Tropospheric ozone depletion events and air mass origin at Arrival Heights (Antarctica)

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by

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Tropospheric ozone depletion events and air mass origin at Arrival Heights (Antarctica)

Abstract: Surface ozone (O\textsubscript{3}) measurements made between 1997 and 2003 at Arrival Heights, Antarctica (77.8°S, 166.7°E), show sudden decreases in O\textsubscript{3} mixing ratios during Antarctic springtime. These low O\textsubscript{3} events are often correlated with elevated concentrations of bromine oxide (BrO). The air mass origin during these O\textsubscript{3} depletion events was investigated by calculating 5-day back trajectories. Trajectory analysis revealed that air masses had either contact with sea-ice, which was correlated with enhanced BrO columns, or were transported across the Antarctic continent, which led to O\textsubscript{3} depletion events without elevated BrO concentrations. In 1997-1998 less frequent high BrO events were observed at Arrival Heights probably due to increased sea ice coverage in the Ross Sea during these El Niño years.

1. Introduction

The phenomenon of sudden springtime ozone (O\textsubscript{3}) depletion events in Polar Regions has been known for a long time now. First discovered in the Arctic [Bottenheim et al., 1986, Barrie et al., 1988] low O\textsubscript{3} events were also observed in the Antarctic boundary layer [Kreher et al., 1996 and 1997; Wessel et al., 1998; Frieb et al., 2004]. Depletion occurs in spring when the frozen sea and the ground are almost entirely snow-covered. It can be observed from the surface up to ~1.5 km [Bottenheim et al., 2002], and occurs over periods of hours and days with concentrations as low as 0.05 ppb (parts per billion) compared with typical values of about 20 - 30 ppb. These events were correlated with elevated concentrations of filterable bromine (especially Br/BrO), giving the first indication, that reactive halogen species are involved in the destruction of O\textsubscript{3} [Barrie et al., 1988; Foster et al., 2001]. Later satellite observations confirmed that indeed large regions with elevated BrO concentrations exist over the polar regions in springtime [Wagner et al., 2001]. These observations showed particularly high BrO concentrations over sea-ice regions, reinforcing current ideas about the general nature of reactions leading to depletion and suggesting that sea-ice is implicated.

1.1 Ozone destruction mechanism

A mechanism for the sudden tropospheric O\textsubscript{3} depletion events is the autocatalytic release of BrO involving heterogeneous reactions on sea-salt surfaces [Fan and Jacob, 1992]. O\textsubscript{3} destruction happens in a mechanism involving several steps; the basic reactions are:

\begin{align*}
Br + O_3 & \rightarrow BrO + O_2 \\
BrO + HO_2 & \rightarrow HOBr + O_2 \\
HOBr + hv & \rightarrow OH + Br \\
BrO + BrO & \rightarrow 2Br + O_2 \\
& \rightarrow Br_2 + O_2 \\
Br_2 + hv & \rightarrow 2Br
\end{align*}

Removal of Br atoms from the chain occurs through reactions with organic compounds such as formaldehyde.
Catalytic reactions alone are not sufficient to explain the release of the observed high BrO mixing ratios (up to 50 ppt) within a few days. Autocatalytic heterogeneous reactions involving sea-salt aerosol, brine or frost flowers (see Section 1.2) are necessary for the release of photochemically active gases such as Br₂.

\[
\text{(HOBr)}_g \rightarrow \text{(HOBr)}_{aq} \tag{6}
\]

\[
\text{HOBr} + \text{H}^+_{aq} + \text{Br}^- \rightarrow \text{(Br}_2\text{)}_{aq} + \text{H}_2\text{O} \tag{7}
\]

\[
\text{(Br}_2\text{)}_{aq} \rightarrow \text{(Br}_2\text{)}_g \tag{8}
\]

Every HOBr has the potential to release two Br atoms to the gas phase. Under particular circumstances this mechanism can lead to an exponential growth of gaseous reactive bromine, the so-called bromine explosion [Platt and Lehrer, 1997; as cited by Frieß et al., 2004].

1.2 Origin of brominated species

While it is now reasonably certain that brominated species are derived from sea salt bromide, many aspects of the chemistry involved in this process are not fully understood; for example, how sea salt and bromine reach the snow surface and how they become activated to undergo the necessary reactions. Three major processes can be envisaged (Figure 2).

1. Frost flowers

Open water in the Arctic and Antarctic is soon covered with a thin layer of young ice. On the surface of this young ice, large crystals called frost flowers can grow (Figure 1). Frost flowers are thought to have a high specific surface area that would provide favourable sites for bromine activation [Rankin et al., 2002]. They also exhibit enhanced salinities and bromide ion concentrations of about three times that of bulk seawater [Perovich and Richter-Menge, 1994; Rankin et al., 2002]. Frost flowers are very fragile structures that can readily be windblown and redistributed to the snow surface, where they then constitute an available source of sea salt [Wolff et al., 2003]. Kaleschke et al. [2004] concluded from their modelling study that most of the observed O₃ depletion events could be correlated to frost flowers.

![Figure 1](image_url)

Figure 1. Frost flowers on sea ice covering a lead: Stellar dendrites of about 1 to 2 cm height on young sea ice (Courtesy of Stefan Kern, University of Hamburg). The photograph was taken at 75°58'N 25°34'E, 24 March 2003. The air temperature was about −18°C [Kaleschke et al., 2004].
2. Migration of brine
The second process is the upward migration of sea salt enriched brine from the sea ice to the snowpack. During freezing of sea water a highly concentrated brine solution exists on the surface of the growing ice crystals. It was suggested that by capillary forces this brine can travel up the snowpack [Perovich and Richter-Menge, 1994; Dominé et al., 2004]. Intrusions of basal brine up to 17 cm from the sea-ice surface were observed. However, the uppermost snow layer was not significantly affected by basal brine [Dominé et al., 2004].

3. Sea salt aerosol
The third process is the transport of sea salt aerosol generated by sea-spray to the snow. Over the ocean, sea-salt aerosols represent a huge reservoir for reactive halogens. Heterogeneous processes on the surface of the sea salt particle lead to the liberation of activated halogen species. However, in Polar Regions this process is probably not as efficient as the other two [Rankin et al., 2000].

Figure 2 illustrates all three possible processes.

![Figure 2](image)

Figure 2. Illustration of the three main processes suspected of supplying sea salt ions to marine snow: wind-transport of sea spray, upward migration from sea ice, and wind-blown frost flowers [Dominé et al., 2004].

Independent of the mechanism of how sea-salt bromine reaches the snowpack, it can be expected that air masses depleted in O_3 originate from the sea ice covered ocean. However, no clear relationship between surface O_3 depletion events and wind direction could be observed [Frieß et al., 2004]. This is not unexpected since the local wind direction at the Antarctic coast is of limited value for estimating source regions. Complex dynamical processes with large variability due to travelling cyclones and katabatic winds influence the wind direction at the Antarctic coast [Kottmeier and Fay, 1998]. Back trajectory calculations are a common technique used to determine the origin of an air mass.
2. Site, instruments and trajectory model

2.1 Site

Arrival Heights (77.8°S, 166.7°E) is located on the Hut Point Peninsula on Ross Island in the Ross Sea. The site can be reached from Scott Base and McMurdo Station, but it is remote from local atmospheric emissions. The laboratory is situated on the top of a hill at an altitude of 250 m above the sea ice allowing for good spectroscopic viewing horizons.

![Figure 4: Map showing Ross Island with Arrival Heights](image)

2.2 Ozone measurements

Surface ozone mixing ratios at Arrival Heights have been performed since 1997 with a commercial ozone monitor (Dasibi O₃ Monitor), which is based on short path UV absorption (71 cm path length in sample cell). In 2002, a second O₃ analyser was installed (Thermo Environmental Instruments, Model 49C). This analyser, which also operates with short path UV absorption, was run parallel with the Dasibi for one year in order to provide consistency for the O₃ time series. The surface O₃ measurements are available at a temporal resolution of 1 hour, an accuracy of 2 ppb and a detection limit of 1 ppb. Automatic calibrations are performed once a day.

2.3 Bromine oxide measurements

Ground-based observations of BrO slant column densities (SCDs) using zenith-sky UV/visible absorption spectroscopy have been made in the Antarctic at Arrival Heights since 1995. The SCD is the integrated atmospheric BrO concentration along the light path of the spectrometer. These observations have been supplemented with multi-axis measurements since 1999 and additionally during spring 2002 with BrO measurements using direct sunlight.

The latter two types of observation provide more accurate information on the tropospheric component of the BrO column due to the longer light path through the troposphere while zenith-sky observations are strongly weighted towards the stratospheric part of the BrO column. For details refer to Kreher et al. [1996] and Kreher et al. [1997].
2.4 Back-trajectory model

Three-dimensional 5-day back-trajectories were calculated every 12 hours (noon and midnight of each day) using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT_4) model developed by the National Oceanic and Atmospheric Administration (NOAA) and Australia’s Bureau of Meteorology [Draxler and Hess, 1997, and 1998]. The model can process various meteorological data sets; here NCEP re-analysed 6-hourly wind fields were used as input to the model. The trajectory model considers both horizontal and vertical components of motion. The back trajectories were calculated for end points located over Arrival Heights at three different altitudes: 100 m, 500 m, and 1500 m above ground level, at noon and midnight of each day.

3. Results

All surface O₃ measurements from Arrival Heights from 1997 until mid-2004 were plotted and visually examined for O₃ depletion events. These events occurred normally between the end of August and the middle of October. Graphs of the spring season surface O₃ mixing ratios together with zenith sky BrO column observations can be found in the appendix.

For these depletion events, 5-day back trajectories were calculated for noon and midnight of each day using the HYSPLIT4 model. Trajectories at 100, 500 and 1500 m were then examined for origin and height changes. On days when the O₃ mixing ratios decreased rapidly or when BrO concentrations were high, trajectories were calculated every 6 hours and additionally for the heights: 50, 1000 and 3000 m. Comparison between these three additional altitudes and the three standard altitudes 100, 500 and 1500 m revealed that the standard altitudes were representative of the general behaviour of the air masses. For higher clarity only the three standard heights will be presented in the illustrations in this report.

For ozone depletion events in the years 1997 to 2003 over 860 5-day back trajectories were calculated. Careful study of these trajectories in conjunction with O₃ and BrO concentrations revealed that three different cases can be distinguished. In the following, these three different cases will be presented and discussed. Initially, these cases will be described and discussed for the year 2000 (Section 3.1); the discussion of these findings is then extended to other years (Section 3.2).
3.1 Ozone depletion events and air mass origin in 2000

The year 2000 is an exceptional year regarding the frequency and characteristics of observed O$_3$ depletion events. Figure 5 shows surface O$_3$ mixing ratios and BrO columns for the spring of 2000. Marked with red circles are certain events that will be discussed in this paper.

![Surface O$_3$ mixing ratios and BrO columns in 2000](image.png)

**Figure 5**: Surface O$_3$ mixing ratios and zenith sky BrO columns observed at Arrival Heights during the spring season 2000 (adapted from K. Kreher). Time is given in Julian Days (JD) with 230 = 18 August and 300 = 27 October.

Three different situations were identified in the spring season 2000:

**Situation 1: Low O$_3$, high BrO**

On 24 and 25 August 2000 high BrO columns were observed at Arrival Heights. This was followed by a sudden decrease in surface O$_3$ mixing ratios on the 26 and 27 August. The first interesting fact to note is that there seemed to be a time lag of around one day between high BrO columns and low O$_3$ mixing ratios. Secondly it can be seen that event with low O$_3$ and high BrO are correlated with air masses that were coming from the sea and that had some sea-ice contact prior to their arrival at Arrival Heights as shown in Figure 6.
Figure 6: 5-day back trajectories from 25 to 27 August 2000. Trajectories are shown for three different heights: 100 m above ground (red), 500 m above ground (blue) and 1500 m above ground (green). The change in air mass origin, especially for the surface trajectory (red) can be clearly seen at the beginning and at the end of this depletion event. Note: Trajectories are calculated for UTC time, which lags 12 hours behind New Zealand Standard time.
Situation 2: Low $O_3$, average BrO

Some very distinctive $O_3$ depletion events were observed between 18 and 25 September 2000. On 20 September $O_3$ mixing ratios suddenly dropped to 1.2 ppb (the lowest concentration observed during the 6 years observation period). However, no increase in BrO columns was observed during this time in September. The 5-day back trajectories for this time are depicted in Figure 7.

![Figure 7: 5-day back trajectories from 18 to 21 September 2000. Trajectories are shown for the three different heights: 100 m, 500 m, 1500 m; the colour code is the same as in Figure 6. Air masses arriving at this time originate from inner Antarctica. The height diagrams show that layers are well stratified and hardly any mixing occurs.](image-url)
The air masses that reach Arrival Heights between 18 and 21 September 2000 have their origin on the polar plateau. From there they descend to Ross Island without any mixing. Layers are well stratified. During this time period none of the trajectories originated over the sea ice or had any extended contact with the sea ice.

**Situation 3: Average O\textsubscript{3} and average BrO**

In order to compare Situation 1 and 2 with a 'control case', a period of average O\textsubscript{3} mixing ratios and average BrO columns was identified and trajectory calculations for this time period performed. From 27 September to 7 October, O\textsubscript{3} mixing ratios varied between 25 and 33 ppb, which is an average concentration during this time of the year. Figure 8 shows 5-day back trajectories calculated for 1 to 6 October. These are representative of the whole time period.

Air masses arriving at this time at Arrival Heights had no extended sea-ice contact. Air masses from different heights had very different origins. Near surface trajectories originated predominantly from the inner part of the Antarctic continent. Atmospheric mixing as indicated by vertical moving air masses is more frequent than in comparison with Situation 2. However, a stratification of layers can be seen here as well. This situation will be assumed as the 'normal' situation that is characterised by average O\textsubscript{3} mixing ratios and average BrO columns.
3.2 Ozone depletion events and air mass origin in other years

Trajectory analyses were also performed for the years 1997, 1998, 2001, 2002 and 2003. Since the 1999 O₃ dataset was not complete, it was not included in this study. While events for the spring season 2000 were studied in detail, analysis of other years is at best preliminary. Further work is necessary.

O₃ depletion events during all years were identified; trajectories for 3 different heights (100, 500 and 1500 m) were calculated and visually examined for noticeable patterns. Most of the events appear to be similar to the described situations in 2000. However, some events are different from the model situations, they were grouped into a class of 'undefined' events.

In 1997 three minor O₃ depletion events were observed (12 - 14 September [not analysed due to missing meteorology data], 3 - 5 and 21 - 25 October), none of which coincided with significantly enhanced BrO columns. The lowest O₃ mixing ratio in this year was detected on 23 October with a value of 14 ppb. Trajectory analysis showed that air masses on 3 - 5 and 21 - 25 October had their origin the Ross Sea region. However, none of the trajectories was close to the sea ice surface (with the exception of trajectories that arrived on 24 October at 12 UTC at Arrival Heights). Since no elevated BrO columns were observed, this might indicate that O₃ destruction took place on the sea ice and that only halogen and O₃ depleted air parcels were transported to Arrival Heights.

In 1998 several short-term O₃ depletion events occurred between 13 and 26 September. On 13 - 14 and 20 - 24 September air masses originated at the other site of the Antarctic continent. They appeared to be well stratified suggesting that conditions similar to Situation 2 prevailed. Air masses that arrive on 15 - 19 September respectively 500 m above Arrival Heights have their origin in heights of 2000-3000 m over the Antarctic Plateau. These events were also called ‘undefined’ since neither Situation 1 nor Situation 2 conditions were present.

In 2001 one major O₃ depletion event happened on 14 - 16 September. This event was, preceded by elevated BrO concentrations on 13 September. Trajectories which that had sea ice contact arrived on 14 September; the O₃ depletion observed during this time can be characterised by Situation 1 conditions. However, the observed elevated BrO concentrations on 13 September cannot be explained at this stage.

In 2002 several O₃ depletion events with simultaneously high BrO columns were observed (29 - 31 August, 12 - 21 September). Nearly all trajectories had sea-ice contact prior to their arrival at Arrival Heights. This and elevated BrO columns indicate that Situation 1 conditions are present. O₃ depletion was much earlier than usually observed during 2002; elevated BrO columns and slightly decreased O₃ mixing ratios were detected as early as 22 August.

In 2003 several O₃ depletion events were observed, some coincided with elevated BrO columns (9 - 16 October), others not (18 - 23 September). On 1 - 3 September BrO concentrations were high, without significant O₃ loss. Air masses, which arrived on 18 - 21 September, originated in an area between South America and the Antarctic Peninsula. O₃ depletion but no elevated BrO was observed, indicating that O₃ destruction probably happened elsewhere and only air parcels depleted of O₃ were transported to Arrival Heights. The contrary situation was present in the beginning of September when high BrO columns but no O₃ destruction was observed. Trajectories during this time originated in the Ross Sea region in altitudes of more than 1500 m. No explanation is available for the depletion event on
9 – 16 October. Though BrO columns are elevated only few air masses with sea ice origin were found (sea ice influence on 13 October).

All findings are summarized in Table 1. The large number of 'undefined' events, especially in 2003 emphasises the need for further and more in depth investigations.

Table 1: Trajectory analysis for the years 1997-2003 (without 1999).

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4. Discussion

Analysis of over 860 5-day back trajectories revealed that several characteristic cases of tropospheric O₃ depletion events can be distinguished at Arrival Heights. In the discussion two cases are closer examined. One is situation 1 with low O₃ mixing ratios, above average BrO columns and trajectories that had sea-ice contact prior to their arrival at Arrival Heights. Situation 2 is characterised by low O₃ mixing ratios, average BrO columns and well-stratified layers with an air mass origin on the Antarctic continent.

4.1 Situation 1

It was suggested by several research groups that young sea-ice or frost flowers provide the necessary conditions for a bromine explosion leading to O₃ destruction [Dominé et al., 2004; Kaleschke et al., 2004; Hollwedel et al., 2004; Wolff et al., 2003; Rankin et al., 2002]. The trajectory analysis in this study showed that during times when enhanced BrO columns were observed at Arrival Heights, air masses had some sea ice contact in the last 5 days prior to their arrival. On the night of 25 August to 26 August 2000, O₃ mixing ratios decreased suddenly from 33 to 19 ppb. This was correlated with a change in air mass for the near surface layer from the Antarctic Plateau to the Ross Sea region as shown in Figure 6. O₃ mixing ratios stayed low until 27 August when the air mass origin changed again, this time from the Ross Sea to the Antarctic interior.

It was emphasized that frost flowers or young ice are essential prerequisites for the bromine explosion. The salinity of sea-ice that is more than one year old is too low for the release of reactive bromine [Lehrer, 1999; as cited by Frieß et al., 2004]. New ice in the Ross Sea region is frequently formed, in the vicinity of the Ross Sea Polynya. With a summer area of 396,500 km², the Ross Sea Polynya is the largest polynya to form regularly around Antarctica [Arrigo and van Dijken, 2003]. It extends along the entire ice shelf, driven by offshore winds that push the pack ice away from the coast, exposing surface waters to the cold atmosphere. Frazil ice is thus formed and herded downwind. In this process brine-rich water and frost flowers can form, providing high salinity and a large surface area for heterogeneous reactions. The Ross Sea Polynya is depicted in Figure 9. Though this illustration shows its extent in summer, the winter area is of 20,230 km² is still very large [Arrigo and van Dijken, 2003].

Figure 9: Sea-ice concentrations in the Ross Sea on 1 January 1999 derived from the DMSP SSM/I satellite [Nihashi et al., 2005]. The white area represents the Ross Sea Polynya.
Sea-ice concentrations for August 2000, when enhanced BrO columns and O$_3$ depletion were observed, are available from the National Snow and Ice Data Center (NSIDC) [Cavalieri et al., 1997]. Sea-ice coverage is measured using passive microwave instruments (Scanning Multichannel Microwave Radiometer (SMMR) and Special Sensor Microwave/Imager (SSM/I)) on board the Defence Meteorological Satellite Program (DMSP) satellites. Figure 10 shows Antarctic sea-ice concentrations from 25 to 27 August 2000. The Ross Sea Polynya is clearly visible as an area of reduced sea-ice concentration (marked by the white rectangle in Figure 10).

![Figure 10: Depicted on the left are total sea ice concentrations (SSMI/DMSP F13) [Cavalieri et al., 1997] for 25, 26 and 27 August 2000. The white rectangle highlights an area of reduced sea-ice concentration, the Ross Sea Polynya. On the right are 5-day back trajectories for the same days, same colour code as in Figure 6.](image)

It can be seen from Figure 10 that the trajectories on 25 and 26 August travel along the coast where reduced sea ice concentrations are represented by green and blue colours. If these regions of reduced ice coverage are also sources of young ice, it is likely that reactive bromine can be transported to Arrival Heights. Reaction of reactive bromine with O$_3$ will produce BrO (Reaction 1). Enhanced BrO columns of 11.5 to 13.5 \times 10^{14}$ molec cm$^{-2}$ were observed on 25 August 2000. Lowest O$_3$ mixing ratios were observed on the morning of 26 August.
BrO measurements are performed continuously during the day- and twilight period (solar zenith angle (SZA) < 95). However, for clarity only observations made at an SZA of 90 are used in this study. It seems that a time lag between BrO maximum and O₃ decrease exists, with O₃ lagging slightly behind BrO. This points towards more complex processes than the simple reaction between Br and O₃ (Reaction 1).

It was emphasized that transport can play a major role in O₃ depletion events [Spicer et al., 2002; Avallone et al., 2003; Tarasick and Bottenheim, 2002]. The question is whether reactive bromine is formed upwind and then transported to Arrival Heights where O₃ destruction takes place locally, or whether parcels of O₃-depleted air, containing also residual gas-phase halogens are transported.

The lifetime of reactive bromine (Br + BrO) is relatively short; it is in the order of a few minutes to half a day [Avallone et al., 2003]. Therefore transport of reactive bromine is only possible from the direct vicinity of Arrival Heights. Frieb et al. [2004] reported that surface ozone destruction is only observed if air masses at ground level originate from the sea ice surface. They assumed a threshold of 100 m. Below this height they believed the air would be well mixed and able to take up reactive bromine or sea salt aerosols from the sea ice. For the ozone depletion event from 25 to 27 August these conditions are fulfilled for the trajectories arriving at Arrival Heights on 26 August at 00 and 06 UTC. Even if air parcels travelling over the sea ice can transport BrO, they have to be below 100 m above the sea-ice in order to cause O₃ destruction, which could perhaps explain the observed time lag between BrO and O₃ concentration.

Another interesting aspect that can be inferred from Figure 10 is that the sea ice concentration in the Ross Sea region shows a surprisingly high daily variability. The area of the Ross Sea Polynya, as marked by the white rectangle, shows lower sea ice concentrations on 26 August. The day before, 25 August, was characterised by high wind speeds of up to 27 m s⁻¹ (meteorology data derived for Arrival Heights from the National Climate Database). Since the Ross Sea Polynya is mainly wind-driven, a major storm event can enlarge open water areas and enhance the proportion of young ice. Kreher et al. [1997] reported that high BrO events at Arrival Heights in 1995 coincided with high surface winds, blowing snow and poor visibility. High wind speeds also favour the inland transport of sea-salt aerosol and the distribution of fragile frost flowers creating conditions for further bromine explosions.

Since wind speed has been attributed as the major factor for the opening of the Ross Sea Polynya, changes in wind speed will influence the sea-ice concentrations in the Ross Sea region significantly. Recent investigations [Arrigo and Dijken, 2004] related the sea-ice extend in the Ross Sea region to the El Niño/Southern Oscillation (ENSO). During El Niño years, the low-pressure system that is typically stationed over East Antarctica shifts eastwards, eventually settling over the Ross Sea. This is related to diminishing wind speeds [Kwok and Cosimo, 2002; as cited by Arrigo and van Dijken, 2004] and may switch from an offshore to an onshore flow resulting in heavier sea ice conditions than average. During the El Niño year 1997-1998 the Ross Sea exhibited the greatest sea-ice cover, while during the La Niña year 1999-2000 the least sea-ice cover was observed [Arrigo and Dijken, 2004]. This coincides with BrO column measurements at Arrival Heights that show no significant enhancements during the years of 1997 and 1998, but 2 and 3 high BrO events in the years 1999 and 2000 respectively. This might suggest that the presence of enhanced BrO levels is related to open leads in the ice pack.
4.2 Situation 2

Situation 2 is characterised by low \( \text{O}_3 \) mixing ratios, average \( \text{BrO} \) columns and well-stratified layers with an air mass originating from the Antarctic continent. From 18 to 24 September 2000, severe \( \text{O}_3 \) depletion events occurred with \( \text{O}_3 \) mixing ratios dropping twice below 5 ppb. The lowest of all occurred on 20 September with 0.9 ppb. However, no enhanced \( \text{BrO} \) columns were observed during this time at Arrival Heights (Figure 5). Analysis of the 5-day back trajectories revealed that the air mass origin was on the Antarctic plateau and that the vertical motion was very small resulting in a well stratified air mass without atmospheric mixing (Figure 7).

No obvious source for reactive bromine on the Antarctic plateau could be identified. However, there is considerable evidence that long-range transport might play a major role in \( \text{O}_3 \) depletion events [Tarasick and Bottenheim, 2002; Barrie and Platt, 1997; Bottenheim et al., 1990]. Since the lifetime of \( \text{O}_3 \) is in the order of a week [Avallone, et al., 2003], 7-day back trajectories were calculated for the 18 to 25 of September 2000. The trajectories for 18 and 19 September are shown in Figure 11, together with \( \text{BrO} \) columns derived by the Global Ozone Monitoring Experiment (GOME) aboard the European research satellite ERS-2.

![Figure 11](image-url)
An area of extremely high BrO concentrations can be seen in the Weddell Sea region. The calculated 7-day back trajectories show an origin not far from the areas of elevated BrO. Transport of the resulting parcels of O₃ depleted air across the Antarctic continent within a week is possible. A detailed analysis of trajectories in the Antarctic lower troposphere showed that errors owing to atmospheric wind shear and interpolation errors of the vertical wind component may lead to position uncertainties of up to 1000 km after 5-days integration time [Kottmeier and Fay, 1998]. This uncertainty will increase for 7-day back trajectories; however, 7-day back trajectories have successfully been applied before [Lee et al., 2004]. Due to the large areas of elevated BrO a large scale effect is expected so that an uncertainty of the air mass origin of more than 1000 km seems acceptable.

![Figure 12: 7-day back trajectories arriving at Arrival Heights on the 18 September 12 UTC showing the days of travel, same colour code as in Figure 6](image)

The trajectory that reaches Arrival Heights on the 18 September 12 UTC at an altitude of 1500 m above the ground has its origin off the coast of Dronning Maud Land (Figure 12). On the 14 September it passes an area where the German Antarctic Station Neumayer (70°39'S, 8°15'W) is located. At Neumayer surface O₃ and BrO measurements were also performed. Results were recently published and show a remarkable coincidence with the trajectory calculations (Figure 13).
Enhanced BrO columns were observed at Neumayer Station on 12, 13 and 14 September, which is consistent with measurements by GOME (Figure 11). O₃ mixing ratios are as low as 5 ppb on some of these days. If an air parcel that was measured on 14 September at Neumayer Station is transported to Arrival Heights within one week this could explain low O₃ mixing ratios at Arrival Heights without elevated BrO columns. A condition for this to happen is that the air mass remains coherent and is not dispersed by atmospheric mixing. From the vertical motion of these trajectories a very stable stratification can be assumed. Similar results can be obtained for air masses arriving at Arrival Heights on 19 September at 12 UTC. To test the assumption of reduced mixing and limited vertical motion, trajectories for 1000, 3000 and 4000 m were additionally calculated (Figure 14).
Figure 14: Trajectories for 100, 500, 1000, 1500, 3000 and 4000 m height, arriving on 19 September 2000, 12 UTC at Arrival Heights.

Some form of disturbance to the stable layering can be seen prior to 14 September. However, after this only very limited vertical motion seem to happen. The area of high BrO concentrations is traversed on the 14th indicating that again O₃ depleted air could be transported across the whole Antarctic continent.
5. Conclusions and outlook

Over 860 5-day back trajectories during times of tropospheric O\textsubscript{3} depletion events were calculated and studied in order to find a correlation between these events and air mass origin. Trajectories were presented and discussed in detail for the year 2000 where three distinct situations could be identified.

Events with low O\textsubscript{3} and high BrO columns coincided with the arrival of air masses that had sea-ice contact (Situation 1). This indicates that similar processes of halogen activation, involving sea ice surfaces as proposed for Arctic and other Antarctic regions, also take place at Arrival Heights. Satellite derived sea-ice concentration images revealed areas of low sea ice coverage along the ice shelf. The Ross Sea Polynya might act as a source for young sea ice and frost flowers that are thought to be prerequisites for bromine explosion events. High wind episodes can lead to a remarkable high short-term variability of sea ice coverage, also fostering the formation of new ice.

Mainly changes in wind velocities lead to the correlation of ENSO and sea ice coverage of the Ross Sea. BrO measurements at Arrival Heights were below average during the El Niño years 1997-1998 when sea ice coverage in the Ross Sea region was heavier than usual. In contrast 2 and 3 high BrO events were observed in the La Niña years 1999-2000, when sea ice coverage was below average.

Low O\textsubscript{3} events in September 2000 showed average BrO columns and air masses originating in Dronning Maud Land on the other side of the Antarctic continent (Situation 2). The trajectory analysis indicated that vertical motion on a synoptic scale was very small and that the air mass remained coherent while the air was over the Antarctic Plateau. 7-day back trajectories linked high BrO concentrations in the Weddell Sea with the transport of O\textsubscript{3} depleted air masses across the Antarctic continent. O\textsubscript{3} and BrO measurements at the German Antarctic Base Neumayer in September 2000 showed high BrO columns and O\textsubscript{3} destruction 6 days prior to observed O\textsubscript{3} depletion events at Arrival Heights. It was speculated that by coincidence a quasi langrangian experiment was performed and that the same air mass was probed once at Neumayer and 6 days later at Arrival Heights.

The trajectory analysis for Arrival Heights during tropospheric O\textsubscript{3} depletion events revealed some interesting coherences; however, this analysis is preliminary. Trajectories for the year 2000 were investigated in detail. Other years were studied in a much more superficial way. Moreover, trajectories were only calculated for O\textsubscript{3} depletion events (with the exception of control case Situation 3) and were not studied with statistical tools. Calculation of back trajectories on a higher temporal and vertical resolution would be desirable for all times and not only during O\textsubscript{3} depletion events. The calculation of covariance ellipses as performed by Kottmeier and Fay [1998] could verify the results of the visual examination presented in this paper. Also, calculating the time that an air mass spent in direct contact with the sea ice [Frieß et al., 2004] would improve the understanding of heterogeneous halogen activation.

One prerequisite for a bromine explosion is a stable stratified boundary layer [Frieß et al., 2004; Tarasick and Bottenheim, 2002]. These meteorological conditions were not incorporated in this study. Information about atmospheric stratification would help to understand why elevated BrO and decreased O\textsubscript{3} mixing ratios cannot always be observed simultaneously.
In particular, the speculation that parcels of depleted air can be transported across the Antarctic continent needs more investigation. Surface $O_3$ measurements and vertical $O_3$ profiles from other Antarctic sites (especially South Pole and McMurdo) could shed some light on this unusual event.

In this paper sea-ice data from NSIDC was used in the form of images. However, a more accurate result could be achieved if the data is transferred to a common map grid and comparisons are made directly within this grid. This was beyond the scope of this project but will be pursued in future work.

In general, it can be said that this project is not yet finished and that more study and work is necessary. Some points were already raised in this outlook. Technical requirements such as computer software and data resources are established now. A preliminary trajectory analysis was performed and revealed some interesting aspects worth pursuing. However, in order to study this problem comprehensively and produce publishable results more work is needed.

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6. References


Fan, S. M., and D. J. Jacob (1992), Surface ozone depletion in the Arctic spring sustained by bromine reactions on aerosols, *Nature*, 359, 522-524


7. Appendix
O$_3$ mixing ratios and BrO columns during the spring seasons 1996 - 2003

(All illustrations by K. Kreher)