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Ozone loss episodes in the free Antarctic troposphere, suggesting a possible climate feedback

H. K. Roscoe,[1] K. Kreher,[2] U. Friess [3]

Abstract. Sudden loss of tropospheric ozone well above the boundary layer was observed on three occasions at two coastal sites in Antarctica in spring 1995. Back trajectories show that the air sampled the boundary layer near the northern edge of the sea ice (1000 km from the coast) between 3 and 5 days previously. Enhanced BrO observed over sea ice in spring suggests that such ozone loss is common offshore, hence it may cause a small climate effect whose sign would create positive feedback, if sea ice reduced during warming.

1. Introduction

Sudden loss of ozone in the tropospheric boundary layer in polar spring is well known in the Arctic (Bottenheim *et al.*, 1986, Barrie *et al.*, 1988, European Commission 1997), and has been observed in the Antarctic (Wessell *et al.*, 1998). In the Arctic, there was usually a simultaneous increase in BrO in the boundary layer (European Commission, 1997). The origin of the BrO is disputed, with sea salt in snow (McConnell *et al.*, 1992) and recycling (catalytic) reactions on snow surfaces (Tang & McConnell, 1996) being suggested. BrO removes ozone via:

$$
\begin{array}{lll}
2\,\mathrm{Br} + 2\,\mathrm{O_3} & \rightarrow 2\,\mathrm{BrO} + 2\,\mathrm{O_2} & \\
\mathrm{BrO} + \mathrm{BrO} & \rightarrow 2\,\mathrm{Br} + \mathrm{O_2} & \\
\quad\text{or} & \rightarrow \mathrm{Br_2} + \mathrm{O_2} \;\text{ and }\; \mathrm{Br_2} + h\upsilon & \rightarrow 2\,\mathrm{Br} \\
\text{Net}\quad 2\,\mathrm{O_3} & \rightarrow 3\,\mathrm{O_2} &
\end{array}
$$

However, the removal rate of $\mathrm{Br_y}$ by other mechanisms is large enough that there is dispute whether the above reactions are sufficient to account for the observed removal rates, hence the suggestion of recycling.

In Antarctica, Kreher *et al.*, (1997, KR) and Wessell *et al.*, (1988) have observed less complete ozone loss in the free troposphere than in the boundary layer events in the Arctic. KR showed that tropospheric BrO was similarly enhanced during these events.

Unlike the Arctic, in Antarctica in spring the sea-ice edge is far from most observing sites and katabatic winds from the interior are common at the coast. Air from the interior is unlikely to be depleted in ozone, as clean ice and snow react slowly with ozone (Galbally & Roy, 1980). Hence few events of in-situ surface loss are observed at coastal sites, but much may occur offshore if the source of BrO is sea salt on ice or in aerosol.

In this paper, we expand on the observations of KR, show some new observations relevant to their events, calculate a range of back trajectories, examine the correlation between ozone loss and trajectory origin, and discuss the consequences.

2. Measurements

Ozonesonde profiles from McMurdo showed significant reductions at altitudes between 1 and 3.5 km on selected days in spring 1995 (KR), summarised in Table 1. This is above the boundary layer, which usually has a thickness of less than 0.5 km in much of Antarctica (Connolley, 1996). Not previously reported is a similar ozone-loss event in an ozonesonde profile from Neumayer on 2 August 1995 (Figure 1).

KR also reported enhanced BrO at Arrival Heights (a New Zealand station 3 km from McMurdo) coincident with the ozone reductions at McMurdo. Kreher *et al.* (1997b) demonstrated from the variation of slant column of BrO during the day on 15 and 16 September that the enhanced BrO must lie in the troposphere. On 25 August there was too little variation in solar zenith angle to demonstrate conclusively that the enhanced BrO was in the troposphere, but the enhancement was so large and sudden, and disappeared so suddenly, that tropospheric origin is very probable. A similar BrO-enhancement event occurred at Neumayer on 2 August 1995, when the slant column of BrO at 90° solar zenith angle reached 12×10^{14} molec cm^{-2}, compared to less than 2×10^{14} molec cm^{-2} on adjacent days (Kreher *et al.*, 1997b).

Temperature profiles from McMurdo, simultaneous with an ozone loss event (Figure 2), show small inversions at altitudes well above the boundary layer. Such inversions are characteristic of air masses of different origin, and suggested that calculation of back trajectories would be fruitful; the fact of ozone loss suggested they might reveal a surface origin for the depleted layers as occurs so frequently in the Arctic, as investigated by Wessel *et al.* (1998).

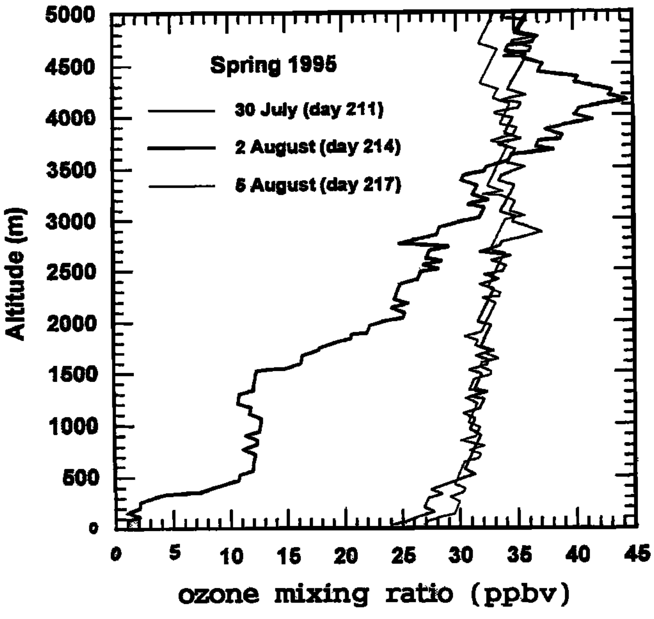

Fig. 1. Ozone profiles measured at Neumayer, Antarctica (71°S, 8°W) on selected days in July and August 1995. On 2 August, there is significantly less ozone below 3 km than on nearby days, and the amount of ozone loss is different in different layers.

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[1] British Antarctic Survey, NERC, Cambridge, UK

[2] National Institute for Water & Atmospheric Research, NZ

[3] University of Heidelberg, Germany

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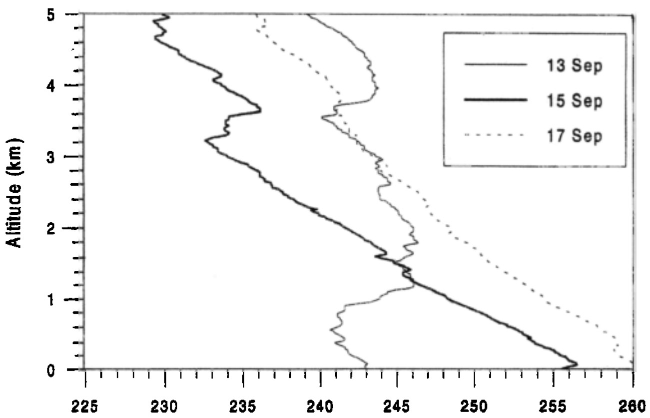

Fig. 2. Temperature profiles measured at McMurdo in Antarctica (78°S, 167°E) on selected days in September 1995. Tropospheric ozone loss was observed on 15 September. All profiles show inversions in the free troposphere, suggesting layers of air of differing origin. Many layers change their structure between adjacent days, suggesting frequent changes in origin.

3. Trajectory calculations

Back trajectories were calculated from ECMWF operational analyses, using Fortran code at the British Atmospheric Data Centre (BADC). The programs interpolated within the reduced resolution of 2.5° of the analyses stored at BADC. Mixing and errors were investigated by calculating trajectories ending at ±1° from the sites (Figure 3) and at 6-hour intervals. The 6-hour intervals also allowed us to bracket the times of sonde measurements: McMurdo measurements were made at about 03:30Z (25 Aug) and 02:00Z (15 Sep), Neumayer at about 10:50Z (2 Aug). Trajectories were calculated backwards for 5 days, in pressure co-ordinates (Figure 4). Results are summarised in Table 2.

4. Discussion

It is clear by eye from Tables 1 and 2 that some of the ozone loss at McMurdo and Neumayer correlates with trajectories which sampled the boundary layer near the sea-ice edge between 3 and 5 days previously, with varying degrees of mixing from continental or non-boundary layer air. Wessel *et al.* (1998) examined a similar event at Neumayer at 1 to 2 km on 24 Sept 1993 (day 267), and found that one trajectory arriving at 1 km had intersected the sea-ice boundary 3.5 days earlier.

Figure 5 illustrates the noisiness of the data. The intercept on the "number of trajectories" axis is 0.7 ±1.8 (*i.e.* includes zero). The correlation coefficient is 0.58, which is significant at the 97% level with 15 data points (*e.g.* Press *et al.*, 1986).

Complete loss of boundary-layer ozone is observed in the Arctic spring close to sea ice. If all of our trajectories ending at a given pressure intersected sea ice, then the air might be presumed to be unmixed and so fully depleted. If the vertical sampling interval of the trajectories were equal to the thickness of the boundary layer, Figure 5 would then have 10 out of 10 trajectories for complete ozone loss (30 to 36 ppbv), a slope of 0.033 ppbv^{-1}. Because the sampling interval is about 1 /km and the thickness of the boundary layer is about 0.5 km, we would expect a slope of about 0.017 ppbv^{-1}; the regression line of Figure 5 has a slope of 0.014 ±0.005 ppbv^{-1}, agreeing within the error bars.

Although the Antarctic snow-pack is now known to be a source of NOx in summer (Jones *et al.*, 2000), the source is thought to be stimulated by sunlight and so would be small in spring. The air above the Southern Ocean contains very little NOx (Ayers *et al.*, 1997). In a low NOx environment, typical ozone production rate is less than 0.55 ppbv/day in summer, less in the reduced UV of spring (Ayers *et al.*, 1997). Production at 0.55 ppbv/day corresponds to 20 days to recover.

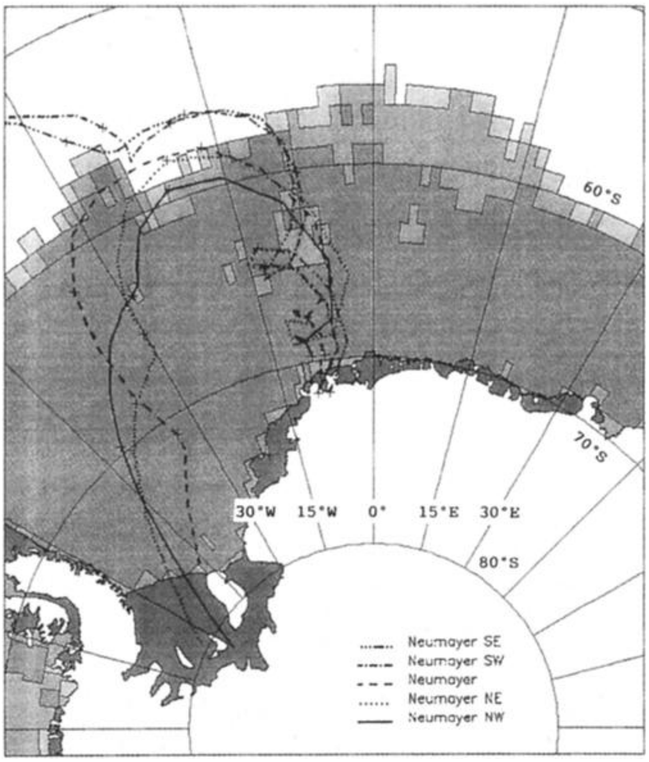

Fig.3. Calculated 5-day back trajectories arriving at Neumayer at 06:00Z on 2 August 1995 at 700 hPa. The darkest grey is shelf ice; three paler shades represent sea-ice cover from satellite data. Trajectories were also calculated to arrive at ±1° of the station, which could illustrate mixing between the two northerly trajectories and the three which originate closer to the continent.

Because some BrO was observed at the same time as the ozone-poor air, ozone loss will continue in transit. The possibility of such a long lifetime for BrO was established by McElroy *et al.* (1999), who observed an episode of major BrO enhancement in the Arctic free troposphere in spring. Together with the long recovery time via NOx, this suggests that an ozone deficit may continue for much longer than the 3 to 5 days we observed - at least a month. The deficit would then be further mixed into the free troposphere and would be sustained.

GOME measurements show a ring of doubled BrO around Antarctica between latitudes of 63° and 71°S in late August 1997

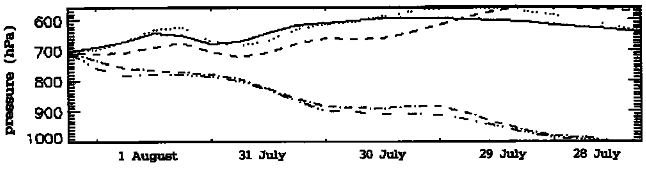

Fig. 4. Pressure (altitude) variations of the calculated back trajectories shown in Figure 3. The two which intersect the surface 4.7 days previously were the northerly trajectories in Figure 3. They passed close to the sea-ice edge at their most North-West plus symbols in Figure 3 (midnight on 28 July), after which their uplift started in the plot above.

Table 1. Ozonesonde profiles at McMurdo and Neumayer on selected days in spring 1995, relative to the free-tropospheric mean (22 Aug to 30 Sept at McMurdo, 30 July and 5 Aug at Neumayer): 30 ppbv at 0 km, increasing to 38 ppbv at 5 km at McMurdo and to 35 ppbv at 5 km at Neumayer.

		------------- O_3 difference (ppbv) ---------		
approx. altitude (km)	p (hPa)	(a) McMurdo 25 August	(b) McMurdo 15 Sept	(c) Neumayer 2 August
0	1000	-5	-10	-29
0.6	925	-5	0	-19
1.3	850	-10	-2	-19
2.9	700	0	-6	-5
5.1	500	0	0	0

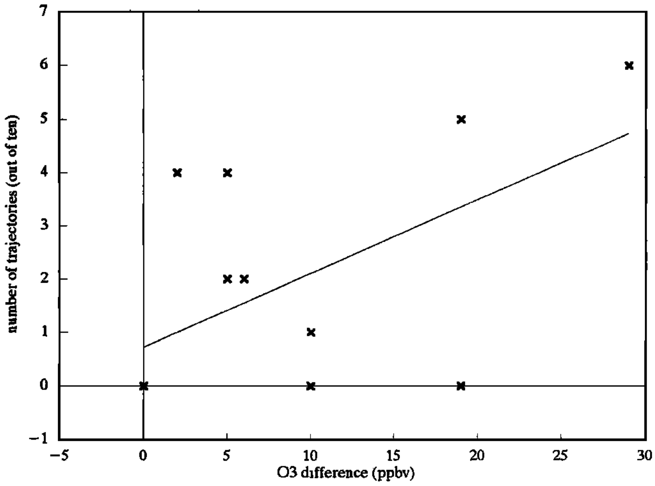

Fig. 5. Correlation between ozone deficits in Table 1 and numbers of trajectories sampling sea ice in Table 2, where ten trajectories close to the ozonesonde launch site and launch time are calculated backwards from each standard altitude. The line is the regression line with ozone deficit as the independent variable.

(Tanzi et al., 1999). This suggests surface ozone loss occurs throughout the sea ice in spring, unobserved because there are no surface sites in the sea ice and because satellite measurements of ozone changes in the unpolluted troposphere are difficult due to the large ozone amounts intervening in the stratosphere.

But if offshore ozone loss is indeed widespread in spring, why are so few events observed at coastal sites? Probably, the frequent storms of the Southern Ocean would mix ozone-poor air over a swath exceeding 1000 km horizontally and several km vertically (unlike our events where ozone-poor air was transported en masse and occupied 1 to 2 km vertically). The dilution would render the ozone loss unobservable, except as a deficit relative to models if models were to become sufficiently accurate. This thesis is supported by the wind speeds of less than 5 m/s in the trajectories during our events. From offshore at Neumayer (defined as from SW to E, clockwise) such light winds were only experienced for 4.3% of the time in August and September 1995 (courtesy http://www.awi-bremerhaven.de/MET/Neumayer/obsequery2.html). Furthermore, Kottmeier & Fay (1998) examined trajectories arriving at the surface at Neumayer, and found that in July to September from 1993 to 1995 the majority originated over the Plateau - origin from the sea-ice edge is rare.

Ozone is a more significant greenhouse gas in the free troposphere than at the surface because it is colder in the free troposphere. The typical loss observed (15 ppbv between 1 and 3 km) is about 3 DU. In a radiative-convective model (Lacis *et al.*, 1990) this gives a surface cooling of 0.02 K at mid-latitudes. A more recent radiative-convective model suggests 0.02 K for the global mean (Forster & Shine, 1997).

If the ozone loss is sustained as we argue above, and so later mixes to higher altitudes, these radiative-convective models suggest that the change could be up to 0.05 K, and so become significant by regional standards. A GCM calculation by Mickley *et al.* (2001) suggests that a well-mixed change of 3 DU would gve a radiative forcing of 0.10 W m^{-2} (equivalent to a surface temperature change of about 0.04 K). At high latitudes, these values would be expected to differ because of differences in amount of daylight, albedo, solar angle and ozone profile, but the three-dimensional radiative model of Kiehl *et al.* (1999) suggests a radiative forcing of 0.12 W m^{-2} (also equivalent to a surface temperature change of about 0.05 K) for a 3 DU change throughout the troposphere at 70° N in spring. A more exact calculation would need further studies with a GCM, but these existing calculations suggest that we can expect the magnitude of the temperature change to be of order 0.05 K.

If this natural process of ozone loss were reduced in an enhanced-CO_2 world because the sea-ice edge moved further southwards, so that the sea ice received less UV light for BrO production, a small positive feedback would result.

Table 2. Trajectories from McMurdo and Neumayer on selected days in spring 1995. Back trajectories were calculated from the indicated locations and ±1° latitude and longitude (5 trajectories from each location, time and pressure), and at the two standard times adjacent to ozonesonde measurements. The table quotes the number of trajectories out of ten which intersected 980 hPa over sea ice or over sea within 300 km of sea ice, the number of days (d) earlier that they did so, and the environment where they did so (M=marine, I2=two thirds sea ice).

approx. altitude (km)	end p (hPa)	n n traject.	n days	environ.	n n traject.	n days	environ.	n n traject.	n days	environ.
(a) 25Aug McMurdo		23Aug, 00+06Z			25Aug, 00+06Z			26Aug, 00+06Z		
0	1000	1	3d	I2	4	4d	I1toI3	1	5d	M
0 6	925	2	3d	I2orI3	2	4d	I1orI2	1	5d	M
1.3	850	0			1	4d	MorI1	0		
2.9	700	0			0			0		
5.1	500	0			0			0		
(b) 15Sep McMurdo		13Sep 00+06Z			15Sep 00+06Z			17Sep 00+06Z		
0	1000	0			0			0		
0.6	925	0			0			0		
1.3	850	0			4	3-5d	I2orI3	0		
2.9	700	0			2	4d	I1toI3	0		
5.1	500	0			0			0		
(c) 2Aug Neumayer		30Jul 06+12Z			2Aug 06+12Z			5Aug 06+12Z		
0	1000	0			6	3-4d	I2orI3	6	1d	I3
0.6	925	0			5	3-4d	I2orI3	3	1d	I3
1.3	850	0			0			0		
2.9	700	2	5d	I2orI3	2	5d	M orI1	0		
5.1	500	0			0			0		

5. Conclusion

Lower tropospheric ozone loss in the Antarctic spring persists for several days and mixes into the free troposphere. Loss may occur over large areas offshore, and may be sustained for very much longer than the 3 to 5 days we observe, causing a major deficit in regional free-tropospheric ozone. If so, we speculate that this would give rise to a regional cooling of the order of 0.05 K; if sea ice were reduced in an enhanced-CO$_2$ world, the feedback would therefore be positive.

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