Stratospheric ozone reaches new minima above McMurdo Station, Antarctica, between 1998 and 2001

Chris Kröger,1 Mark Hervig,2 Bruno Nardi,3 Larry Oolman, and Terry Deshler
Department of Atmospheric Science, University of Wyoming, Laramie, Wyoming, USA

Stephen Wood
New Zealand National Institute of Water and Atmospheric Research Ltd., Central Otago, New Zealand

Sylvia Nichol
New Zealand National Institute of Water and Atmospheric Research Ltd., Wellington, New Zealand

Received 3 September 2002; revised 25 May 2003; accepted 11 June 2003; published 11 September 2003.

[1] Ozone sonde measurements were performed annually in late winter and early spring from McMurdo Station, Antarctica, between 1998 and 2001, continuing a record starting in 1986. Mean column ozone during the same 47 day period in all four years are at least 11% below the average during the same period of the 1986–1997 record in the total column and at least 24% below the 1986–1997 record in the 12–20 km column. Average column ozone of 2000 and 2001 is also clearly below the minima observed between 1986 and 1997, with 2001 the lowest on record. These observations of lowest ozone are consistent with predictions and observations of peaking halogen abundance in the lower stratosphere around 2000 and a very slow decline thereafter. Such low ozone values are a combined consequence of stratospheric halogens and a continual and cold polar vortex. Man-released halogens mainly affect the 12–20 km ozone column, while the ozone column above and below the 12–20 km column stays about constant. Several kilometer deep ozone-depleted layers with mixing ratios below 0.1 ppmv appeared about 10 days earlier in 2001 than in 1998. Integrated ozonesonde measurements are compared to TOMS and Dobson spectrophotometer data with generally very good agreement. Measurement differences are largest when the vortex edge is close to McMurdo and decrease with increasing distance to the vortex edge region. The analysis of the vortex edge location at 400 K and 550 K shows that nearly all measurements were performed inside the polar vortex at 400 K, but extravortex air was sampled on occasion above 550 K. The earlier departure of the polar vortex edge above 550 K south of McMurdo led in 2000 to very high column ozone, both in the total column and in the 12–20 km column, which occasionally exceeds maximum observed values since 1986. Synchronous temperature measurements show correlations between high temperature, high ozone mixing ratio, and extravortex air.

INDEX TERMS: 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; KEYWORDS: polar, ozone depletion, stratosphere, ozonesonde, polar vortex


1. Introduction

[2] Significant ozone depletion over the Antarctic continent has occurred annually every austral spring since the late 1970s and the current situation will lead to strong ozone depletion for many years to come. Liberation of chlorine from reservoir molecules on the surface of polar stratospheric clouds (PSCs) (or, to a lesser degree, on volcanically released sulfuric acid droplets) causes the severe ozone destruction via photochemical reactions [Solomon, 1999]. The formation of PSCs is a natural phenomenon and, for
Given stratospheric water vapor and HNO₃ mixing ratios, strictly temperature dependent, while the chlorine and most other halogens have been contributed by human activity. Although the impact of chlorine compounds released into the atmosphere on the ozone layer was predicted by Molina and Rowland [1974], it took the findings of Farman et al. [1985] and others since then that lead to the signing of the Montreal Protocol in 1987. The rate of growth of CFCs and related compounds in the atmosphere has since decreased considerably. Tropospheric concentrations of all major CFCs, namely CFC-12, CFC-11, CFC-113, methyl chloroform, and tetrachloride were all stabilized or decreasing by 1996 [Montzka et al., 1996]. At a transport time of 4–6 months for air entering the stratosphere through the tropopause [Boering et al., 1995] and several more years to reach the middle stratosphere where chlorine is released from CFC’s [e.g., Seinfeld and Pandis, 1998], the peak chlorine concentration in the stratosphere was predicted to occur before 2000 [World Meteorological Organization, 1998; Montzka et al., 1996]. This prediction is supported by Engel et al. [2002]. However, emissions of the potent ozone-depleting CBrClF₂ (halon-1211) have remained fairly constant despite the Montreal Protocol regulations [Montzka et al., 1999], which may delay the recovery of the ozone layer by impeding the decline of ozone-depleting halogens in the atmosphere. Additionally, increasing CO₂ amounts in the atmosphere may alter stratospheric temperatures which could arguably lead to accelerated ozone-depleting reaction rates there [Shindell et al., 1998].

Heterogeneous halogen chemistry that significantly depletes ozone depends on the occurrence of PSCs. However, PSCs form on the condition that the polar vortex is stable and the air inside can cool below the PSC dew or frost point, depending on the ambient thermo-dynamical conditions. When the polar vortex is destabilized and deformed by strong atmospheric disturbances, the cold temperatures inside the polar vortex are not sustained and only few PSCs produced. A “warm” polar vortex explains the comparable chlorine amounts the significantly smaller size of the ozone hole and relatively high ozone observations in the Austral spring of 2002 compared to the presented measurements. (The measurements of 2002 are not further described here, refer to TOMS data.) The less severe nature of the northern hemisphere ozone hole is equally the consequence of a frequently disturbed polar vortex.

2. Instrumentation

Ozone measurements are performed with commercial electrochemical cell (ECC) ozonesondes, developed and described by Komhyr [1969]. The ozonesonde consists of

a Teflon piston pump and a Teflon sensor. The cathode half-cell contains a buffered KI solution and the anode half-cell contains a saturated KI solution. Any sampled ozone molecule reacts with iodide inside the cell releasing the flow of two electrons in the external cell circuit. The resulting electrical current is proportional to the ozone concentration for a known pump flow rate. The pumps of the ozonesondes experience an efficiency decrease of up to 25% at 5 hPa ambient pressure and are therefore individually calibrated prior to flight [Harder, 1987]. A Vaisala radiosonde provides temperature and pressure data. The balloon ascent rate and data transmission rate leads to a vertical resolution of approximately 20 m on ascent, and up to 40 m on descent. Approximately every third day between /C24 20 August and the end of October one ozone profile is measured.

The standard operating method at McMurdo has used a 1% KI buffered solution. While the 1% KI buffered solution is considered the standard [Komhyr, 1969, Komhyr et al., 1995], some authors report better accuracies with the 0.5% buffered KI solution [Boyd et al., 1998], or with the 2% unbuffered solution [Johnson et al., 2002]. According to Boyd et al. [1998], the 1% KI solution overestimates ozone concentrations. In their comparison flights, the 1% KI solution showed 3–8% positive ozone concentration differences and about 5% more in total column ozone. In the same report the 0.5% KI solution compared better to Dobson spectrophotometer measurements. A hysteresis effect after encountering high ozone is noted [Johnson et al., 2002], which is most significant for 1% KI solutions at higher altitudes. Johnson et al. [2002] reports measurement differences up to 10% at flight ceiling. The standard 1% buffered KI solution was maintained for all McMurdo measurements since 1986, except in 1999, when the 0.5% buffered KI solution was used. Consequently consistently lower ozone measurements should be expected in 1999.

3. Data and Analysis

3.1. Description

[7] Ozone measurements in the lower stratosphere above McMurdo between days ~230 and ~305 (late August to end of October) in 1998–2001 are shown in Figure 1. The simultaneous 1998–2001 temperature contours are plotted in Figure 2. Every year a drop in ozone mixing ratios below 0.05 ppmv is observed between 350 and 500 K before day 280, where nearly the full 150 K potential temperature range can be seen such depleted in 1998, 2000, and 2001. About three weeks before the end of winter, on day 245, measurements show that ozone mixing ratios range from 0.5 to 3 ppmv between 350 and 500 K, thus ozone is reduced by more than 95% over a period of less than 4 weeks. Although 1999 ozone is depleted to the same degree as the other years, ozone in 1999 appears less adversely affected by displaying a significantly smaller depth of the 0.05 ppmv isopleth. This is despite the fact that the 0.5% KI solution used leads to relatively lower ozone measurements. The start of ozone depletion seems to be earlier each successive year, and ozone mixing ratios <0.1 ppmv are observed ~10 days earlier in 2001 than in 1998. The beginning of ozone recovery is indicated by a decreasing depth of the ozone-depleted layer and by an increasing ozone mixing ratio up to
6 ppmv and temperatures $\geq -35^\circ$C above the 550 K region. All years show signs of ozone layer recovery by day 300.

### 3.2. Analysis

[8] The simultaneous ozone rich air and high temperatures after day 280 in 2000 and 2001 suggest extra vortex air. To categorize air as vortex or extravortex air, the relative location of the polar vortex edge to McMurdo Station ($77.81^\circ$S, $166.67^\circ$E) at two isentropic levels is plotted in Figure 3. The polar vortex edge is here defined as a region rather than an exact line, which better reflects the nature of the vortex boundary. Vortex edge analysis was performed with the 00 UT NCAR/NCEP reanalysis potential vorticity and wind speed data on the 400 K and 550 K isentropic surfaces. Data are provided on a $2.5^\circ$ horizontal grid. An 11th degree polynomial was fitted to 21 grid points below 40$^\circ$S along longitude 167.5 E. This polynomial was differentiated to obtain the slope and curvature. The analysis was then confined to 87.5$^\circ$S and 45$^\circ$S. The vortex edge center is defined as the maximum slope in the potential vorticity function, and the south- and northward extensions of the vortex boundary are determined from the inflection points on either side of the maximum slope. In case the potential vorticity function exhibits several maxima, a plausibility condition has to be fulfilled that the wind speed at the center of the vortex boundary has to be greater than one half of the maximum wind speed along the longitude.

[9] Figure 3 shows that observations of ozone rich air and high temperatures in Figures 1 and 2 after day 280 above 550 K are associated with movement of the vortex edge to the south of McMurdo. On the other hand, the almost continuously ozone-depleted layer at 400 K after day 260 in all years is shown in Figure 3 to be vortex air. The vortex edge rarely crossed south of McMurdo at this altitude. All years show a correlation of ozone mixing ratio, temperature, and vortex edge location. This correlation indicates in the ozone and temperature measurements in Figures 1 and 2 the altitude where the vortex edge crosses over McMurdo.

[10] Total and 12–20 km column ozone is determined from each ozonesonde measurement and shown in Figure 4. Total column ozone is calculated by extrapolating from the balloon burst altitude assuming constant ozone mixing ratio. The error introduced by this method depends on the burst altitude and is larger when the burst altitude is lower. An error of $\sim$5% at midlatitude location has been estimated by McPeters et al. [1997], when the burst altitude coincides with the point of highest ozone partial pressure at 400 K ($\sim$16 km). Obviously the same burst altitude leads to underestimation if the measurement is performed during deep ozone depletion, when mixing ratios approach 0 ppmv. We calculated total column ozone for one flight at the end of August reaching 31.1 km. Then we calculated total column ozone for the same flight, but starting the extrapolation at 20 and 25 km. The 20 km extrapolation results in 81% of the 31.1 km value, and extrapolating from 25 km results in 96% of the same value. To avoid predictable discrepancies only measurements exceeding 25 km are used for total column extrapolation. The 12–20 km column on the other hand is a direct result from the measurement. Focusing on the 12–20 km column is more representative for quantifying ozone loss than total column ozone, since it is the major ozone depletion zone and ozone differences due to dynamical effects can be largely excluded.

[11] In Figure 4 the 1998–2001 column ozone is comparable to the low range (observed minimum between 1986 and 1997 for any given day) between days 240 and 275,
most notable in the 12–20 km column. After this day increasing ozone above 500 K shifts column ozone toward or above the mean. Total column ozone in 2000 exceeds the upper range on several occasions, also reflected in the 12–20 km column. Total and the 12–20 km column ozone of 1999 rank amongst the lowest. This is surprising since ozone mixing ratios below 0.1 ppmv in 1999 covered only a fraction of the vertical extent of 1998, 2000, and 2001 and thus low ozone depletion appeared less strong. The 0.5% KI solution used in 1999 has been shown to measure less ozone than the 1% KI solution [Boyd et al., 1998]. This effect may become more pronounced at higher altitudes after water evaporation from the censor solutions and consequently a further increase in KI solution concentration. Investigations by Davies et al. [2000] and Johnson et al. [2002] reported a height dependent increase of up to 12% at flight ceiling for 1% KI solutions compared to 0.5% KI solutions. The second author reports also a stronger hysteresis effect in

![Figure 4](image-url)

**Figure 4.** Total and 12–20 km column ozone for 1998–2001. The shading shows the range (minimum and maximum observed ozone) between 1986 and 1997. The white line is the average observed ozone for this date between 1986 and 1997.

![Figure 5](image-url)

**Figure 5.** Mean total and 12–20 km column ozone for the period beginning day 237 and ending day 283. The full bar shows the total column ozone, the black bar is the 12–20 km column, and the gray bar is the difference between the total and 12–20 km ozone columns. The mean and minimum of the 1986–1997 record are identical to the ones in Figure 4.
the 1% KI solution after the ozonesonde has sampled ozone. These results suggest explanations of the observed relatively low column ozone in 1999, but further study is necessary on the dependence of the measured ozone amount on the strength of the KI solution.

The mean ozone column \( \bar{A} \) for a certain time period is used to compare yearly ozone depletion quantitatively:

\[
\bar{A} = \frac{\sum (A^* \Delta t)}{T},
\]

with \( A \) the mean column ozone between two measurements, \( \Delta t \) the time between the two measurements, and \( T \) the time period including days 237 to 283 (47 days). The time period is chosen such that it is representative for inside vortex measurements. In addition to the 1998–2001 measurements the comparison includes 1993, the average of 1986–1997, and the measured minima between 1986 and 1997. The lower and upper integration boundaries are days 237 and 283, respectively. When a measurement is not available for either the start or finish day, a linear interpolation of the ozone column is performed between the nearest preceding and following measurement to this day. Results are shown in Figure 5 and in Table 1. Ozone of 1993 and 1998–2001 is below the average for total and 12–20 km column. The 12–20 km column shows a downward trend between 1998 and 2001 and is below the 1986–1997 minimum beginning in 2000. In 2001 the 12–20 km column is 44% below the average, 35% below 1993, and 12% below the 1986–1997 minimum. Hence 2001 displays the strongest ozone depletion in the 12–20 km column in our record. The total column exceeds the 1986–1997 minimum except in 1999, but is below the 1986–1997 average. The difference between the total and 12–20 km column ozone in Table 1 remains approximately constant, indicating that ozone depletion is limited to the 12–20 km layer. The difference is comparable to the 1986–1997 average (<5%) in 1998, 2000, and 2001; however, the 1986–1997 minimum total and 12–20 km column difference is 13% below the average difference. Ozone depletion in 1993 was enhanced by volcanic aerosol in the lower stratosphere, which led to notable ozone loss also outside the 12–20 km layer. The large deviation of the 1999 difference is likely due to the use of the 1% KI solution after the ozonesonde has sampled ozone.

Table 1. Percentage of Mean Total and 12–20 km Column Ozone Between Days 237 and 283 With Respect to the 1986–1997 Record Average\(^a\)

<table>
<thead>
<tr>
<th>Year</th>
<th>12–20 km Column, %</th>
<th>Total Column, %</th>
<th>Difference Total and 12–20 km Column, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1993</td>
<td>91</td>
<td>90</td>
<td>89</td>
</tr>
<tr>
<td>1998</td>
<td>76</td>
<td>89</td>
<td>95</td>
</tr>
<tr>
<td>1999</td>
<td>70</td>
<td>78</td>
<td>82</td>
</tr>
<tr>
<td>2000</td>
<td>61</td>
<td>85</td>
<td>97</td>
</tr>
<tr>
<td>2001</td>
<td>56</td>
<td>85</td>
<td>99</td>
</tr>
<tr>
<td>1986–1997</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>minimum</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)See also Figure 5.

Figure 6. Comparison of total column ozone [DU] from ozonesondes, TOMS, and Dobson spectrophotometer measurements for 1998–2001. Ozonesonde total column ozone is extrapolated assuming constant ozone mixing ratio above balloon burst altitude.
of the 0.5% KI solution as compared to the 1% KI solution used in all other years, which, as explained earlier, is most influential at higher altitudes with measurement differences up to 10% at flight ceiling.

4. Comparison of In Situ and Remote Measurements

Ozonesonde total column ozone is compared to the ground based Dobson spectrophotometer by NIWA at Arrival Heights near McMurdo and to the satellite-borne Earth Probe TOMS (http://toms.gsfc.nasa.gov/eptoms/ep.html). Aside from instrumental errors, common error sources include: (1) the measurement path (While the in situ measurements are along a line of flight, TOMS and the Dobson spectrophotometer each measure along a specific line of sight.), (2) spatial and time difference (the TOMS data was limited to data within 24 hours of ozonesonde launch and 320 km radius around McMurdo; Dobson spectrophotometer measurements were performed daily and use a line of sight toward the north while the prevailing winds move ozonesondes to the east), (3) obscured sunlight or moonlight; these measurements are not as accurate as those made using direct sunlight [Basher, 1982]. The measurements made using obscured sun have a small cloud correction applied to them.

Total column ozone from ozonesonde, TOMS, and Dobson spectrophotometer measurements for 1998–2001 are compared in Figure 6. The agreement is excellent on most occasions. Larger discrepancies can be attributed to the above noted error sources, which become more pronounced when the air masses undergo strong dynamical changes or are located close to the polar vortex edge. In 2000 and 2001, deviations are largest after day 285 when the vortex edge is above McMurdo at 550 K (see Figure 3). The vortex edge at 400 K and 550 K was near McMurdo on day 290 in 1999, and the difference between ozonesonde and TOMS measurement is ~70 DU, notably more than on any other occasion in 1999. Most likely TOMS measured outside the polar vortex on day 290 while the ozonesonde sampled air within or at the edge of the vortex. The Dobson spectrophotometer measured outside the vortex edge on day 290, but on day 291 inside, hence showing good agreement with TOMS on day 290 and with the ozonesonde on day 291. The strong variation in ozone measurement from a single instrument during this period is an indication of the rapid movement of the vortex edge rather than an indication for significant instrument variations.

The assumption of significant measurement differences due to vortex edge proximity is investigated further in Figure 7. The difference between ozonesonde and TOMS/Dobson spectrophotometer measurements is plotted as a function of the distance of the inner boundary of the polar vortex edge region to McMurdo. The distance of the vortex edge to McMurdo is calculated at the 550 K isentropic surface, because this surface approximately separates the ozone loss region from air above, which is stronger influenced by vortex motion (see Figures 1 and 3).
measurement difference is defined as ozonesonde measurement minus TOMS measurement or minus Dobson spectrophotometer measurement, respectively. The majority of measurements in 1998–2001 were taken more than 5° south of the vortex edge, clearly inside the polar vortex. The difference for these data is only weakly correlated to the vortex edge distance, but once the vortex edge approaches McMurdo latitude, the error increases rapidly, most notably in 1999, 2000, and 2001. A Gaussian least squares line is fitted to the absolute value of the difference, revealing a decreasing difference with increasing distance to the vortex edge in all years. The slope of the linear fit is negative except for TOMS in 1998. The reason that this comparison is different may be a limited number of vortex crossings after day 275, when 1998 ozone depletion would lead to significant ozone concentration gradients across the vortex edge. Close proximity to the vortex edge before day 260 would not lead to large measurement differences since ozone variation across the polar vortex edge is small prior to the onset of significant ozone depletion. The measurement difference for all three instruments is negligible on day 290, despite the fact that the polar vortex edge crosses McMurdo at 550 K.

[16] While the linear fit is based on the absolute value of the measurement difference, the actual measurement differences are plotted in Figure 7. This is to show that while in 1998, 2000, and 2001 the measurement differences are mainly positive (1998) or spread evenly around the zero line (2000, 2001), the majority of differences in 1999 are negative. This means that the ozonesonde measures mostly higher ozone than TOMS and the Dobson spectrophotometer when a 1% KI solution is used, but mostly less ozone than the remote instruments when a 0.5% KI solution was used in 1999. A similar observation has been made by Gill [2001], and is consistent with the conclusions made by Boyd et al. [1998] and Johnson et al. [2002] that 1% KI solutions lead to higher ozone measurements than 0.5% KI solutions.

5. Summary and Conclusion

[17] This paper presents ozone profile measurements of 1998–2001 for the period from the end of August until the beginning of November. The data are evaluated with respect to measurements taken between 1986 and 1997, to the distance of the polar vortex edge, and to two remote measurements.

[18] The year 2001 exhibits lowest ozone on our record since 1986 in the 12–20 km column, followed by 2000, 1998 and 1999. All four years are well below the measurement average of 1986–1997, and 2000 and 2001 are also below the 1986–1997 minima. Ozone outside the 12–20 km region was not significantly affected by ozone depletion during 1998–2001, as the nearly constant difference between the total and 12–20 km column ozone shows for 1998, 2000, 2001 and the 1986–1997 average. The ozone sensor solution used in 1999 (0.5% KI solution) resulted in lower ozone measurements above 20 km than the 1% KI solution used in all other years. This is consistent with findings by Boyd et al. [1998]. This led to low total column ozone measurements in 1999 despite the fact that vertical extensions of the ozone-depleted layer is a fraction of the extension in 1998, 2000, and 2001.

[19] Every year ozone mixing ratios were reduced from >1 ppmv to <0.05 ppmv in the 12–20 km layer, at least a 95% reduction. Observations of ozone mixing ratios of <0.1 ppmv appeared nearly two weeks earlier in 2001 than in 1998. Total and 12–20 km column ozone is near the lower range of the 1986–1997 record before day 275. After day 285, ozone relaxes to the 1986–1997 mean in the total column, and occasionally exceeds the upper range in 2000. The vertical extension of the 0.1 ppmv isopleth is strictly confined between the 350 K and 500 K isentropic surfaces (~12–20 km), but spans this depth only in 2001 and 1998. Temperatures >−30°C above 650 K and after day 280 are correlated with high ozone mixing ratios (>6 ppmv). Vortex edge analysis has shown that this air is of extravortex origin. To characterize these ozone measurements with respect to the polar vortex required developing an analytical definition of the region representing the polar vortex edge. On the basis of this definition, most measurements around 400 K in 1998–2001 were performed inside the polar vortex, while extravortex air was occasionally sampled above 550 K, in particular after day 280. The distance to the vortex edge has indications for comparison of ozonesondes and remote ozone measurements from TOMS and Dobson spectrophotometer. The measurement difference increases rapidly if the vortex edge is closer than 5° latitude to McMurdo, but there is no obvious dependency if all measurements are performed clearly inside the vortex. Ozonesonde measurements are more often larger than TOMS or Dobson spectrophotometer when a 1% KI solution is used, but are clearly smaller when a 0.5% KI solution was used in 1999.

[20] Major ozone depleting halogen accumulations are now at their maximum in the stratosphere, thus in the absence of large volcanic eruptions the low ozone measurements of 1998–2001 are a consequence of continued chlorine and halogen saturation in the lower stratosphere and sustained cold polar vortices. These years may stand as records for Antarctic ozone loss.

[21] Acknowledgments. The important work of Lyle Womack and Jason Gonzales on the instruments is gratefully acknowledged. The operation of the Dobson spectrophotometer was supported by the New Zealand Foundation for Research Science and Technology and by Antarctica New Zealand. This research was funded by the National Science Foundation, Office of Polar Programs. Gratitude is expressed for the helpful suggestions by the reviewers.

References


