Electrochemical concentration cell (ECC) ozonesonde pump efficiency measurements and tests on the sensitivity to ozone of buffered and unbuffered ECC sensor cathode solutions

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[1] On the basis of extensive laboratory and field tests of electrochemical concentration cell (ECC) ozonesondes, a height-dependent artifact in ozone profile measurements was found that is primarily due to side reactions of the phosphate buffers used in the "standard" 1% potassium iodide sensing solution. The influence of the buffers was revealed as a result of new, direct measurements of the ozonesonde pump flow rate efficiency made in an environmental chamber using an oil bubble flowmeter developed at National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL). The new flow rate measurements give pump efficiency correction factors that are 2 and 15% greater at 100 and 5 hPa, respectively, than those used in currently recommended procedures. Profile measurements using ozonesondes with differing ECC sensor solutions, on dual-sonde balloons and experiments in a simulation chamber, show that the impact of the buffers is most pronounced above the ozone partial pressure maximum. The effect is about a 10–15% overmeasurement of ozone at an altitude of 30 km. Careful consideration must be given to the combination of the sensing solution composition and pump efficiency correction if representative ozone profiles are to be obtained from ozonesonde measurements. *INDEX TERMS:* 0394 Atmospheric Composition and Structure: Instruments and techniques; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* Ozonesonde, iodometric method, intercomparison

1. Introduction

[2] The electrochemical concentration cell (ECC) ozone instrument, developed by *Komhyr* [1969], combines the basic principle of the reaction of ozone and iodide within a redox cell sensor coupled to a nonreactive air-sampling Teflon pump. The ozone instrument, when interfaced with a balloon-borne radiosonde, provides a simple, reliable, and relatively inexpensive method to measure ozone concentrations from the surface to altitudes of about 35 km.

[3] The earliest ECC ozonesonde sites began measuring ozone profiles in the late 1960s. Since then, ozonesondes have become important in monitoring tropospheric and lower stratospheric ozone. For example, trends derived from ozonesonde data at several sites are a significant part of ozone assessments [*World Meteorological Organization* (*WMO*), 1998; *SPARC*, 1998] and other studies [*Logan et al.*, 1999]. Ozonesondes have also been used extensively in projects such as SHADOZ [*Thompson and Witte*, 1999; *Thompson et al.*, 2002] and MATCH [*Schulz et al.*, 2001] where data are gathered and compared from many different locations. Therefore it is important that ozonesonde data sets be consistent.

[4] Two potential obstacles to consistency are changes in the manufactured instruments and differences in the operating guidelines used to prepare the ozonesondes for flight. Since each ozonesonde flight represents a new instrument, manufacturers must provide consistent, high-quality sondes. Table 1 lists the two different manufacturers of ECC ozonesondes, the model production dates, and design changes.

[5] The guidelines for preparing ozonesondes for flight and data processing may be from one of the current manuals provided by the two manufacturers, the original 4A NOAA technical memorandum [*Komhyr*, 1986], or some modified

Table 1. Electrochemical Concentration Cell Ozonesonde Models and Manufacturers

Manufacturer	Model Number	Years Manufactured	Design
Science Pump	1A	1968	initial ECC ozonesonde model
Science Pump	3A	1968–1981	rectangular pump
Science Pump	4A	1978–1995	cylindrical piston pump
Science Pump	5A	1986–1997	start of digital data acquisition
Science Pump	6A	1995 to present	
EN-SCI	1Z	1993–1998	
EN-SCI	2Z	1997 to present	molded plastic sensor cell

version of one of the manuals. Modifications or changes to the above manuals are aimed at optimizing data or performance of the ozonesondes. Some changes may be simple and can be applied simply by reprocessing the data. One example of this type of change would be using a different average pump efficiency correction factor (PCF), which accounts for the reduced volumetric flow rate of the ozonesonde pump at pressures below 300 hPa. Other changes, aimed at improving precision and accuracy, may affect the physical characteristics of the ozonesonde measurement. Changing the composition of the ozone sensing solution falls into this category. Experimental tests would then be required to determine empirical corrections to prior data in order to maintain a consistent data set.

[6] New ozonesonde models or changes in procedures are often tested through organized intercomparison campaigns. These field and laboratory intercomparisons have been the guide for monitoring the consistency, precision, and accuracy of ozone profile measurements made by various groups. The SPARC Report [*SPARC*, 1998] lists 12 major ozonesonde intercomparisons completed since 1970. *Kerr et al.* [1994] analyzed the results of the 1991 WMO international ozonesonde intercomparison and found that ECC ozonesonde precision had improved considerably. A few years later, the results from the 1995 Mauna Loa ozone intercomparison (MLO3) [*McPeters et al.*, 1999] and the 1996 Jülich Ozonesonde Intercomparison Experiment (JOSIE) [*Smit et al.*, 1998] also showed good precision among ECC ozonesondes. However, the NOAA/CMDL ozonesondes, in both intercomparisons, measured higher ozone in the stratosphere, about 5% high near the ozone peak and steadily increasing to 15–20% high by the end of the profile. Since all ECC groups from the JOSIE-1996 intercomparison, including NOAA/CMDL, were using the standard 1% potassium iodide (KI) buffered sensing solution, the higher pump flow correction factors used to process the data by NOAA/CMDL resulted in the higher measured ozone amount. However, additional measurements of PCFs using the new oil bubble flowmeter were consistent with earlier data processing. This prompted the investigation of the ECC ozonesonde response to sensing solution composition reported on here.

2. Ozone Measurement

2.1. Iodometric Methods

[7] This paper presents the results of experiments investigating the characteristics of ECC ozonesondes under laboratory and field conditions. However, various ozone/iodometric measurement methods [e.g., *Littman and Benoliel*, 1953; *Byers and Saltzman*, 1959; *Kopczynski and Bufalini*, 1971; *Van De Wiel et al.*, 1978] offer an excellent source of information, even though these studies may differ in the type of sensor, composition of the potassium iodide sensing solutions, and concentration of ozone measured. Nevertheless, it is appropriate to briefly discuss some of the results from these earlier tests as they often apply to the fundamental operation of the ECC ozonesonde.

[8] The iodometric "wet method" for measuring ozone is based on the fast reaction of ozone and iodide (I^-) producing iodine (I_2) in an aqueous solution, represented by equation (1).

$$2KI + O_3 + H_2O \rightarrow 2KOH + I_2 + O_2 \tag{1}$$

Many of the earlier iodometric methods used titration procedures to determine the quantity of iodine produced. The molar amount of iodine equals the molar amount of ozone assuming that the stoichiometric yield is 1:1. However, validation of the 1:1 yield has often shown conflicting results [*Birdsall et al.*, 1952; *Flamm and Anderson*, 1975]. Much of the uncertainty stems from the use of a variety of KI sensing solutions, pH buffers, and sensors [*Saltzman and Gilbert*, 1959; *Boyd et al.*, 1970; *Dietz et al.*, 1973; *Pitts et al.*, 1976; *Lanting*, 1979]. However, one experimental observation that was common to many of the references on iodometric stoichiometry tests is a secondary reaction producing additional iodine. Higher ozone to iodine ratios from approximately 1:1.1 to 1:1.25 were often observed (10 to 25% too much iodine). *Saltzman and Gilbert* [1959] noted that the phosphate buffers appeared to be responsible for this effect and suggested a hypothetical mechanism where additional hypoiodite ion (IO^-) may be produced by the reaction of iodide (I^-) and dihydrogen phosphate ion ($H_2PO_4^-$), eventually leading to excess iodine.

2.2. Electrochemical Concentration Cell

[9] The ECC ozonesonde, described by *Komhyr et al.* [1986, 1995], uses a platinum electrode electrochemical cell sensor. An ozone molecule in air, forced into the sensor cathode chamber by the ozonesonde's nonreactive gas sampling pump, reacts with the iodide in the sensing solution to form an iodine molecule. The iodine molecule is converted back to iodide and simultaneously two electrons of current flow through the cell's external circuit. Thus the sensor's output current is proportional to the rate at which ozone enters the sensor. Ozone partial pressure can then be computed from equation (2) if the flow rate and cell current (typically 0–6 microamperes) are known.

$$P_{O3} = 4.307 \times 10^{-4} (I - I_{BG}) T_p T_{100} PCF, \tag{2}$$

where
P_{O3} Ozone partial pressure, millipascals;
I Cell output current, microamperes;
I_{BG} Cell background current, typically 0-0.1 μamps;
T_p Temperature of sonde pump, K;
T_{100} Flow rate in seconds per 100 cm^{-3} of airflow;
PCF   Pump flow rate correction factor, 1/efficiency.

[10] The ozonesonde volumetric flow rate (T_{100}), during a typical balloon flight, is relatively constant from surface pressure to about 300 hPa and then begins to steadily

Table 2. Ozonesonde Pump Efficiency Calibrations Measured by Various Methods[a]

	Model Number	Number Calibrated	Pressure, hPa						
			100	50	30	20	10	7	5
Torres [1981]	3A	43	1.010	1.026 (0.012)	1.038 (0.013)	1.056 (0.015)	1.098 (0.017)	1.130 (0.021)	
Torres [1981]	4A	7	1.000	1.015	1.027	1.038	1.063	1.084	
Komhyr [1986]	4A		1.011 (0.005)	1.015 (0.006)	1.022 (0.008)	1.032 (0.009)	1.055 (0.010)	1.070 (0.012)	1.092 (0.014)
Komhyr et al. [1995]	4A	13	1.007 (0.005)	1.018 (0.005)	1.029 (0.008)	1.041 (0.012)	1.066 (0.024)	1.087 (0.026)	1.124 (0.027)
Harder [1987]	5A	10	1.056 (0.015)	1.082 (0.015)	1.104 (0.020)	1.125 (0.026)	1.169 (0.031)	1.198 (0.032)	1.231 (0.033)
Deshler (UWYO)[b]	1Z		1.023 (0.008)	1.041 (0.011)	1.055 (0.013)	1.073 (0.016)	1.127 (0.026)	1.171 (0.035)	1.225 (0.046)
Deshler (UWYO)	5A		1.021 (0.009)	1.035 (0.011)	1.049 (0.014)	1.067 (0.018)	1.129 (0.030)	1.182 (0.040)	1.248 (0.053)
Deshler (UWYO)	all[c]	658	1.022 (0.011)	1.037 (0.013)	1.049 (0.016)	1.066 (0.020)	1.120 (0.032)	1.166 (0.040)	1.224 (0.051)
Rosen (verbal communication, 1987)	5A	15	1.030	1.041	1.058	1.072	1.100	1.123	1.150
Rosen (verbal communication, 1989)	5A	15	1.025	1.039	1.055	1.074	1.114	1.139	1.180
De Backer et al. [1998][d]	1Z		1.030	1.048	1.067	1.085	1.126	1.153	1.183
NOAA/CMDL	1Z	78	1.030 (0.011)	1.049 (0.012)	1.066 (0.014)	1.086 (0.018)	1.138 (0.024)	1.188 (0.028)	1.244 (0.036)
NOAA/CMDL	2Z	31	1.038 (0.012)	1.056 (0.012)	1.071 (0.010)	1.089 (0.010)	1.143 (0.015)	1.187 (0.022)	1.245 (0.028)
NOAA/CMDL	5A	8	1.029 (0.008)	1.052 (0.012)	1.069 (0.015)	1.091 (0.017)	1.151 (0.018)	1.201 (0.025)	1.279 (0.021)
NOAA/CMDL	6A	46	1.037 (0.013)	1.058 (0.016)	1.078 (0.018)	1.099 (0.019)	1.159 (0.025)	1.213 (0.032)	1.276 (0.044)
NOAA/CMDL	all[c]	305	1.033 (0.010)	1.052 (0.012)	1.070 (0.013)	1.089 (0.014)	1.145 (0.020)	1.195 (0.027)	1.260 (0.037)

[a] Values given are pump calibration factors (1/efficiency) with the 1-sigma standard deviations given directly below in parentheses for available data.
[b] University of Wyoming Balloon Group.
[c] Average of all ozonesonde pump calibration factors (including recovered instruments) for that specific group.
[d] Based on measurements fit to empirical correction formula using parameter $b = 0.20$.

decrease owing to the relative increase in resistance from pumping against the cathode solution fluid head, dead space in the cylinder of the piston pump, and pump leakage [*Komhyr et al.*, 1995; *Steinbrecht et al.*, 1998]. Equation (2) accounts for the decrease in flow rate by multiplying by a pump correction factor, which is a function of ambient pressure. The PCF value is simply the inverse of the pump efficiency. Table 2 lists several PCF measurements including the current "standard" values based on experimental measurements by *Komhyr et al.* [1986], which differ by as much as 15% at 5 hPa from the higher NOAA/CMDL values, reported on here.

[11] In addition to the differences in PCF values, Table 3 lists four different ECC cathode sensor solutions used in operating procedures. The "standard" sensor solution, given by *Komhyr* [1986], and the most recent Science Pump Manual [*Science Pump Corporation*, 1996], is the 1% KI buffered (1% KI-b) solution. However, *EN-SCI Corporation* [1996] recommends using 0.5% KI buffered (0.5% KI-b) sensor solution, which is simply the 1% KI-b diluted by one half. NOAA/CMDL began using a 2% KI unbuffered (2% KI-u) sensor solution in 1998. The most recent ozonesonde intercomparison project (JOSIE-2000) held at Jülich, Germany, investigated the differences in ECC ozonesonde response using the various cathode sensor solutions in Table 3, except for the 1.5% KI-b solution, which has not been in use since approximately 1985.

[12] Besides major intercomparison projects, there have been other laboratory tests [*Tarasick et al.*, 1998] and field tests investigating the accuracy and response of ECC ozonesondes. The buffered KI cathode sensing solutions often showed higher ozone readings compared to a UV ozone analyzer in surface experiments or inside an environmental chamber [*Barnes et al.*, 1985] and can also depend upon the background value (I_{BG}) used [*Thornton and Niazy*, 1982; *Reid et al.*, 1996]. Several dual flight experiments by *Davies et al.* [2000] showed differences between ozonesondes using 1% KI-b, 0.5% KI-b, and 2% KI-u sensor solutions. The largest difference was near the top of the profile, above 30 km, where the 2% KI-u profile was about 10–12% lower than the 1% KI-b ozonesonde measurement.

[13] In summary, the iodometric method for measuring ozone has been studied extensively in absorption/titration methods and in ECC ozonesondes. Many of the experiments have shown similar results with respect to high ozone measurements and a hysteresis effect. The phosphate buffers were considered as a likely source of additional side reactions leading to observed stoichiometric ratios that are greater than the ideal 1:1 ratio expected from the ozone to iodine reaction as discussed by *Saltzman and Gilbert* [1959]. The accuracy and precision of ECC ozonesondes also depends on the pump characteristics at low ambient pressures. Therefore we investigated the characteristics of the ECC ozonesonde through sensor response experiments (using different sensing solution recipes), pH sensitivity tests, ozone pump flow calibration factor measurements, and dual ozonesonde flights.

3. Experimental Section

3.1. Methods

[14] Science Pump Corporation model 6A and EN-SCI Corporation model 1Z and 2Z ozonesondes were used in all

Table 3. Most Widely Used Electrochemical Concentration Cell Ozonesonde Cathode Sensor Solutions and Ingredients

Sensor Solution	KI, g/L	Buffers: g/L and (M)		KBr, g/L
		$NaH_2PO_4 \, H_2O$	$Na_2HPO_4 \cdot 12H_2O$	
1.5% KI-b[a]	15	7.5 (0.021)	1.88 (0.014)	37.5
1.0% KI-b[b]	10	5.0 (0.014)	1.25 (0.009)	25
0.5% KI-b[c]	5	2.5 (0.007)	0.63 (0.005)	12.5
2% KI-u[d]	20	0	0	0

[a] Science Pump ECC 1A Manual, [*Science Pump Corporation*, 1968]; *Barnes et al.*, [1985].

[b] *Komhyr* [1986]; Science Pump ECC 6A Manual [*Science Pump Corporation*, 1996].

[c] EN-SCI ECC 2Z Manual [*EN-SCI Corporation*, 1996]; *Boyd et al.* [1998].

[d] Currently used at all NOAA/CMDL sites.

of the laboratory and field tests presented here. The cathode and anode solutions were made with A.C.S. "analyzed" reagent grade chemicals and HPLC deionized water. All anode solutions used in these tests were prepared in the standard manner by saturating the respective cathode solutions with potassium iodide. A Thermo Environmental Instruments (TEI) 49C Ozone Calibrator was used as the ozone source in all of the stoichiometric ozonesonde sensitivity and pH tests. The calibrator showed very good agreement ($-0.2 \pm 2.5\%$ at $5-25$ ppbv and $-0.1 \pm 0.5\%$ from $25-250$ ppbv) when compared to a National Institute of Standards (NIST) standardized Dasibi Model 1003-AH UV ozone analyzer.

[15] All ozonesonde flow rates were measured in the laboratory using a 100 cm^{-3} soap-film bubble flowmeter. The flow rate time (T_{100} in equation (2)) was corrected to account for evaporation of the soap bubble solution. The correction can be estimated from the room temperature and relative humidity; however, we used a separate ozonesonde to determine the correction directly by measuring the flow from filtered laboratory air followed by measuring the flow from a humidified air source. For example, the correction for Boulder, Colorado, shows a seasonal dependence, ranging from 2.1 to 3.3% in Figure 1. This correction is typically not applied in current published operating guidelines. However, *Schmidlin et al.* [1998] reported that dry air and a humidity correction is used when measuring the flow rate of ECC ozonesondes with a soap bubble flowmeter at NASA Wallops Flight Facility.

3.2. Cathode Solution Sensitivity Tests

[16] More than 100 sensitivity tests were conducted with ozonesondes sampling from a TEI 49C Ozone Calibrator operating at laboratory pressure and temperature. The calibrator ozone concentrations were adjusted every 10 min to simulate typical midlatitude ozone profile partial pressures. Three ozonesondes, each containing a different sensor solution composition, were compared simultaneously while sampling the output of the ozone calibrator. The primary goal of the sensitivity tests was to determine which of the sensing solution ingredients had the greatest effect, if any, on the ozonesonde response.

[17] Figure 2 summarizes the tests showing the effect of adjusting the amount of KI used in unbuffered sensor solutions (left) versus adjusting the buffer concentrations (right) in the standard 1% KI-b solutions. Increasing the KI concentration from 0.5% to 4% KI resulted in an overall

increase by $5-7\%$ in the ozonesonde response, but all four solutions yielded ozone values within $\pm5\%$ of the calibrator values. Adjusting the KBr showed the least amount of sensitivity with less than 5% differences observed when the amount of KBr was varied from 0 to 10%. The right side of Figure 2 shows the much greater effect on ozonesonde response when the buffers were adjusted from 0 to 4 times the standard concentration of 0.01 M. Ozonesondes using the standard 1% KI-b sensor solution matched the concentration of the ozone calibrator at the beginning of the simulated profile, but measured 13% higher ozone near the end of the test. Increasing the buffer concentration by a factor of 4 increased the difference to 30% higher ozone. The hysteresis effect was also much greater when the buffer concentration was increased. Further tests indicated that the acidic buffer ($NaH_2PO_4 \cdot H_2O$) was responsible for the excess ozone measured and hysteresis effect observed.

[18] Since the unbuffered sensor solutions showed good results, additional tests were carried out to determine the relationship of ozonesonde response with the pH of the cathode sensing solution.
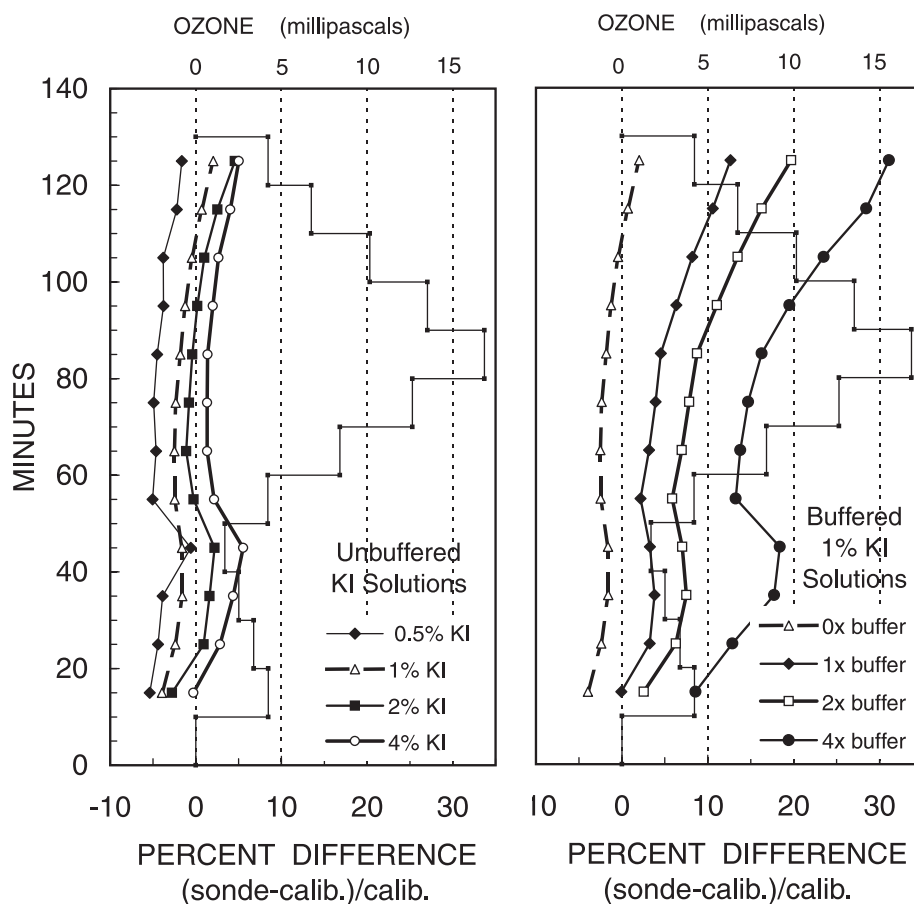
3.3. The pH Sensitivity Tests

[19] Figure 3 shows the experimental setup used to determine the ozonesonde response as a function of pH. The pH of the cathode sensing solution was monitored during the tests by inserting a micro pH electrode directly into the bubbling cathode solution. The pH electrode remained in the solution throughout each test and did not show any effect on the ECC ozonesonde measurements. The pH of the standard buffered cathode solution (1% KI-b) was always constant at a neutral 6.9 throughout the test. However, the pH of an unbuffered 2% KI-u solution initially varied from 6.0 to 6.7 and always increased, partly owing to the production of potassium hydroxide from equation (1).

[20] The pH of the cathode sensing solution was adjusted during the tests by controlling the ambient carbon dioxide entering through the ozone calibrator. This was done by adding a removable sodium hydroxide column to the inlet of the calibrator air pump to remove CO_2, as shown in
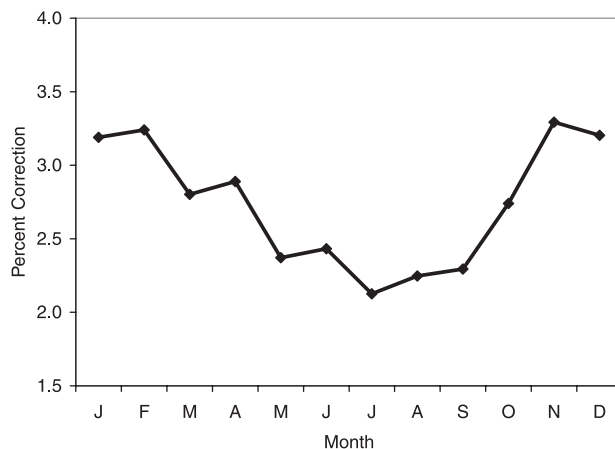
Figure 1. Average correction for the T_{100} time (in equation (2)) measured with a soap bubble flowmeter at Boulder, Colorado, when the ozonesonde is sampling unsaturated room air. The typical standard deviation for each month is $\pm0.4\%$.

Figure 2. (left) Surface ozonesonde sensitivity tests of cathode sensor solutions using various unbuffered potassium iodide (KI) concentrations; (right) zero to four times the buffer concentration for the standard 1% KI buffered sensor solutions.

Figure 3. Eliminating CO_2 would represent the upper pH operating conditions for the unbuffered cathode solution, similar to ambient stratospheric conditions where the mass of CO_2 sampled is about 50 times lower than at the surface.

[21] Figure 4 shows the results of pH and measured ozone using the 2% KI-u, 1% KI-b, and 0.5% KI-b cathode sensing solutions. The dashed lines represent the ozone calibrator settings at 200 and 30 ppbv. The ozonesonde mixing ratio (thick line) and pH (thin line) were monitored for about 3 hours. The four black dots along the pH line in each of the graphs represent times when the CO_2 scrubber was connected and removed during each test. Figures 4a and 4b show results from an EN-SCI 2Z and a Science Pump Corporation 6A model using the 2% KI-u sensing solution. After the CO_2 scrubber was initially connected (first dot), the pH of the unbuffered cathode solution would begin increasing after 2 to 3 min, eventually stabilizing at a pH of about 9 after 1 hour. Upon removal of the scrubber, the pH remained stable for about 2 min then dropped rapidly as CO_2 was absorbed back into the cathode solution, eventually stabilizing near 7.5. The scrubber was connected again to maximize the pH a second time and removed for the final time during the 30 ppbv ozone measurement. Even though the pH changed considerably in the unbuffered solutions, the sonde response remained very stable throughout the test and was always within 2% of the calibrator concentration at 200 ppbv. The response showed a small

hysteresis effect, about 5–7% excess ozone, when the calibrator ozone output was decreased to 30 ppbv.

[22] The pH of the buffered solutions, in Figures 4c and 4d, showed no fluctuation in pH, remaining at 6.9. The ozone response was stable each time the CO_2 scrubber was connected and removed. However, the buffered solutions measured higher ozone than the calibrator output. The standard 1% KI-b solution in Figure 4c showed the largest difference, reading 210 ppbv (5% high) at the beginning of the test and increasing to 225 ppbv (12% high) after 2 hours, and showed a significant hysteresis effect when ozone was dropped from 200 to 30 ppbv. The 0.5% KI-b solution results (Figure 4d) were also higher, but only increased from an initial 3% to about 7% higher measured ozone compared to the calibrator. The hysteresis effect was about one-half as large compared to the 1% KI-b solution. These results are in agreement with the pattern observed in the surface tests of buffered solutions in Figure 2.

[23] In a second set of pH tests we investigated how much the buffer capacity could be reduced and still maintain a stable, neutral pH. The pH of the neutral phosphate solution depends on the ratio of the molar concentrations of the weak acid $H_2PO_4^-$ and its conjugate base $HPO_4^=$, as shown in equation (3) [e.g., *Bettelheim and March*, 1988].

$$pH = 7.21 + \log \frac{[HPO_4^=]}{[H_2PO_4^-]} \qquad (3)$$
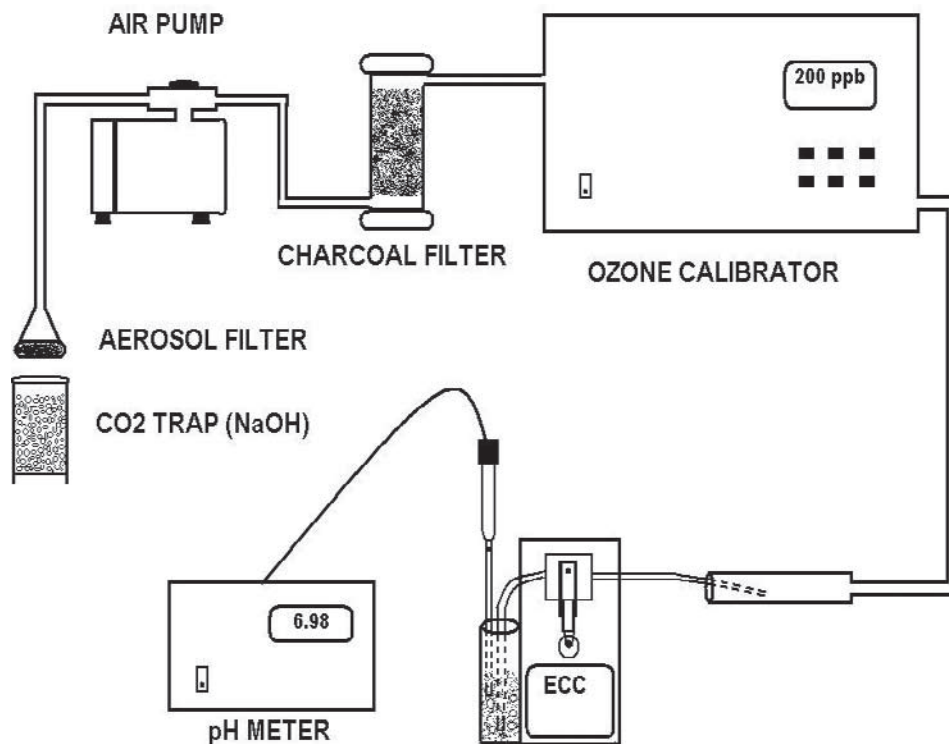
Figure 3. Experimental diagram for the electrochemical concentration cell (ECC) ozonesonde pH sensitivity tests. The ozonesonde sampled a constant ozone source while the pH of the cathode sensor solution was monitored continuously. The pH of unbuffered sensor solutions could be adjusted between 6.0 and 9.3 by connecting or removing the carbon dioxide trap.

Therefore the reduction in buffer concentration could potentially decrease the high ozonesonde measurement and hysteresis effect and still maintain a relatively constant pH but at a lower buffer capacity or lower resistance to pH changes. Figure 5 shows the results when 1% KI-b solutions were prepared with the buffer concentration reduced successively from one-half (5a) to one-eighth (Figure 5c) of the standard 0.01 M. Each successive dilution in the buffer quantity improved the ozonesonde measurement, while the pH remained stable. A dilution to 1/16th buffers (not shown) began to show some signs of drifting pH, but only by about 0.2 pH units during the entire test. The response of the ozonesonde with 1/16th buffers was very close to that of the ozone calibrator and very similar to the 2% KI-u solution ozone measurements.

[24] In Figure 5d, the unbuffered 1% KI solution with 25 g/l KBr, showed a spike (about 9% excess) during the rapid drop in pH at 200 ppbv, and also at the 30 ppbv calibrator levels. Preceding the spike in Figure 5d, the ozonesonde was reading about 3% low. Since it appears that the larger spike may be related to the presence of KBr, an additional test was run with a new ozonesonde containing a sensor solution consisting of 25 g/L KBr (2.5%) in the cathode chamber and saturated KBr in the anode. The results of the pH sensitivity test showed that the KBr-only solutions responded much lower than KI solutions and gave a more distinct pattern of a slow, decreasing response to ozone when the pH was increasing, followed by a 50% upward spike after the CO_2 scrubber was removed. Therefore the presence of KBr in an unbuffered KI sensor solution appears to add an increased pH dependence to the ozonesonde response.

3.4. Pump Efficiency: Pump Calibration Factor Measurements

[25] Originally, *Komhyr* [1969] used a bag inflation method to measure ozonesonde pump flow rates at reduced pressures. Estimated corrections were applied to the measured pump correction factors to account for actual flight conditions, when the cathode solution evaporates and reduces the head pressure that the pump works against. These average PCF values (referred to as Komhyr-1986 throughout this paper) are given in the 1986 Operations Handbook for 4A ECC ozonesondes, including the *Science Pump Corporation* [1996], and *EN-SCI Corporation* [1994] instruction manuals. The revised 1996 EN-SCI manual recommends slightly higher PCF values, measured by *Komhyr et al.* [1995] using a dual-sonde RPM technique.

[26] The NOAA/CMDL pump correction factors, given in the summary from Table 2, were determined by a new method using an oil bubble flowmeter. The apparatus, shown in Figure 6, is nearly identical to the typical sidearm burette soap bubble flowmeter used to measure volumetric flow rates. The only difference is that the soap solution is replaced with Dow Corning 704 silicon diffusion pump oil. The extremely low vapor pressure of the oil eliminates any errors from evaporation and eventual boiling that would occur at low pressures using a soap and water solution. The pump being calibrated uses a separate sensor cell containing 2 mL of the diffusion pump oil to simulate the typical head
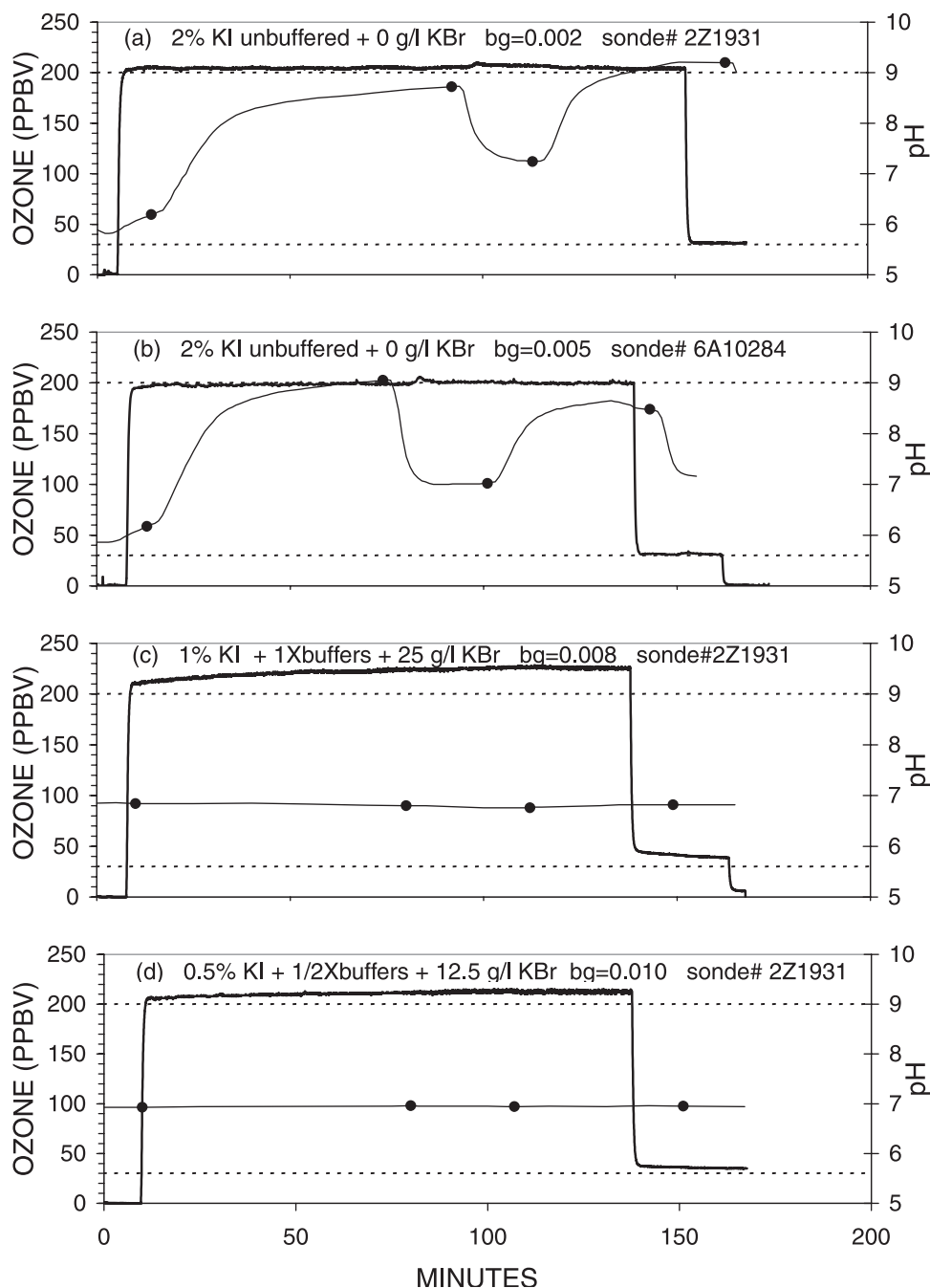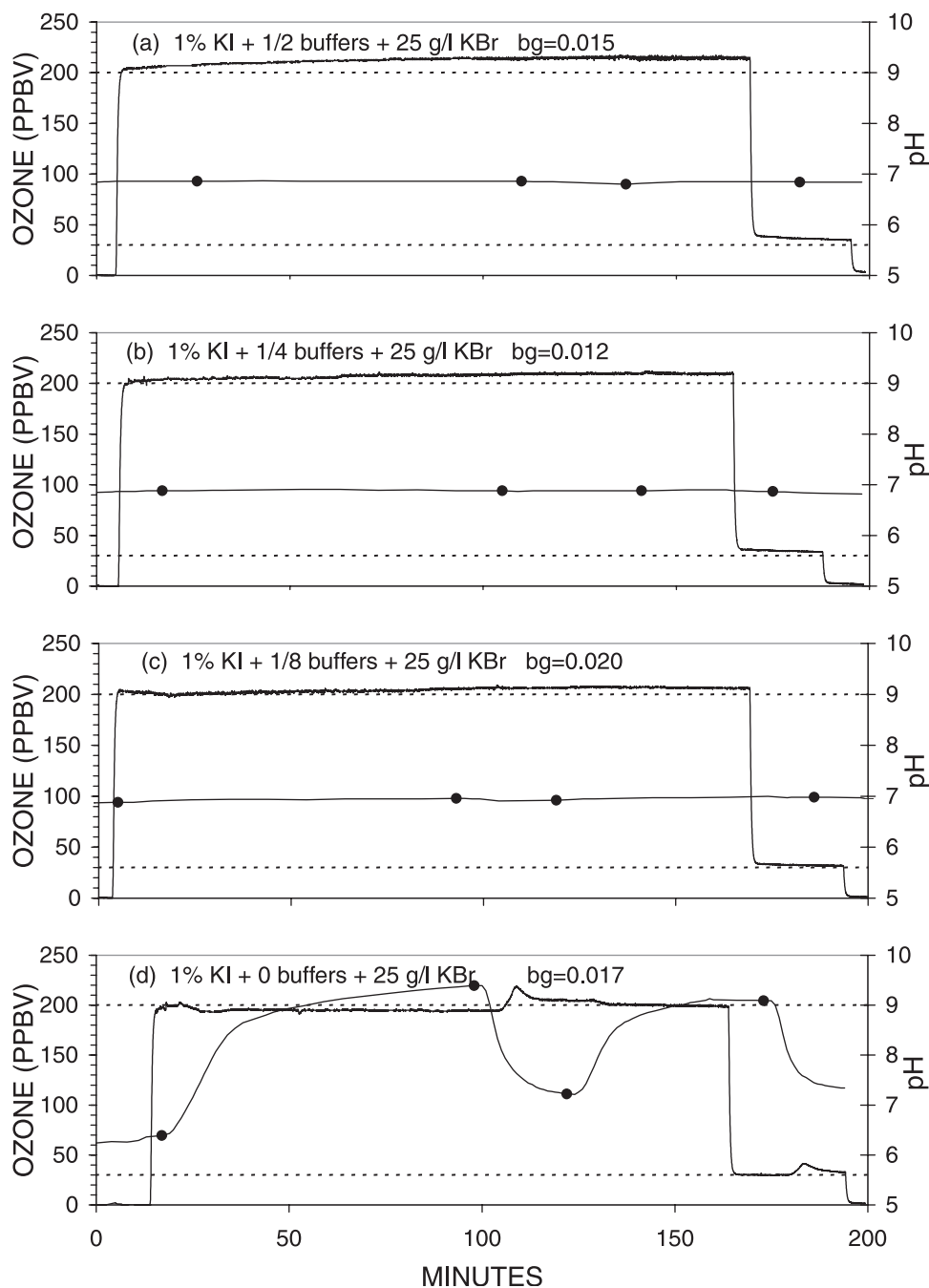
Figure 4. Results of pH sensitivity tests for (a, b) 2% KI unbuffered sensor solutions, (c) the standard 1% KI buffered, and (d) 0.5% KI buffered sensor solution. The tests were run at calibration levels (dashed lines) of 200 parts per billion followed by 30 parts per billion ozone for about 140 and 20 min, respectively. The ozonesonde O_3 mixing ratio is the thick, solid line. The pH of the sensor solution is the thin solid line. The four large dots on the pH lines represent when the CO_2 filter was attached (first and third dot) and removed (second and fourth dot) from the ozone calibrator air inlet in order to adjust the pH of the sensor solution. The ozonesonde background (bg) is given in microamps.

pressure that the pump works against. JOSIE simulation experiments showed that about one third of the 3 mL of cathode solution evaporates by the end of a typical ozonesonde flight. Therefore 2 ml of diffusion pump oil, which has nearly the same density as water, is a good approximation of the fluid head pressure.

[27] The PCF measurements were made with the ozonesonde and oil bubble flowmeter placed inside a Standard Environmental Systems vacuum chamber (1 m^3). The chamber has a glass observation window in the door and a mechanical arm, which can be controlled from outside the chamber to raise and lower the oil fluid level in the Tygon tubing in order to produce the bubbles. Two optical sensors, coupled to a stopwatch, measure the speed of the oil film bubble traveling through the burette. The pump temperature was maintained at around $25-28°C$ during the calibration

Figure 5. As in Figure 4, but showing results of pH sensitivity tests for the standard 1% KI buffered sensor solutions with decreasing amounts of buffers: (a) one-half, (b) one-quarter, (c) one-eighth, and (d) zero buffers.

by placing water-filled, sealed cans around the pump and motor. The pump temperature data were also used to correct for the ideal gas volume during the flow measurements. Fans in the chamber helped to maintain a stable burette temperature during the 90-min calibration. Seven flow (bubble speed) measurements were made at each pressure level beginning at surface and followed by 100, 50, 30, 20, 10, 7, and 5 hPa. The chamber pressure, monitored by an MKS model 622 pressure transducer, was stabilized at ±0.02 hPa for about 2 min before beginning the flow measurements. The precision of the bubble speed time was better than 1% for the seven measurements. During

the return to surface pressure, repeat measurements at 20 and 30 hPa were made and always found to be within 3% of the PCFs measured during the ascent (decreasing pressure). Figure 7 illustrates the difference between the average NOAA/CMDL measurements and the Komhyr-1986 PCFs along with the University of Wyoming bag deflation method. The uncertainties in ozonesonde flow rate measurements become larger as pressure decreases. This is due to the greater likelihood that the measurement technique may restrict or alter the airflow at each lower pressure level. In the case of the oil bubble flowmeter, consideration was given to whether the weight and drag of the bubble film
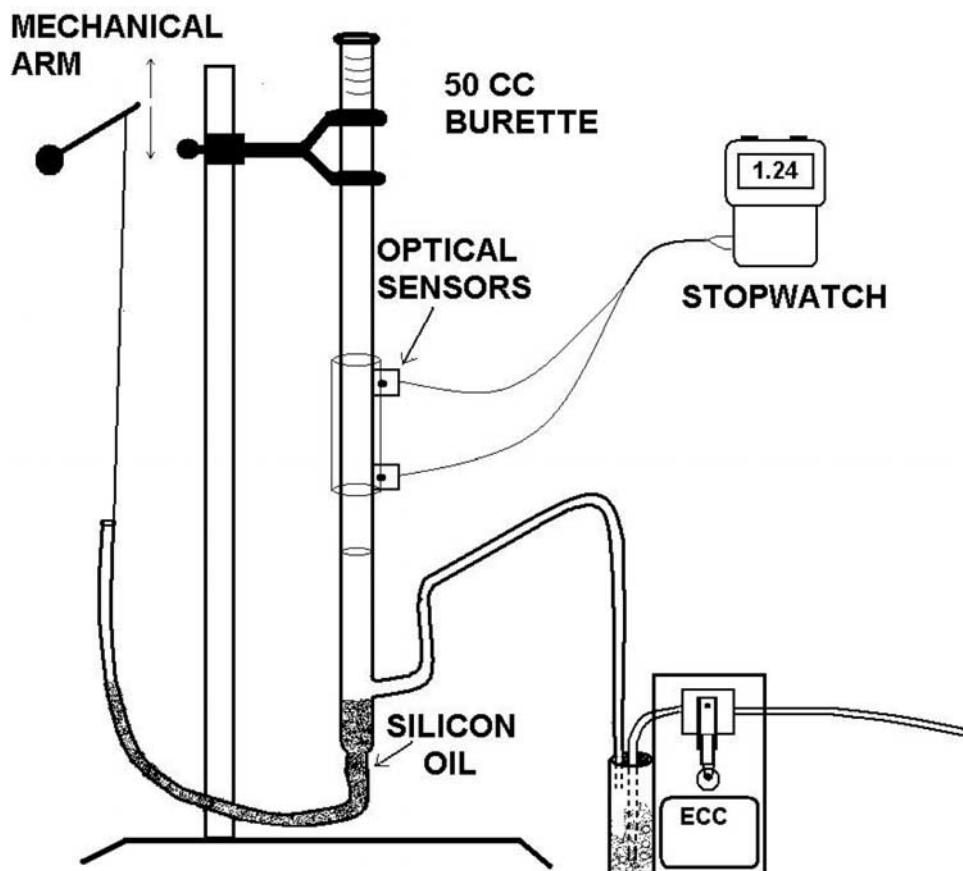
Figure 6. Oil bubble flowmeter used to measure pump correction factors from 100 to 5 hPa. The apparatus is set up inside a 1 cubic meter environmental chamber. Volumetric flow is determined from the speed of the oil bubble film passing the optical detectors.

would induce a small pressure differential in the air flowing through the burette, resulting in artificially slow time measurements (high pump correction factors). This potential bias was checked by calibrating a gear/lobe type pump used on balloon-borne aerosol counters flown by the University of Wyoming Atmospheric Science Balloon Group. This pump design is considered to be nearly 100% efficient at low pressures when operating under no head pressure. The efficiency of the gear pump was not confirmed in advance, but it is reasonable to expect that the volumetric flow rate will decrease slightly or at best remain constant at lower pressures. The pump was geared down to match the flow rate of a typical ozonesonde (220 mL/min). Diffusion pump oil was initially run through the pump to fill as much dead air space as possible. The volumetric flow rate remained essentially constant from surface to 20 hPa as shown in the average PCF curve in Figure 7, then the PCF increased only slightly to 1.035 at 5 hPa. Therefore the oil bubble flow method accurately measured PCF values down to an ambient pressure of approximately 10 hPa but may be measuring 3.5% too high at 5 hPa, assuming that the gear/lobe pump design is 100% efficient.

[28] Prior to developing the oil bubble flowmeter method, many of the earlier NOAA/CMDL ozonesondes were calibrated by the University of Wyoming group using the *Harder* [1987] bag deflation method. Both methods show good agreement in Figure 7. However, the slightly higher

average PCF values measured by the oil bubble flowmeter is partly due to the head pressure from the 2 mL of oil that the ozonesonde pumps against. The bag deflation method did not use any additional head pressure. Several calibration tests showed that the head pressure is insignificant at ambient pressures greater than 10 hPa, but at 5 hPa the PFCs were about 2–3% higher when pumping against 2 mL of oil versus no head pressure.

4. JOSIE Intercomparison Results for NOAA/ CMDL Ozonesondes

[29] The World Calibration Facility for ozonesondes at the Research Center in Jülich, Germany, uses an environmental chamber to simulate temperature, pressure, and ozone from surface pressure to 6 hPa as described by *Smit and Kley* [1998]. The ozone reference instrument consists of a fast-response dual-beam UV photometer, developed by *Proffitt and McLaughlin* [1983]. Four ozonesondes can be tested simultaneously during one profile simulation.

[30] The first Jülich Ozone Sonde Intercomparison Experiment (JOSIE) campaign was held in 1996 [*Smit et al.*, 1998], organized under the auspices of the Environmental Division of the World Meteorological Organization. Eight different ozonesonde groups were present, representing four major types of ozonesondes. Three groups used Science Pump Corporation 5A and 6A ECC ozonesondes
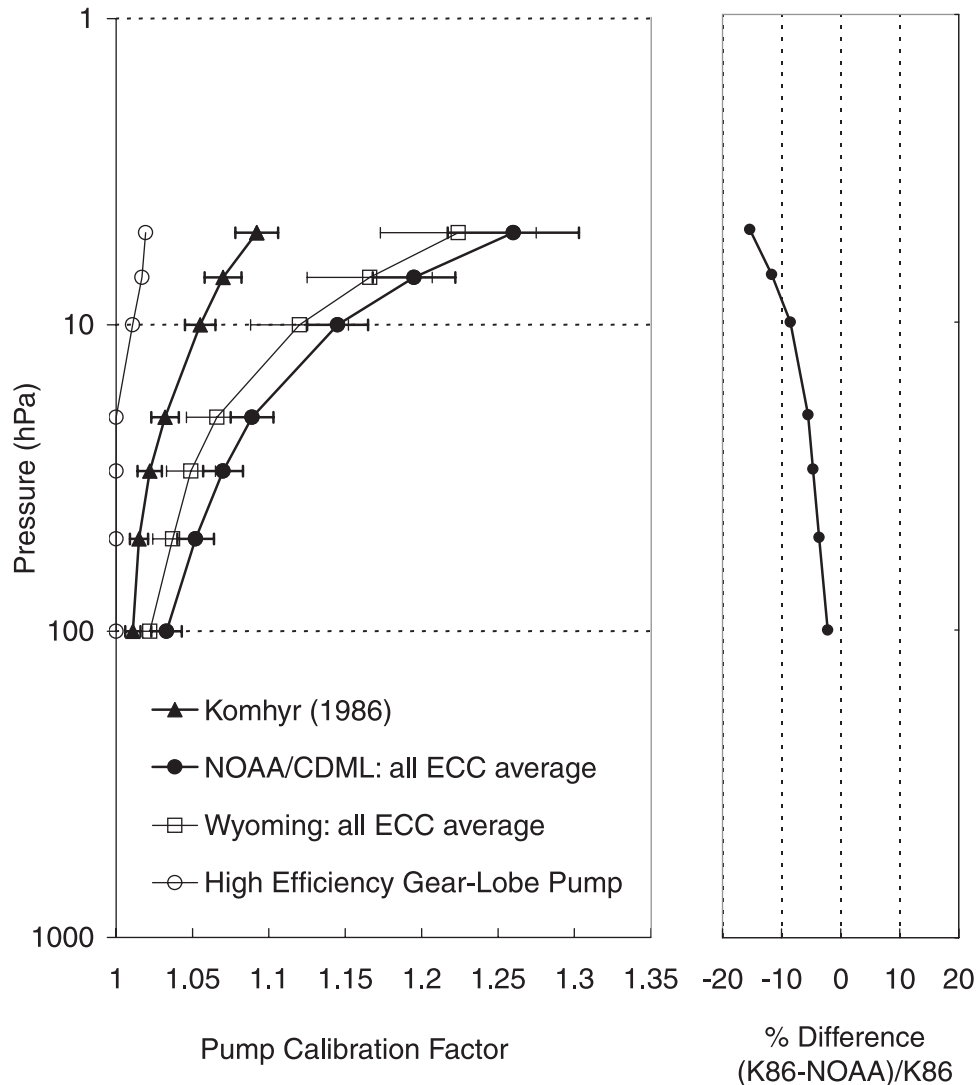
Figure 7. (left) Pressure (hectopascals) versus pump correction factors (PCF) for the standard *Komhyr* [1986], the NOAA/CMDL average oil bubble flowmeter, and the Wyoming bag method. The nearly 100% efficient gear-type pump PCF curve measured by the oil bubble flowmeter is also shown. (right) The percent difference between Komhyr-1986 and the NOAA method.

and processed data using the Komhyr-1986 PCF values. NOAA/CMDL used EN-SCI model 1Z ozonesondes and PCF values measured by the oil bubble flowmeter method. All four participating ECC groups, including NOAA/CMDL, used 1% KI-b cathode sensing solutions.

[31] Table 4 summarizes the comparisons of the integrated total ozone from NOAA/CMDL ozonesondes and the UV photometric reference profile. In JOSIE-1996, the NOAA/CMDL ozonesondes measured 8–13% higher total integrated ozone than the reference UV photometer. This percentage was not a constant offset but typically showed a steady increase beginning near the ozone peak and reaching a maximum difference of about 15–17% by the top of the profile, as shown in one of the midlatitude simulations in Figure 8a. The other ECC sonde groups showed very good agreement with the UV photometer, typically within ±4% [*Smit et al.*, 1998]. Again, the difference in results stemmed from the use of newly measured higher pump correction factors by NOAA/CMDL.

[32] During the second JOSIE campaign (September 2000), NOAA/CMDL used the 2% KI-u cathode sensing solution and both EN-SCI (2Z) and Science Pump Corporation (6A) ozonesondes. The PCF values measured were similar to those used in JOSIE-1996. The agreement in total integrated ozone between the UV photometer and NOAA/CMDL ozonesondes improved to a range of −2 to +6%. Figure 8b shows an ozone profile from a JOSIE-2000 simulation using an EN-SCI 2Z model. All three 2Z ozonesondes measured more ozone than did the 6A model ozonesondes. This difference contributed to the overall larger standard deviation in the profiles we observed in JOSIE-2000 compared to using only EN-SCI ozonesondes in JOSIE-1996.

[33] Figure 9 summarizes the average difference between the ozonesonde and UV photometer profiles for all of the NOAA/CMDL measurements during JOSIE-1996 and JOSIE-2000 campaigns. The greatest difference between the two campaigns appears in the stratosphere, above

Table 4. Summary of Jülich Ozonesonde Intercomparison Experiment for the NOAA/CMDL Ozonesondes[a]

Simulation Number	Pump	Cathode Solution	Background microamps	Integrated Ozone (DU) Sonde	Integrated Ozone (DU) UV_Ref	%Difference
			JOSIE 1996			
SIM 25 midlatitude	1Z0974	1% KI-b	0.061	404	374	+ 8
SIM 26 midlatitude	1Z0971	1% KI-b	0.060	394	356	+10
SIM 27 midlatitude	1Z0972	1% KI-b	0.047	341	305	+12
SIM 28 Tropical	1Z1003	1% KI-b	0.065	300	265	+13
SIM 29 Tropical	1Z1035	1% KI-b	0.049	262	243	+8
SIM 30 midlatitude	1Z1036	1% KI-b	0.060	389	359	+8
			JOSIE 2000			
SIM 89 midlatitude	6A9992	2% KI-u	0.010	338	337	<1
SIM 90 midlatitude	2Z1860	2% KI-u	0.011	354	334	+6
SIM 91 Tropical	6A8885	2% KI-u	0.015	203	206	−1
SIM 92 Tropical	2Z1567	2% KI-u	0.00	203	195	+4
SIM 94 Sub-Tropical	6A8839	2% KI-u	0.00	270	277	−2
SIM 94 Sub-Tropical	2Z1610	2% KI-u	0.00	289	277	+4

[a] All JOSIE–1996 ozonesondes used 1% KI buffered sensor solutions, while JOSIE-2000 ozonesondes used 2% KI unbuffered. The integrated amount (Dobson units) for the ozonesonde and the UV photometer reference profile and percent differences (sonde-UV)/UV are also given.

20 km, where the ozonesondes using the 2% KI-u solutions in JOSIE-2000 compared much better with the reference UV photometer; however, they were slightly worse (4–8% too low) below 10 km. High instrument backgrounds would be considered a potential reason for the lower ozone measurement, but the backgrounds measured during JOSIE-2000 were very low, less than 0.015 microamperes. One month after the completion of the campaign, all six ozonesondes were checked in the NOAA/CMDL laboratory and were found to agree within 2% of the TEI 49C UV photometric calibrator at concentrations from 0 to 200 ppbv.

[34] During JOSIE-1996 the ozonesonde backgrounds, listed in Table 4, were significantly higher using the 1% KI-b sensor solutions. This is partly due to the slower decay observed in ozonesonde response after the surface ozone tests and not allowing enough time for the background to drop lower. The high artifact background may explain why the measured ozone was 3–5% lower than the UV photometer in the surface to 10 km region, where the lower ozone levels are more sensitive to instrument background values used in equation (2).

5. Field Tests

5.1. Dual Ozonesonde Flights

[35] Dual ozonesonde instruments were flown by NOAA/CMDL at Boulder, Colorado, Suva, Fiji, and South Pole Station, and by the University of Wyoming Balloon Group (UWYO) at McMurdo Station, Antarctica. The dual flights provided side-by-side comparisons of the ozonesondes using the standard 1% KI-b sensor solution with 2% KI-u (Table 5) and 0.5% KI-b solutions (Table 6). The ozonesonde profiles were computed using the NOAA/CMDL or UWYO pump correction factors. The integrated total column ozone, in Dobson units (DU), includes a residual amount (above burst altitude) that was computed by two methods: by using a constant mixing ratio (CMR) extrapolation and from satellite-derived ozone averages based on climatology from the solar backscattered ultraviolet (SBUV) instrument data from *McPeters et al.* [1997]. The total ozone column from the 1% KI-b sondes averaged 11% higher than the

sondes using 2% KI-u solutions. The profile from a Boulder dual flight in Figure 10a shows that the percentage difference tended to increase with altitude, which is the same pattern observed in Figure 11 for all five NOAA/CMDL dual flights comparing 1% KI-b and 2% KI-u sensor solutions. The increasing difference with altitude is also similar to the 1% KI-b versus the reference UV measured ozone profile comparisons in Figure 9 for the JOSIE-1996 results.

[36] The total column ozone measurements from the ozonesondes were also compared to measurements from NOAA/CMDL and National Institute of Water and Atmospheric Research (NIWA) Dobson spectrophotometers and the NASA Total Ozone Mapping Spectrophotometer (TOMS). The 1% KI-b ozonesonde total was approximately 12% greater than the NOAA Dobson spectrophotometer measurements at Boulder and at South Pole, while the 2% KI-u sondes were within ±2%. The UWYO group 1% KI-b ozonesondes were about 6% greater than the NIWA Dobson spectrophotometer at McMurdo Station, but the 2% KI-u sondes were 5–10% lower. The greater differences observed in total column ozone measurements at McMurdo Station in October can often occur owing to the large ozone gradients existing near the polar vortex edge at the time of the ozone hole period [*Deshler and Hofmann*, 1991; *Nardi et al.*, 1999].

[37] A balloon package carrying six ozonesondes was flown during a joint project between NOAA/CMDL and UWYO on 20 June 1996 to compare the performance of the standard 1% KI-b sensor solution with the 0.5% KI-b solution, recommended for use by *EN-SCI Corporation* [1995]. Figure 10b shows the average ozone profile measured from the ozonesondes using the two sensing solutions. The plastic balloon burst at 30 km (15 hPa) so the total column ozone value includes a relatively large residual amount above the balloon burst altitude. Dobson spectrophotometer 65 was set up at the launch site and recorded 290 Dobson units in total column ozone. The ozonesondes using the 0.5% KI-b solutions agreed very well with the Dobson spectrophotometer, averaging about 2% higher in total ozone, while the 1% KI-b solution profiles averaged 6% higher. The ozonesonde data were
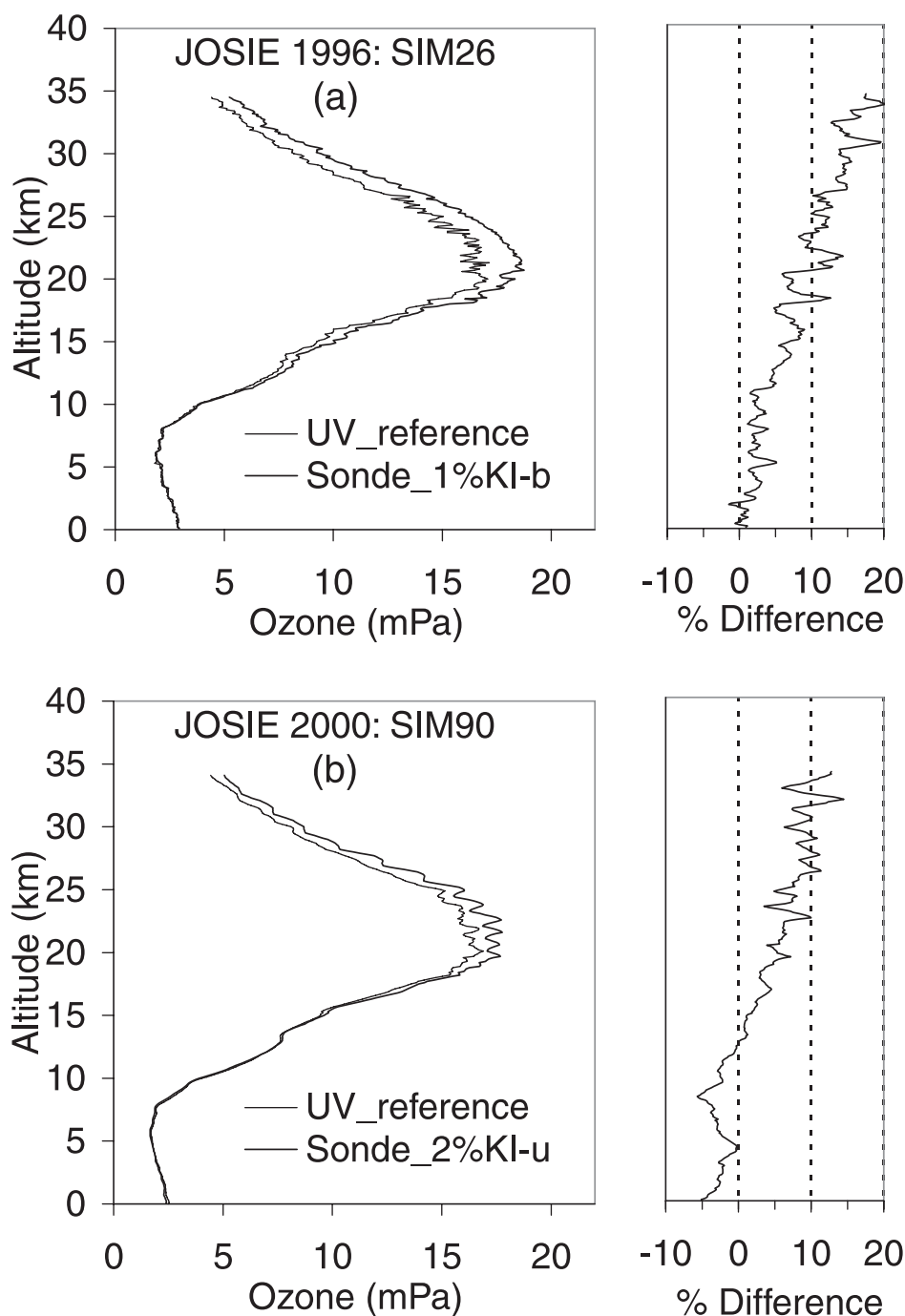
Figure 8. Ozone partial pressure (millipascals) profiles from the Jülich Ozonesonde Intercomparison Experiments: (a) 1996 and (b) 2000. The thick line is the NOAA/CMDL ozonesonde compared to the reference UV photometer (thin line). One percent KI buffered sensor solutions were used in 1996 and 2% KI unbuffered sensor solutions in 2000. National Ocean and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) pump correction factors were used to process the ozonesonde profile data. The percent differences shown were computed by (sonde-UV)/UV.

processed using NOAA/CMDL measured pump calibration factors. The calculated total ozone difference would be about 2% lower using the PCFs recommended by EN-SCI [*Komhyr et al.*, 1995], i.e., 1.060 at 15 hPa versus the NOAA/CMDL PCF of 1.10 at 15 hPa. The results of this six-sonde flight were similar to those reported by *Boyd et al.* [1998] from three dual-ozone soundings at Lauder, New Zealand, which compared 1% KI-b and 0.5% KI-b sensor solutions.

5.2. Surface Measurements

[38] ECC ozonesondes are not typically used to monitor surface ozone, but operating the ozonesondes in an ambient, urban environment for several hours is a more rigorous test
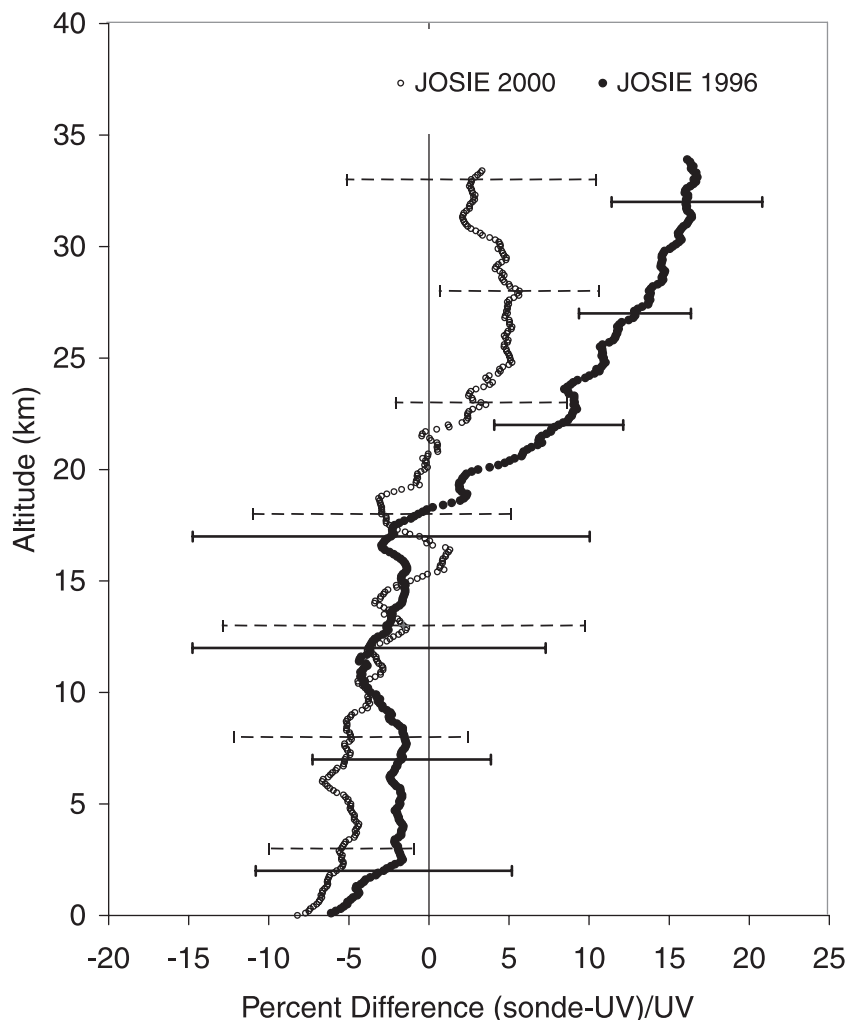
Figure 9. Average differences (smoothed) between the NOAA/CMDL ozonesondes and the UV photometric reference from the six simulated profiles at JOSIE-1996 (1% KI buffered sensor solutions) and JOSIE-2000 (2% KI unbuffered sensor solutions).

of the cathode sensing solutions than running under clean laboratory conditions. Surface ozone tests were performed on the roof of the NOAA building in Boulder, Colorado, on 18 different days in the spring and summer of 1999 and 2000. Ozonesondes were run simultaneously alongside a UV photometric surface ozone analyzer (TEI model 49). The ozonesondes were set up inside an air-conditioned room with 1.7-m-long intake tubing extending outside and taped next to the intake tube of the UV ozone analyzer. Figure 12 shows the results of four EN-SCI ozonesondes running simultaneously during a test on 23 August 1999. Each ozonesonde contained one of the four cathode solutions listed in Table 3 (0.5% KI-b, 1.0% KI-b, 1.5% KI-b, and 2% KI-u). The measurements began in the morning and ended at 1550 LT, when ozone was near the 90 ppbv peak for the day. The ozonesondes using the 2% KI-u and 0.5% KI-b solutions measured 0–2% more ozone than did the UV photometric ozone instrument. However, they both began tailing off slightly by 1–4% after about 6 hours of sampling, which may have been due to evaporation of the cathode solution and thus reduced collection efficiency from the smaller amount of solution. The 1% KI-b and 1.5% KI-b solution ozonesondes closely followed the fine structure in the ozone

mixing ratio measured by the UV photometer ozone instrument but were about 7 and 14% higher, respectively.

[39] Figure 13 shows the average of the differences from all 18 days of the NOAA/CMDL ambient surface tests, which compared ozonesondes using the 1% KI-b and the 2% KI-u cathode sensing solutions with the UV photometer. The 2% KI-u solutions averaged within 1–2% of the UV photometric ozone analyzer while the 1% KI-b sondes showed an increasing ozone response (higher ozone) with time, measuring about 9% more ozone after 4 hours. Only two surface experiments were performed using ozonesondes containing the 0.5% KI-b sensor solutions, but both tests showed the ozonesonde measurements were within ±2% of the UV photometer. Overall, the ozonesonde surface data were very consistent and the sensors using unbuffered cathode sensor solutions did not show any inconsistencies when sampling under urban conditions.

6. Discussion and Conclusions

[40] ECC ozonesonde characteristics were investigated through sensor response tests and volumetric flow measure-

Table 5. Dual Ozonesonde Flights Using 1% KI Buffered and 2% KI Unbuffered Cathode Sensing Solutions[a]

Site	Date	Pump	Cathode Solution	Sonde (CMR)	Sonde (SBUV)	Total Ozone (DU) Dobson	Total Ozone (DU) TOMS	Percent Difference from Dobson CMR	SBUV
Boulder	29 Jan.	1Z0672-r	1% KI-b	340 (40)	330 (30)	305	304	+11	+8
	1998	1Z1100-r	2% KI-u	306 (35)	301 (30)	305	304	+0.3	−1
Fiji	29 April	6A4469	1% KI-b	277 (52)	262 (37)	none	261		
	1998	6A4462	2% KI-u	255 (46)	244 (37)	None	261		
South Pole	22 April	6A3480	1% KI-b	299 (18)	311 (28)	none	none		
	1998	6A3483	2% KI-u	257 (12)	273 (28)	none	none		
South Pole	11 Oct.	6A3511	1% KI-b	112 (22)	108 (18)	none	103		
	1998	6A3509	2% KI-u	98 (12)	98 (12)	None	103		
South Pole	11 Jan.	6A6367	1% KI-b	305 (28)	302 (25)	266	283	+15	+14
	1999	6A6368	2% KI-u	269 (23)	271 (25)	266	283	+1	+2
McMurdo	31 Oct.	1Z1504	1% KI-b	176 (34)	165 (27)	163	168	+8	+1
	1997	1Z1503	2% KI-u	155 (29)	149 (27)	163	168	−5	−9
McMurdo	21 Sept.	1Z1533	1% KI-b	153 (32)	146 (27)	138	148	+11	+6
	1998	1Z1514	2% KI-u	138 (29)	135 (27)	138	148	0	−2
McMurdo	14 Oct.	1Z1531	1% KI-b	167 (34)	155 (22)	163	146	+2	−5
	1998	1Z1532	2% KI-u	149 (30)	135 (27)	163	146	−9	−17
McMurdo	18 Oct.	1Z1519	1% KI-b	276 (46)	259 (29)	241	274	+15	+7
	1998	1Z1520	2% KI-u	246 (39)	235 (29)	241	274	+2	−2

[a] The "Sonde" total column ozone includes the residual amount (in parentheses) based on the constant mixing ratio extrapolation (CMR), or climatology from (SBUV), *McPeters et al.* [1997]. The table also includes total column ozone from the Dobson Spectrophotometer and the Total Ozone Mapping Spectrometer (TOMS) when data were available. Percent difference is (sonde-Dobson)/Dobson.

ments at reduced pressures to determine new pump efficiency correction factors (PCF).

[41] The oil bubble flowmeter technique was found to accurately measure PCFs down to an ambient pressure of 10 hPa, based on results from measurements of a gear/lobe pump that is assumed to have a nearly 100% efficient design. At 5 hPa the difference was only 3.5%. So the PCF values may be 3.5% too high. This would be nearly in agreement with the 5% difference observed when comparing ozonesonde profile measurements at surface pressures versus a similar profile under actual flight ambient pressures. The PCFs measured by the oil bubble flowmeter are 2 and 15% greater than the standard Komhyr-1986 values at 100 and 5 hPa, respectively.

[42] The other equally important variable influencing the determination of ozone amount is the response of the ozonesonde sensor. Laboratory tests at surface pressure compared ozonesonde measurements with NIST traceable UV photometric ozone analyzers. The tests focused on different cathode sensing solutions, which included the standard 1% potassium iodide buffered solution (1% KI-b), the 0.5% KI buffered solution (one half dilution of the standard 1% KI-b) and the 2% KI unbuffered solution. Additional tests, whereby individual ingredients of the sensor solutions were adjusted, showed that the buffers, primarily the weak acid phosphate ($NaH_2PO_4 \cdot H_2O$), are responsible for slower side reactions that increase the ozonesonde response. For example, ozonesondes using the standard 1% KI-b sensor solutions can drift to approximately 5–7% too high at constant ozone conditions. Under typical ozone profile simulations the difference can be as much as 15% higher ozone due to the hysteresis effect from the buffer reactions which are dependent on past exposure to ozone as well as the buffer concentration. Ozonesonde tests using 4 times the standard buffer in a 1% KI sensor solution measured as much as 30% excess ozone. However, a 1/16th reduction in the buffer concentration showed ozonesondes giving nearly perfect agreement with a UV photometric ozone calibrator. These laboratory tests were consistent with results from the JOSIE-1996 ozone simu-

Table 6. One Dual and One Six-Ozonesonde Flight Comparing 1% KI Buffered and 0.5% KI Buffered Sensing Solutions[a]

Site	Date	Pump	Cathode Solution	Sonde (CMR)	Sonde (SBUV)	Total Ozone (DU) Dobson	Total Ozone (DU) TOMS	Percent Difference from Dobson CMR	SBUV
McMurdo	12 Oct.	1Z1493	1% KI-b	143 (25)	139 (24)	140	150	+2	+1
	1999	1Z1492	0.5% KI-b	137 (23)	135 (24)	140	150	−2	−4
Laramie	20 June	1Z0485	1% KI-b	325 (78)	305 (58)	290	none		
	1996	1Z0859	1% KI-b	333 (82)	309 (58)	290	none		
	1996	1Z1205	1% KI-b	327 (77)	308 (58)	290	none		
Average			1% KI-b	328 ± 4	307 ± 2	290	none	+13	+6
	1996	1Z0483	0.5% KI-b	294 (67)	285 (58)	290	none		
	1996	1Z0972	0.5% KI-b	312 (72)	298 (58)	290	none		
	1996	1Z1201	0.5% KI-b	304 (71)	291 (58)	290	none		
Average			0.5% KI-b	303 ± 9	291 ± 7	290	none	+4	+0.3

[a] The "Sonde" total column ozone includes the residual amount (in parentheses) based on the constant mixing ratio extrapolation (CMR), or climatology from (SBUV), *McPeters et al.* [1997]. The table also includes total column ozone from the Dobson Spectrophotometer and the Total Ozone Mapping Spectrometer (TOMS) when data were available. Percent difference is (sonde-Dobson)/Dobson.
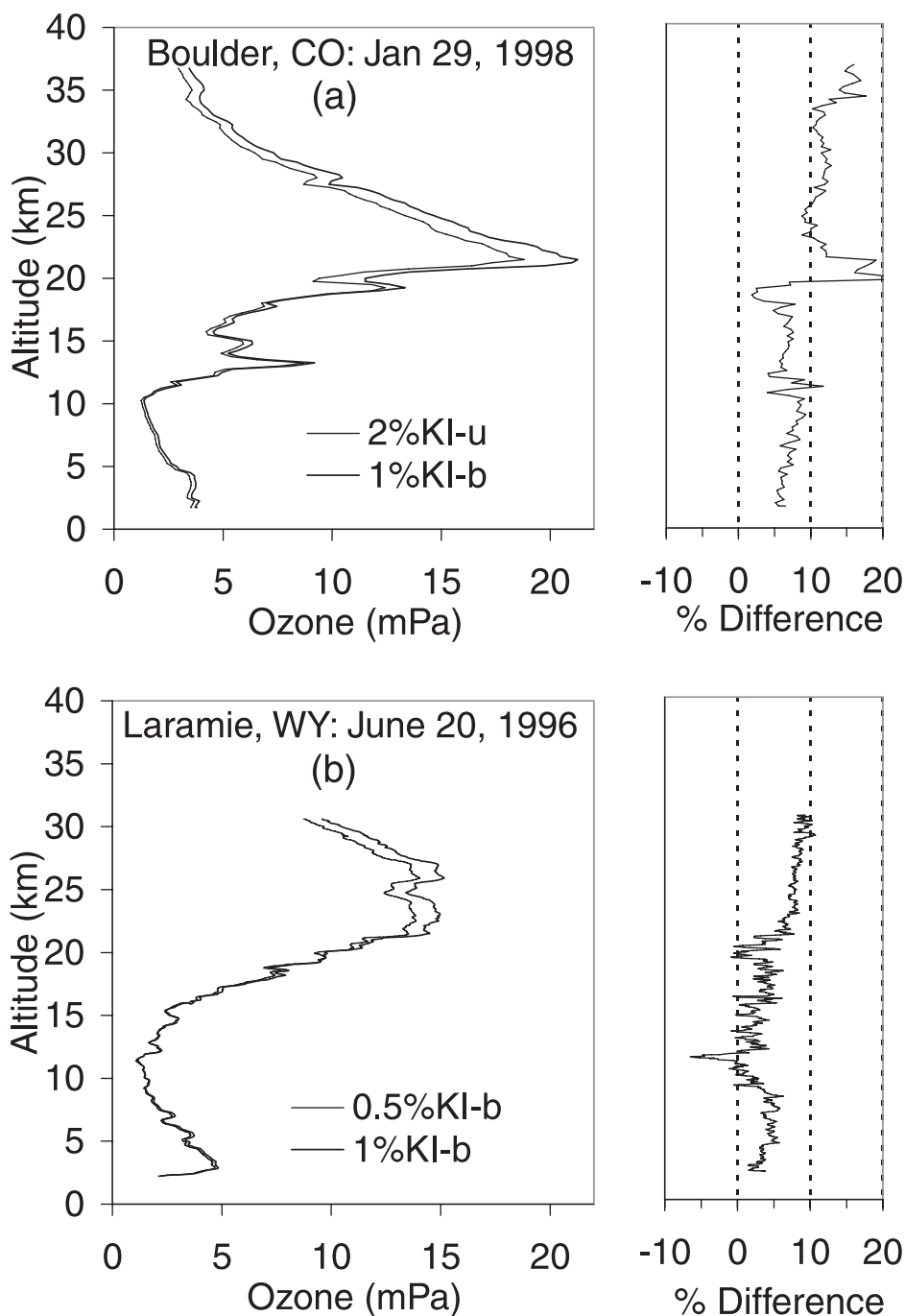
Figure 10. (a) Dual-ozonesonde flights comparing 1% KI buffered (thick line) and 2% KI unbuffered (thin line) sensor solutions at Boulder, Colorado. (b) The average of a six-sonde flight comparing 1% KI and 0.5% KI buffered (thin line) sensor solutions at Laramie, Wyoming.

lation tests and several dual ozonesonde flights in showing that the higher measurements by NOAA/CMDL ozonesondes using buffered sensor solutions were not a constant offset but typically began increasing just below the stratospheric ozone peak and were about 15 ± 4% high near the maximum altitude (~35 km). Even though the tests showed higher ozone measurements for the NOAA/CMDL ozonesondes, the standard 1% KI buffered sensing solutions showed very good results in JOSIE-1996 intercomparisons when ozonesonde data were processed using the standard Komhyr-1986 pump efficiency correction factors. The influence of the buffers on the sensor response may, to some degree, be compensated by these smaller pump efficiency correction factors.

[43] Ozonesondes using the 2% KI unbuffered cathode sensor solutions compared within ±2% of surface UV photometric ozone measurements showed a reduced hysteresis effect and only a slight sensitivity in the pH range of 6 to 9.3. Total column ozone comparisons of 2% KI-u ozonesondes to the UV reference in the JOSIE-2000 intercomparison tests and to Dobson spectrophotometer measurements were generally within ±5%. However, it is
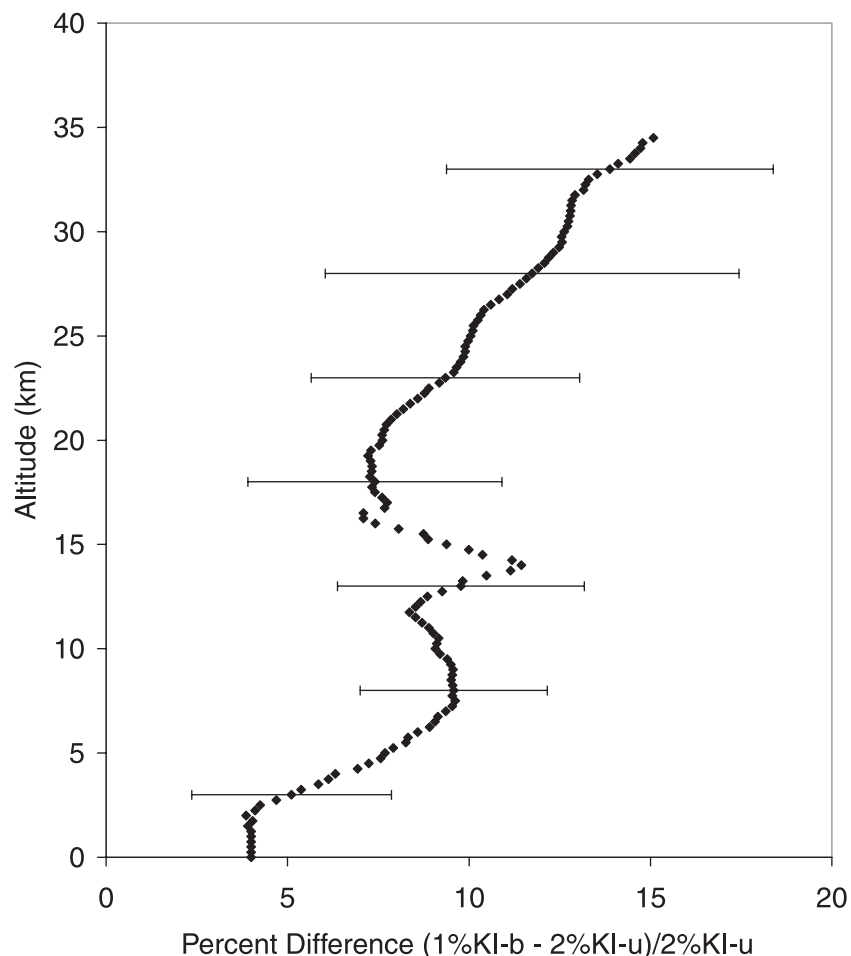
Figure 11. Average difference (smoothed curve) between the 1% KI buffered and 2% KI unbuffered sensor solution ozonesondes from the five NOAA/CMDL dual flights. A one standard deviation line is shown at 5 km intervals.

important that the higher pump efficiency correction factors, measured by the NOAA/CMDL oil bubble flowmeter method or the University of Wyoming bag deflation method, be used to process the data; otherwise, the total column ozone will be too low. In addition, the surface flow rate should be corrected for evaporation of the soap solution when measurements are made using a soap bubble flow-meter. Room temperature air will generally give a 0–4% increase in the measured T_{100} time, depending on the relative humidity. Finally, potassium bromide appears to add a pH dependent component to the ozonesonde response and therefore should not be used with the 2% KI-u sensor solution.

[44] The 0.5% KI buffered solution was not tested as extensively as the 1% KI buffered and 2% KI unbuffered solutions, but the ozonesondes using the 0.5% KI buffered solutions did compare well with UV photometric methods in surface laboratory and ambient surface tests. In the stratosphere it appears to give a response somewhere between the ozonesondes using 1% KI-b and 2% KI-u sensor solutions. EN-SCI recommends using the *Komhyr et al.* [1995] pump correction factors with the 0.5% KI buffered solutions, which are slightly higher than the stand-ard Komhyr-1986 values.

[45] Electrochemical concentration cell ozonesondes are important instruments used to accurately measure and monitor tropospheric and lower stratospheric ozone. There are several differences in the type of sensing solution used as well as the pump correction factors applied in processing data, but the right combination, as discussed above, can give good ozone measurement results. Future investigations of the characteristics of ozonesondes through laboratory experiments, field tests, and intercomparison projects are important for maintaining data quality and understanding how potential differences in data sets may be explained among various ECC ozonesonde groups.

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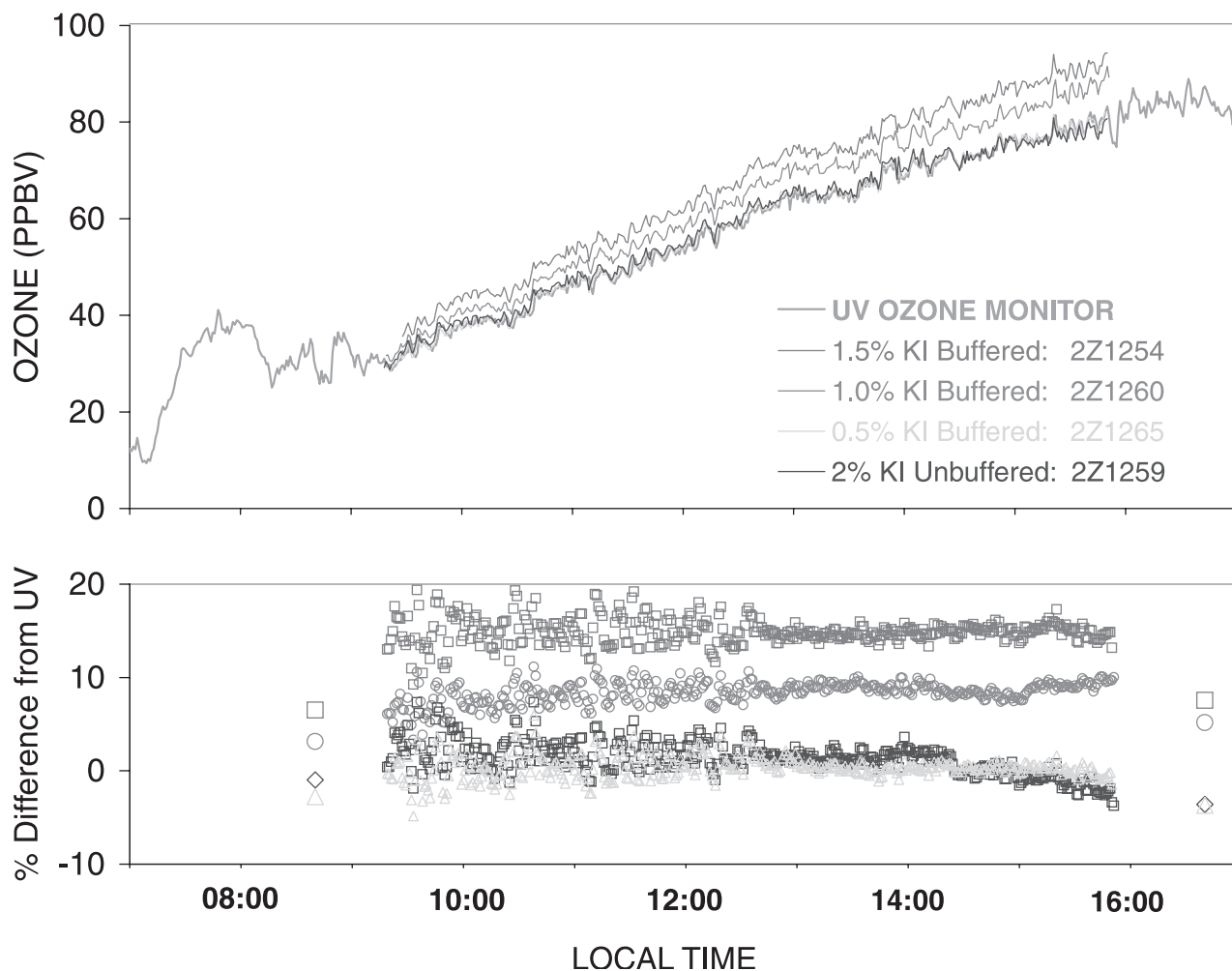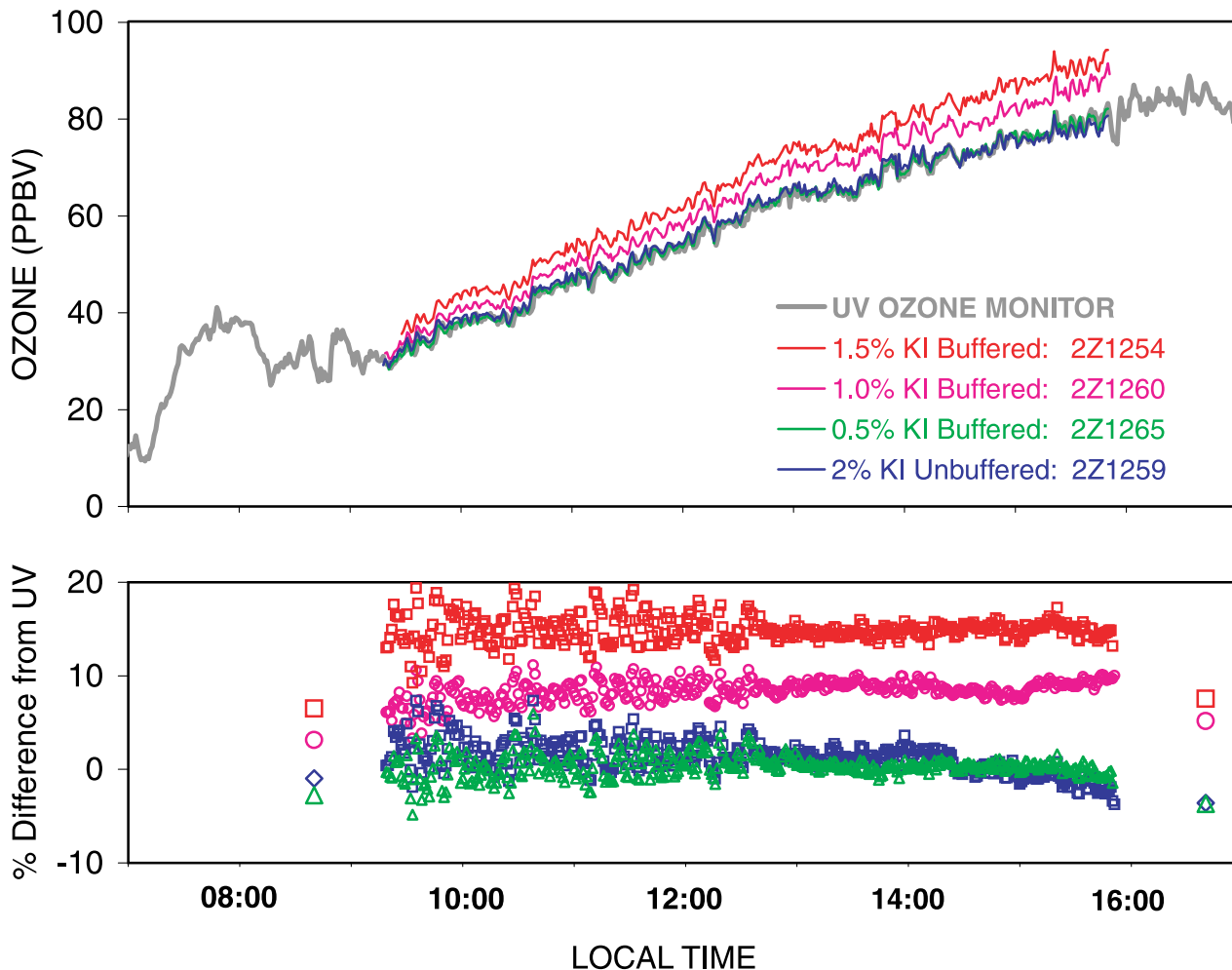
Figure 12. (top) Ambient surface tests comparing four ECC ozonesondes using the ozonesonde sensor solutions listed in Table 3 with a UV photometric ozone monitor at Boulder, Colorado (23 August 1999). (bottom) The percent difference (sonde-UV)/UV along with the 100 part per billion ozone calibrator checks (colored symbols) in the laboratory prior to and after the ambient measurements. See color version of this figure at back of this issue.

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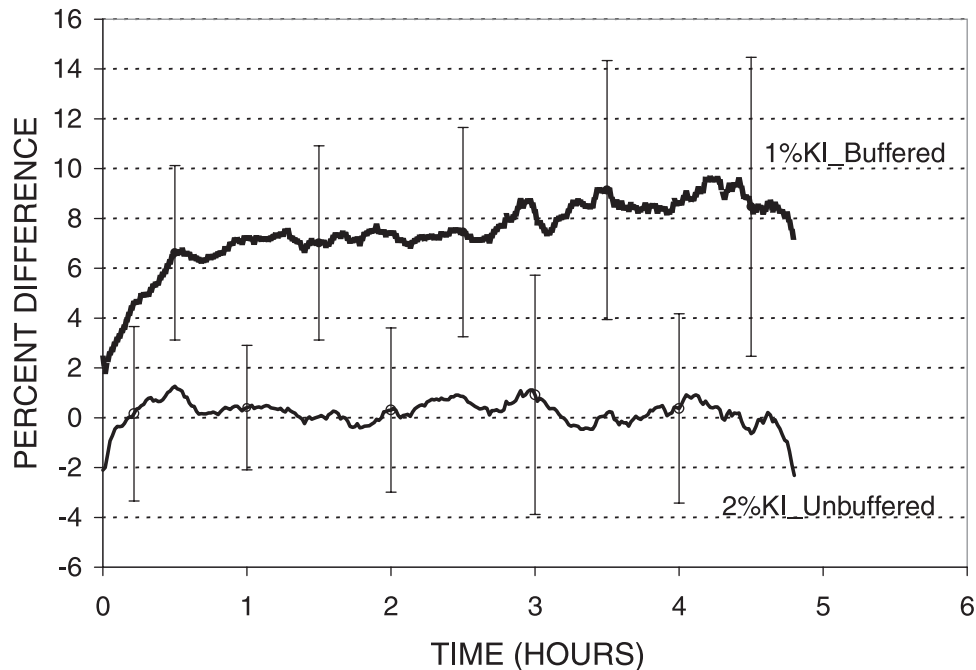
Figure 13. Summary of all surface ozonesonde and UV photometer comparison experiments using 1% KI buffered and 2% KI unbuffered sensor solutions. The percent difference is (sonde-UV)/UV. The standard deviation bars are 1 sigma. All tests were conducted during daytime hours in the spring and summer months.

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Figure 12. (top) Ambient surface tests comparing four ECC ozonesondes using the ozonesonde sensor solutions listed in Table 3 with a UV photometric ozone monitor at Boulder, Colorado (23 August 1999). (bottom) The percent difference (sonde-UV)/UV along with the 100 part per billion ozone calibrator checks (colored symbols) in the laboratory prior to and after the ambient measurements.