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An assessment of ECC ozonesondes operated using 1% and 0.5% KI cathode solutions at Lauder, New Zealand

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Abstract. The effects of reducing the concentration of the potassium iodide (KI) cathode electrolyte from 1% to 0.5% in electrochemical concentration cell (ECC) ozonesondes flown at Lauder, New Zealand (45° S, 170° E) have been investigated. Four studies were made to assess these effects: 1% and 0.5% KI ozonesonde performance was compared directly in three dual flights, one year of 1% KI and one year of 0.5% KI ozonesonde profiles were compared with near-simultaneous lidar profiles, integrated ozonesonde profiles were compared with Dobson spectrophotometer measurements over the same period, and ascent and descent profiles were compared for both KI concentrations. Ozonesondes flown with a 1% KI solution showed positive differences of 3% to 8% in the ozone profile and ~5% in the ozone column compared with the 0.5% KI ozonesondes, which also showed better agreement in profiles and ozone column compared with the lidar and Dobson spectrophotometer measurements respectively.

Introduction

Laboratory calibration tests carried out by Environmental Science (EN-SCI) Corporation, manufacturer of ECC ozonesondes (W. Komhyr, personal communication, 1996), as well as by the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) [*Johnson et al.*, 1997] have shown that ozonesondes using the standard 1% KI cathode solution consistently overestimate ozone from 2% to 15-20% above the ozone maximum. Use of a 0.5% KI cathode solution (1% KI solution, including KBr and buffers, diluted by half) was found to largely correct the overestimates. Based on these results, and revised instructions for ozonesonde preparation [*EN-SCI Corporation*, 1996], ozonesondes flown at Lauder since August 1996 have used a 0.5% KI solution.

In this study, three dual soundings (two EN-SCI 1Z-series ozonesondes flown together, with 1% and 0.5% KI cathode solutions) were made to directly compare differences between the two solutions. In addition, between August 1995 and July 1997, encompassing one year of 1% KI ozonesondes and one year of 0.5% KI ozonesondes, comparisons with lidar ozone profiles and Dobson spectrophotometer ozone columns were made. Ascent and descent ozone profiles for both KI concentrations were also compared over the same two years.

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The ECC ozonesonde described by *Komhyr et al.*, [1969; 1995] consists of a battery-powered Teflon piston pump and Teflon sensor containing a buffered KI solution in the cathode half cell and a saturated KI solution in the anode half cell. When an ozone molecule enters the sensor, iodine is formed, which the cell converts to iodide, causing the flow of two electrons in the cell's external circuit. Ozone concentrations are calculated based on the sensor current and the pump volumetric air flow rate. The ozone lidar, operated at Lauder by the Dutch National Institute of Public Health and the Environment (RIVM) and the National Institute of Water and Atmospheric Research Limited (NIWA), measures ozone using the DIAL (Differential Absorption Laser) technique [*Swart et al.*, 1994, *Brinksma et al.*, 1997]. Dobson spectrophotometer 72, operated at Lauder by NOAA/CMDL and NIWA, was compared against the World Standard Dobson Instrument 83 in February, 1997, showing a maximum difference of +0.4% for direct-sun observations in the air-mass range 1.15 to 3.2.

The standard operating procedure at Lauder for the 1% KI sondes has been to scale ozone data by 0.9743 to match revised ozone absorption coefficients used with Dobson spectrophotometers [*Komhyr et al.*, 1993]. However, since the purpose of this paper is to directly compare the performance of 1% KI and 0.5% KI solutions, the 1% KI data used here have not been scaled. Therefore, apart from the different solution concentrations, the preparation and data processing of the ozone soundings were the same. A pre-launch sensor background current was applied as a constant offset through the flight. Corrections to ozone for decreases in pump efficiency at pressures below 200 hPa were based on pump efficiencies determined during the STOIC campaign [*Komhyr et al.*, 1995].

Results from the dual ozone soundings

Three dual ozone soundings were performed at Lauder, coinciding with the seasonal ozone maximum (October 1996), the seasonal minimum (March 1997) and a mid-range period (June 1997). Results from these soundings are presented in Figure 1. The percentage differences have been smoothed by averaging the high resolution data into 1 km bins. The statistical uncertainty in the differences, due to the variance in the high resolution data, is 0.4% to 0.9% below 20 km and 0.1% to 0.4% above 20 km.

Tropospheric differences between the two configurations range from 0 to 10% and most likely result from intrinsic changes in the solution chemistry. In addition to this effect, differences in the lower stratosphere may result from the steep ozone gradient in this region if there are differences in the response time of the sensors. This is likely for the second sounding between 15 and 20 km, as the response time, measured prior to launch, was 27% slower for the 1% KI sonde compared to the 0.5% KI sonde. For the first and third soundings, pre-launch response times for the ozonesonde pairs were similar. Above the

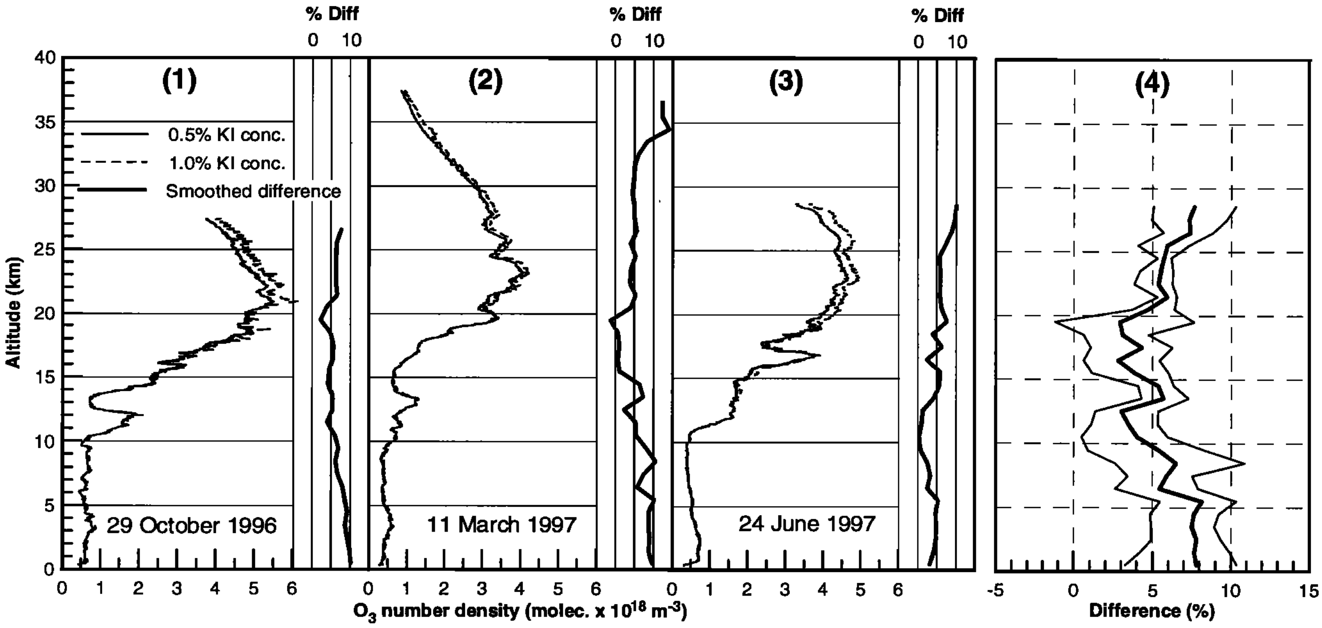

Figure 1. Panels (1), (2), (3) show the ozonesonde profiles obtained from the three dual soundings. The continuous thick lines show percentage differences smoothed into 1 km bins, derived using the formula ((1% sonde-0.5% sonde)/0.5% sonde) x 100. Panel (4) shows the resultant percentage difference profile obtained by averaging the three difference profiles (thick line). Also shown are the minimum and maximum 1 km binned values (thin lines).

ozone maximum at ~20 km, the percentage differences vary initially from 4% to 5% in the second sounding (with lowest ozone values) to ~6.5% in the first sounding.

The mean percentage difference profile is shown in panel (4) of Figure 1. Although derived from a set of only three comparisons, the profile shows a generally increasing percentage difference between the 1% KI and 0.5% KI sondes above 20 km. It is also consistent with a difference profile obtained by NOAA/CMDL from a six ozonesonde flight performed at the University of Wyoming in June 1996 (B. Johnson, personal communication, 1997). It should be stressed, however, that this curve may be applicable only to Lauder.

A summary of ozone column measurements for the three dual flights is presented in Table 1. Measurements were made with Dobson spectrophotometer 72 on the afternoon before the dual soundings, and then early the next morning. These have been interpolated to estimate the ozone column at the mid-point of the soundings. An ozone column value for the ozonesondes was calculated by integrating the profiles and using the simultaneous lidar profile integrated from the burst altitude to 50 km to determine the residual. Likewise, an ozone column value for the lidar was calculated by integrating the profile and using the simultaneous 0.5% KI sonde profile integrated from the surface to 7 km to determine the residual. The ozone column derived from the 0.5% KI sondes is consistently ~5% lower than the 1% KI sondes and, in two cases of three, shows better agreement with the Dobson and lidar ozone column. The result from the second 0.5% KI sonde is 4% lower than the Dobson spectrophotometer and 3% lower than the lidar ozone column. The greatest differences between the second dual sonde profiles and the simultaneous lidar measurement occurred between 15 and 19 km and could result from the steep ozone gradient in this region and the exponential response time of the ECC sensor.

Table 1. Comparison of Dobson spectrophotometer total ozone with integrated ozonesonde and lidar profiles.

Date	Dobson (DU)	Dobson (DU §)	0.5% Sonde	1% Sonde (DU total/residual ‡)	Lidar
961029	353 (pm)	348	349/102	363/102	346/14
961030	344 (am)				
970311	260 (pm)	255	245/16	256/13	252/11
970312	253 (am)				
970624	297 (pm)	296	304/69	318/69	307/14
970625	295 (am)				

Bass and Paur [1985] O_3 absorption cross-sections used for Dobson.
§ Estimated Dobson O_3 amount for the mid-point of the sounding.
‡ Residual determined from above the peak altitude of the sonde profile and below the lowest point of the lidar profile.

Comparison of near-simultaneous ozonesonde and lidar measurements

Since the installation of the lidar system in November 1994 ozonesondes have been launched near to the time of a lidar measurement when possible. Comparisons of near-simultaneous measurements (within 24 hours of each other), made over a two year period, are summarized in Figure 2 where differences between lidar and 1% KI sondes (flown between August 1995 and July 1996), and lidar and 0.5% KI sondes (flown between August 1996 and July 1997) are shown. 28 comparisons were made in the first year, and 27 comparisons in the second year.

The results show consistently better agreement, above 20 km, between the 0.5% KI sonde and the lidar than between the 1% KI sonde and the lidar. Differences between the 0.5% KI sonde and lidar are seldom statistically significant. Below 20 km the standard deviations become too large to allow meaningful comparison of the two sonde configurations.

These results, together with further field and laboratory studies, should eventually allow homogenization of the 1% and 0.5% KI Lauder databases. For example, also shown in Figure 2 is the result of adding the mean percentage difference curve from panel

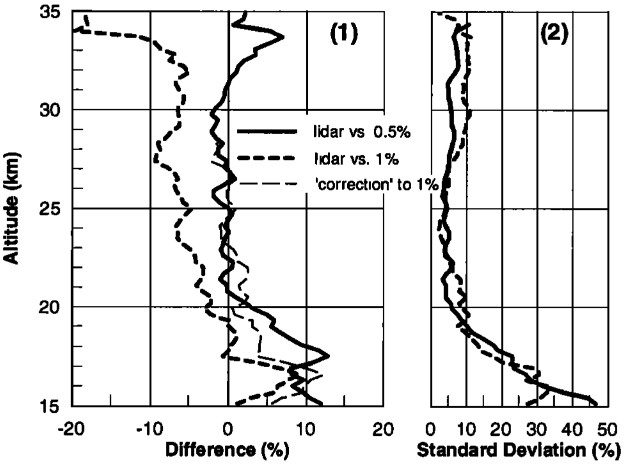

Figure 2. Comparison of lidar and ozonesonde near simultaneous measurements over a two year period. Panel (1) shows the mean of the percentage differences in O_3 number density of ((lidar-sonde)/sonde) x 100, and the results of applying a 'correction' to the lidar vs. 1% difference profile; and panel (2) shows the standard deviation of the percentage differences.

(4) of Figure 1 to the lidar vs. 1% KI sonde profile. The limited number of dual soundings means that this result is indicative only. However the proximity of the curve to the 0% error line and the lidar vs. 0.5% KI curve suggests that, with other supporting measurements, a correction to the Lauder data record should be possible.

Comparison of quasi-simultaneous ozonesonde and Dobson spectrophotometer measurements

Since most ozonesondes at Lauder are flown during daylight hours, simultaneous ozone column measurements from Dobson spectrophotometer 72 are often available. An ozone column amount is determined from the sounding by integrating the profile from the surface to the burst altitude, and using a 40° to 50° S zonal mean SBUV climatology [*McPeters et al.*, 1997] to estimate the residual column from the burst altitude to 1 hPa.

Normalization factors calculated by dividing the Dobson ozone column by the integrated ozonesonde profile are presented in Figure 3. The Dobson spectrophotometer value used is the direct-sun observation made closest to the mid-point of the sounding and with no more than 3 hours separating the measurements. The mean normalization factor to the end of July 1996 is 0.957±0.016 (1σ, 48 comparisons), and from August 1996 to July 1997 the mean is 1.006±0.022 (1σ, 35 comparisons). These results confirm the differences between the 1% and 0.5% KI sondes derived from comparisons with lidar (Figure 2), and show good agreement between the Dobson spectrophotometer and integrated 0.5% sonde profile column amounts, suggesting that the 0.5% KI sondes have better absolute accuracy.

Comparison of ascent and descent profiles: A comment on sensor recovery rates

The possibility that the sensor background current in 1% KI ozonesondes is influenced by previously measured ozone can be examined, independent of other measurements, by comparing balloon ascent and parachute descent profiles in the troposphere. The troposphere is the only suitable part of the profile where this

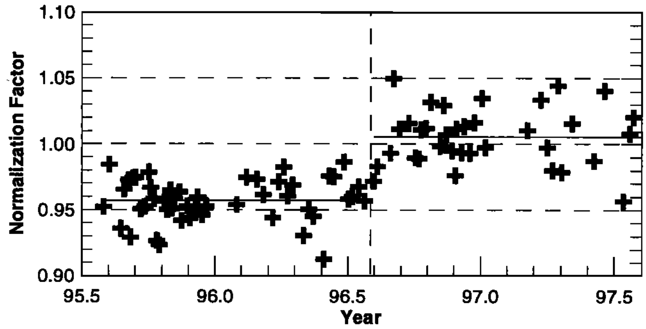

Figure 3. Normalization factors derived by comparing integrated ozonesonde profiles (plus SBUV climatology from burst to 1hPa) with Dobson spectrophotometer ozone columns. The continuous lines show the mean value for each ozonesonde configuration. The dashed vertical line indicates the point where the solution concentration was changed.

comparison can be made as the ascent and descent rates of the ozonesonde are similar, and changes in ozone are, generally, relatively small. Profiles using the two solution concentrations are compared in Figure 4.

The results show that 0.5% KI ozonesondes display little or no evidence of being affected by high ozone amounts in the stratosphere by the time the ozonesonde re-enters the troposphere on descent. Although this does not show that sensors containing a 0.5% KI solution are not affected when measuring high ozone, it suggests that the recovery rate of the sensor is more rapid. The 1% KI ozonesonde ascent and descent profiles show a continued marked offset. The mean difference would represent a 2% to 3% offset above 20 km. This supports the premise that the differences shown in Figures 1 and 2 above 20 km are due, at least in part, to an increase in the background current of the 1% KI ozonesondes after exposure to high ozone amounts.

Conclusions and Discussion

The results obtained from this study show that ECC ozonesondes charged with a 0.5% KI cathode solution (standard 1% KI

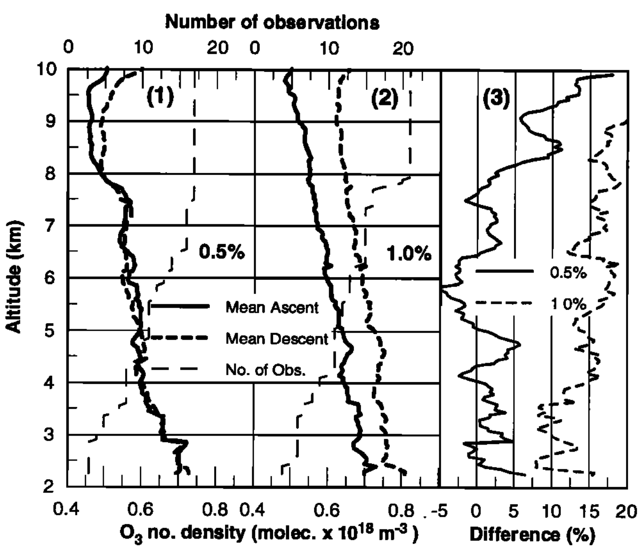

Figure 4. Comparison of ascent and descent profiles made (1) between August 1996 and July 1997 with 0.5% KI solution and (2) between August 1995 and July 1996 with 1% KI solution. Panel (3) shows the mean of the percentage differences for the two configurations.

solution, including KBr and buffer concentrations, diluted by half), yield more accurate ozone measurements than sondes charged with a 1% KI solution, when prepared according to standard procedures and the data processed as outlined above. Possible sources for the observed differences in the 1% and 0.5% KI ozonesondes include intrinsic changes in the chemistry of the electrolyte, changes in the chemistry induced by evaporation during the flight, differences in background current deviation from the initial measured value after measuring high ozone, and differences in the sensor response times.

Using 1% and 0.5% KI ozonesondes, laboratory studies [*Johnson et al.*, 1997] have shown differences in measured ozone when evaporation is negligible and before high ozone is sampled, suggesting that there are intrinsic changes in the chemistry of the O_3 to I_2 conversion reaction. This possibility is also supported by the tropospheric results shown in Figure 1.

Changes in the solution volume from evaporation during the flight could affect the reaction differently for the 1% and 0.5% KI solutions. Throughout the period discussed in this study ozonesonde packages were configured to ensure pump temperatures of 20 to 25 °C at launch decreasing to 10 to 15 °C by the top of the sounding. Based on such profiles estimated typical evaporative losses from the cathode cell are 0.4 to 0.6 ml from a total of 3 ml. The effects of the resultant increase in the KI concentration may be offset, in part, by ozone passing through the cell unreacted due to the lowered solution head, making it difficult to assess how differently the two solutions are affected. While it is unlikely that this alone could account for the observed differences, further investigation is necessary.

Laboratory tests by EN-SCI Corporation and *Johnson et al.* [1997] and the results of the ascent and descent profile comparison support the premise that differences in the performance of the 1% and 0.5% KI sondes are due, at least in part, to a greater deviation in the background current of the 1% KI sondes after exposure to high ozone. Differences in background current sensitivity to high ozone may depend on the buffer solution concentration, which was also halved, and is a topic of current research.

Pre-launch measurements of the time it took for the sensor output current to drop from 4 to 1.5 mA showed that the response times for the 1% and 0.5% KI sondes were not statistically significantly different. Furthermore, changes in sensor response during a sounding caused by changes in solution volume and temperature and atmospheric pressure [*Komhyr et al.*, 1995] would be independent of the solution concentration.

An important issue when comparing the relative performance of 1% and 0.5% KI ozonesondes is the application of pump efficiency correction curves. For example, the JOSIE campaign [*Smit et al.*, 1996] showed that good results can be obtained using a 1% KI solution by application of pump efficiency corrections based on measurements by *Komhyr* [1986], which give nearly constant ECC pump efficiencies of 1.0 up to 200 hPa, gradually decreasing to 0.916 at 5 hPa. However, more recent measurements [*Komhyr et al.*, 1995; *Harder*, 1987] have shown lower efficiencies by 1 to 12% between 100 and 5 hPa, suggesting that use of the 1986 pump efficiency corrections masks the overestimation of ozone by the 1% KI ozonesondes.

A more complete assessment of the accuracy of ozonesondes containing the 0.5% KI solution will require laboratory tests and comparisons with more ozone profiling instruments. Laboratory tests are planned and a campaign is currently being conducted to compare quasi-simultaneous ozone profiles from satellite-borne platforms such as SAGE II and HALOE with ozonesonde, lidar, and microwave radiometer instrument profiles.

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