Atmospheric comparison of electrochemical cell ozonesondes from different manufacturers, and with different cathode solution strengths: The Balloon Experiment on Standards for Ozonesondes

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[1] A balloon flight to compare 18 ozonesondes with an ozone photometer and with ozone column measurements from Dobson and Brewer spectrophotometers was completed in April 2004. The core experiment consisted of 12 electrochemical concentration cell ozonesondes, 6 from Science Pump Corporation (SP) and 6 from ENSCI Corporation (ES), prepared with cathode solution concentrations of 0.5% KI (half buffer) and 1.0% KI (full buffer). Auxiliary ozonesondes consisted of two electrochemical concentration cell sondes with 2.0% KI (no buffer), two reconditioned sondes, and two Japanese-KC96 sondes. Precision of each group of similarly prepared ozonesondes was <2–3%. The six ozonesondes prepared according to the manufacturer's recommendations (SP, 1.0% KI, ES 0.5% KI) overestimated the photometer measurements by 5–10% in the stratosphere, but provided ozone columns in good agreement with the ground-based spectrophotometer measurements. This is consistent with the difference (~5%) in ozone photometer and column measurements observed during the experiment. Using cathode cell concentrations of 1.0% KI for ES sondes caused overestimates of the photometer by 10–15% and of ozone column by 5–10%. In contrast, 0.5% KI in SP sondes led to good agreement with the photometer, but underestimates of ozone column. The KC96 sondes underestimated the photometer measurements by about 5–15% at air pressures above 30 hPa. Agreement was within 5% at lower pressures. Diluting the solution concentration and the buffers from 1.0% to 0.5% KI causes an approximately linear pressure-dependent decrease in ozone for both SP and ES sondes, ratio (0.5 KI/1.0 KI) = 0.9 + 0.024 * $\log_{10}$(Pressure).

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1. Introduction

[2] Atmospheric ozone, which exists over wide concentration and altitude ranges, plays essential roles in the chemical and radiation balance of both the troposphere and stratosphere. These balances in turn have large impacts on the biosphere. Measurements of ozone abundance provide a measure of the impact of anthropogenic activities on the atmosphere, which have been responsible for anomalously high tropospheric ozone and low stratospheric ozone. For these reasons global ozone monitoring networks have been in place since the late 1960s, and ozone trend studies are a continuing effort [*Logan*, 1994; *Ancellet and Beekmann*, 1997; *World Climate Research Programme*, 1998; *Logan et al.*, 1999; *Tarasick et al.*, 2005; *Oltmans et al.*, 2006; *Terao and Logan*, 2007]. For vertical distributions of ozone these studies are limited to ozonesondes since the late 1960s, to Dobson Umkehr, since 1957, the International Geophysical Year, and to the satellite SBUV and SAGE measurements since the late 1970s. Of these only

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ozonesondes provide measurements below about 20 km [*World Climate Research Programme*, 1998].

[3] Ozonesondes consist of an inert pump, usually Teflon, an electrochemical cell facilitating a reaction between ozone and iodide, a means of detecting the small electric current generated, and an interface to a standard radiosonde for the measurement of air temperature and pressure. The instruments are light in weight and can easily be flown to 35 km on small balloons. The first application of electrochemical cells to atmospheric ozone measurements led to the Oxford-Kew ozonesonde which evolved into the Brewer-Mast (BM) ozonesonde [*Brewer and Milford*, 1960], which consists of a single electrochemical cell and a potential applied across the silver anode and platinum cathode immersed in an alkaline potassium iodide (KI) solution. *Kobayashi and Toyama* [1966] developed the KC sonde which is also a galvanic cell, but with a platinum cathode and carbon anode immersed in a neutral KI solution. This instrument built upon some earlier work by *Komhyr* [1964]. *Komhyr* [1969] developed the ECC sonde by splitting the electrochemical cell into two half-cells each containing a platinum electrode, and using KI solutions of differing concentrations. All of these ozonesondes rely on the titration of ozone in a KI sensing solution according to the redox reaction,

$$2KI + O_3 + H_2O \rightarrow 2KOH + I_2 + O_2, \qquad (1)$$

as air containing ozone is bubbled through the sensing solution. For each ozone molecule two electrons are released. For atmospheric concentrations of ozone this reaction will provide a current of a few microamperes.

[4] Ozonesondes are designed as single-use instruments that require minimum preparation before use. The primary operating principles and chemistry of the ozonesondes in use today, primarily ECC, have not changed significantly; however, the manufacturing, preparation, solution concentration, and data analysis techniques have evolved. This has led to considerable efforts to assess the accuracy, precision, and stability of the various sonde types [*Attmannspacher and Dütsch*, 1970; *Barnes et al.*, 1985; *Hilsenrath et al.*, 1986; *Margitan et al.*, 1995; *Thompson et al.*, 2007; *Smit et al.*, 2007]. Here this effort is continued with an analysis of a field experiment conducted as a continuation of WMO-recommended ozondesonde intercomparisons. Thus it is an extension of the WMO-recommended laboratory work on ECC sondes [*Smit et al.*, 2007]. The purpose of the Balloon Experiment on Standard Operating procedures for Ozonesondes (BESOS) was to compare randomly selected ozonesondes from the two ECC manufacturers, Science Pump Corporation (SP) and EN-SCI Corporation (ES), against an ozone reference during deployment of the ozonesondes on a balloon platform to make atmospheric measurements. In addition subsets of the ozonesondes from each manufacturer were operated using different cathode cell solution strengths, 0.5, 1.0, and 2.0% KI.

2. Ozonesonde Description and Previous Comparisons

2.1. ECC Ozonesondes

[5] ECC sondes consist of Teflon or molded plastic cathode and anode cells containing platinum electrodes and connected by an ion bridge, a Teflon pump with Teflon intake tubing, a pump motor, and electronics for interfacing with a radiosonde transmitter. The cathode cell contains a KI solution which includes phosphate buffers to maintain a roughly neutral solution. The anode contains a solution saturated with KI. As an ozone molecule passes through the cathode solution, it reacts with the iodide to form an iodine molecule (1). The iodine is converted back to iodide on the platinum electrode and two electrons flow through the cell's external circuit, allowing the measurement of current, which is proportional to the amount of ozone entering the chamber [*Komhyr*, 1986; *Komhyr et al.*, 1995a]. The relationship between ozone partial pressure and the cell current, E, is obtained from the ideal gas law and Faraday's first law of electrolysis. Thus

$$P_{O3} = R/(2 \bullet F) \bullet (E - E_{BG}) \bullet T_{pump}/(FR \bullet PE), \qquad (2)$$

where P_{O3} = ozone partial pressure, R = universal gas constant, F = Faraday's constant, E_{BG} = cell background current (typically $\sim$0.1 μA), Tpump = temperature of the air passing through the pump, FR = pump flow rate, PE = pump efficiency = 1/pump flow correction factor. PE is used to correct for the decrease in pump efficiency at low pressures.

[6] Several methods to determine pump efficiency for the Teflon pump used [*Komhyr*, 1967] at various altitudes are in use throughout the working community and have resulted in different correction equations. The most commonly used is the efficiency determined in the 1980s using a differential oil manometer [*Komhyr*, 1986]. This efficiency was updated in 1989, generally referred to as the STOIC efficiency correction [*Komhyr et al.*, 1995a]. The differences are very small, and only significant (1–2%) below 20 hPa pressure. Other equations include the NOAA and Wyoming average equations [*Johnson et al.*, 2002], and the NASA Wallops Flight Facility curves [*Schmidlin et al.*, 1996]. These average pump efficiencies were determined by individual pump characterizations using an oil bubble flowmeter in a vacuum chamber (NOAA), a bag deflation method in a vacuum chamber (Wyoming), and an evacuated chamber inflation (NASA). Additionally, instead of using an average, some laboratories individually measure the pump efficiency of each sonde prior to use. In general these alternate methods indicate substantially lower (5–10%) pump efficiencies at pressures less than 20 hPa compared to *Komhyr* [1986] and *Komhyr et al.* [1995a].

[7] An assumption in the data reduction is that the ratio of I_2:O_3 is 1:1 at all altitudes and for any amount of ozone entering the chamber. Prior to the electrochemical technique, past iodometric methods to validate the 1:1 stoichiometry yielded higher ratios (ranging from 1.1:1 to 1.53:1) of too much iodine [e.g., *Birdsall et al.*, 1952; *Saltzman and Gilbert*, 1959; *Boyd et al.*, 1970; *Flamm and Anderson*, 1975]. *Saltzman and Gilbert* [1959] suggested that higher yields of I_2 could be due to secondary reactions involving activated oxygen. Most activated oxygen would lose energy quickly via molecular collisions; however, some could react with iodide and per phosphoric acid, leading to excess I_2 [*Saltzman and Gilbert*, 1959], and ultimately to measured values of ozone that are too high. The extent of these side reactions is dependent on the amount of ozone introduced to

Table 1. Chemical Composition of the Aqueous Solutions for the Cathode Cell of ECC and KC96 Ozonesondes Used[a]

			P_H – Buffer			
Sensing Solution Type	Name	KI, g/L	$NaH_2PO_4 \cdot H_2O$, g/L	$Na_2HPO_4 \cdot 12H_2O$, g/L	KH_2PO_4, g/L	KBr, g/L
1.0% KI, full buffer	1.0 KI	10	1.25	5.0	0	25
0.5% KI, half buffer	0.5 KI	5	0.625	2.5	0	12.5
2.0% KI, no buffer	2.0 KI	20	0	0	0	0
JMA-KC96	KC96	0.4	0	35.3	14	340

[a]For the anode sensing solution the relevant cathode solution (full or half buffered) is saturated with KI for the ECC sondes. The name will be used in the text to refer to the various possibilities.

the system and the concentrations of buffers present. Additionally, as the sonde ascends, there will be some evaporation inside the cathode cell, thus increasing the KI and buffer concentrations. Tests performed by *Komhyr* [1969] indicated an increase of ~5% in measured ozone when cathode sensing solution concentration and buffers were doubled from 1.0% to 2.0%. Comparisons described here and elsewhere [*Johnson et al.*, 2002] indicate the buffers may play a large role in this difference. Together these results indicate that the efficiency of the conversion of O_3 to I_2 increases in the stratosphere. This increase in the O_3:I_2 stoichiometry has not been accounted for in the application of a pump efficiency factor, and in fact may negate the importance of these corrections.

[8] Current standard operating procedures consist of an initial preparation 3–7 d before launch to confirm that the sondes have pumps which draw <100 mA, pump head pressures >70 kPa, and vacuum pressures >53 kPa. The instrument is then conditioned with high ozone for 30 min prior to filling the cells with cathode and anode solution for storage until flight. The high ozone conditioning is done to passivate active ozone absorption sites in the Teflon pump, tubing, and cells. Sonde components exposed to high ozone include the tubing and pump, and, depending on the laboratory, the cathode chamber. For the flight described here the cathode chamber was included in the high ozone exposure. The second stage of instrument preparation occurs within 24 h of flight. The preparations consist of replacing the cathode and anode solutions, checking the instrument response to moderate (~5 μA) and zero ozone, and measuring the flow rate. Each sonde's background is expected to decrease to <0.1 μA when sampling ozone free air for several minutes.

[9] There has always been some deviation in the strength of the KI solutions used in the cathode cells of ECC sondes. In the 1980s solution strengths of 1.0% and 1.5% were in use at different laboratories [*Komhyr et al.*, 1995a; *Barnes et al.*, 1985]. In the middle 1990s, after ES began manufacturing ozonesondes and some environmental chamber tests of the new ozonesondes were completed [*Smit et al.*, 2007], ES recommended diluting the standard 1.0% KI cathode solution by one half (0.5% KI solutions) for use in their ECC sondes. In addition *Johnson et al.* [2002] explored the possibility of increasing the KI solutions to 2.0% with no buffer, on the basis of earlier iodometric method literature indicating that the buffers may be responsible for secondary reactions increasing the 1:1 response of ozone to iodide [*Saltzman and Gilbert*, 1959]. In all cases, the anode solution is produced by saturating the cathode solution with KI crystals. The solution formulas for the three solutions commonly in use in ECC sondes today are given in Table 1, along with the solution used for the KC96 sondes.

[10] An initial assessment of the differences caused by the change from 1.0% to 0.5% has been provided by *Boyd et al.* [1998], *Johnson et al.* [2002], and *Smit et al.* [2007]. BESOS also included a test of the 0.5, 1.0, and 2.0% KI solutions, hereafter referred to as 0.5 KI, 1.0 KI, and 2.0 KI, as well as the Japanese KC96 sondes.

[11] In contrast to ECC sondes Japanese KC sondes use a single cell with a carbon anode and platinum cathode. Two electrodes are immersed in a solution composed of KI with phosphate buffers and KBr, see Table 1. When ozone is introduced into the solution reaction (1) proceeds, creating free iodine molecules which then convert to iodide by taking 2 electrons at the platinum cathode and 2 hydroxyl ions get neutralized by releasing 2 electrons at the carbon anode. As a result, current flows in an external circuit between electrodes. The ozone amount is deduced from the current value.

[12] KC sondes tend to show relatively low ozone concentration in the lower atmosphere and high ozone in the upper atmosphere. Laboratory experiments found that this was partly due to solution-temperature-dependent reactions, response time, and a background current dependent on exposure to ozone. The new algorithm to correct for these effects and the experimentally determined pump efficiency [*Fujimoto et al.*, 2004] were applied for the data reported here. Degassing of the solution prior to 2 d before use, conditioning the pump and tubing with high ozone for 10 min, and a check of the reaction current on the day before flight were done in accordance with standard procedures described in the Observer's Handbook [*Japan Meteorological Agency*, 1997].

2.2. Previous Ozonesonde Comparisons

[13] Some of the earliest ozonesonde intercomparisons were carried out at the Hohenpeissenberg Observatory in 1970 and 1978. In 1970 there was a comparison of six different types of wet chemistry sondes that were either commonly used or in development at the time. It was concluded that the four commonly used sondes (BM, KC, ECC, Brewer-type Italy) produced similar results when the data were modified by a single multiplicative factor to normalize the integrated ozonesonde profiles to an independent measurement of total ozone [*Attmannspacher and Dütsch*, 1970]. The 1978 campaign again compared the four commonly used sonde types, all of which had undergone some changes in design since the first campaign in 1970. The ECC sonde was shown to measure 12% higher ozone values in the lower troposphere than the other types

of sondes (i.e., BM and KC), but there were no other regular height-dependent differences. Additionally, it was recognized during this campaign that the reliability of the instruments varied between types and also between operating crews [*Attmannspacher and Dütsch*, 1981].

[14] The Balloon Ozone Intercomparison Campaign (BOIC) was held at Palestine, Texas in 1984, and consisted of a series of three balloon missions. Sondes were prepared using either the standard-at-that-time NOAA or NASA methods and then flown with an in situ UV photometer. Between ~60 and 10 hPa, the NOAA sondes measured within ±5% of the UV photometer [*Hilsenrath et al.*, 1986], while differences with the NASA sondes were larger. The differences between the two types of sondes were attributed to the concentration of sensing solution used (NOAA used 1.0% KI solution while NASA used 1.5% KI solution) and to the preparation methods [*Hilsenrath et al.*, 1986].

[15] The Stratospheric Ozone Intercomparison Campaign (STOIC) was held at the Jet Propulsion Laboratory's Table Mountain Facility in California in 1989 [*Margitan et al.*, 1995]. This experiment compared, among many ozone measurements, pairs of ozonesondes flown within 1–2 h of each other. The sondes were prepared according to methods used by either NOAA or NASA. At this time, NOAA still used 1% KI sensing solution and charged the cells 2–3 d before flight time, while NASA used 1.5% KI sensing solution and charged the cells nearly 1 month before flight [*Komhyr et al.*, 1995a]. In general, the ozone profiles measured by the two different sondes were highly similar and differences below 450 hPa of up to 8% were attributed to natural ozone variations measured by sondes that were flown on different balloons and released up to 2 h apart [*Komhyr et al.*, 1995a]. Above ~10 hPa, results from the two sonde types diverged and this difference was partially attributed to different sonde pump efficiency corrections used [*Komhyr et al.*, 1995a].

[16] In 1991 four ozonesonde types (German BM, ECC, KC, Indian BM) were compared on ten flights of balloon gondolas carrying 7–8 ozonesondes [*Kerr et al.*, 1994]. The flights, conducted at Vanscoy, Canada, indicated improvements in the performance of most sondes since the previous comparison. Of the four sonde types the ECC sondes had the best precision, standard deviations <5% through most of the profile. The KC sonde precision was similar while the BM sondes had precisions on the order of 5–10%. The Indian BM sonde was comparable to the ECC sondes, which formed the majority of the instruments, through most of the profile. In contrast the German BM (KC) sonde showed greater (less) ozone than the ECC sondes in the troposphere, and then less (greater) ozone than the ECC sondes in the stratosphere. Comparing the integrated profiles to independent total ozone measurements indicated average differences of 2–4% for all sondes.

[17] In 1989 ECC and Brewer-Mast ozonesondes were compared with a UV differential absorption lidar above Haute Provence, France. The sondes differences were about 15%, Brewer-Mast <ECC, similar to previous comparisons, while the lidar measurements fell between the sonde measurements, somewhat closer to the ECC sondes [*Beekmann et al.*, 1994]. In 1991 ECC and Brewer-Mast ozonesondes were compared with a UV differential absorption lidar, and an airborne UV photometer, also above Haute Provence. The ECC, Brewer-Mast sondes and lidar could only be compared with the airborne photometer in the troposphere, <8 km. This comparison indicated that while the precision of all measurements was <10%, there was a significant difference between the ECC ozone measurements and the other measurements. Comparing all instruments with the median of all measurements indicates that the ECC sondes overestimated tropospheric ozone by 25%, while the Brewer-Mast, UV photometer, and lidar under predicted the median by 1–7% [*Beekmann et al.*, 1995]. *Reid et al.* [1996] compared ECC sondes with a chemiluminescent analyzer in the troposphere and found that the measurements agreed within 4%, provided a constant background current correction was used.

[18] The Jülich Ozone Sonde Intercomparison Experiment (JOSIE) consisted of three sets of experiments completed in 1996, 1998, and 2000, under quasi-flight conditions inside the environmental simulation chamber at the Research Center Jülich [*Smit and Kley*, 1998; *Smit and Straeter*, 2004a, 2004b]. The experiments in 1996 were designed to assess the performance of the major ozonesonde types (ECC, BM and KC) and were attended by representatives of eight laboratories involved in the WMO-GAW ozonesonde network. The focus was on assessing whether differences in instrument preparation and data analysis from each laboratory would cause significant differences in the measurements. There were a total of 6 ozone profiles measured. The emphasis so far in the analysis of this experiment has been on the three differently manufactured ECC ozonesondes (EC-Z, SP-6A, and SP-5A) and the operating procedures of the different laboratories using these sondes. All sondes were prepared using 1.0 KI. Under simulated midlatitude conditions, with data processed according to *Komhyr* [1986], all of the sondes compared well with the reference UV photometer in tropospheric conditions; however, EC-Z sondes increasingly overestimated ozone in the stratosphere, increasing to ~8% at the highest altitudes, while the SP-6A sondes agreed with the photometer within 5% through the stratosphere [*Smit et al.*, 2007].

[19] In 1998, the JOSIE experiment's aim was to compare the quality of newly manufactured ECC-sondes by both ES and SP. Twenty-six ECC-sondes, 13 sondes from each manufacturer (SP-6A and EC-Z), randomly picked from stocks at different sounding sites, were tested. Again, 1.0 KI-buffered solution was used in simulated midlatitude conditions. Both types of sondes showed a positive bias in relation to the photometer (~5–10%) at chamber pressures below ~200 hPa. Between 200 and 50 hPa both sondes agreed within ~5%. At pressures <50 hPa the ES sondes overestimated ozone by over 10% while the SP sondes underestimated ozone [*Smit et al.*, 2007]. As a result of this comparison one manufacturer (EC) recommended reducing the solution strength in their sondes to 0.5%.

[20] JOSIE 2000 addressed the use of different cathode sensing solution strengths (1.0 KI-full-buffered, 0.5 KI-half-buffered, 2.0 KI-unbuffered) (Table 1) in both EC-Z and SP-6A sondes. Seven ozone measurement stations operating ECC-sondes were involved. The smallest relative biases (less than 5%) were achieved with SP-6A sondes using 1%-buffered solution and with EC-Z sondes using 0.5%-half-buffered solution [*Smit et al.*, 2007]. Overall, the JOSIE

Table 2. Characteristics of the Ozonesondes (Both Core and Auxiliary Experiment) Flown on the BESOS Gondola Including Manufacturer and Model, Cathode Solution Strength, Flow Rate in Laboratory, Background Current Measured in the Laboratory the Day Before Flight and Just Prior to the Flight at the Balloon Site, and the Laboratory Responsible for the Preparation in the Lab and Before Flight for Each Ozonesonde[a]

Sonde Type	Cathode Solution	Flow Rate Measured in Lab, ml min^{-1}	Background in Lab, μA	Background Just Prior to Flight, μA	Responsible Laboratory	Experiment
SP-6A	1.0 KI	220.51	0.07	0.04	Met. Svc Canada	core
SP-6A	1.0 KI	220.99	0.05	0.05	NASA WFF	core
SP-6A	1.0 KI	211.64	0.04	0.03	NASA WFF	core
ES-2Z	1.0 KI	212.80	0.05	0.05	Meteo Swiss	core
ES-2Z	1.0 KI	215.13	0.06	0.05	Met. Svc Canada	core
ES-2Z	1.0 KI	215.22	0.06	0.06	Met. Svc Canada	core
SP-6A	0.5 KI	217.55	0.01	0.04	NASA-GSFC	core
SP-6A	0.5 KI	218.58	0.01	0.07	Meteo Swiss	core
SP-6A	0.5 KI	220.18	0.02	0.05	NASA-GSFC	core
ES-2Z	0.5 KI	216.68	0.03	0.04	FMI	core
ES-2Z	0.5 KI	215.44	0.03	0.05	FMI	core
ES-2Z	0.5 KI	217.94	0.02	0.08	Meteo Swiss	core
SP-6A	2.0 KI	224.32	0.00	0.06	Meteo Swiss	aux
ES-2Z	2.0 KI	216.73	0.02	0.04	NOAA-CMDL	aux
ES-1Z (reused)	1.0 KI	217.23	0.06	0.05	NASA WFF	aux
ES-1Z (reused)	1.0 KI	228.70	0.08	0.05	U. Wyoming	aux
KC96	see Table 1	411.00	0.08	0.03	JMA	aux
KC96	see Table 1	410.00	0.10	0.02	JMA	aux

[a]The laboratories which participated are Meteorological Service Canada, NASA–Wallops Flight Facility (WFF) and Goddard Space Flight Center (GSFC), Meteo Swiss, Finnish Meteorological Institute (FMI), NOAA–Climate Monitoring and Diagnostics Laboratory (CMDL), Japanese Meteorological Agency (JMA), and University of Wyoming.

2000 experiment found that the best agreements with the photometer were found with the manufacturers' recommendations for KI sensing solution strengths, for SP sondes a 1.0% full-buffer solution and for ES sondes a 0.5% half-buffer cathode solution [*Smit et al.*, 2007].

3. BESOS: Balloon Gondola, Preparation, and Flight Logistics

[21] BESOS was designed to compare randomly selected SP and ES ozonesondes against an UV photometer ozone reference during an atmospheric profile measurement. Subsets of the ozonesondes from each manufacturer were operated with 1.0 KI (recommended by SP) and 0.5 KI (recommended by ES), Table 1. Table 2 shows the distribution of the cathode solutions used among the 12 core sondes and the 6 auxiliary sondes. The 12 core sondes consisted of 6 SP and 6 ES sondes. Three from each group were prepared with 1.0 KI and three with 0.5 KI. The auxiliary sondes consisted of one SP and one ES sonde prepared with 2.0 KI, two reconditioned ES sondes prepared with 1.0 KI, and two Japanese KC96 sondes. Air pressure and temperature were measured by a Vaisala radiosonde. Preparation and preflight characteristics of the 18 ozonesondes are also listed in Table 2, including the laboratory responsible for preparation. The preparation of all the SP and ES sondes followed exactly the same procedure. The temperature of each sonde pump was measured with a thermistor inserted into a hole bored into the Teflon block near the pump by the manufacturer. These holes have been provided by the manufacturers since the JOSIE experiments [*Smit et al.*, 2007]. The measurement in flight from each ozonesonde consisted of the ozone current and pump temperature.

[22] The ozone reference instrument was a fast response dual beam ozone UV-photometer [*Proffitt and McLaughlin*, 1983]. The measurement consists of a comparison of the absorption at 254 nm from two cells open to the atmosphere, with one cell filtered of ozone. This is the same photometer as used in the JOSIE chamber experiments, but modified for balloon-borne flight, and was provided by the Research Centre Jülich.

[23] Eight laboratories, Table 2, involved in ozonesonde measurements were involved in BESOS. Representatives from five of these laboratories prepared the 12 core ozonesondes for flight, and 2 of the 4 auxiliary ECC ozonesondes, while the KC96 sondes were prepared by JMA. Each laboratory was responsible for 2 or 3 ozonesondes for both the advance preparation and the day of flight preparation. The other two laboratories prepared a fraction of the auxiliary experiment ozonesondes, Table 2.

[24] The 12 core ozonesondes were new and were initially prepared between 5 and 8 d prior to flight, thus within the normal preflight preparation period. The advance preparation of the sondes followed standard recommendations, section 2.0. For BESOS the cathode cell was included in the 30 min of high ozone conditioning. The preflight preparations also followed standard recommendations. For background checks in the laboratory, for flow rate measurements, and for the day of flight background checks, compressed air with zero ozone and zero relative humidity (RH) was used.

[25] Ozonesonde flow rates were measured using a standard soap bubble flowmeter, measuring the flow rate of the air leaving the exhaust port of the cathode cell after it had bubbled through 3 mL of cathode solution. In this case water from the cathode solution evaporates into the dry zero air stream, thus increasing the volume of the exhaust air stream by the additional water vapor. To estimate this addition, and thus the true pump flow rate, we assume the air leaving the exhaust port of the cathode solution is saturated. This causes the measured flow rate to

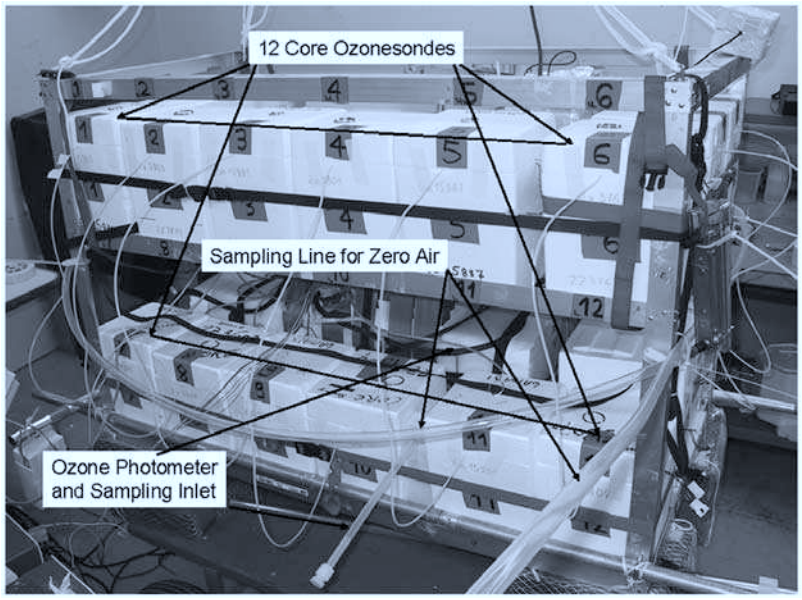

Figure 1. Picture of gondola showing ozonesonde, ozone photometer placement and sampling configuration, and the configuration for sampling zero air to establish background.

be approximately 3.6% greater than the true pump flow rate. The flow rate used for data analysis was corrected for this effect using $(1 - (1 - RH/100)*e_s(T)/P)$ [*Smit and Straeter*, 2004b, p. 18]. P is the atmospheric pressure, $e_s(T)$ saturated water vapor pressure at T, the air temperature during measurement.

[26] To accommodate an early morning balloon release and the logistics of preparing the gondola containing 18 ozonesondes, the photometer, and data acquisition and telemetry system, the final ozonesonde preparations were completed the afternoon prior to flight, and the gondola assembled. This was approximately 15–16 h prior to flight. A picture of the gondola, displaying the sampling arrangement for the 12 core ozonesondes is shown in Figure 1. The auxiliary ozonesondes are on the ends and back side of the gondola, with the photometer and data acquisition system in the middle. The air pressure and temperature were measured with a Vaisala RS-80 radiosonde. An additional independent radiosonde was attached to the gondola to measure GPS altitude, pressure, and temperature. At balloon burst there was a difference between the gondola pressure (8.1 hPa) and the auxiliary ozonesonde pressure (8.5 hPa). The auxiliary ozonesonde altitude calculated from the pressure was compared to the GPS altitude; however, the GPS altitude was too intermittent to allow a definitive conclusion concerning the absolute accuracy of either pressure sensor. In view of this no corrections were made to the pressure measured on the gondola. The data were transmitted in real time and stored on board. The final ozonesonde background prior to flight was obtained within 1 h of the flight using zero air and a Teflon manifold to allow all sondes to measure background at the same time (Figure 1). The sonde backgrounds were all similar, range of 0.02–0.08 μA, and are listed in Table 2.

[27] Data collected from the gondola came from three instrument groups: ozonesonde current and pump temperature, reported at 1 Hz from 18 ozonesondes, air pressure and temperature reported at 0.08–0.17 Hz, and photometer measurements averaged to 0.1 Hz. For analysis the 1 Hz ozonesonde data were averaged over the sampling frequency for air pressure and temperature. This averaging does not degrade the resolution of the ozone measurement since the instrument has a time constant exceeding these frequencies. These averaged ozonesonde current and pump temperatures, at 0.08–0.17 Hz, for each ozonesonde were then processed using the standard algorithm (equation (2)) to convert current to ozone partial pressure. A background for each sonde was accounted for by subtracting the final background measured prior to flight for each sonde from the measurements (equation (2)). The high-altitude (air pressure <300 hPa) ozonesonde data were processed in two ways: (1) correcting for decreasing pump flow rate efficiency at low pressure and (2) using no pump efficiency correction. The standard pump correction applied here is from *Komhyr* [1986], who estimated pump efficiencies of: 0.993, 0.982, 0.969, 0.948, 0.935, 0.916 and 0.890 at pressures of 100, 50, 20, 10, 7, 5 and 3 hPa. These efficiencies are 1–2% higher at pressures of 20–7 hPa compared to *Komhyr et al.* [1995a], and 5–10% higher than the averages of several laboratory measurements on a large number of pumps [*Johnson et al.*, 2002]. Thus the *Komhyr* [1986] correction results in the least correction to low-pressure ozone measurements.

4. BESOS Flight Results

4.1. Core Experiment: Six SP and Six ES Ozonesondes

[28] The balloon was released at 0725 local time (LT) on 13 April 2004, from near Laramie, Wyoming (41.3°N, 105.7°W), surface pressure 780 hPa, elevation 2.2 km. It reached a ceiling of 8.1 hPa, 32.5 km, 100 min after release. The descent required 35 min. The instruments landed approximately 50 km downwind (41.0°N, 105.1°W). During the flight total ozone was measured at the balloon

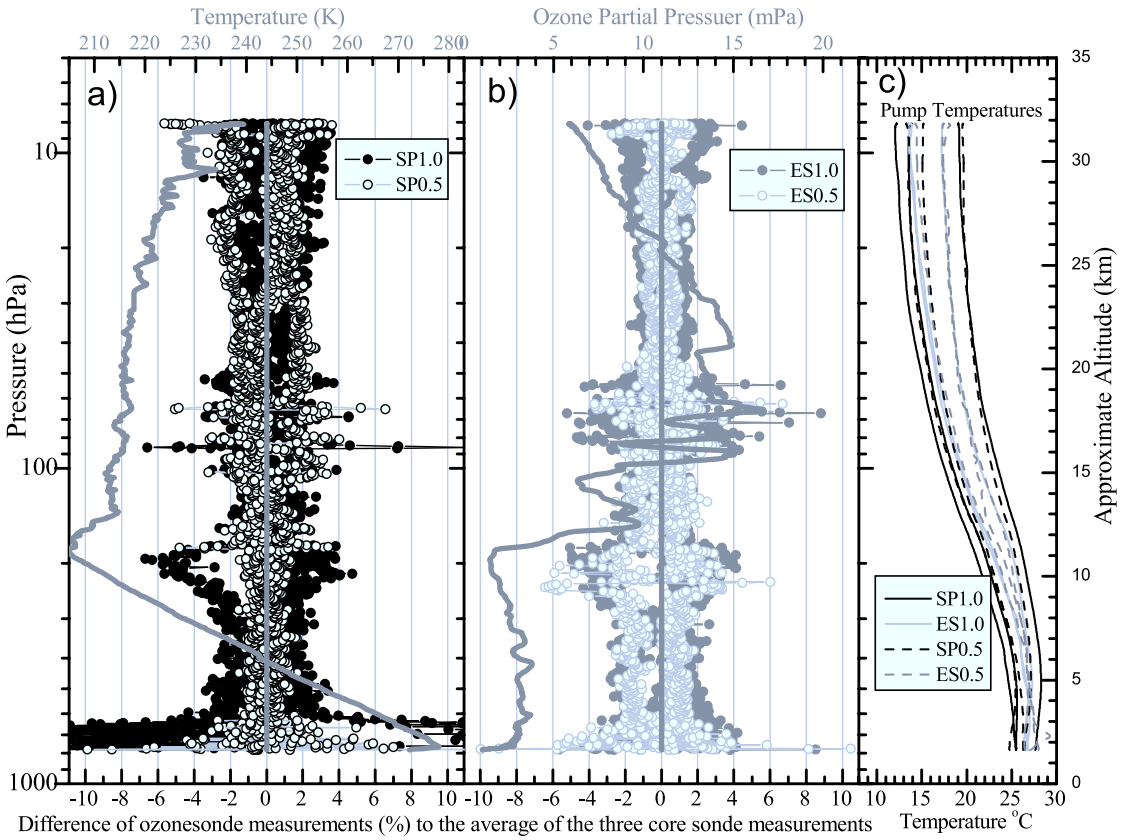

Figure 2. Profiles of ozonesonde precision. The percent differences of each core ozonesonde from the 6–8 s averages of the three ozonesondes in each core group are plotted for (a) SP1.0 and SP0.5 and (b) ES1.0 and ES0.5 ozonesondes. Air temperature is also included in Figure 2a and ozone partial pressure from the average SP1.0 sondes in Figure 2b. (c) Ozonesonde pump temperature for the 12 core ozonesondes.

release location with both a Dobson and Brewer spectrophotometer. Seven Dobson measurements were completed between 0726 and 0823 LT, and seven Brewer measurements between 0851 and 1014 LT. The average column ozone observed during this period was 337 (341) ± 1.7 (1.6) DU from the Dobson (Brewer) spectrophotometers.

[29] The 18 ozonesondes performed well throughout the flight. The 12 core ozonesondes showed little variance within each group of three sondes. Figure 2 displays the percent difference of each of the three core sondes, from the average of those three sondes. The average from each core group represents a 6–8 s average of the three sonde measurements in each group. Also shown are the pump temperatures from each ozonesonde. The SP and ES sondes performed similarly. Differences from the average were <2–3% except in regions where ozone is low, near the surface and just below the tropopause, or where ozone gradients are high, such as between 50 and 100 hPa. The smallest differences (<1%) are observed in the troposphere with SP0.5 and in the stratosphere with ES0.5. Generally smaller differences are observed with 0.5 KI. These estimates of precision are similar to or slightly less than results from *Komhyr et al.* [1995b].

[30] While the ozonesondes performed well, there were some problems with the photometer. Prior to flight the photometer had been in intermittent operation for more than 20 years. Since 1985, and until BESOS, it had been used only in an environmental chamber, and had required little or no maintenance. This pristine environment is optimal for instrument operation, particularly when compared to a flight environment which includes swinging and rotation of the gondola. The low-pressure mercury lamp has a finite lifetime which is determined by degradation of intensity of the 254 nm emitted light and its short-term stability. The short-term stability of the signal intensities is monitored by the photometer. In general, a lamp will be replaced when its average intensity has decreased by 20–30%, usually after 5,000–10,000 h of operation. Short-term stability (of the emitting plasma within the lamp) usually remains acceptable throughout its lifetime; however, short-term stability can be affected by motion of the plasma lamp in a magnetic field. Although lamp instabilities were not seen during chamber tests nor during BESOS preflight and post flight checks, they were present during much of the BESOS flight. We believe these arose from swinging and rotation of the gondola in the Earth's magnetic field. The analysis of these data to remove this effect required careful examination of the measurements to isolate periods when lamp instabilities were at a minimum. In these periods ozone mixing ratios were calculated in 10 s intervals. Measurements were reported only when differences between two independent analyses provided mixing ratios within 0.3% of each other.

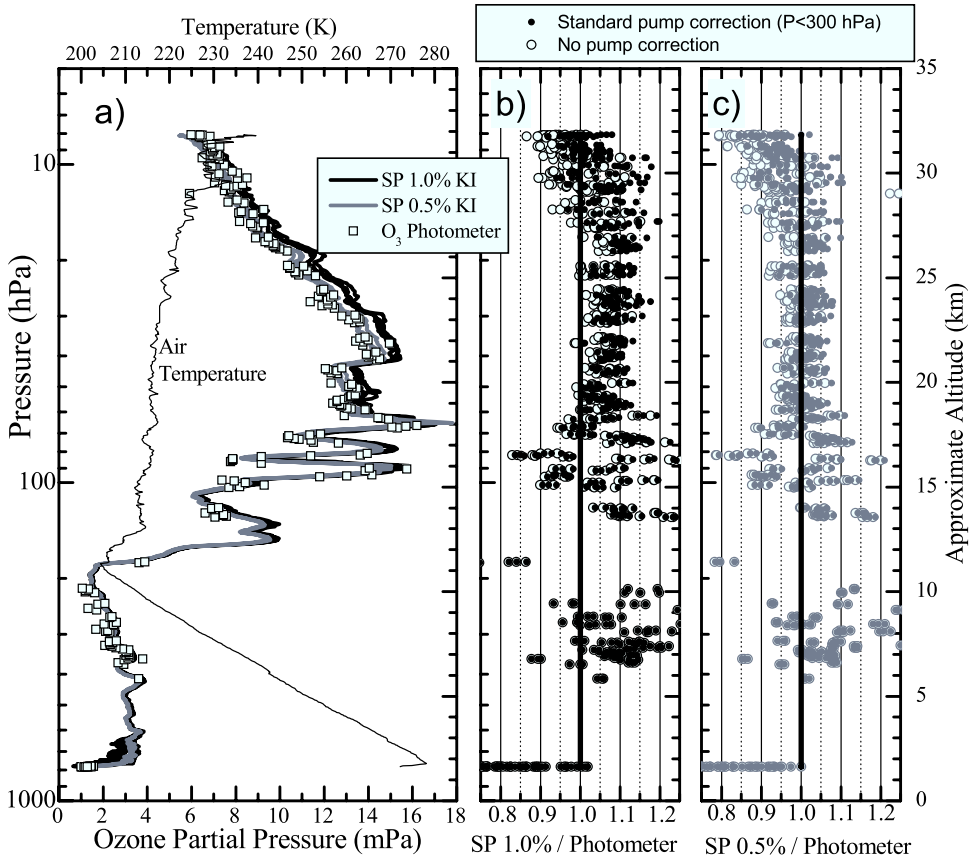

Figure 3. Profiles of (a) air temperature and ozone partial pressure from the ozone photometer, 3 SP1.0 ozonesondes and 3 SP0.5 ozonesondes; (b) ratios of SP1.0 to photometer with and without a pump correction; and (c) ratios of SP0.5 to photometer with and without a pump correction. For the ozonesonde partial pressure profile the measurements were corrected for pump efficiency at air pressures less than 300 hPa, using *Komhyr* [1986].

Altogether approximately one third of the measurements could be recovered, with the first measurements after the surface available only above 6 km. While disappointing, this is still enough to complete some comparisons with the ozonesondes, particularly in the stratosphere.

[31] As a further check, the ozone column calculated from the photometer measurements were compared with an average of the Dobson and Brewer spectrophotometer measurements, although the sparse photometer data creates some uncertainty in the calculations. Estimates were made by integrating the sparse photometer measurements, and by using the average of the 3 SP1.0 and 3 ES0.5 sondes to provide the ozone column from the surface to 60 hPa. The two results are nearly the same. From the surface to 60 hPa an integral of the photometer data indicated 106 DU, while integrals of the 3 SP1.0 and ES0.5 sondes indicated 110 DU. This difference, 4 DU, is 1% of the ground based total column measurements (338, 341 DU). The photometer measurements were extrapolated to the top of the atmosphere assuming both the SBUV climatology for 41°N in April (40 DU, ~12% of the column) [*McPeters et al.*, 1997] and constant ozone mixing ratio, which was 47 DU (~14% of the column) for the photometer measurements. *Fioletov et al.* [2006] show a good correlation between SBUV and SAGE II ozone measurements over middle and high latitudes. The results indicate that the photometer underestimated the remote spectrophotometer measurements by 3.4 (5.7)% for the constant mixing ratio (SBUV) extrapolations, resulting in an average difference of −4.5% between the photometer and the remote measurements. Such a difference is within the 5% underestimation observed in previous comparisons of in situ photometers with remote measurements [*Hilsenrath et al.*, 1986].

[32] The fundamental measurements for the core experiment involving 12 ozonesondes and the photometer are shown in Figures 3 and 4. Figures 3a and 4a present the temperature and ozone profiles from the photometer and 6 ozonesonde measurements. The temperature and photometer measurements are repeated on each figure. Figure 3 presents the three SP1.0 and three SP0.5 ozonesonde measurements using the *Komhyr* [1986] pump efficiency correction for high-altitude measurements. Figure 4 is similar but presents the three ES1.0 and ES0.5 measurements. Profiles of the ratio of each ozonesonde to the photometer are shown in Figures 3b and 4b for 1.0 KI and Figures 3c and 4c for 0.5 KI. The ratios are shown for both the *Komhyr* [1986] pump efficiency correction and for no correction.

[33] The photometer variations and limited data preclude definitive comparisons in the troposphere, and thus assess-

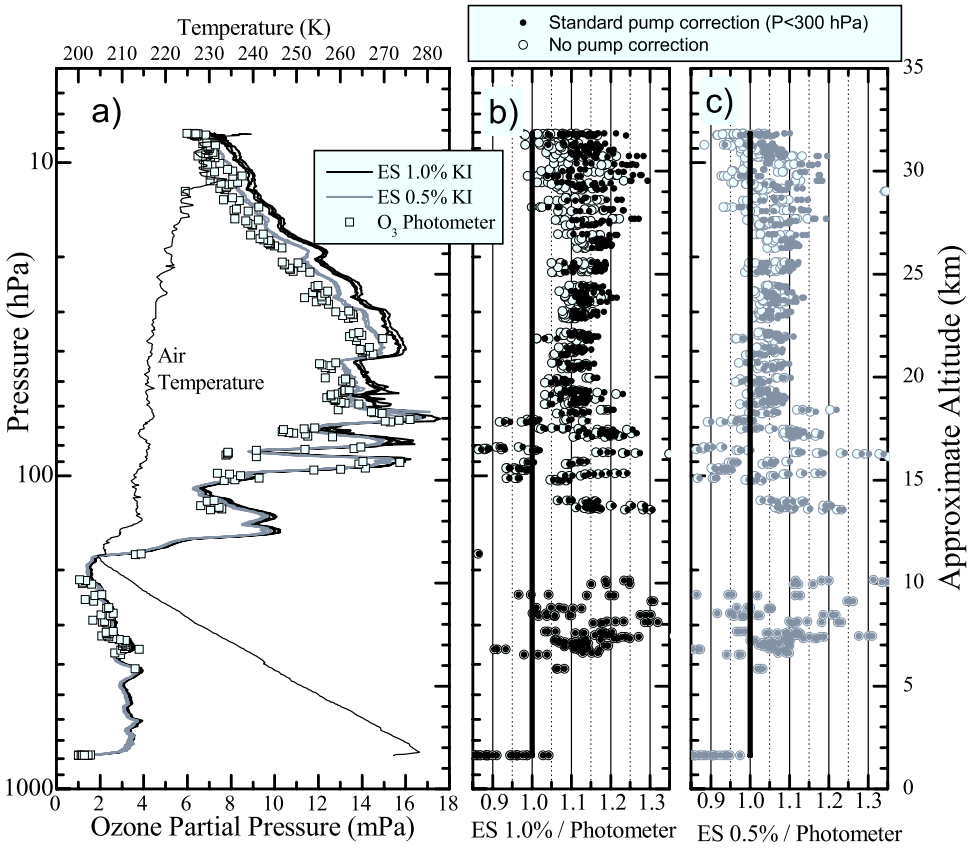

Figure 4. Same as Figure 3 except for ES ozonesondes.

ments of the accuracy of the tropospheric ozonesonde data. The conclusion that these measurements provide is that tropospheric measurements from any ozonesonde configuration can provide measurements with a precision of <2–3% for ozone >3 mPa. As ozone decreases below 3 mPa the error increases, see the measurements near 200 hPa in Figure 2. Thus the absolute precision is no better than 0.1 hPa.

[34] For SP sondes Figures 3b and 3c indicate that the best agreement with the photometer is obtained using SP0.5, with a pump correction. The SP1.0 measurements are 5–10% above the photometer throughout the stratosphere. This difference is diminished if no pump correction is applied. For ES sondes Figures 4b and 4c indicate that ES1.0 overestimates stratospheric ozone, by 10–15%, even with no correction for pump efficiency, while ES0.5 measurements are 5–10% above the photometer, similar to SP1.0 measurements. While the manufacturers' recommendations (SP1.0 and ES0.5) provide a similar difference to the photometer in the stratosphere, the best agreement with the photometer is found using SP0.5.

[35] Considering that some stations which transitioned from SP to ES sondes have not adopted the ES recommendations of 0.5 KI, the 12 core ozonesondes were used to compare the difference between 0.5 KI and 1.0 KI in both the SP and ES sondes. Figure 5a presents the ratios of measurements with 0.5 KI compared to 1.0 KI for both SP and ES sondes. The ratios are quite similar, and essentially linear with $\log_{10}$(pressure) throughout the profile, with some variation of the ES0.5:ES1.0 ratio in the upper troposphere. As a simple approximation to a transfer function for homogenizing data sets, the 0.5 KI to 1.0 KI ratios were fit with a linear equation in log of pressure, for measurements between 625 and 8 hPa. The equation, ratio (0.5 KI/1.0 KI) = 0.90 + 0.024 * $\log_{10}$(Pressure), captures the primary pressure-dependent effect of the different solution strengths within an uncertainty of ±1–2%.

[36] The response of the SP and ES sondes for each of the solution types can also be compared directly. Ratios of the ozonesonde measurements (SP/ES) for the three cathode solution strengths used are shown in Figure 5b. For 0.5 KI and 1.0 KI the three measurements from each sonde type were averaged prior to forming the ratio. For the 2.0 KI, only one sonde of each type was flown. As shown in Figure 5b the ratio of the sonde performance is to a good approximation independent of the cathode solution used. The ratio is nearly constant between 0.96 and 0.98 until pressure is <100 hPa, then the ratio increases nonlinearly until the difference exceeds 10%. To estimate this difference the 0.5 KI data were fit with a quadratic in log pressure, between 780 and 8 hPa. This relationship, shown on Figure 5b, also does a reasonable job for the 1.0 KI ratios, but deviates some from the 2.0 KI ratios. Similar comparisons of the two sonde types using 1.0 KI are available from measurements on 9 dual ozonesonde flights in the Arctic [*Kivi et al.*, 2007]. Those data, although presented in the opposite sense to Figure 5b, show the same tendency: reasonably constant difference of 3% up to 15 km, then a difference which gradually increases to >5% at 25 km. Kivi et al. fit their difference to a cubic in altitude (km), rather than a quadratic

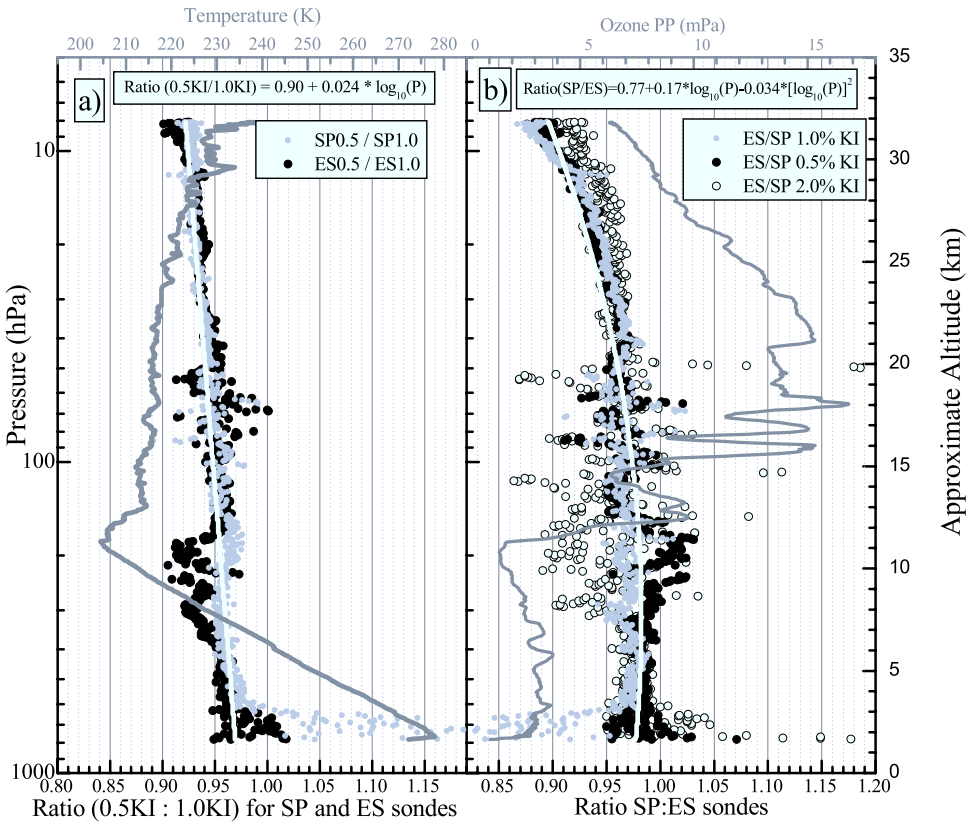

Figure 5. (a) Profiles of air temperature and the ratios of the 0.5 KI measurements to the 1.0 KI measurements for both SP and ES ozonesondes. The ratios were fit with a straight (white) line, over the pressure range 625 to 8 hPa, providing the equation shown in Figure 5a. (b) Profiles of ozone and the ratios of SP to ES sondes for the three cathode KI concentrations used. The 0.5 KI SP:ES ratios over the pressure range 780 to 8 hPa were fit with the quadratic equation shown in Figure 5b, providing the white line in Figure 5b, which also does a reasonable job of fitting the 1.0 KI data.

in log pressure. The larger ratios which appear in the region of ozone laminae, 150–50 hPa, may indicate differences in response time of the two sonde types. In this case the largest differences are observed when 2.0 KI unbuffered solutions are used.

4.2. Auxiliary Ozonesonde Measurements, 2.0 KI, Reused ECC (ES), and KC96 Sondes

[37] Measurements from the SP and ES sondes flown with 2.0 KI and with the two reused ES sondes using 1.0 KI are shown in Figure 6 along with temperature and photometer data. For the 2.0 KI sondes the differences with the photometer are 5–15% underestimates for SP and 0 ± 5% estimates for ES (Figures 6b and 6c). Pump efficiency corrections improve the comparison for both SP and ES ozonesondes. More aggressive pump efficiency corrections [*Johnson et al.*, 2002] would improve the comparison for the SP2.0 sonde, but not the ES2.0 sonde. Similar to results with other solution strengths, the SP sonde measures less than the ES sonde for the same solution strength (Figure 5b).

[38] The reused ES1.0 ozonesondes clearly overestimate the photometer measurements (Figure 6a), similar to results from the new ES1.0 ozonesondes (Figure 4a). Figure 6d presents the ratio of the two reused ES1.0 sondes with an average of the three new ES1.0 measurements. With the exception of an unexplained excursion near 200 hPa by one reused sonde, the reused ES1.0 sondes match the new ES1.0 sondes within $<\pm 5\%$.

[39] The two KC96 ozonesonde profiles are shown in Figure 7 compared with the photometer. In contrast to the ECC ozonesondes with varying cathode cell solution strengths, the KC96 ozonesondes underestimate the photometer measurements in the troposphere and lower stratosphere, pressures >60 hPa, by over 10%. At pressures below 30 hPa, the KC96 sondes overestimate the photometer by 5–10%. Comparing the two KC96 sondes (Figure 7c) indicates agreement with each other within 2–5%, with some divergence at pressures less than 40 hPa.

4.3. Averages and Integral Comparisons

[40] The ratios of ozonesonde to photometer measurements were averaged over different pressure intervals to summarize ozonesonde performance as a function of altitude. Averages and standard deviations of the ratios are shown for the whole flight (780–8 hPa), troposphere (420–200 hPa), region of high ozone gradient (100–60 hPa), and middle stratosphere, 60–8 hPa, in Figure 8. The manufacturer's recommended configurations, SP1.0 and ES0.5 (Figure 8a), overestimate the photometer measurements by 3–7% in the stratosphere. Accounting for the decrease in pump efficiency at low pressures leads to larger over-

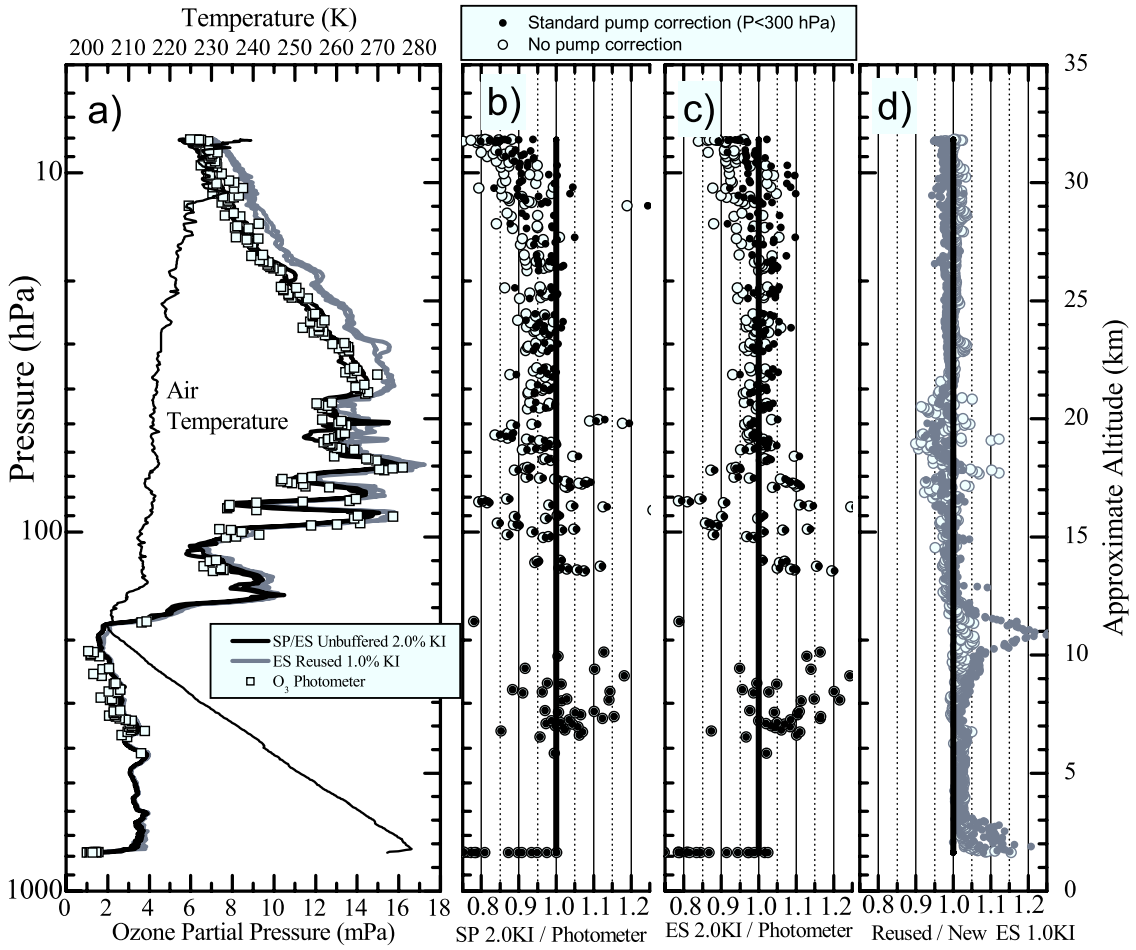

Figure 6. Profiles of (a) air temperature and ozone partial pressure from the ozone photometer, one SP2.0 and one ES2.0 ozonesonde, and 2 reused ES1.0 ozonesondes; (b) ratios of SP2.0 to photometer with and without a pump correction; (c) ratios of ES2.0 to photometer with and without a pump correction; and (d) ratios of the two reused ES1.0 measurements (open and solid gray circles) to the average of the three new ES1.0 ozonesondes. For the ozonesonde partial pressure profile the measurements were corrected for pump efficiency at air pressures less than 300 hPa, using *Komhyr* [1986].

estimates between 60 and 8 hPa. The SP0.5 sondes display quite good agreement with the photometer (Figure 8b), particularly in the stratosphere. Use of a pump efficiency correction in this case improves the comparison between 60 and 8 hPa. The ES1.0 ozonesondes overestimate the photometer by 10% or more. The reused ES1.0 results follow closely the new ES1.0 results again suggesting that ozonesondes can be reused without serious problems. The SP2.0 and KC96 results are shown in Figure 8c. The SP/ES2.0 ozonesondes provide reasonable comparisons with the photometer. The differences between SP2.0 and ES2.0 is similar to differences between the two sonde types at other KI concentrations (Figure 5b). For the 2.0 KI solutions correcting for pump efficiency improves the comparison. The KC96 sondes are different than the ECC sondes, indicating less ozone than the photometer between the surface and 60 hPa. This difference dominates all the average ratios except for the interval between 60 and 8 hPa, where the KC96 sondes slightly overestimate the photometer. This underestimation of ozone in the troposphere by KC96 ozonesondes has been noted before [*Fujimoto et al.*, 2004].

[41] The ozonesonde measurements were integrated to calculate total ozone. The ozone profiles shown in Figures 3, 4, 6, and 7 were extrapolated to the top of the atmosphere assuming both the SBUV climatology for 41°N in April (40 DU) [*McPeters et al.*, 1997] and constant ozone mixing ratio (42–58 DU, depending on final ozonesonde measurement). The extrapolation at constant mixing ratio increases the total ozone estimates on the order of 0.5–5% of the ozone column, dependent on the final ozone amount measured for the sonde. Total column ozone from each of the ozonesondes, both with and without a pump correction for the ECC sondes, is compared with the Dobson and Brewer spectrophotometer measurements in Figure 9. Including the *Komhyr* [1986] pump correction increases the total column estimates by about 2% for the SBUV extrapolation, and by about 4% for the extrapolation at constant mixing ratio. The extrapolation of the ozonesonde measurements above 8 hPa using the SBUV climatology provides a better comparison with the total column measurements than the

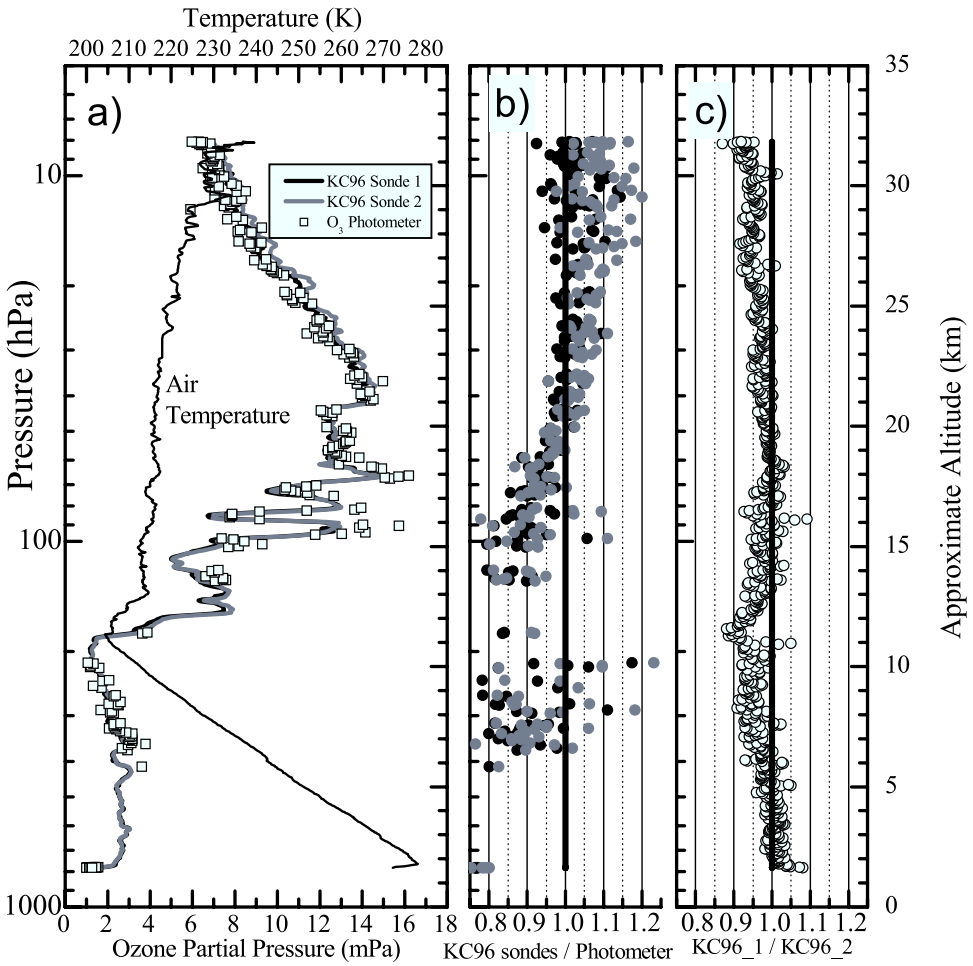

Figure 7. Profiles of (a) air temperature and ozone partial pressure from the ozone photometer and two KC96 ozonesondes, (b) ratios of the two KC96 sondes to the photometer, and (c) ratios of the two KC96 sondes flown.

extrapolation at constant mixing ratio for all the core experiment ozonesondes except the SP0.5 sondes. In contrast extrapolation at constant mixing ratio improves total column estimates from the auxiliary ozonesondes SP/ES2.0 and KC96 (Figures 9c and 9d).

[42] Figures 9a and 9b indicate that the best total column results are obtained with SP1.0 and ES0.5 with the correction for pump efficiency being somewhat inconsequential, changing slight underestimates to slight overestimates. In contrast SP0.5 and SP/ES2.0 ozonesondes underestimate total ozone even when accounting for pump efficiency. The new and reused ES1.0 sondes perform similarly, overestimating total ozone by 3–5% if no pump correction is applied. For the 2.0 KI sondes the difference between the SP and ES measurements is in the same direction (SP < ES) as the differences between SP and ES for both 1.0 and 0.5 KI, although the magnitude of the difference is slightly lower. The KC96 sondes underestimate total ozone by 5–10% using the SBUV climatology for extrapolation. Extrapolation at constant mixing ratio improves these differences to <5%.

4.4. Comparisons With JOSIE 2000

[43] The performance of SP and ES sondes have been compared to photometer measurements in the laboratory (JOSIE, 2000) using the same three cathode solution strengths tested here, 0.5 KI, 1.0 KI, and 2.0 KI. The UV photometer used in the environmental simulation chamber was the same instrument as used for BESOS. Its performance in the laboratory was much more stable than in the field. Thus Figures 3, 4, and 6 have direct analogues from JOSIE 2000 [*Smit et al.*, 2007]. The ozonesonde measurements from Figures 3, 4, and 6 were converted to relative difference (%) to the photometer, for a comparison with the JOSIE 2000 laboratory results [*Smit et al.*, 2007, Figure 7], which were recalculated using the same procedures as for the balloon-borne data, that is, constant background subtraction, using the background measured just before flight. The results are shown in Figure 10, for altitudes above 18 km, pressures less than 70 hPa. There were not enough photometer measurements below this altitude from the balloon flight to warrant a comparison. Figure 10 indicates that the JOSIE 2000 and BESOS results are reasonably consistent for all 6 sonde and solution strength combinations. The averages of the laboratory measurements for all the SP and ES variations lie generally at the lower boundary of the balloon measurements, with a slightly better agreement observed with the ES sondes. A significant fraction of the balloon-borne measurements exceed the

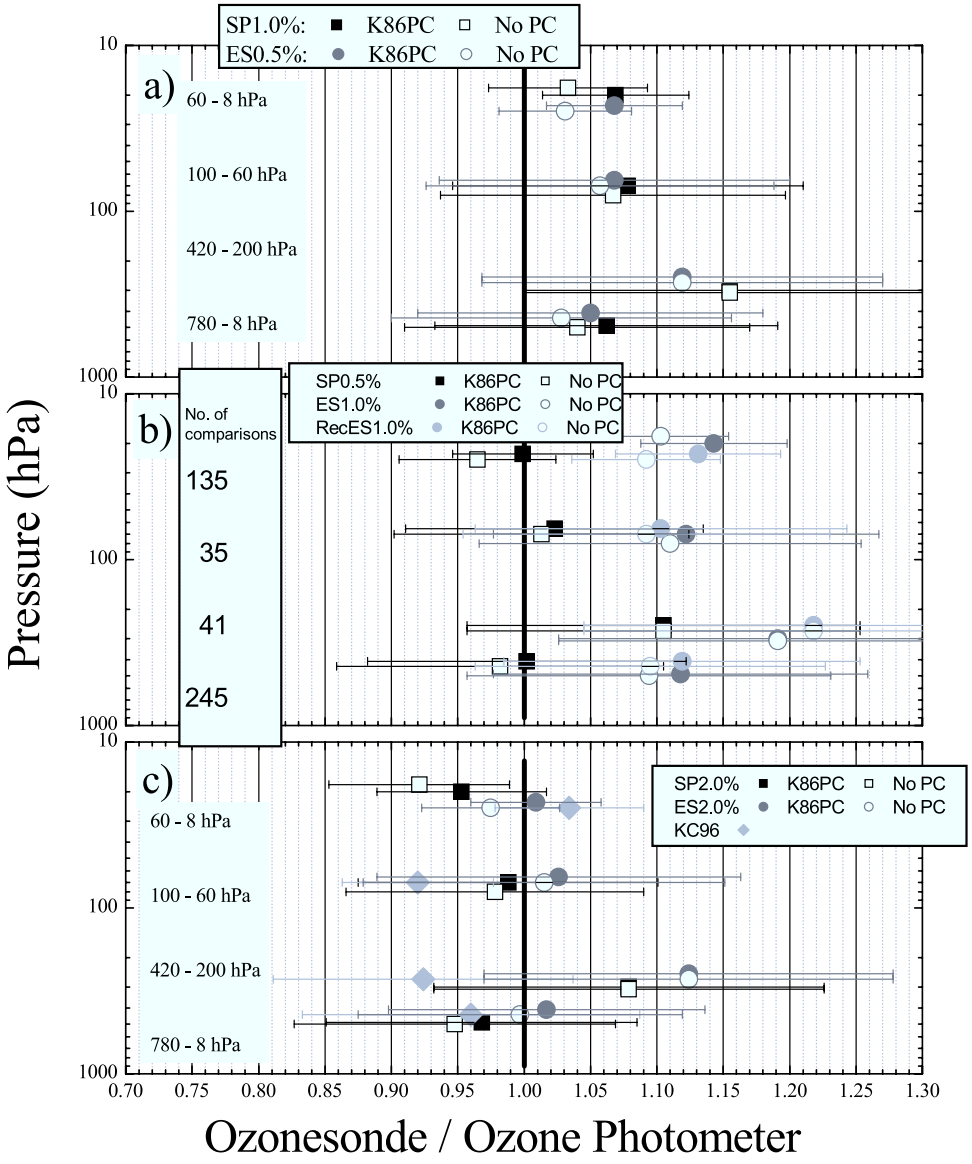

Figure 8. Ratios of ozonesondes to photometer averaged over different pressure ranges using both the *Komhyr* [1986] pump correction (K86PC) and no pump correction (No PC) for (a) the manufacturers' recommendations (SP1.0, ES0.5), (b) SP0.5 and the new and reused ES1.0 sondes, and (c) average of SP and ES sondes flown with 2.0 KI and the two KC96 sondes. The pressure ranges are shown on the left in Figures 8a and 8c. Only slight pump corrections are applied at pressures >200 hPa, thus there is no noticeable change for the results in the 420–200 hPa range. The number of ozone photometer comparisons in each pressure range are shown on the left in Figure 8b.

upper standard deviation of the laboratory measurements while the majority lie in the region between the average and upper standard deviation of the laboratory measurements. The differences between SP and ES sondes is similar. ES sondes are generally 5–10% more sensitive to ozone than SP sondes when the same cathode solution is used in both sondes.

5. Discussion

[44] For this ozonesonde intercomparison the in situ measurements were compared to a photometer flown with the ozonesondes, while integral columns of the ozonesonde measurements were compared with two remote spectrophotometers, a Dobson and a Brewer operated at the balloon launch site. The summary comparisons of ozonesondes with these references are shown in Figures 8 and 9. The conclusions drawn from Figures 8 and 9 differ. Comparisons with the in situ photometer (Figure 8) indicate that the SP0.5 or ES2.0 combinations provide the best measurements, while the manufacturer's recommendations, and more widely used combinations, SP1.0 and ES0.5, overestimated ozone by 3–8%. In contrast ozone column comparisons (Figure 9) indicates that both SP1.0 and

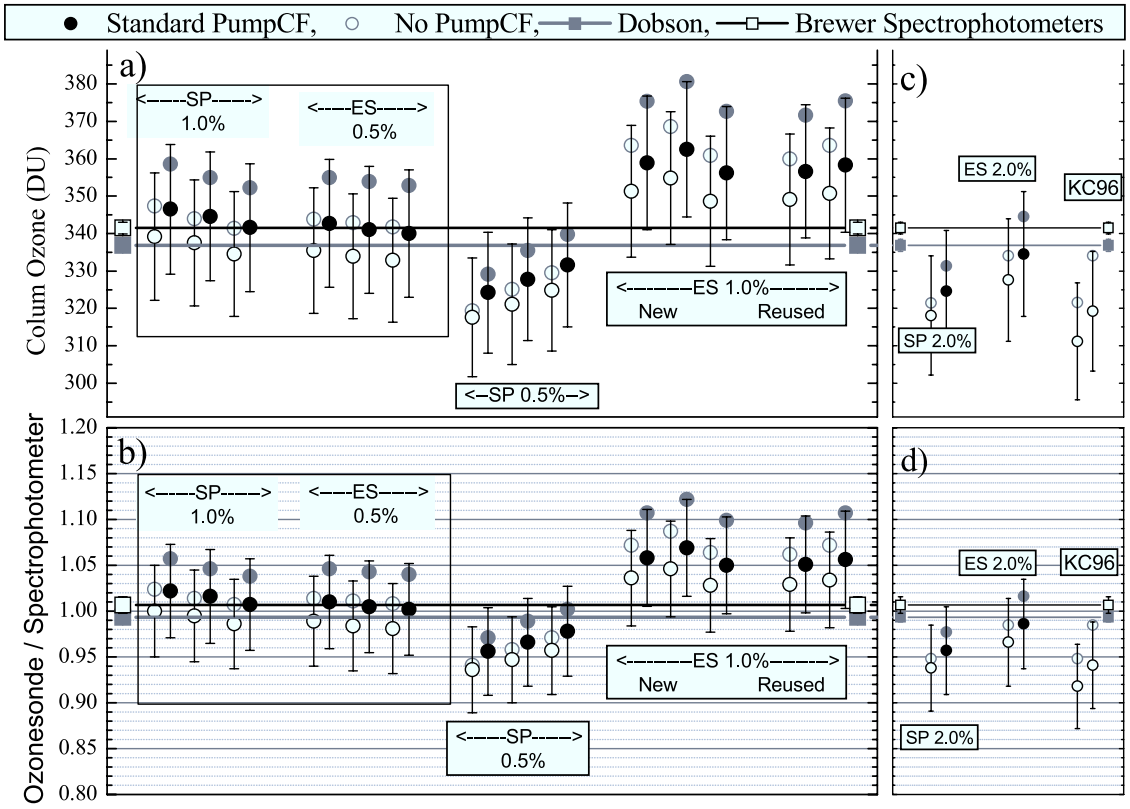

Figure 9. (a) Integrated ozone from the 12 core ozonesondes (3 SP1.0, 3 ES0.5, 3 SP0.5, and 3 ES1.0), two reused ES1.0 ozonesondes (circles with error bars), and from Dobson and Brewer spectrophotometers located at the launch site (lines with boxes and error bars). The ozonesonde measurements are extrapolated using both the SBUV climatology (40 DU for April at 41°N) (solid and open black circles) [*McPeters et al.*, 1997] and at constant ozone mixing ratio above the last ozone measurement (solid and open gray circles without error bars). Results with and without the standard pump efficiency correction [*Komhyr*, 1986] for measurements at low air pressures are shown. The error bars indicate a precision of 5%. The standard deviation of the seven Dobson and Brewer spectrophotometer measurements completed during the balloon flight do not exceed the symbol sizes. (b) As in Figure 9a but ratios of integrated total ozone from the ozonesondes to the average of the Dobson and Brewer measurements. (c and d) Same as Figures 9a and 9b for the other four auxiliary ozonesondes flown (1 SP2.0, 1 ES2.0, and 2 KC96). Results from the manufacturer's recommendations for solution strength are enclosed in the box in Figures 9a and 9b.

ES0.5, the manufacturer's recommendations, provide the best results, while SP0.5 underestimates ozone by up to 5%. The ozone column from the ES2.0 sonde also agrees well with the remote measurements.

[45] The ozonesondes individually, and as groups, performed with precisions of approximately ±2% throughout the flight (Figure 2). Accuracies for the Dobson and Brewer remote spectrophotometer measurements are thought to be ±2% with precisions of 1% [*Holland and Thomas*, 1975; *Basher*, 1982; *Huber et al.*, 1995]. These values are consistent with the variations observed during the flight operations, which were less than 1% over the 1–2 h measurement period. Precision of the photometer measurements during flight were observed to be ±5%. This is poorer than anticipated, and measured in the past [*Hilsenrath et al.*, 1986], and probably results from the in flight difficulties experienced by the photometer, discussed earlier. Integration of the photometer measurements using two techniques to account for tropospheric ozone produced similar results indicating that the photometer ozone columns are less than the remote column measurements by 3.5 (5.7)% using constant mixing ratio (SBUV) for extrapolation of the column. This result is within the precision of the measurement, agrees with similar comparisons completed by *Hilsenrath et al.* [1986], and is fully consistent with the summary comparisons for ozonesonde performance (Figures 8 and 9). Thus combinations of ozonesonde type/cathode cell concentration which overestimated the photometer (SP1.0, ES0.5) by ~5% provided ozone columns in close agreement with the remote measurements. Combinations which agreed with the photometer throughout the flight provided ozone columns which underestimated the remote measurements (SP0.5, ES2.0). This result is, however, somewhat at odds with the comparison with the laboratory measurements, which could be interpreted as indicating that the balloon-borne photometer

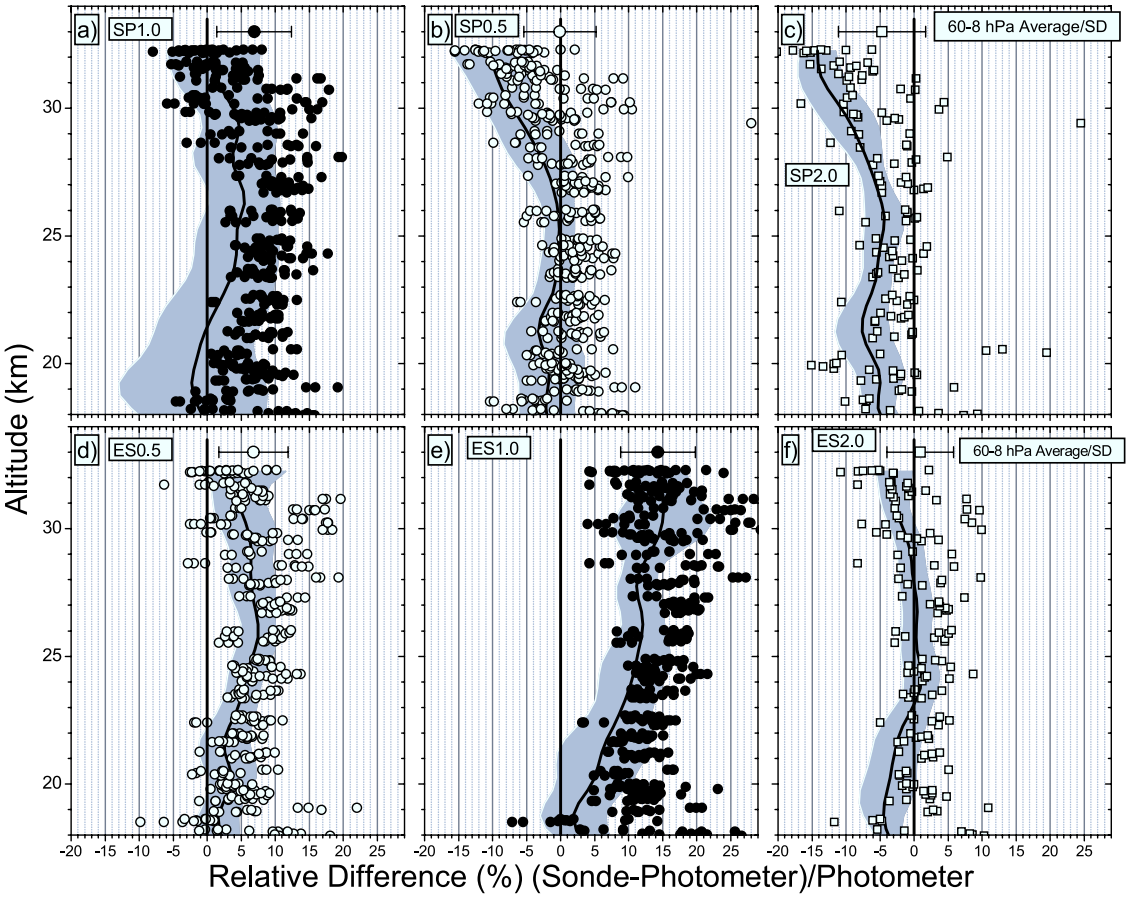

Figure 10. Relative differences (ozonesonde-photometer)/photometer as a percent for balloon-borne and laboratory [*Smit et al.*, 2007, Figure 7] measurements at air pressures of less than 70 hPa for (a) SP1.0, (b) SP0.5, (c) SP2.0, (d) ES0.5, (e) ES1.0, and (f) ES2.0. The number of balloon-borne photometer measurements at higher pressures were too few to warrant a comparison with the laboratory measurements. The laboratory results represent the mean (solid line) and standard deviation (shaded area) of approximately eight individual measurements for each sonde type and solution strength (JOSIE 2000). The balloon measurements for Figures 10a, 10b, 10d, and 10e are the measurements from the three core sondes flown at 0.5 KI (open circles) and 1.0 KI (solid circles). The balloon measurements in Figures 10c and 10f are the result of the single SP/ES sondes flown at 2.0 KI (open boxes). The single data point at 36 km in each panel indicates the mean and standard deviation for the set of balloon-borne comparisons shown in that panel. For this comparison the JOSIE results are processed in the same way as the balloon measurements.

measured slightly less than it did in the laboratory comparisons, if we assume ozonesonde performance in these two situations was on average the same (Figure 10).

6. Summary, Conclusions, and Recommendations

[46] A balloon flight containing 14 new ECC ozonesondes (7 Science Pump (SP), 7 ENSCI (ES)), 2 previously flown ES ozonesondes, 2 KC96 ozonesondes, an ozone photometer, and a Vaisala temperature and pressure sensor was completed on 13 April 2004 from near Laramie, Wyoming, USA. At the balloon launch site ozone columns of 337 ± 1.7 DU (341 ± 1.6 DU) were measured during the flight with Dobson (Brewer) spectrophotometers. Of the 14 new ECC sondes, three of each type, were activated with 1.0% KI cathode solution, three of each type with 0.5% half buffered KI cathode solution. These 12 ozonesondes formed the core experiment. The other two new ECC sondes, 1 ES and 1 SP, were activated with 2.0% unbuffered KI solution. In addition two reused ES sondes were activated with 1.0% KI. The KC96 sondes use primarily a KBr solution. The exact solution cell concentrations are specified in Table 1. The ECC ozonesonde data were analyzed both with and without a correction for loss of pump efficiency at air pressures below 300 hPa. The correction applied is the *Komhyr* [1986] recommendation, which leads to an increase in ozone of 1–8% for pressures between 100 and 8 hPa and an increase of the ozone column from ozonesondes on the order of 2–4%. The manufacturer's recommendations, 1.0% KI for SP sondes and 0.5% KI for ES sondes are a subset of the 12 core ozonesondes. Of the other two core experiment combinations, only the 1.0% KI solution in ES sondes is known to have been in regular use at some stations. Including 0.5% KI in SP sondes was done for completeness.

[47] The change of ozonesonde response when the solution strength is increased from 0.5% to 1.0% KI is similar for both SP and ES sondes. A simple linear transfer function, Ratio (0.5 KI/1.0 KI) = 0.9 + 0.024 * $\log_{10}$(pressure) captures, within ±2%, the pressure-dependent variation of this ratio. Although somewhat nonlinear, there is a similar increase in ozone sensitivity for ES sondes, compared to SP sondes, when the same cathode cell concentrations are used. This increase is nearly the same for 0.5, 1.0, and 2.0% KI concentrations, and can be represented with a quadratic function in $\log_{10}$(pressure).

[48] The precision of all ozonesondes was high. The range of measurements compared to the average of each group of similarly prepared ECC sondes was generally <2%, increasing to 4–5% near the surface, tropopause, and where ozone gradients were large. Although precision of the ozonesonde measurements was high in the troposphere, the precision and availability of data from the ozone photometer was limited in the troposphere, thus no conclusions can be made concerning ozonesonde accuracy in the troposphere. The photometer problems arose, we believe, because of motion in the Earth's magnetic field affecting the plasma lamp of the photometer. As a result data from this instrument were reduced to about one third of the anticipated data, and were concentrated in the stratosphere.

[49] The primary goal of the experiment was to investigate, with an atmospheric measurement, the variation in response of SP and ES ozonesondes for the two primary KI solutions in use today, 1.0% and 0.5% KI. These 4 combinations formed the 12 core ozonesondes which, along with the 6 auxiliary ozonesondes, were compared in situ with the ozone photometer and their integrals with the remote column measurements. The comparisons with these two references does not lead to the same conclusions since ozone columns from the sparse photometer data, estimated in several ways, were found to underestimate the column measurements by about 5%, which is within the precision of the photometer and similar to previous comparisons of ozone photometers and column measurements [*Hilsenrath et al.*, 1986]. Further work to reconcile these differences, or to repeat such an ozonesonde intercomparison, requires the development of a stable in situ ozone photometer that can be used in the laboratory and in the field, and can be shown to provide ozone columns in agreement with ground-based standards.

[50] The 6 ozonesondes comprising the manufacturer's recommendations were found to overestimate the photometer by 5–10% in the stratosphere, but provide ozone columns in good agreement with the remote column measurements. This difference is in line with the difference in ozone photometer and column measurements observed. Using a correction [*Komhyr*, 1986] for loss of pump efficiency at low pressures leads to an average increase of 4% at pressures below 60 hPa, thus agreement with the photometer is improved if no correction for pump efficiency is made, while the pump correction affects only slightly the correspondence with column measurements.

[51] The use of 1.0% KI solution in ES sondes is not recommended. This leads consistently to overestimates of ozone by 5–15% when compared to reference instruments. Correcting for pump efficiency increases this error. This characteristic was observed for both new and reused ES sondes, indicating that the reuse of recovered ozonesondes is reasonable if they are prepared as a new sonde. In contrast the use of 0.5% KI in SP sondes was found to underestimate the photometer measurements, and thus also the column measurements. Thus of the standard concentrations in primary use, only 0.5% KI used in SP sondes leads to measurements which provide better comparisons with reference instruments when pump efficiency is accounted for.

[52] The use of 2.0% unbuffered KI solutions in ES sondes provided measurements which are in good agreement with the reference instruments. The results for SP sondes with a 2.0% unbuffered KI solution are similar to those with 0.5% KI solutions in SP sondes. Both underestimate total ozone by up to 5%. For these sondes better results are found when a pump correction is used. The KC96 sondes underestimate ozone at pressures above 50 hPa, and then overestimate ozone at pressures <60 hPa.

[53] The overall conclusions from this experiment are not as clear as had been hoped. It was shown that randomly selected ozonesondes perform with high precision, when prepared with similar techniques and solution strengths. In comparison with column measurements the results support the use of 1.0% KI in SP sondes, and 0.5% KI in ES sondes, which are the manufacturer's recommendations, while comparisons with the in situ photometer suggests these combinations overestimate ozone in the stratosphere. Comparing these in situ balloon-borne measurements with a similar laboratory experiment [*Smit et al.*, 2007] indicates overlap of the two results within uncertainty limits; however, there is a small systematic difference. This may suggest small variations in instrument performance (either ozonesonde or photometer) between the experiments, or small difficulties in reproducing an atmospheric environment within a laboratory. In addition questions have been raised about the importance of corrections for decreases in ozonesonde pump efficiency at low pressure. Clearly, in spite of the progress, there are additional details to be addressed concerning ozonesonde performance.

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