

File Revision Date:

September 27, 2017

Data Set Description:

PI: Dr. Richard Querel

Instrument: ECC ozonesonde

Site(s): Lauder 45.0446S, 169.684E)

Measurement Quantities: Pressure, Geopotential height, Temperature, Ozone partial pressure, Humidity, Internal sonde temperature, and since October 1998, wind speed and direction, and package location.

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Reference Articles:

Publications concerned specifically with the Lauder ozonesonde programme include:

1. Bodeker, G.E.; Boyd, I.S.; Matthews, W.A. (1998). Trends and variability in vertical ozone and temperature profiles measured by ozonesondes at Lauder, New Zealand: 1986-1996. *Journal of Geophysical Research* 103(D22): 28661-28681.
2. Boyd, I.S.; Bodeker, G.E.; Connor, B.J.; Swart, D.P.J.; Brinksma, E.J. (1998). An assessment of ECC ozonesondes operated using 1% and 0.5% KI cathode solutions at Lauder, New Zealand. *Geophysical Research Letters* 25(13): 2409-2412.
3. McGee, T.J.; Gross, M.; Singh, U.; Kimvilakani, P.; Matthews, W.A.; Bodeker, G.E.; Connor, B.J.; Tsou, J.J.; Proffitt, M.; Margitan, J. (1997). Vertical profile measurements of ozone at Lauder, New Zealand during ASHOE/MAESA. *Journal of Geophysical Research* 102: 13283-13289.
4. Lu, J.; Mohnen, V.A.; Yue, G.K.; Atkinson, R.J.; Matthews, W.A. (1997). Intercomparison of stratospheric ozone profiles obtained by Stratospheric Aerosol and Gas Experiment II, Halogen Occultation Experiment, and ozonesondes in 1994-1995. *Journal of Geophysical Research* 102: 16137-16144.
5. McDermid, I.S.; Bergwerff, J.B.; Bodeker, G.E.; Boyd, I.S.; Brinksma, E.J.; Connor, B.J.; Farmer, R.; Gross, M.R.; Kimvilakani, P.; Matthews, W.A.; McGee, T.J.; Ormel, F.T.; Parrish, A.; Singh, U.; Swart, D.P.J.; Tsou, J.J. (1998). OPAL: Network for the detection of stratospheric change ozone profiler assessment at Lauder, New Zealand 2. intercomparison of revised results. *Journal of Geophysical Research* 103(D22): 28693-28699.
6. McDermid, I.S.; Bergwerff, J.B.; Bodeker, G.E.; Boyd, I.S.; Brinksma, E.J.; Connor, B.J.; Farmer, R.; Gross, M.R.; Kimvilakani, P.; Matthews, W.A.; McGee, T.J.; Ormel, F.T.; Parrish, A.; Singh, U.; Swart, D.P.J.; Tsou, J.J.; Wang, P.H.; Zawodny, J. (1998). OPAL: Network for the detection of stratospheric change ozone profiler assessment at Lauder, New Zealand 1. blind intercomparison. *Journal of Geophysical Research* 103(D22): 28683-28692.

Other publications which have made use of the Lauder ozonesonde data or other vertical profile data from Lauder include:

1. Planet, W.G.; Miller, A.J.; DeLuisi, J.J.; Hofmann, D.J.; Oltmans, S.J.; Wild, J.D.; McDermid, I.S.; McPeters, R.D.; Connor, B.J. (1996). Comparison of NOAA-11 SBUV/2 ozone vertical profiles with correlative measurements, *Geophysical Research Letters* 23: 293-296.
2. Brinksma, E.J.; Meijer, Y.J.; McDermid, I.S.; Cageao, R.P.; Bergwerff, J.B.; Swart, D.P.J.; Ubachs, W.; Matthews, W.A.; Hogervorst, W.; Hovenier, J.W. (1998). First lidar observations of mesospheric hydroxyl, *Geophysical Research Letters* 25: 51-54.
3. Brinksma, E.J.; Meijer, Y.J.; Connor, B.J.; Manney, G.L.; Bergwerff, J.B.; Bodeker, G.E.; Boyd, I.S.; Liley, J.B.; Hogervorst, W.; Hovenier, J.W.; Livesey, N.J.; Swart, D.P.J. (1998). Analysis of record-low ozone values during the 1997 winter over Lauder, New Zealand. *Geophysical Research Letters* 25(15): 2785-2788.

Papers published in conference proceedings include:

1. Matthews, W.A. (1994). Tropospheric ozone at 45°S. In: R.D. Hudson (ed.) *Quadrennial Ozone Symposium*, NASA CP-3266, Greenbelt, Md, pp. 7-10.
2. McGee, T.J.; Gross, M.R.; Singh, U.; Matthews, W.A.; Hofmann, D.J.; Godin, S.; Komhyr, W.; Barnes, R. (1996). "A comparison of ozone lidar measurements with chemical sonde measurements". Presented at *Quadrennial Ozone Symposium*, L'Aquila, Italy, September, 1996. Oltmans, S.J.; Hiram L, I.; Lefohn, S.A.; Eckhart, H.; Galbally, I.E.; Matthews, W.A.; Brunke, E.-G.; Meyer, M.; Lathrop, J.A.; Johnson, B.J. (1996). "Ozone changes in the troposphere over the past twenty years". Presented at *Quadrennial Ozone Symposium*, L'Aquila, Italy, September, 1996.

Unpublished conference presentations include:

1. Bodeker, G.E.; Matthews, W.A.; Boyd, I.S. (1995). "Long-term trends in vertical ozone profiles at 45°S". Presented at the XXI general assembly of the International Union of Geodesy and Geophysics, Boulder, Colorado, USA, July 1995.
2. Bodeker, G.E.; Matthews, W.A.; Boyd, I.S. (1996). "Altitude dependence of long-term ozone trends at 45°S". Presented at *American Geophysical Union Western Pacific meeting*, Brisbane, Australia, July 1996.
3. Tsou, J.J.; Connor, B.J.; Parrish, A. (1996). "NDSC microwave ozone profile measurements in mid-latitude southern hemisphere: validation, variation, and trend analysis". Presented at *1st SPARC General Assembly*, Melbourne, 2-6 December 1996.
4. Bodeker, G.E.; Boyd, I.S.; Matthews, W.A. (1997). "Long-term trends in ozone and temperature profiles measured at 45°". Presented at the *International Symposium on Atmospheric Chemistry and Future Global Environment*, Nagoya, Japan, 11-13 November 1997.
5. Bodeker, G.E.; Matthews, W.A.; Boyd, I.S. (1996). "The altitude dependence of southern hemisphere mid-latitude ozone depletion". Presented at the *13th annual conference of the South African Society for Atmospheric Sciences*, Cape Town, South Africa, 31 October-1 November 1995.
6. Deaver, L.E.; Tsou, J.J.; Russell, J.M.; Connor, B.J. (1996). HALOE Ozone Profile Intracomparisons with the NDSC Ground-Based Microwave Measurements from Lauder, New Zealand. Presented at the *Upper Atmosphere Research Satellite Science Team Meeting*, Hampton, Virginia, USA, 25 March 1996.

7. Connor, B.J. (1997). Lauder ozone profiles (sonde, microwave and lidar). Presented at SPARC/IOC Ozone Trends Assessment, Hampton, Virginia, March, 1997.

Other general reference papers are:

1. Komhyr W.D., Electrochemical concentration cells for gas analysis, Ann. Geophys, vol. 25, pages 203-210, 1969.
2. Komhyr W.D., Barnes R.A., Brothers G.B., Lathrop J.A., Opperman D.P., Electrochemical concentration cell ozonesonde performance evaluation during STOIC 1989, Journal of Geophysical Research, vol. 100, no. D5, pages 9231-9244, May 20, 1995.

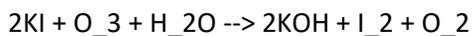
Instrument Description:

The ozonesondes flown as part of this programme have included the 4A, 5A, and 6A series ECC sondes manufactured by the Science Pump Corporation and the 1Z series ECC sondes manufactured by the EN-SCI corporation [Komhyr, 1969]. The 4A sondes were flown from August 1986 to October 1989, 5A sondes between August 1989 and June 1994, 6A sonde on occasional backscattersonde flights and 1Z sondes from July 1994 to the July 1996, although there are a few exceptions to this sequence. The 1Z series ECC ozonesonde (the primary sondes used at Lauder after 4 May 1994) consists of a rigid mainframe on which is mounted a motor driven Teflon/glass gas sampling pump, a thermistor for measuring pump temperature, an ozone sensing electrochemical concentration cell, and an electronics interface box. For ascent into the stratosphere, the instrument is encased in a molded polystyrene weatherproof box. During flight the instrument is coupled to a Vaisala, Incorporated, 403 MHz RS-80-15 meteorological radiosonde. Coupling is achieved through TMAX HMOS electronic interface circuitry. Measured parameters telemetered to the ground receiving station are ozone, sonde pump temperature, air pressure, air temperature and humidity.

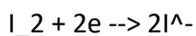
The ozone sensor of the ECC ozonesonde is made of two bright platinum electrodes immersed in potassium iodide (KI) solutions of different concentrations contained in separate cathode and anode chambers. The chambers are linked with an ion bridge that, in addition to providing an ion pathway, retards mixing of the cathode and anode electrolytes thereby preserving their concentrations. The electrolytes also contain potassium bromide (KBr) and a buffer whose concentrations in each half cell is the same. Driving electromotive force for the cell, of approximately 0.13V, is provided by the difference in potassium iodide concentrations in the two half cells. Thus, an external battery is not needed to drive the cell.

Algorithm Description:

When ozone in air enters the sensor, iodine is formed in the cathode half cell according to the relation



The cell converts the iodine to iodide according to



during which time two electrons flow in the cell's external circuit. Measurement of the electron flow (i.e., the cell current), together with the rate at which ozone enters the cell per unit time, enables ozone concentrations in the sampled air to be derived from

$$PO_3 = PCF \times 4.307E-3 \times (i_m - i_b) \times T_p \times t$$

where

PO_3: is the ozone partial pressure in nbars (1 mPa = 10 nbar).
 PCF: is the pump efficiency correction function.
 i_m: is the measured sensor output current in microamps.
 i_b: is the sensor background current (i.e., the residual current emanating from the cell in the absence of ozone in air) in micro amps.
 T_p: is the pump temperature in kelvins.
 t: is the time in seconds taken by the sonde gas sampling pump to force 100 ml of air through the sensor.

The PCF varies from sonde to sonde and with ambient air pressure. It also depends on pump leakage, the pump dead volume, and the pump head (the back pressure exerted on the pump by the pump sensor cathode electrolyte). The PCF for each sonde has not been measured as part of this ozonesonde programme. Rather, a pump correction curve, appropriate to each series of ozonesonde, has been used. This curve is a third order polynomial fit to pump corrections published in ozonesonde instruction manuals, as a function of $\ln(\text{Pressure})$:

$$\text{PCF} = C_0 + C_1 \ln(P) + C_2 \ln(P) \ln(P) + C_3 \ln(P) \ln(P) \ln(P)$$

The C_0 to C_3 coefficients used for the series of sondes flown were:

	C_0	C_1	C_2	C_3
4A and 5A:	1.79130E+00	-4.95597E-01	1.08781E-01	-8.10444E-03
1Z:	1.584515+00	-4.29117E-01	1.08876E-01	-9.22500E-03

The errors introduced through the uncertainty in the PCF are discussed in the following section.

The background current (i_b) is measured before the launch and is assumed to remain constant through the flight. The errors introduced by this assumption are discussed further below. Likewise, the time taken by the sonde gas sampling pump to force 100 ml of air through the sensor is assumed to remain constant.

The geopotential height difference between two levels (1 and 2) can be calculated with the following algorithm:

$$\begin{aligned} \text{Sat1} &= 6.1078 \cdot 10^{((7.5 \cdot \text{Temp1}) / (237.3 + \text{Temp1}))} \\ \text{WaterMix1} &= (0.622 \cdot (\text{Humd1} / 100.0) \cdot \text{Sat1}) / (\text{Press1} - (\text{Sat1} \cdot \text{Humd1} / 100.0)) \\ \text{VirtTemp1} &= (\text{Temp1} + 273.15) \cdot (1 + 0.61 \cdot \text{WaterMix1}) \\ \text{Sat2} &= 6.1078 \cdot 10^{((7.5 \cdot \text{Temp2}) / (237.3 + \text{Temp2}))} \\ \text{WaterMix2} &= (0.622 \cdot (\text{Humd2} / 100.0) \cdot \text{Sat2}) / (\text{Press2} - (\text{Sat2} \cdot \text{Humd2} / 100.0)) \\ \text{VirtTemp2} &= (\text{Temp2} + 273.15) \cdot (1 + 0.61 \cdot \text{WaterMix2}) \\ \text{DeltaZ} &= (287.05 / 9.80665) \cdot ((\text{VirtTemp2} + \text{VirtTemp1}) / 2.0) \cdot \ln(\text{Press1} / \text{Press2}); \end{aligned}$$

where

Temp1, Temp2: Are the temperatures at the two levels, measured in degrees Celsius.

Press1,Press2: Are the pressures at the two levels, measured in hPa.

Humd1,Humd2: Are the humidities at the two levels, measured in percent.

Sat1,Sat2: Are the saturated water vapour pressures at the two levels.

WaterMix1,WaterMix2: Are the water vapour mixing ratios at the two levels.

VirtTemp1,VirtTemp2: Are the virtual temperatures at the two levels.

DeltaZ: Is the geopotential height difference between level1 and level2 in meters.

Expected Precision/Accuracy of Instrument:

The data contained in the ozonesonde data files are:

- 1) Time after launch in minutes
- 2) Pressure in hPa
- 3) Geopotential height in meters
- 4) Temperature in Kelvin
- 5) Ozone partial pressure in mPa
- 6) Humidity in percent
- 7) Internal temperature in degrees Celsius

Except for the primary index variable, the time after launch, for which the error is assumed to be zero, accuracy and precision for all of these quantities must be calculated.

Pressure:

If an environmental chamber is not available for the calibration of the every pressure sensor, as in our case, a pressure offset error can be calculated from analysis of a large data set of calibrated pressure sensors. This was found to be 0.258 ± 0.671 hPa, indicating that on the whole, the pressure sensors tends to underestimate the pressure. The random error (precision) was estimated at 0.2 hPa.

Temperature:

The random error in the temperature is specified as 0.2C. Additional error is introduced since radiative heating of the temperature sensor may cause the reading to be overestimated, while cooling through ventilation may cause the reading to be underestimated. The Vaisala operating manual gives the necessary corrections as a function of the current solar zenith (SZA) angle and ambient pressure. However, the attitude of the ozonesonde package varies through the flight with the result that it cannot always be determined whether the sensor is radiatively heated by the sun or shaded by the ozonesonde package or cloud cover and cooled, thereby introducing a further error.

Humidity:

The random error in the humidity is specified as 3%. The systematic error was assumed to be zero.

Internal temperature:

The random error in the internal temperature sensor was assumed to be 0.2C, while the systematic error was assumed to be zero.

Geopotential height:

The geopotential height is calculated using the hydrostatic equation modified for the inclusion of water vapour as described above. Therefore the temperature, pressure and humidity measurements are required to calculate the geopotential height. Since the errors in these quantities are not normally distributed, it is not possible to use the standard least squares propagation of errors approach. It is therefore necessary to make use of a Monte Carlo error model. In this case 100 flights were simulated, with a geopotential height profile for each flight being calculated as follows:

- 1) The probability density functions (PDFs) for the pressure, temperature, humidity and pressure offset errors are integrated. The PDF is a Gaussian profile whose width is specified by the random measurement error (first standard deviation) and whose offset from the Y axis is determined by the systematic error. The Monte Carlo technique makes use of the fact that by randomly selecting values on the ordinate of the integrated PDF plot, and reading off the appropriate values for the required parameters on the abscissa, the population of the selected values will be constrained to the Gaussian PDFs. For the temperature, there is additional uncertainty introduced by the radiation correction. The temperature PDF is created from a constant value between two extremes, specified by the measured temperature and the radiation corrected temperature, with half Gaussian curves at each end specified by the random error in the temperature measurement.
- 2) At the start of each flight a pressure offset value is selected by selecting a random number between 0 and 1, and reading off the pressure offset from the integrated PDF plot. It is assumed that this pressure offset will remain constant through the flight.
- 3) The initial altitude is set to the surface altitude (370 m in this case). Pressure, temperature and humidity errors for the surface measurements are determined in a similar way to the pressure offset value.
- 4) For each data record in the flight, pressure, temperature and humidity errors are determined as they were at the surface. The errors are added to the measured values and the change in geopotential height is calculated between levels n-1 and n using the modified hydrostatic equation.

Statistical analysis of the 100 geopotential height profiles calculated in this way, is used to determine the first standard deviation in the positive and negative direction for the geopotential height for each data record.

Ozone partial pressure:

Errors in each of the terms used to calculate the ozone partial pressure (see equation above) must be estimated.

Pump efficiency correction factor:

If an environmental chamber is not available for the calculation of a pump efficiency correction curve for every ozonesonde, as in our case, it is necessary to estimate the uncertainties in the PCF from other measurements. We obtained a file of 435 measured pump efficiency correction curves from Terry Deshler for a variety of ozonesonde types. Statistical analysis of these data was used to determine the uncertainty in the pump correction curves, for each type of ozonesonde, at each pressure level. However, the mean of the pump correction curves for the 1Z sondes was significantly higher than the values listed in the ECC ozonesonde instruction manual by the EN-SCI corporation. The reason for this is

that there are conflicting techniques for the measurement of the pump efficiency. This introduces additional error into the pump efficiency corrections.

Measured ozonesonde current:

The random error in the ozonesonde current was assumed to be 2% as used by [Komhyr et al. 1995].

Background current:

The behaviour of the background current during an ozonesonde flight is not well understood. Komhyr suggested that the background current resulted largely from residual sensitivity of the ozonesonde sensor to oxygen. In this case it would be appropriate to assume that the background current decreases from its measured surface value in proportion to the atmospheric pressure. Special treatment and pre-conditioning of ECC sensor platinum electrodes in recent years has significantly reduced sensor background current compared to values observed in the past. The newer sensors apparently exhibit little, if any, sensitivity to oxygen. In this case it would be more appropriate to assume that the background current remains constant during the flight. It has also been suggested however, that the background current is influenced by previously measured ozone. In addition to these errors, there is a random error in the background current of 2%.

Time to pump 100 ml:

The error in this quantity was assumed to be zero.

Overall error in ozone partial pressure:

To estimate the overall error in the ozone partial pressure profile, 100 flights were simulated, using the Monte Carlo technique to estimate the errors, as follows:

- 1) Pump correction PDFs for each pressure level and internal temperature PDFs are integrated.
- 2) Before the start of the simulated flight, the random number for the selection of the pump efficiency correction curve error is selected. This number is applied throughout the flight to ensure that the curve has the correct form.
- 3) For each data record the error in the background current is estimated by assuming that it lies randomly between its surface value, and its pressure scaled value and the 2% uncertainty at these limits. This of course makes no provision for background currents being influenced by previous ozone levels. This problem will be examined in future. The internal temperature error is calculated using the Monte Carlo technique and is added to the measured internal temperature value. The ozone partial pressure for that record is then calculated.

Statistical analysis of the 100 ozone partial pressure profiles calculated in this way, is used to determine the first standard deviation in the positive and negative direction for the ozone partial pressure for each data record.

Discussion:

Errors in the pressure profile become noticeable above 25 km as a result of errors in the pressure offset and random errors in the pressure measurement. These in turn, together with the temperature errors, result in rapidly increasing geopotential height errors above 25 km. Initially, below 200 hPa, the measured ozone partial pressure is a lower estimate, since if anything, the ozone background current

will be lower than the assumed constant value as a result of the pressure scaling. Above 200 hPa, when the pump efficiency correction curve is used, these errors are compounded by the pump efficiency uncertainty.

If the ozone partial pressure profile is indexed by geopotential height rather than time after launch, the errors would be bigger for a particular altitude, since there is also uncertainty in the altitude value. This will be particularly important in the case of large vertical gradients in the ozone partial pressure since a small error in altitude could result in much higher or lower ozone values being assumed. These effects have not been investigated here and those people using these data and indexing the data by altitude should change the maximum and minimum estimates of the ozone at each level appropriately i.e. at level N move up and down and for each level whose altitude falls within the altitude uncertainty at level N, the specified ozone values should be examined (if the ozone levels are above or below the maximum and minimum values at level N, the max and min values at level N should be changed accordingly).

Clearly the errors in the pressure profile could be improved through accurate calibration of the pressure sensor, thus removing the pressure offset error, and leaving only the random error. Shading of the temperature sensor removes the need for a radiation correction and will significantly reduce the error in the temperature. Measurement of the pump efficiency curve for each sonde would significantly reduce the error in the ozone partial pressure profile, as would a better understanding of the behaviour of the background current during the flight.

This error analysis applied to the ozonesonde files is discussed more thoroughly (including plots of mean errors for each type of sonde) in the following publication:

Bodeker, G.E.; Boyd, I.S.; Matthews, W.A. (1998). Trends and variability in vertical ozone and temperature profiles measured by ozonesondes at Lauder, New Zealand: 1986-1996. *Journal of Geophysical Research* 103(D22): 28661-28681.

Instrument History:

Ozonesonde flights have been performed at Lauder since the beginning of August 1986. Although electrochemical concentration cell (ECC) ozonesonde have been used throughout the measurement period, different types of ECC sondes have been used. Initially 4B series ozonesonde were used, followed by 4A, then 5A and finally 1Z. Differences in performance characteristics for each of these types of sondes (eg. differences in pump efficiencies) have been taken into account when creating the homogeneous data base of vertical ozone profiles.

To remove the uncertainty in the temperature introduced by the radiation correction, temperature sensors have been shaded on flights from 28 March 1996 onwards.

From July 1996 the 1Z series sonde were flown using a 0.5% KI solution rather than the usual 1% solution. The reasons for making this change and the effects on performance of the ozonesonde is discussed in:

Boyd, I.S.; Bodeker, G.E.; Connor, B.J.; Swart, D.P.J.; Brinksmas, E.J. (1998). An assessment of ECC ozonesondes operated using 1% and 0.5% KI cathode solutions at Lauder, New Zealand. *Geophysical Research Letters* 25(13): 2409-2412.

Since October 1998 a GPS based Marwin ground receiving system has been used periodically at Lauder to receive data from the ozonesondes interfaced to GPS radiosondes. In addition to generating data at higher vertical resolution, it also make available wind speed and direction data.

December 2012: Digicora III ground station replaced the Marwin.

April 2015: Digicora III was (software) upgraded to MW41.

RS92 and RS41 being used with ENSCI Z ozonesondes.