both sondes with SST2.0 exhibited a significant negative bias with values of −(7–15)% for SPC-6A and −(3–8)% for ENSCI-Z sondes depending on altitude. The smallest average relative bias was achieved for the SPC-6A sonde with SST1.0 and for ENSCI-Z sonde with SST0.5 or SST2.0.

[37] Throughout the entire ozone profile systematic features of the different SST are seen by comparing the performance of ENSCI-Z and SPC-6A sondes (Figure 8). For both sonde types there is a systematic change in the ozonesonde readings of about 5–15% with differing SST. A change from SST1.0 to SST0.5 or from SST0.5 to SST2.0 produces a change in the ozone reading up to 5–10%, depending on the altitude. A maximum ozone difference of more than 10% can be expected when changing from SST1.0 to SST2.0. Integrated over the entire profile, the

Table 7. Survey of Average Background Current (±1σ) Before and After Exposure of Ozone Obtained During Pre-flight Preparations of the Sondes "Flown" During JOSIE 1996, 1998 and 2000

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
Background current, μA		0.02–0.05	0.05–0.11	0.00–0.03	0.03–0.11
Background contribution to ozone partial pressure, mPa		0.07–0.17	0.2–0.4 mPa	0–0.1 mPa	0.1–0.4 mPa
Background contribution to surface ozone at mid latitude		2–5%	2–10%	0–3%	3–10%

ozone column of both sonde types decreases by about 3% in case of a change from SST1.0 to SST0.5 and by about 6–7% when changing from SST0.5 to SST2.0.

6. Results From JOSIE 1996–2000

6.1. Instrumental/Operating Uncertainties

[38] The JOSIE experiments have shown that for ECC-ozonesondes a precision better than ±(3–5)% can be achieved, particularly in the stratospheric region between the tropopause and 25 km. However, some outliers in the troposphere and in the stratosphere above 25 km altitude are observed. Causes of these outliers are different in the two regions of the atmosphere.

6.2. Troposphere: Background Current and its Correction

[39] Due to the relatively low ozone concentrations in the troposphere compared to the stratosphere, the correction for the background current can have a significant impact on tropospheric values [*Smit et al.*, 1994; *Reid et al.*, 1996]. For ECC-sondes the conventional method of correction prescribed by *Komhyr* [1986] assumes the background current to be dependent on the oxygen partial pressure, i.e., decrease proportional with pressure. Laboratory studies [*Thornton and Niazy*, 1982, 1983; *Smit et al.*, 1994] did not show any oxygen dependence on the background current and recommended a constant background current correction throughout the ozone profile. The background current can also depend on exposure to ozone during pre-flight preparations [*Smit et al.*, 1994]. During the JOSIE experiments, as part of the pre-"flight" preparation, the background current was measured before and after pumping for 10 min air with ozone (150–200 ppbv) through the sensor. Each time before the background current was measured the sensor was flushed for 10 min with ozone free air.

[40] The overall results for the background currents of JOSIE 1996–2000 are summarized in Table 7 for the ENSCI-Z and SPC-6A sonde types and different SST. The background currents of the SPC-6A and ENSCI-Z sondes are of the same magnitude and both are significantly larger after exposure to ozone. This enhancement effect of the background current, from values 0–0.05 μA before ozone exposure to 0.05–0.11 μA after exposure to ozone, is most likely due to "memory" effects of the sensor caused by reaction of ozone in the sensing cathode solution. However, in JOSIE 2000 no indication of any influence of the SST on the background current was observed.

6.3. Pump Temperature: Internal and External

[41] The standard procedure for measuring the pump temperature during JOSIE 1996–2000 was to tape a thermistor to the outside of the Teflon block of the pump near to

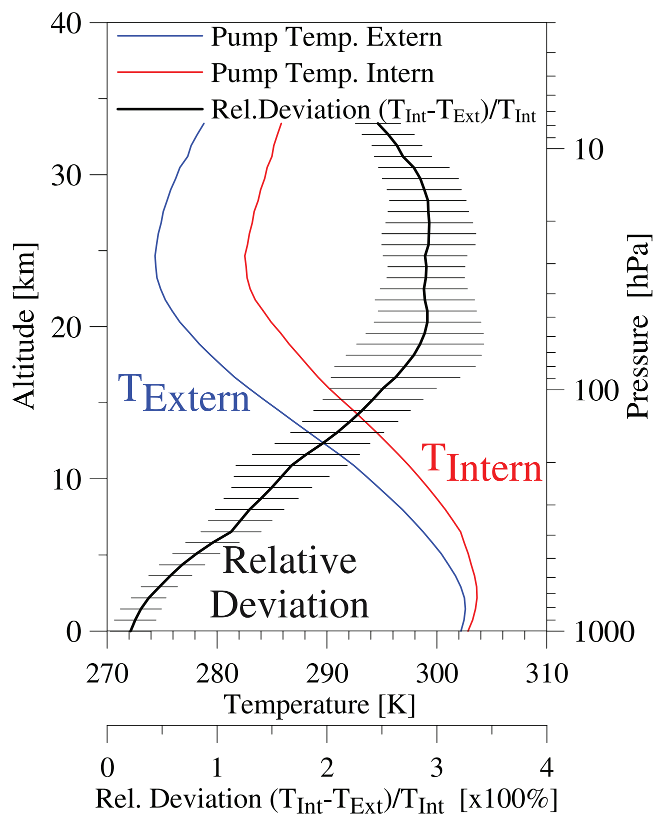

Figure 9. JOSIE 2000: Internal and external pump temperature and their relative differences as a function of altitude obtained from combined internal and external temperature measurements over an ensemble of 8 ECC-sondes (3 ENSCI-Z and 5 SPC-6A) tested during JOSIE 2000.

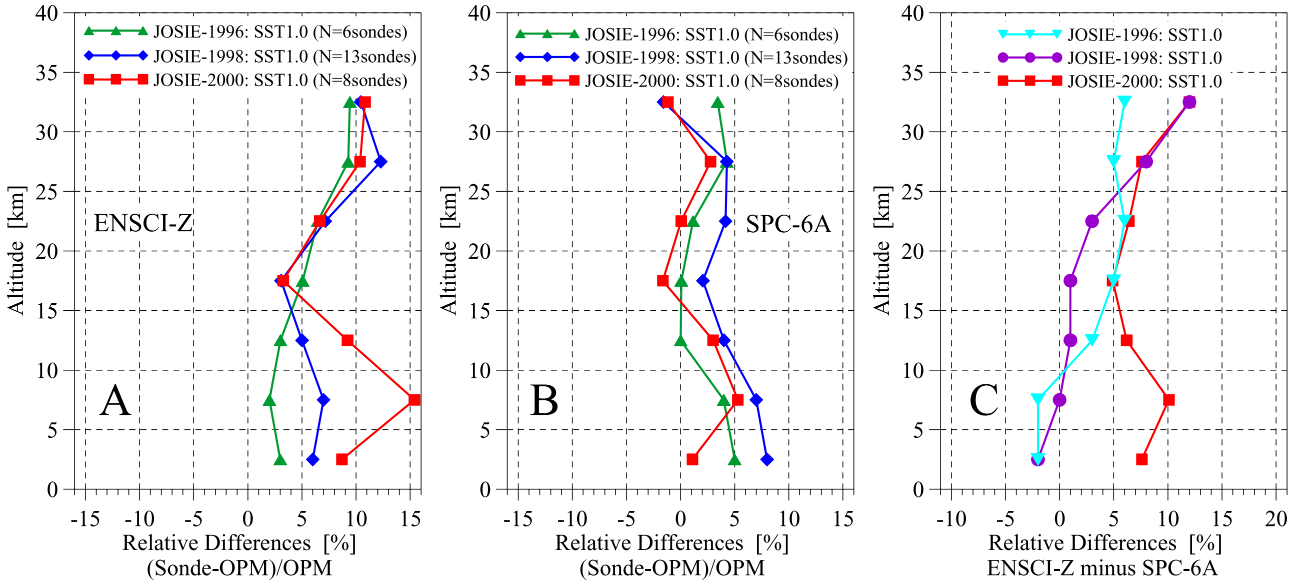

Figure 10. JOSIE: Differences of ENSCI-Z (A) and SPC-6A sondes (B) relative to UV-photometer (OPM) and relative differences between both sonde types (C). ECC-sondes were prepared according to *Komhyr* [1986] with SST1.0 during JOSIE 1996, 1998 and 2000. All data were processed with pump correction from *Komhyr* [1986], pressure dependent background correction and no total ozone normalization (Table 2). Data are averaged over 5 km altitude bins.

and at the same height as the tube outlet from the block (going to the cathode cell) - henceforth known as the 'external pump temperature'. All presented data are based on the use of the measured external pump temperature. Nowadays, both ECC-sonde manufacturers provide their sondes with a hole drilled into the Teflon block. This allows the thermistor to be positioned close to the piston and to measure the 'internal pump temperature'. Figure 9 shows the typical evolution of the internal and external pump temperatures as a function of pressure derived from measurements over an ensemble of 8 ECC-sondes (3 ENSCI-Z and 5 SPC-6A) tested during JOSIE 2000. Because of frictional heating of the moving piston of the pump the internal pump temperatures are 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 toward 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. The observed differences indicate that using the internal pump temperature ($T_{P,Int}$) instead of the external pump temperature ($T_{P,Ext}$) can lead to 0–3% larger ozone readings depending on pressure, i.e., altitude (Figure 9) while the corresponding total ozone normalization factor would be 1–2% lower than the reported values in Table 7. Considering Figure 8 it would cause an additional overestimation of ozone for SPC-6A (SST1.0) and ENSCI-Z (SST1.0 and SST0.5), while for SPC6-A (SST0.5) it would bring it closer to the photometer measurements. However, the results are just based on a few measurements and need more simultaneous measurements of internal and external pump temperature during flight operation to draw final conclusions.

6.4. Different ECC-Sonde Types With Different Sensing Solutions

[42] JOSIE 1996 showed that the differences among ECC-sonde types (SPC-5A, SPC-6A and ENSCI-Z operated with SST1.0) and UV-photometer were largely due to differences in the preparation and correction procedures of the various laboratories. Consistent results were obtained for ECC-sondes operated by the procedures described by *Komhyr* [1986] (Figure 10). In the troposphere and lower/middle stratosphere up to 35 km altitude, the precision is ±(3–5)% with a positive bias of the order of 5–10% relative to UV-photometer. These results are in good agreement with field comparisons that evaluated the performance of ECC-sondes in the troposphere and in the stratosphere [e.g., *SPARC-IOC-GAW*, 1998; *Lemoine and De Backer*, 2001; *Fioletov et al.*, 2006]. *Ancellet and Beekmann* [1997] compared regular ozone soundings (SPC-5A) with simultaneous tropospheric Lidar measurements and observed a systematic difference of ECC-sondes of about 4 ± 3% relative to the Lidar. Comparisons of ECC-sondes (mostly SPC-5A) versus lidar/microwave ozone profiles in the stratosphere indicate that ECC-sondes tend to overestimate ozone by about 2 ± 3% at altitudes above 20 km [*SPARC-IOC-GAW*, 1998].

[43] The JOSIE experiments all indicated that, when operated under similar conditions, following guidelines of *Komhyr* [1986] and using SST1.0, the SPC-6A and ENSCI-Z sondes both overestimate ozone (Figure 10). In the middle stratosphere above 25 km altitude the ENSCI-Z-sonde measures 5–10% more ozone than the SPC-6A sonde. Below 25 km the differences between both sonde types and the UV-photometer were less than 5% during JOSIE 1998 but were 10–15% during JOSIE 2000. The experiments show that characteristics of the two ECC-sonde types are not always the same, even when operated under the same conditions. They exhibit systematic differences of

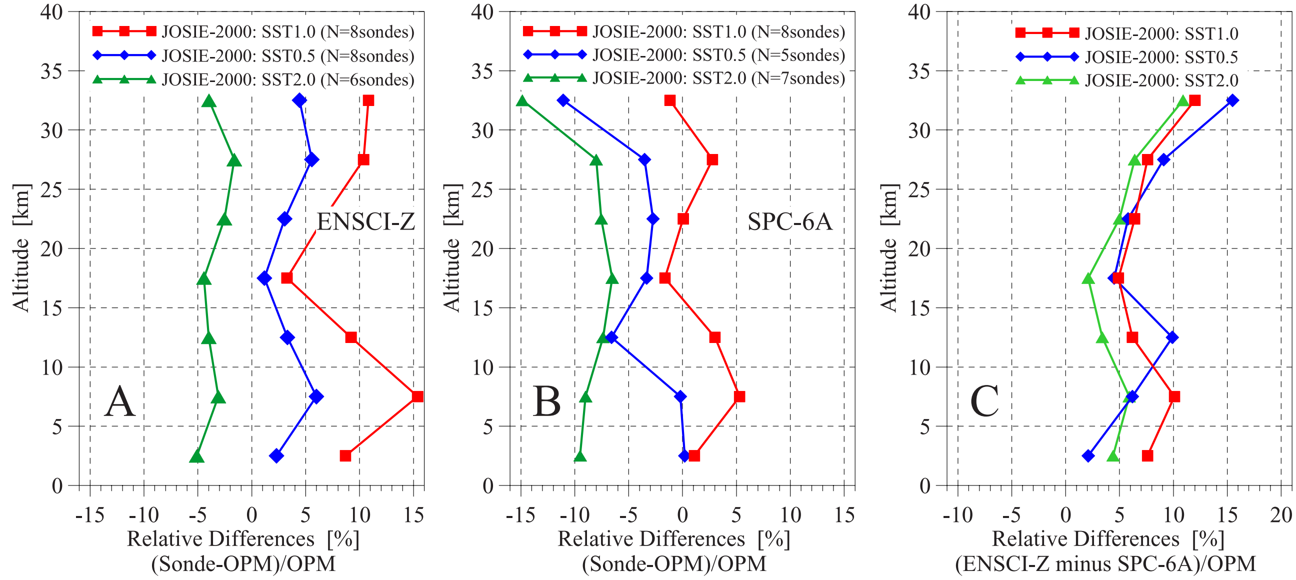

Figure 11. JOSIE: Differences of ENSCI-Z (A) and SPC-6A sondes (B) relative to UV-photometer (OPM) and relative differences between both sonde types (C) for use of SST1.0, SST0.5 and SST2.0 during JOSIE 2000. All sondes were prepared according to *Komhyr* [1986]. All data were processed with pump correction from *Komhyr* [1986], pressure dependent background correction and no total ozone normalization (Table 2). Data are averaged over 5 km altitude bins.

∼5% in the stratosphere and 5–10% in the troposphere which can vary from JOSIE campaign to campaign. Differences larger than the 3–5% precision of the sondes can get significant and probably depend on manufacturer batch to batch (Figure 10). However, the origin of these differences is not known at the present.

[44] ECC-sondes, operated with SST1.0, tend to overestimate ozone, even in the altitude region above 25 km where the conventional pump correction by *Komhyr* [1986] and *Komhyr et al.* [1995] is probably too low [*De Backer et al.*, 1998; *Johnson et al.*, 2002]. This is most likely compensated by the increasing sensitivity of the ECC-sonde as the sensing solution evaporates [*Johnson et al.*, 2002]. The increased sensitivity to ozone at increasing concentration of sensing solution was addressed by *Komhyr* [1969] and *Barnes et al.* [1985]. The enhanced sonde readings are most pronounced for ENSCI-Z sondes operated with SST1.0. In order to compensate, the ENSCI-Z manufacturer recommended reducing the concentration of the cathode sensing solution by using SST0.5 [*EN-SCI Corporation*, 1996].

[45] JOSIE 2000 shows that independent of the SST, the performance characteristics of the ENSCI-Z and SPC-6A sondes are different (Figure 11). The relative differences between both sonde types as a function of altitude are very similar for SST1.0, SST0.5 and SST2.0. When both sonde types are operated with the same SST the ENSCI-Z sonde readings are about 5–10% higher than the SPC-6A sonde throughout almost the entire vertical ozone profile. Above 25–30 km altitude the differences increases up to 10–15%, primarily caused by the declining response of the SPC-6A sonde (Figure 11b).

[46] Good results are achieved for SPC-6A sondes with SST1.0 and ENSCI-Z sondes with SST0.5. Both sonde types exhibit a bias relative to the UV-photometer less than 5% (Figures 11a and 11b) and the lowest relative differences between both sonde types with values of 2–5% at all altitudes (Figure 12).

7. Summary and Conclusions

[47] Since 1996 three JOSIE experiments to assess the performance of ECC ozonesondes in comparison to a UV-photometer have been conducted in the environmental simulation facility at the Research Centre Juelich. The 1996 experiments focused on differences in sonde preparation and data analysis procedures. The 1998 experiments compared primarily the performance of the SPC-6A and ENSCI-Z sondes from the two manufacturers. JOSIE 2000 addressed the influence of the use of the three most widely used sensing solution types (SST1.0, SST0.5 and SST2.0) on the performance of both sonde types.

[48] The JOSIE simulations showed that when the sondes are prepared and analyzed according to exactly the same procedures as *Komhyr* [1986], i.e., pressure dependent background and *Komhyr* 1986 pump correction factors, then the precision of all three ECC-sonde types is better than 5% and accuracy is within ±(5–10)%. However, the ENSCI-Z sonde overestimated ozone by about 5% when operated with 1% KI, full buffer cathode sensing solution. In the troposphere and stratosphere up to 35 km altitude, the precision of all three ECC-sonde types was better than 5%.

[49] Even when SPC6A and ENSCI-Z sondes are prepared and operated according to exactly the same procedures, JOSIE results demonstrate that instrumental differences can affect the performance of both sonde types. Below 20 km the differences are 5% or less, but the larger values of 5–10% observed during JOSIE 2000 might indicate that they can differ from one manufacturer batch to another. Above 20 km, in particular, the ENSCI-Z sonde measures 5–10% more ozone than the SPC-6A sonde. The

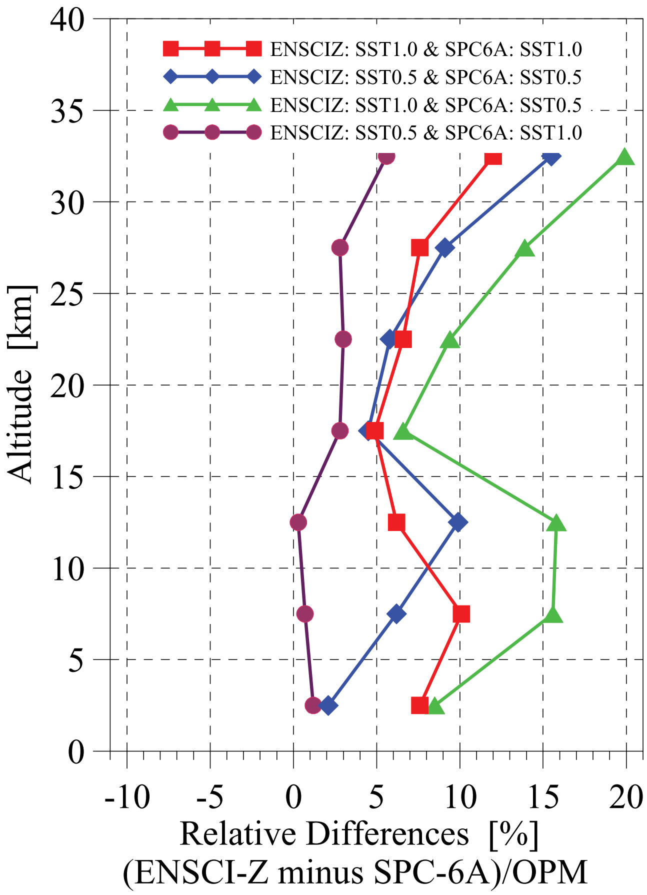

Figure 12. JOSIE 2000: Relative differences between ENSCI-Z and SPC-6A sondes in case of different combinations of SST1.0 and SST0.5 sensing solutions. All sondes were prepared according to *Komhyr* [1986]. All data were processed with pump correction from *Komhyr* [1986], pressure dependent background correction and no total ozone normalization (Table 3). Data are averaged over 5 km altitude bins.

cause of the observed differences is not understood, although variation in pump flow efficiency at lower pressures might be a factor. The unknown evolution of the KI and phosphate buffer concentrations caused by evaporation during a sounding may also play a role. Further, using the internal pump temperature (thermistor embedded in pump) instead of the external pump temperature (thermistor located outside pump at inlet tube) as was used during JOSIE can lead to 0–3% larger ozone readings depending on pressure, i.e., altitude while the corresponding total ozone normalization factor would be 1–2% lower.

[50] There is a significant difference in the ozone readings when sondes of the same type are operated with different sensing solutions. Both sonde types exhibit a systematic change of sensitivity, about 5–10% over the entire profile, when the sensing solution is changed from SST1.0 to SST0.5 or from SST0.5 to SST2.0. From laboratory experiments [*Johnson et al.*, 2002] it is known that this change of sensitivity is mostly caused by the phosphate buffer with only a minor contribution from the KI-concentration. Thus a difference of 10–15% can be expected for different sonde types operated with different sensing solutions when all other procedures and pump flow corrections to the data, are the same. Standardization of operating procedures for ECC-sondes yields a precision better than ±(3–5)% and an accuracy of about ±(5–10)% up to 30 km altitude.

[51] The best total ozone comparisons are achieved for SPC-6A sondes with SST1.0 and ENSCI-Z sondes with SST0.5. For both sonde types the bias relative to the UV-photometer is less than 5% and the relative differences between both sonde types is only 2–5% at all altitudes. These combinations match the manufacturer recommendations on the use of sensing solution type: SPC-6A sondes (SST1.0: 1% KI & full buffer) and ENSCI-Z (SST0.5: 0.5%KI & half buffer), respectively.

[52] JOSIE results demonstrate that differences in ECC-sonde instrument or SST can influence trends derived from sonde profile records. For ozone sounding stations doing long term measurements, changing the sensing solution or ECC-sonde type can introduce a change of 5% or greater in the ozone time-series. Systematic differences in procedures among station procedures further complicate trend interpretation. It is sometimes recommended that "transfer functions" based on comparisons like JOSIE be used to compare trends among stations. For example, if a consistent SST is used, normalization factors for ENSCI-Z sondes relative to total ozone from the UV-photometer are 6–7% lower than for the SPC-6A sondes. However, variations within the profile need to be accounted for. A single transfer value may be appropriate for the region 20–30 km where most ozone is found [*Fioletov et al.*, 2006], but above 30 km and in the troposphere the same value may not hold.

[53] JOSIE has added to our knowledge about the performance of different ozonesonde types and the effect of the various preparation and data correction procedures on the ozone measurement. Ozonesondes have gone through modifications since they were first manufactured and are likely to continue to do so. This adds uncertainty to trend analysis and reinforces the need for regular evaluation of ozonesondes. Periodic testing of ozonesondes directly from the manufacturer and adoption of standard operating procedures will ensure more confidence in the ozonesonde measurement.

[54] JOSIE activities are conducted with detailed documentation of procedures [*Smit and Straeter*, 2004a, 2004b] and many participants have agreed to a standard set of practices and procedures for ozonesondes. Sonde to sonde differences with SST1.0 and SST0.5 were tested in April 2004 in a field situation during the WMO-sponsored Balloon Experiment on Standards for Ozone Sondes (BESOS), [Deshler et al., Field test of ECC-ozonesondes from different manufacturers, and with different cathode solution strengths, and of KC96 ozonesondes: Results of the BESOS balloon flight, submitted to *Journal of Geophysical Research*, 2007]. Preliminary results indicate that the JOSIE-simulation chamber experiments resemble the real atmosphere with respect to sonde -to-sonde and sonde-to-UV-photometer comparisons. However, research is required to gain a more fundamental understanding of variability in instrument background signal and pump efficiency in order to quantify remaining uncertainties in ozonesonde performance.

[55] **Acknowledgments.** We want to thank Volker Mohnen (University of Albany), John Miller, Michael Proffitt and Len Barrie (WMO/AREP) for their personal engagement, contributions and arranging financial support for JOSIE. Many thanks to Dieter Kley (Research Centre Juelich) for his encouragement in establishing JOSIE as a unique facility for ozonesonde quality assurance. Also many thanks to Manfred Helten for assistance in conducting the JOSIE campaigns. Special thanks to Gilbert Levrat from Aerological Station Payerne, Switzerland, Dave Ross from NASA/GSFC-Wallops Flight Facility, USA, Jim Kerr from Environment Canada, Canada, and Greg Bodeker from National Institute of Water and Atmospheric Research, New Zealand for their assistance at the JOSIE-campaigns. Karin Thomas of KT-Consulting many thanks for assistance in the data analysis. Further, we are grateful to all other people involved in the JOSIE-missions for their encouraging support and fruitful discussions. JOSIE was sponsored by WMO/GAW, QA/SAC-Germany and FZJ/HGF. We are grateful to three anonymous referees for many helpful comments and suggestions.

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