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**Br<sub>2</sub>, BrCl, BrO and surface ozone in coastal Antarctica**

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# Br<sub>2</sub>, BrCl, BrO and surface ozone in coastal Antarctica: a meteorological and chemical analysis

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## Abstract

There is much debate over the source of bromine radicals in the atmosphere that drives polar boundary layer ozone depletion events (ODEs), but there is strong evidence to suggest a source associated with the sea ice zone. Here we report the first high temporal resolution measurements of Br<sub>2</sub>, BrCl and BrO in coastal Antarctica, made using a Chemical Ionisation Mass Spectrometer (CIMS). Mixing ratios ranged from instrumental detection limits to 13 pptv for BrO, 45 pptv for Br<sub>2</sub>, and 6 pptv for BrCl. We find evidence for blowing snow as a source of reactive bromine both directly during a storm and subsequently from recycling of bromide deposited on the continental snowpack.

An unusual event of trans-continental air mass transport might have been responsible for severe surface ozone depletion observed at Halley. The halogen source region was the Bellingshausen Sea, to the west of the Antarctic Peninsula, the air mass having spent 3 1/2 days in complete darkness prior to arrival at Halley. We, further, identify an artefact in daytime BrCl measurements arising from conversion of HOBr, similar to that already identified for CIMS observations of Br<sub>2</sub>. Model calculations using the MISTRA 0-D model suggest a 50–60 % conversion of HOBr to Br<sub>2</sub>, and 5–10 % conversion to BrCl. Careful data filtering enabled us to use the halogen observations, in conjunction with the MISTRA model, to explore the temperature dependence of the Br<sub>2</sub>:BrCl ratio. We find evidence of a ratio shift towards Br<sub>2</sub> at temperatures below ~-21 °C, suggesting a relationship with hydrohalite (NaCl·2H<sub>2</sub>O) precipitation. This suite of Antarctic data provides the first analogue to similar measurements made in the Arctic.

## 1 Introduction

The first published measurements of tropospheric ozone depletion events (ODEs) were reported from Barrow, Alaska (Oltmans, 1981), followed by a more detailed study in March 1985 at Alert, Nunavut (Bottenheim et al., 1986). A study by Barrie et al. (1988) was the first to link these ODEs to bromine. Since the first observations of boundary

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layer (BL) ODEs in the Antarctic in the mid-1990s (Kreher et al., 1996; Wessel et al., 1998) and the coincident detection of BrO (Kreher et al., 1997), many more Antarctic field studies have taken place (Rankin et al., 2002; Wolff et al., 2003; Jones et al., 2006). Roscoe and Roscoe (2006) showed, through analysis of historical ozone data from Halley, that ozone depletion events were evident as far back as 1957/58.

During such events, ozone concentrations can fall from background amounts (typically 30–40 ppbv) to below instrumental detection limits (roughly a few parts per billion by volume, ppbv) within a few minutes and remain suppressed for on the order of hours to days. The chemical destruction of ozone is driven by halogens (especially bromine radicals) that have a source associated with the sea ice zone (e.g. Jones et al., 2006). Although our knowledge of ODEs has increased greatly since their discovery, some of the key processes involved are not yet fully understood (Simpson et al., 2007).

The atmospheric boundary layer in Antarctica is unique. It is separated from polluted air masses by the Southern Ocean (Simpson et al., 2007) and has been described as very clean (Wessel et al., 1998). A recent study by Hamilton et al. (2008) has highlighted the presence of a “chemical equator” near, but not coincident with, the ITCZ (Intertropical Convergence Zone) during the Austral monsoon season. This region of inhibited interhemispheric mixing makes it difficult for polluted air masses from Asia to contaminate the Antarctic troposphere, meaning conditions in Antarctica differ greatly from the Arctic which succumbs to “Arctic Haze” events (Barrie et al., 1989). The snowpack plays a key role in determining the chemical composition of the polar BL as it is a major source of trace gases (e.g. NO<sub>x</sub>, HCHO, H<sub>2</sub>O<sub>2</sub>) (Grannas et al., 2007). Many snowpack emissions cause an increase in OH radical concentrations thereby enhancing the oxidising capacity of the BL.

We now know that heterogeneous reactions lead to the activation of Br<sub>2</sub> and BrCl, via uptake of HOBr onto aqueous salt solutions /aerosol/ surface snowpack (Fickert et al., 1999), and it is widely accepted that bromine catalytic reaction cycles (the “bromine explosion”) are responsible for surface ozone destruction (Simpson et al., 2007 and references therein). There is still much debate over the source of bromine in the atmo-

sphere that drives ODEs, but there is strong evidence to suggest a source associated with the sea ice zone.

In 2007, year round measurements were made at the British Antarctic Survey station Halley (75°35' S, 26°19' W), in coastal Antarctica, using a Chemical Ionisation Mass Spectrometer (CIMS). During the austral spring and summer, the CIMS was configured to perform high resolution measurements of BrO, Br<sub>2</sub> and BrCl. In addition, concurrent measurements of surface ozone and local meteorology were made. This is the first such suite of measurements in Antarctica, and enables us to test our ideas of ozone depletion chemistry, and to contrast it with similar measurements made in the Arctic.

We present here the first high resolution measurements of Br<sub>2</sub> and BrCl made in Antarctica, and analyse them in terms of the broader meteorological situation at play during the onset and termination of ODEs. For contrasting case studies, we use the 0-D version of the MISTRA model (von Glasow et al., 2002) to investigate the different meteorological conditions present during ODEs, and the role halogens play in each event. In order to explore potential halogen source regions, we use the 0-D MISTRA model to consider emissions from a specific source region, identified using HYSPLIT air parcel back trajectories.

## 2 Experimental methods

### 2.1 Halley research station

Measurements were made at Halley, an Antarctic coastal research station operated by the British Antarctic Survey (BAS) and situated on the Brunt Ice shelf, 35 m above sea level. Halley is effectively located on a promontory that extends out into the Weddell Sea and of note, to the south and west is a large area of open water with associated newly-forming sea ice (Precious Bay). Although the prevailing wind direction throughout the year is easterly, traversing hundreds of kilometers of undisturbed snow, strong directional changes to westerlies/south-westerlies often occur, especially in the spring

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and summer months. This results in air masses with very different histories arriving at Halley.

The instruments used for this field campaign were housed in the CASLab (Clean Air Sector Laboratory) which is situated about 1 km south of the main base in an area that is exposed to minimal disturbance by vehicles or base pollution. A more detailed description of the Halley region and site layout is given in Jones et al. (2008).

The measurement campaign ran between January 2007 and February 2008. During the year, the CIMS operated alternately in two different modes; (i) a high pressure mode which measured, separately, OH and RO<sub>2</sub> and (ii) a low pressure mode measuring a variety of trace gases including HNO<sub>4</sub>, HCl, HNO<sub>3</sub>, SO<sub>2</sub>. In early spring, BrO, BrCl and Br<sub>2</sub> were added to the suite of low pressure measurements and included over the subsequent low-pressure mode measurement periods. The first direct sunlight at Halley at the end of the polar winter occurs on 13 August, thus the observations reported here almost all fall within the sunlit spring time.

Boundary layer conditions at Halley are well documented (Anderson and Neff, 2008), with a recent study by Jones et al. (2010) drawing attention to its importance in understanding the vertical extent of ODEs. The low vertical height, and stable BL structure found at Halley dominates during the Spring (August–October), giving us an opportunity to employ the marine boundary layer chemistry model (MISTRA), in 0-D form, to test our understanding of the chemical interactions occurring in coastal Antarctica.

## 2.2 CIMS instrument description

The CIMS technique has been used to detect many atmospheric trace gases (Huey et al., 1995, 1998, 2004; Berresheim et al., 2000; Leibrock and Huey, 2000; Sjostedt and Abbatt, 2008), but its use as a high-resolution halogen detector is of most importance to this present study. While the CIMS technique is well documented (e.g. Huey et al, 2004; Davis et al, 2004), we describe here features that were specific to the configuration at Halley.

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Within the CIMS ionisation region, a mixture of nitrogen doped with a few parts per million by volume (ppmv) of SF<sub>6</sub> was added to the flow tube after passing through a <sup>210</sup>Po ion source. This synthesised the reagent ion SF<sub>6</sub><sup>-</sup> in the ion source via associative electron attachment (Huey et al., 2004). The use of SF<sub>6</sub><sup>-</sup> as a reagent ion can be limited due to its slow second-order reaction with water (Huey et al., 1995; Arnold and Viggiano, 2001), but Slusher et al. (2001) have found that it is viable at dew points below ~-20 °C, such as are frequently found in polar regions.

Air was continuously sampled via a Teflon inlet tube, passing through this larger sample inlet to the smaller flow tube. From there, sampled air mixed with ions from the ion source where reactions can occur for the length of the flow tube. A small amount of air from the flow tube is sampled and then electrostatically accelerated by ion optics into the quadrupole mass filter and an ion detector which can detect multiple ion masses on each pass (Huey et al, 2004). Rate coefficients for the reactions of the molecules with SF<sub>6</sub><sup>-</sup> were measured relative to SO<sub>2</sub>, as the rate coefficient for reaction (1) has been measured over a wide range of pressures and buffer gases (Slusher et al, 2001). SO<sub>2</sub> is also used as the calibration gas for the instrument.



An automated 3-way sampling valve allows for switching between two flow paths, measurement mode and zero mode, without disrupting the required constant flow (maintained by the diaphragm pump). The measurement mode is equivalent to a straight Teflon tube, whereas the zero mode configuration draws ambient air through nylon wool (used as a scrubber) before entering the CIMS to obtain background signal values for SO<sub>2</sub>. The measurements were all corrected for humidity (due to the slow second-order reaction of SF<sub>6</sub><sup>-</sup> with H<sub>2</sub>O) and converted to mixing ratios.

CIMS data for Br<sub>2</sub> and BrCl measured in the Arctic (Foster et al., 2001; Spicer et al., 2002) have previously been published. A recent paper highlights a different CIMS technique for detection of BrO, Br<sub>2</sub>, and BrCl in the Arctic (Liao et al., 2011). Although

there are many similarities in the instrumental setup to that described here, the main difference to note is the use of  $I^-$  for the reagent ion, not  $SF_6^-$  as mentioned above.

## 2.3 Supporting observations

Surface ozone was measured at the CASLab, using a Thermo Electron model 49C, which has a detection limit of 1 ppbv, and a precision of 1 ppbv. Data were recorded as 1 min averages of 10 s observations. Measurements of wind speed and wind direction were carried out at the main station, some 1 km from the CASLab. The anemometers and vanes were located at a height roughly 10 m above the snow surface, and have an accuracy of about  $0.5 \text{ m s}^{-1}$  for wind speed and  $5^\circ$  for wind direction (König-Langlo et al., 1998). Data are also output every 1 min.

## 2.4 MISTRA, a box model specific description

To explore features in the CIMS observations, we used the 0-D version of the Marine Boundary Layer (MBL) chemistry model, MISTRA (von Glasow et al., 2002).

MISTRA includes descriptions of meteorology, microphysics and thermodynamics as well as a multiphase chemistry module (von Glasow et al., 2002). The chemistry module includes chemical reactions in the gas phase, in and on aerosol particles and takes into account transfer between the gas and aqueous phase. The complete set of chemical reactions incorporated in the multi-phase chemistry module are solved using the kinetic pre-processor (KPP) (Damian-Lordache., 1996) which allows easy changes of the chemical mechanism.

Dry deposition of gases onto the sea and snow surface is calculated using the resistance model described by Wesely (1989), and photolysis rates are calculated online by the method of Landgraf and Crutzen (1998).

Recent model developments have included an extension of the sulphur chemistry (von Glasow and Crutzen, 2004) and an improved description of the iodine aqueous phase and of the aqueous phase in general (Pecht et al., 2007). The recently-

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developed snow photochemistry module (Thomas et al., 2011) was not used in our calculations.

For our work, MISTRA was modified to be representative of Antarctic conditions. This was achieved by implementing measurements from Halley station, which include: aerosol size distribution and composition (Rankin and Wolff, 2003; Jaenicke, 1988), local meteorology (Anderson and Neff, 2008), and measurements of local chemical composition in the model.

## 2.5 Air mass histories and halogen flux derivation

Back trajectory analyses using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model were used, both to track air mass origins and to derive fluxes of halogens for the MISTRA calculations. HYSPLIT is available via the NASA ARL READY website ([www.ready.noaa.gov/ready/open/hysplit4.html](http://www.ready.noaa.gov/ready/open/hysplit4.html)) (Rolph, 2012; Draxler and Rolph, 2012). Back trajectories were driven by meteorological fields from the NCEP Global Data Assimilation System (GDAS) model output, and calculated using model vertical velocity at a resolution of  $1^\circ$  by  $1^\circ$ .

Information on sea ice concentration was obtained from the satellite-borne AMSR-E instrument (Sprenn et al., 2008) which provides information at a resolution of 6.25 by 6.25 km. Air parcel trajectories were superimposed over sea ice concentration maps and used to estimate the amount of time an air parcel had spent in the BL over areas of open water and leads, and thereby the halogen source region.

We initially calculated the flux of bromine (assuming all bromine was released as  $\text{Br}_2$ ) required to achieve the night-time maximum  $\text{Br}_2$  mixing ratio for a specific event. The  $\text{Br}_2$  was emitted into the model at a fixed rate for the period of passage over open water.

For each event, the flux of  $\text{Br}_2$  into the model required to reproduce the observed night-time  $\text{Br}_2$  mixing ratio was derived. The flux was a function of boundary layer height, as well as time spent over open water en route to Halley.

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### 3 Results and discussion

#### 3.1 Overall timeseries

Although this was a year round measurement campaign at Halley, the CIMS instrument was only configured for detection of Br<sub>2</sub>, BrCl and BrO for specific periods. Here we focus on a measurement period in austral spring, from 12 August to 18 September 2007, a time which, according to previous work at Halley (Saiz-Lopez et al., 2007), is likely to have active bromine chemistry. While the CIMS technique has been used in other field campaigns (Foster et al., 2001; Spicer et al., 2002; Neuman et al., 2010; Liao et al., 2011a, b), it is now acknowledged that day time observations of Br<sub>2</sub> suffer from an artefact (Neuman et al., 2010). For this reason we distinguish between day time and night time observations and only consider night time data for discussion unless otherwise stated (see also Sect. 3.2).

Table 1 gives details of instrument performance, as well as a summary of the halogen measurements. Figure 1 presents the time series of Br<sub>2</sub>, BrCl, BrO and O<sub>3</sub> together with concurrent meteorological observations of local wind speed/direction and local temperature for the entire measurement period.

There is considerable variability in the Br<sub>2</sub> and BrCl observations over the measurement period which is strongly linked to the prevailing meteorology and thus air mass origin. Relatively low and invariant Br<sub>2</sub> and BrCl is generally associated with easterly winds with continental origin and higher temperatures. The highest mixing ratios of both Br<sub>2</sub> and BrCl are associated with surface ozone depletion events and air arriving at Halley from across the sea ice zone to the west.

BrO exhibits a clear diurnal cycle throughout the period of CIMS observations, with night time minima around instrumental detection limits. The characteristic of the day-time maxima vary from day to day, being either (i) a single peak around noon, (ii) a broad flat-topped maximum also around noon, or (iii) double peaks with maxima shortly after sunrise and shortly before sunset. Such double-peaks were also observed by Pöhler et al. (2010) during springtime measurements in the Amundsen Gulf, but were

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not apparent in springtime observations at Barrow, Alaska (Liao et al., 2011a). The BrO maxima at Halley are less obviously correlated with local wind direction than are Br<sub>2</sub> and BrCl. For example, from 27 August until 1 September, while the prevailing wind direction is easterly (implying continental air) and Br<sub>2</sub> and BrCl show little variability, BrO maintains a diurnal structure, and with daily maxima ranging from ~2 ppbv to ~8 ppbv. The presence of a diurnal variability in BrO throughout this measurement period suggests some persistent background bromine/ozone chemistry is active during the day, even when air is not approaching from directly across the sea ice zone. The range of BrO mixing ratios during the measurement period (from instrumental detection limits to ~13 pptv, see Table 1), are in line with previous observations at Halley (Saiz-Lopez et al., 2007) made using a long-path DOAS. BrO mixing ratios showed little association with surface ozone mixing ratios, in contrast to observations in the Arctic (Neuman et al., 2010; Liao et al., 2011a). However, this lack of association is a function both of the limited range of [O<sub>3</sub>] in our data as well as very few observations at [O<sub>3</sub>] <5 ppbv. As Halley comes more under the influence of the sun, there is an increase in the occurrence of the BrO broad flat-topped maximum around noon, and the double peaks with maxima shortly after sunrise and shortly before sunset.

As has already been stated, there is considerable variability in the BrO, Br<sub>2</sub> and BrCl observations over the measurement period. For example there is a period on the 14–16 August where we see the presence of a large ODE (<10 ppb) and a consistently high Br<sub>2</sub> mixing ratio (>10 pptv), yet the diurnal cycle of BrO is maintained for the whole of the two day period. We also see the diurnal structure of BrO maintained (up to 8pptv) on the 30–31 August where air is arriving at Halley from the continent, there is no ODE and very little influence from either Br<sub>2</sub> or BrCl. At other times (e.g. 3–8 September) there are periods with lots of halogen and a high number of partial ODEs, nearly all of which are associated with periods when air has arrived at Halley from over the sea-ice zone.

## 3.2 Case study trajectory analyses

The variability in the data is clearly considerable and complex. In the following sections we explore in more detail the air mass history of three cases with contrasting characteristics, to understand better some of the drivers of the observed variability.

### 3.2.1 Case 1 – classic

Surface ozone depletion events have frequently been associated with stable boundary layers and low wind speeds (Jones et al., 2009). Such an event was observed at Halley on 6<sup>th</sup> and 7<sup>th</sup> September 2007 (see Fig. 2), and for the first time in Antarctica, additional observations of Br<sub>2</sub>, BrCl and BrO were available. The local wind direction throughout this two day period (~250°, see Fig. 1) indicates arrival of air at Halley from over Precious Bay, and is clearly shown by back trajectories for the same time period overlaid on a sea ice density map (Fig. 3). Relatively low wind speeds of around 15 knots (~7 m s<sup>-1</sup>), and very low temperatures (< -40°C) dominate during this period. On both days, ozone depletion started soon after sun rise, with ozone levels on the intervening night returning to background of roughly 28 ppbv after the sun set. This replenishment of ozone depleted air could be indicative of some vertical mixing brought about by changes in heat flux over Precious Bay between night and day (P. S. Anderson, personal communication, 2011). With the consistent wind direction, speed and temperature throughout the period it provides a well-constrained event against which to test the MISTRA model.

Figures 4a and b show both the observations of Br<sub>2</sub> and BrCl and their equivalent modelled output from MISTRA. It is immediately evident that there are several clear differences between the basic model output and the observations. Firstly, according to the model, day time mixing ratios of both Br<sub>2</sub> and BrCl should be zero, but the measurements show a clear day time signal for both Br<sub>2</sub> and BrCl. Secondly, the modelled increase in mixing ratios of both Br<sub>2</sub> and BrCl at the end of the day is delayed by roughly 3 h relative to the observations. Thirdly, observations of BrCl show a first peak around

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noon, followed by a larger peak around 18:00, while the model only simulates a single peak.

Photolytic lifetimes of  $\text{Br}_2$  and  $\text{BrCl}$  are on the order of a minute (Neuman et al., 2010). With such rapid photolysis, daytime concentrations of  $\text{Br}_2$  and  $\text{BrCl}$  would be zero in the absence of a large and persistent flux. Indeed, with its lifetime at high latitudes in spring of roughly 20–50 seconds (Neuman et al., 2010), maintaining the observed mixing ratio of  $\sim 4$  pptv around solar noon would require a flux of  $\text{Br}_2$  of  $6\text{--}8 \times 10^9$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  assuming a typical lower mixing layer height of 50 m (Jones et al., 2008). This is considerably larger than the flux found in other modelling studies (Toyota et al., 2011). It is also considerably larger than the flux we calculated of  $\sim 1 \times 10^8$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  required to reproduce the night-time halogen measurements at Halley during this event. However, laboratory tests (Neuman et al., 2010) have recently shown that CIMS measurements of  $\text{Br}_2$  suffer from an artefact arising from  $\text{HOBr}$  conversion most likely on the CIMS inlet. Output from the MISTRA model show diurnal variation in  $\text{HOBr}$ , with maxima during the day, and an absence at night. The CIMS measurements of  $\text{Br}_2$  from Halley indeed appear to exhibit a daytime interference. Furthermore the data also indicate that  $\text{BrCl}$  suffers from a similar interferent during the daytime.

In light of the potential  $\text{HOBr}$  interferent, model output was re-plotted, incorporating a proportion of modelled  $\text{HOBr}$  into both modelled  $\text{Br}_2$  and modelled  $\text{BrCl}$ . The results are shown in Figures 4c and 4d. It is immediately obvious that inclusion of this artificial “ $\text{HOBr}$  interferent” improved agreement between the model and measurements both in terms of the daytime signal, and in the timing of the night time increase. For  $\text{BrCl}$ , inclusion of the artefact yielded a double peak, as observed in the measurements. This approach suggests that the artefact within daytime  $\text{Br}_2$  measured with CIMS is of the order several tens of percent, while that for  $\text{BrCl}$  is less, at between 5 and 10 %.

Given the evidence for an interferent in the day time measurements of  $\text{Br}_2$  and  $\text{BrCl}$ , we have chosen to colour code all plots to differentiate day/night observations for  $\text{Br}_2$  and  $\text{BrCl}$  by showing all daytime measurements in black. In contrast, a recent assess-

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ment by Liao et al. (2011a) compared Arctic ground-based observations of BrO made using a CIMS with those made by a long-path DOAS. While the spatial distribution of BrO introduced some differences in the data, when air masses were well mixed, the two methods compared extremely well. Given that there was no sign of any interferent in the CIMS observations, we assume that all BrO observations made at Halley are interferent-free, and therefore do not distinguish between daytime and night-time results.

### 3.2.2 Case 2 – evidence for snowpack source?

It has previously been proposed that the coastal snowpack could be a direct source of bromine compounds (Simpson et al., 2007). For this to be the case, the snow would need to have an increased salinity, for example from sea salt aerosol deposition. At Halley, easterly airflow generally has a continental origin, occasionally skirting close to the sea ice edge. Such conditions provide a good test case for the snowpack source hypothesis.

For a 4 day period in September (Fig. 5) wind arrived at Halley from the east. Unusually there also appeared to be higher than background halogen concentrations, and some evidence of ozone depletion, associated with this “continental air”. Looking at air mass pressure from HYSPLIT back trajectories (Fig. 6) reveal that air arriving at Halley on days 1 and 2 had been in the BL since the previous day, whereas air arriving on days 3 and 4 had skirted the coast and had no direct contact with the snow surface or with sea ice.

Some key characteristics for this 4 day period are high wind speeds of 20–40 knots ( $10\text{--}20\text{ m s}^{-1}$ ) converging at the coast with temperatures consistently around  $-20^{\circ}\text{C}$  (only dropping on the last day). Looking at ECMWF Interim reanalysis data (image not shown) it is clear that there is a large storm system present over the Weddell Sea on days 1 and 2. These conditions of high winds associated with a storm in the Weddell sea have previously been associated with blowing snow (Jones et al., 2009). It has been suggested that salty blowing snow could act as bromine source (Yang et al.,

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2008), subsequently triggering the onset of ODEs. The evidence suggests that this is what we are seeing on these two days. Day 2 is associated with direct sea-ice contact (Fig. 6), and we observed higher  $\text{Br}_2$  ( $\sim 4$  pptv) and  $\text{BrO}$  ( $\sim 7$  pptv) on this day than on days 1, 3 and 4. As the wind speeds drop on days 3 and 4 there is a signal of 2–3 pptv of  $\text{BrO}$  present. It is possible that during the storm on the previous days, bromide was deposited on the continental snow (as discussed by Piot and von Glasow, 2008). Potentially this could account for the  $\text{BrO}$  signal of  $\sim 2$  pptv which we see on days 3 and 4. The air mass pressure (from the HYSPLIT back trajectories in Fig. 6) indicate that the air mass was much higher above the snowpack on days 3 and 4 than on the previous days. When combined with the drop in wind speed and likely reduction in aerosol loading aloft, we can understand why we observe a lower  $\text{BrO}$  mixing ratio at Halley on these days.

### 3.2.3 Case 3 – trans-continental transport of ozone-depleted air mass

On 21 August an intriguing event was observed at Halley, that was associated with the highest measured  $[\text{Br}_2]$  and  $[\text{BrO}]$ , and the lowest measured  $[\text{O}_3]$  throughout the entire period of observations. The  $\text{Br}_2$  maximum occurred around sun set, so is not likely to be dominated by the  $\text{HOBr}$  interferent. HYSPLIT back trajectories show that this ozone depleted air mass had arrived at Halley having travelled across the continent of Antarctica from the Bellingshausen Sea, to the west of the Antarctic Peninsula (Fig. 8). As shown by the lower panel of Fig. 8, the air mass had travelled in darkness for the previous 3 1/2 days with no possibility of photochemical reactions taking place. AMSR-E maps (not shown) show open water leads, with associated sea-ice formation processes, at the coastal edge of the Bellingshausen in the region of the air mass trajectories. This area could be seen as the main source of halogen for the air mass, but it could also be argued that the furthest edge of the sea is the greatest halogen source.

South Pole surface ozone data support this interpretation. Figure 9 shows surface ozone measurements from South Pole from the 1–31 August 2007. The outstanding

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feature is the drop in ozone that occurs on 19–20 August. The back trajectories shown on Fig. 8 indicate that the low-ozone air arriving at Halley on 21 August had passed South Pole on 19–20 August. While the drop in ozone at South Pole is modest compared with the Halley observations, the HYSPLIT trajectories suggest that the Halley air mass did not skirt the surface, but travelled at some height over South Pole. The drop in surface ozone of 7–8 ppb on 19 August is consistent with an ozone depleted air mass passing at height over South Pole with only a small influence being evident at the surface. Unfortunately no ozone sonde was launched from South Pole on this day, from which the profile of ozone could be seen. However, ECMWF Interim reanalysis data of temperature and specific humidity both show significant increases, consistent with passage of marine air. Further, Bromwich et al. (1996) suggest that passage of air across the continent along this route is not uncommon.

In an attempt to understand the halogen chemistry occurring during this period of darkness as the air mass traversed the continent, a run in MISTRA was set up to recreate the conditions the air mass would see (Fig. 10). An initial mixing ratio for Br<sub>2</sub> was set at 40 pptv, with the majority of the remaining parameters set for a typical Halley model run. HYSPLIT trajectories were used to determine the length of run required, and the influence of light on the air mass. The result is shown in Fig. 10. It is clear that the initial influence of sunlight is of vital importance in the partitioning of halogen species between Br<sub>2</sub> and BrCl, but it appears that the lack of photolysis thereafter effectively “stalls” the OD reactions. This implies that the majority of ozone depletion would have to occur prior to the period of darkness, although there is some photolytic influence near the end of the run. Although the model run does not show complete ozone depletion as observed at Halley, the run does highlight the transport of the depleted air mass in the dark. We also note that the final [Br<sub>2</sub>] and [BrCl] output from the model run is comparable to the halogen observations from Halley on the 21 August 2007.

### 3.3 Br<sub>2</sub> and BrCl observations

#### 3.3.1 Comparison with Arctic

High resolution ground-based measurements of Br<sub>2</sub> and BrCl were previously made in the Arctic as part of the Alert Polar Sunrise Experiment (PSE) (Foster et al., 2001; Spicer et al., 2002). These measurements were conducted prior to first direct sunlight, and continued for a further two weeks after polar sunrise. In the period following first direct sunlight, Br<sub>2</sub> mixing ratios at Alert ranged from instrumental detection limits to ~25 pptv (Foster et al., 2001), which is comparable to the mixing ratios observed at Halley. For the same period at Alert, reported BrCl mixing ratios ranged from the detection limit to ~35 pptv. This is considerably larger than was observed at Halley.

Laboratory data from Neuman et al. (2010) and results presented here have demonstrated that daytime CIMS measurements of Br<sub>2</sub> can be prone to an artefact from HOBr conversion; Sect. 3.2 of this paper, further, strongly suggests that a similar artefact exists also for BrCl. The PSE measurements were made using an atmospheric-pressure chemical ionisation tandem mass spectrometer technique, which, as pointed out also by Neuman et al. (2010) raises some questions about the validity of the daytime observations. While daytime observations are thus open to question, night time observations should not suffer from an HOBr conversion factor. Figure 5 of Spicer et al. (2002) present a short period of data that distinguishes between daytime and night-time observations, and where night time BrCl mixing ratios reach ~18 pptv. At no time during the Halley observations were BrCl mixing ratios greater than 6 pptv, and as this maximum was recorded at night, it is taken to be interferent-free, and thus not boosted by a contribution from HOBr. The data from Spicer et al. thus suggest that BrCl in the Arctic can reach considerably greater mixing ratios than were measured at Halley. Furthermore, the coincident Br<sub>2</sub> measured at Alert was only ~4 pptv, considerably less than BrCl, and yielding a Br<sub>2</sub>:BrCl ratio of ~0.2. In general, Foster et al. (2001) describe the measured ratio of BrCl to Br<sub>2</sub> in the air to be ~1, although we again note that the data may be subject to an interferent which is not taken into account in their analysis.

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Recent aircraft observations within the marine boundary layer over the Arctic Ocean also used a CIMS to measure halogens during the daytime flights (Neuman et al., 2010). Recognising the issue of an interferent, Br<sub>2</sub> observations are reported as “active bromine”, assumed to represent a lower limit of HOBr + Br<sub>2</sub>. BrCl data are also reported, but mixing ratios were rarely above the 2 pptv detection limit. No night-time BrCl measurements were made with which to compare the Foster et al. results and those from Halley.

### 3.3.2 Br<sub>2</sub>:BrCl ratio at Halley

Figure 11 shows the ratio of Br<sub>2</sub>:BrCl derived from the Halley night time observations, and colour coded for local wind direction. There is considerable variability in the ratio much of which is clearly associated with wind direction and thereby halogen source region. For example, from 10 September onwards, the ratio is very low, as are the mixing ratios of both Br<sub>2</sub> and BrCl (see Fig. 1), resulting from air masses with little/no sea ice contact. These air masses have little/no ozone depletion. On a very few occasions within these continental air masses, the Br<sub>2</sub>:BrCl ratio drops below 1. However, such low ratios can be attributed simply to the extremely low mixing ratios of both species (at or below stated detection limits) rather than a real measure of any chemistry at play. In contrast, air masses with an origin from the sea ice zone (e.g. 3 to 8 September) which are depleted in ozone and enhanced in halogens, have a Br<sub>2</sub>:BrCl ratio clearly in favour of Br<sub>2</sub>, and never less than 1, in contrast to the ratios reported for Alert (Foster et al., 2001) (although note observations from Sect. 3.3.1).

### 3.3.3 Temperature-dependence of Br<sub>2</sub>:BrCl ratio

The ratio of Br<sub>2</sub>:BrCl can be used as an indicator of the chemistry driving release of halogens from the surfaces of salty condensed phase substrate (brine slush, frost flowers, sea salt aerosol etc.). Various factors have been suggested to influence the ratio of Br<sub>2</sub>:BrCl in the air. Foster et al. (2001), attribute their reported ratio to Henry's

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Law coefficients, which at the temperatures of Arctic spring, render Br<sub>2</sub> less soluble (and therefore more easily lost to the atmosphere) than BrCl. The latter, by remaining in the surface film, would also be more likely to decompose through secondary reactions. These conclusions are in line with estimates by Sander et al. (2006), based on thermodynamic data, that at low temperatures (in the region 240 K) the equilibrium reaction BrCl + Br<sup>-</sup> ↔ Br<sub>2</sub>Cl<sup>-</sup> shifts to the right, enhancing the proportion of Br<sub>2</sub>Cl<sup>-</sup> in the system which then dissociates to release Br<sub>2</sub>. In laboratory studies of HOBr uptake on frozen NaCl/NaBr surfaces at temperatures between 253K and 233K, Adams et al. (2002) found that the ratio of product Br<sub>2</sub>:BrCl was a strong function of the reactant Cl<sup>-</sup>:Br<sup>-</sup> ratio in the condensed phase. They found for a mixed salt surface of similar composition to sea spray that the major product was Br<sub>2</sub>, and that BrCl was only produced when Br<sup>-</sup> was significantly depleted. The results were, similarly, interpreted as initial formation of BrCl which, given sufficient Br<sup>-</sup>, then reacted further to generate Br<sub>2</sub>. A further possible factor affecting the ratio of Cl<sup>-</sup>:Br<sup>-</sup> in sea ice surfaces is the precipitation of hydrohalite (NaCl·2H<sub>2</sub>O) once temperatures drop below ~-21°C (Koop et al., 2000).

To explore the sensitivity of the Br<sub>2</sub>:BrCl ratio to variations in temperature, we ran the MISTRA model at a range of polar spring temperatures, 233 K, 240 K and 247 K. The model chemistry includes the temperature-dependent reactions and Henry's Law coefficients described above, but does not include a description of hydrohalite precipitation. The calculated Br<sub>2</sub>:BrCl ratios for each 24 h run are shown in Fig. 12. The modelled ratio is clearly highly temperature-dependent, progressively shifting towards Br<sub>2</sub> as modelled temperatures are reduced. We note also that the calculated ratio is non-linear over this temperature-range, and that for all three temperature scenarios considered here, the ratio of gas-phase Br<sub>2</sub>:BrCl remains greater than or equal to 1.

The question then arises: can we see any signal of temperature-dependence in the Br<sub>2</sub>:BrCl ratio in the observations? To consider this, the Halley observations were filtered according to local wind direction to include only data with a direct sea ice zone origin (200° to 300°); to account for the HOBr interferent, only night time data were con-



to the temperature drop does not show evidence of increase in the Br<sub>2</sub>:BrCl ratio (see Fig 14c). While this is certainly not explicit proof of the role played by hydrohalite precipitation in determining the Br<sub>2</sub>:BrCl ratio, and thereby driving the “bromine explosion” reactions, these data are nonetheless consistent with this mechanism .

## 4 Summary

We have presented here the first suite of high resolution Br<sub>2</sub>, BrCl and BrO measurements made in Antarctica, as well as other supporting data. We have shown contrasting case studies, and used the 0-D version of the MISTRA model (von Glasow et al., 2002) to investigate different meteorological conditions present during ODEs, and the role halogens play in each event as a means of exploring drivers of variability observed in the data.

Our modelling assessments support the results of Neuman et al. (2010) that polar CIMS Br<sub>2</sub> observations are prone to an interferent from HOBr conversion, and further suggest that BrCl suffers from a similar interferent. The conversion of HOBr to Br<sub>2</sub>, and to BrCl, was quantified using the 0-D MISTRA model and found to be ~50–60 % conversion for Br<sub>2</sub> and 5–10 % conversion for BrCl. However, careful filtering of the observations to exclude daytime measurements allows us to explore the data. A similar suite of CIMS halogen observations from Alert were difficult to compare and contrast with those from Halley, due to the presence of the interferent in the day time CIMS halogen measurements. However, we find at Halley that Br<sub>2</sub> is always found in greater quantities than BrCl, but at Alert that is not the case.

In order to explore potential halogen source regions, we used the 0-D MISTRA model to consider emissions from a specific source region, identified using HYSPLIT air parcel back trajectories. An area of open water near Halley (Precious Bay) was the first region considered. As expected, when air arrived at Halley from over this sea ice zone, enhanced halogen and depleted ozone were observed.

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We then looked at an event where slightly elevated levels of BrO and depletion of ozone were associated with air of continental origin. HYSPLIT back trajectories indicated that the air mass had actually arrived at Halley having skirted the coast, and even contacting the sea ice, rather than passing over the continental snow pack. It was argued that a storm system over the Weddell Sea was a source of blowing snow which led to halogen activation and some depletion of ozone. Elevated BrO was also seen on the days after the high winds had dropped, suggesting deposition of halogen rich aerosol to the snow surface leading to halogen re-activation.

An intriguing event of trans-continental transport of ozone depleted air from the Bellingshausen Sea to Halley, coincided with the largest measured ODE in the observation period. Although the air mass spent several days in the dark while crossing the continent, it is possible that the bulk of ozone depletion could have occurred prior to this period of darkness and chemical arrest. An area of open water leads at the coastal edge of the Bellingshausen in the region of the air mass trajectories could be seen as the main source of halogen for the air mass, but it could also be argued that the furthest edge of the sea is the greatest halogen source.

A comparison of the Halley CIMS Br<sub>2</sub> and BrCl observations with those of a similar study in the Arctic highlighted a few differences in the respective measurements. We found that the [BrCl] observed in the Arctic was much greater than we find at Halley, and also that BrCl was even found at higher concentrations than Br<sub>2</sub> at time. This was not found to be the case at Halley. A chemical study of the measurements was carried out using MISTRA as a tool to explore the temperature dependence of the Br<sub>2</sub>:BrCl ratio. We find evidence of a ratio shift towards Br<sub>2</sub> at temperatures below  $\sim -21^\circ$ , suggesting a relationship with hydrohalite (NaCl·2H<sub>2</sub>O).

The data presented here have further highlighted the role of the sea ice zone as a source of halogens responsible for surface ozone depletion. Future work will use the 1-D coupled snow photochemistry model MISTRA-SNOW (Thomas et al., 2011), to study halogen activation. Identifying and investigating these processes is key in understanding what is responsible for triggering ODEs in polar regions.

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## References

Adams, J. W., Holmes, N. S., Crowley, J. N.: Uptake and reaction of HOBr on frozen and dry NaCl/NaBr surfaces between 253 and 233 K, *Atmos. Chem. Phys.*, 2, 79–91, doi:10.5194/acp-2-79-2002, 2002.

Anderson, P. S. and Neff, W. D.: Boundary layer physics over snow and ice, *Atmos. Chem. Phys.*, 8, 3563–3582, doi:10.5194/acp-8-3563-2008, 2008.

Arnold, S. T. and Viggiano, A. A.: Turbulent ion flow tube study of the cluster-mediated reactions of SF<sub>6</sub><sup>-</sup> with H<sub>2</sub>O, CH<sub>3</sub>OH, and C<sub>2</sub>H<sub>5</sub>OH from 50 to 500 torr, *J. Phys. Chem. A*, 105, 3527–3531, 2001.

Barrie, L. A., Bottenheim, J. W., Schnell, R. C., Crutzen, P. J., and Rasmussen, R. A.: Ozone Destruction and Photochemical-Reactions at Polar Sunrise in the Lower Arctic Atmosphere, *Nature*, 334, 138–141, 1988.

Barrie, L. A., Denhartog, G., Bottenheim, J. W., and Landsberger, S.: Anthropogenic Aerosols and Gases in the Lower Troposphere at Alert Canada in April 1986, *J. Atmos. Chem.*, 9, 101–127, doi:10.1007/bf00052827, 1989.

Berresheim, H., Elste, T., Plass-Dulmer, C., Eisele, F. L., and Tanner, D. J.: Chemical ionization mass spectrometer for long-term measurements of atmospheric OH and H<sub>2</sub>SO<sub>4</sub>, *Int. J. Mass Spectrom.*, 202, 91–109, 2000.

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- Bottenheim, J. W., Gallant, A. G., and Brice, K. A.: Measurements of NO<sub>y</sub> Species and O<sub>3</sub> at 82°N Latitude, *Geophys. Res. Lett.*, 13, 113–116, 1986.
- Bromwich, D. H., Carrasco J. F., and Turner J.: A Downward Developing Mesoscale Cyclone Over the Ross Ice Shelf During Winter, *Global Atmos. Ocean Syst.*, 4, 125–147, 1996.
- 5 Damian-lordache, V.: KPP – Chemistry Simulation Development Environment, MS thesis, University of Iowa, Iowa City, USA, 1996.
- Davis, D. D., Eisele, F., Chen, G., Crawford, J., Huey, G., Tanner, D., Slusher, D., Mauldin, L., Oncley, S., Lenschow, D., Semmer, S., Shetter, R., Lefer, B., Arimoto, R., Hogan, A., Grube, P., Lazzara, M., Bandy, A., Thornton, D., Berresheim, H., Bingemer, H., Hutterli, M., McConnell, J., Bales, R., Dibb, J., Buhr, M., Park, J., McMurry, P., Swanson, A., Meinardi, S., and Blake, D.: An overview of ISCAT 2000, *Atmos. Environ.*, 38, 5363–5373, doi:10.1016/j.atmosenv.2004.05.037, 2004.
- 10 Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (<http://ready.arl.noaa.gov/HYSPLIT.php>), NOAA Air Resources Laboratory, Silver Spring, MD, USA, 2012
- Fickert, S., Adams, J. W., and Crowley, J. N.: Activation of Br<sub>2</sub> and BrCl via uptake of HOBr onto aqueous salt solutions, *J. Geophys. Res.*, 104, 23719–23727 doi:10.1029/1999JD900359, 1999.
- 15 Foster, K. L., Plastridge, R. A., Bottenheim, J. W., Shepson, P. B., Finlayson-Pitts, B. J., and Spicer, C. W.: The role of Br<sub>2</sub> and BrCl in surface ozone destruction at polar sunrise, *Science*, 291, 471–474, 2001.
- Grannas, A. M., Jones, A. E., Dibb, J., Ammann, M., Anastasio, C., Beine, H. J., Bergin, M., Bottenheim, J., Boxe, C. S., Carver, G., Chen, G., Crawford, J. H., Domine, F., Frey, M. M., Guzman, M. I., Heard, D. E., Helmig, D., Hoffmann, M. R., Honrath, R. E., Huey, L. G., Hutterli, M., Jacobi, H. W., Klan, P., Lefer, B., McConnell, J., Plane, J., Sander, R., Savarino, J., Shepson, P. B., Simpson, W. R., Sodeau, J. R., von Glasow, R., Weller, R., Wolff, E. W., and Zhu, T.: An overview of snow photochemistry: evidence, mechanisms and impacts, *Atmos. Chem. Phys.*, 7, 4329–4373, doi:10.5194/acp-7-4329-2007, 2007.
- 20 Hamilton, J. F., Allen, G., Watson, N. M., Lee, J. D., Saxton, J. E., Lewis, A. C., Vaughan, G., Bower, K. N., Flynn, M. J., Crosier, J., Carver, G. D., Harris, N. R. P., Parker, R. J., Remedios, J. J., and Richards, N. A. D.: Observations of an atmospheric chemical equator and its implications for the tropical warm pool region, *J. Geophys. Res.-Atmos.*, 113, D20313, doi:10.1029/2008jd009940, 2008.
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- Huey, L. G., Hanson, D. R., and Howard, C. J.: Reactions of SF<sub>6</sub><sup>-</sup> and I<sup>-</sup> with Atmospheric Trace Gases, *J. Phys. Chem.*, 99, 5001–5008, doi:10.1021/j100014a021, 1995.
- Huey, L. G., Dunlea, E. J., Lovejoy, E. R., Hanson, D. R., Norton, R. B., Fehsenfeld, F. C., and Howard, C. J.: Fast time response measurements of HNO<sub>3</sub> in air with a chemical ionization mass spectrometer, *J. Geophys. Res.-Atmos.*, 103, 3355–3360, 1998.
- Huey, L. G., Tanner, D. J., Slusher, D. L., Dibb, J. E., Arimoto, R., Chen, G., Davis, D., Buhr, M. P., Nowak, J. B., Mauldin, R. L., Eisele, F. L., and Kosciuch, E.: CIMS measurements of HNO<sub>3</sub> and SO<sub>2</sub> at the South Pole during ISCAT 2000, *Atmos. Environ.*, 38, 5411–5421, doi:10.1016/j.atmosenv.2004.04.037, 2004.
- Jaenicke, R.: Aerosol Physics and Chemistry, In Landolt-Boernstein “Zahlenwerte und Funktionen aus Naturwissenschaften und Technik”, Springer, Heidelberg, Germany, V 4b, 391–457, 1988.
- Jones, A. E., Anderson, P. S., Wolff, E. W., Turner, J., Rankin, A. M., and Colwell, S. R.: A role for newly forming sea ice in springtime polar tropospheric ozone loss? Observational evidence from Halley station, Antarctica, *J. Geophys. Res.*, 111, D08306, doi:10.1029/2005JD006566, 2006.
- Jones, A. E., Wolff, E. W., Salmon, R. A., Bauguitte, S. J. B., Roscoe, H. K., Anderson, P. S., Ames, D., Clemishaw, K. C., Fleming, Z. L., Bloss, W. J., Heard, D. E., Lee, J. D., Read, K. A., Hamer, P., Shallcross, D. E., Jackson, A. V., Walker, S. L., Lewis, A. C., Mills, G. P., Plane, J. M. C., Saiz-Lopez, A., Sturges, W. T., and Worton, D. R.: Chemistry of the Antarctic Boundary Layer and the Interface with Snow: an overview of the CHABLIS campaign, *Atmos. Chem. Phys.*, 8, 3789–3803, doi:10.5194/acp-8-3789-2008, 2008.
- Jones, A. E., Anderson, P. S., Begoin, M., Brough, N., Hutterli, M. A., Marshall, G. J., Richter, A., Roscoe, H. K., and Wolff, E. W.: BrO, blizzards, and drivers of polar tropospheric ozone depletion events, *Atmos. Chem. Phys.*, 9, 4639–4652, doi:10.5194/acp-9-4639-2009, 2009.
- Jones, A. E., Anderson, P. S., Wolff, E. W., Roscoe, H. K., Marshall, G. J., Richter, A., Brough, N., and Colwell, S. R.: Vertical structure of Antarctic tropospheric ozone depletion events: characteristics and broader implications, *Atmos. Chem. Phys.*, 10, 7775–7794, doi:10.5194/acp-10-7775-2010, 2010.
- Konig-Langlo, G., King, J. C., and Pettre, P.: Climatology of the three coastal Antarctic stations Dumont d’Urville, Neumayer, and Halley, *J. Geophys. Res.-Atmos.*, 103, 10935–10946, doi:10.1029/97jd00527, 1998.

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Koop, T., Kapilashrami, A., Molina, L. T., and Molina, M. J.: Phase transitions of sea-salt/water mixtures at low temperatures: Implications for ozone chemistry in the polar marine boundary layer, *J. Geophys. Res.-Atmos.*, 105, 26393–26402, 2000.

5 Kreher, K., Keys, J. G., Johnston, P. V., Platt, U., and Liu, X.: Ground-based measurements of OClO and HCl in austral spring 1993 at Arrival Heights, Antarctica, *Geophys. Res. Lett.*, 23, 1545–1548, doi:10.1029/96GL01318, 1996.

Kreher, K., Johnston, P. V., Wood, S. W., Nardi, B., and Platt, U.: Ground-based measurements of tropospheric and stratospheric BrO at Arrival Heights, Antarctica, *Geophys. Res. Lett.*, 24, 3021–3024, doi:10.1029/97GL02997, 1997.

10 Landgraf, J., and Crutzen, P. J.: An Efficient Method for Online Calculations of Photolysis and Heating Rates, *J. Atmos. Sci.*, 55, 863–878, doi:10.1175/1520-0469(1998)055<0863:AEMFOC>2.0.CO;2, 1998.

Leibrock, E. and Huey, L. G.: Ion chemistry for the detection of isoprene and other volatile organic compounds in ambient air, *Geophys. Res. Lett.*, 27, 1719–1722, 2000.

15 Liao, J., Huey, L. G., Tanner, D. J., Brough, N., Brooks, S., Dibb, J. E., Stutz, J., Thomas, J. L., Lefer, B., Haman, C., and Gorham, K.: Observations of hydroxyl and peroxy radicals and the impact of BrO at Summit, Greenland in 2007 and 2008, *Atmos. Chem. Phys.*, 11, 8577–8591, 10, <http://www.atmos-chem-phys.net/11/8577/10/5194/acp-11-8577-2011>, 2011a.

20 Liao, J., Sihler, H., Huey, L. G., Neuman, J. A., Tanner, D. J., Friess, U., Platt, U., Flocke, F. M., Orlando, J. J., Shepson, P. B., Beine, H. J., Weinheimer, A. J., Sjostedt, S. J., Nowak, J. B., Knapp, D. J., Staebler, R. M., Zheng, W., Sander, R., Hall, S. R., and Ullmann, K.: A comparison of Arctic BrO measurements by chemical ionization mass spectrometry and long path-differential optical absorption spectroscopy, *Journal of Geophysical Research-Atmospheres*, 25, 116, 14, D00R02, doi:10.1029/2010jd014788, 2011b.

Martin, S., Yu, Y. L., and Drucker, R.: The temperature dependence of frost flower growth on laboratory sea ice and the effect of the flowers on infrared observations of the surface, *J. Geophys. Res.-Ocean.*, 101, 12111–12125, doi:10.1029/96jc00208, 1996.

30 Neuman, J. A., Nowak, J. B., Huey, L. G., Burkholder, J. B., Dibb, J. E., Holloway, J. S., Liao, J., Peischl, J., Roberts, J. M., Ryerson, T. B., Scheuer, E., Stark, H., Stickel, R. E., Tanner, D. J., and Weinheimer, A.: Bromine measurements in ozone depleted air over the Arctic Ocean, *Atmos. Chem. Phys.*, 10, 6503–6514, doi:10.5194/acp-10-6503-2010, 2010.

- Oltmans, S. J.: Surface Ozone Measurements in Clean Air, *J. Geophys. Res.*, 86, 1174–1180, 1981.
- Perovich, D. K. and Richtermenge, J. A.: Surface Characteristics of Lead Ice, *J. Geophys. Res.-Ocean.*, 99, 16341–16350, doi:10.1029/94jc01194, 1994.
- 5 Piot, M. and von Glasow, R.: The potential importance of frost flowers, recycling on snow, and open leads for ozone depletion events, *Atmos. Chem. Phys.*, 8, 2437–2467, doi:10.5194/acp-8-2437-2008, 2008.
- Poehler, D., Vogel, L., Friess, U., and Platt, U.: Observation of halogen species in the Amundsen Gulf, Arctic, by active long-path differential optical absorption spectroscopy, *Proc. Natl. Acad. Sci. USA*, 107, 6582–6587, doi:10.1073/pnas.0912231107, 2010.
- 10 Rankin, A. M., Wolff, E. W., and Martin, S.: Frost flowers: Implications for tropospheric chemistry and ice core interpretation, *J. Geophys. Res.-Atmos.*, 107, 4683 doi:10.1029/2002jd002492, 2002.
- Rankin, A. M. and Wolff, E. W.: A year-long record of size-segregated aerosol composition at Halley, Antarctica, *J. Geophys. Res.-Atmos.*, 108, 4775, doi:10.1029/2003jd003993, 2003.
- Rolph, G. D.: Real-time Environmental Applications and Display sYstem (READY) Website; <http://ready.arl.noaa.gov>, NOAA Air Resources Laboratory, Silver Spring, MD, USA, 2012.
- Roscoe, H. K. and Roscoe, J.: Polar tropospheric ozone depletion events observed in the International Geophysical Year of 1958, *Atmos. Chem. Phys.*, 6, 3303–3314, doi:10.5194/acp-6-3303-2006, 2006.
- 20 Saiz-Lopez, A., Mahajan, A. S., Salmon, R. A., Bauguitte, S. J. B., Jones, A. E., Roscoe, H. K., and Plane, J. M. C.: Boundary layer halogens in coastal Antarctica, *Science*, 317, 348–351, doi:10.1126/science.1141408, 2007.
- Sander, R., Burrows, J., and Kaleschke, L.: Carbonate precipitation in brine &ndash; a potential trigger for tropospheric ozone depletion events, *Atmos. Chem. Phys.*, 6, 4653–4658, doi:10.5194/acp-6-4653-2006, 2006.
- 25 Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., Burrows, J., Carpenter, L. J., Friess, U., Goodsite, M. E., Heard, D., Hutterli, M., Jacobi, H. W., Kaleschke, L., Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner, T., and Wolff, E.: Halogens and their role in polar boundary-layer ozone depletion, *Atmos. Chem. Phys.*, 7, 4375–4418, doi:10.5194/acp-7-4375-2007, 2007.
- 30

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- Sjostedt, S. J. and Abbatt, J. P. D.: Release of gas-phase halogens from sodium halide substrates: heterogeneous oxidation of frozen solutions and desiccated salts by hydroxyl radicals, *Environ. Res. Lett.*, 3, 045007, doi:10.1088/1748-9326/3/4/045007, 2008.
- Slusher, D. L., Pitteri, S. J., Haman, B. J., Tanner, D. J., and Huey, L. G.: A chemical ionization technique for measurement of pernitric acid in the upper troposphere and the polar boundary layer, *Geophys. Res. Lett.*, 28, 3875–3878, 2001.
- Spicer, C. W., Plastringe, R. A., Foster, K. L., Finlayson-Pitts, B. J., Bottenheim, J. W., Grannas, A. M., and Shepson, P. B.: Molecular halogens before and during ozone depletion events in the Arctic at polar sunrise: concentrations and sources, *Atmos. Environ.*, 36, 2721–2731, 2002.
- Spreen, G., Kaleschke, L., and Heygster, G.: Sea ice remote sensing using AMSR-E 89-GHz channels, *J. Geophys. Res.-Oceans*, 113, C02S03, doi:10.1029/2005jc003384, 2008.
- Thomas, J. L., Stutz, J., Lefer, B., Huey, L. G., Toyota, K., Dibb, J. E., and von Glasow, R.: Modeling chemistry in and above snow at Summit, Greenland – Part 1: Model description and results, *Atmos. Chem. Phys.*, 11, 4899–4914, doi:10.5194/acp-11-4899-2011, 2011.
- Toyota, K., McConnell, J. C., Lupu, A., Neary, L., McLinden, C. A., Richter, A., Kwok, R., Semeniuk, K., Kaminski, J. W., Gong, S. L., Jarosz, J., Chipperfield, M. P., and Sioris, C. E.: Analysis of reactive bromine production and ozone depletion in the Arctic boundary layer using 3-D simulations with GEM-AQ: inference from synoptic-scale patterns, *Atmos. Chem. Phys.*, 11, 3949–3979, doi:10.5194/acp-11-3949-2011, 2011.
- von Glasow, R., Sander, R., Bott, A., and Crutzen, P. J.: Modeling halogen chemistry in the marine boundary layer – 1. Cloud-free MBL, *J. Geophys. Res.-Atmos.*, 107, 4341, doi:10.1029/2001jd000942, 2002.
- von Glasow, R., and Crutzen, P. J.: Model study of multiphase DMS oxidation with a focus on halogens, *Atmos. Chem. Phys.*, 4, 589–608, doi:10.5194/acp-4-589-2004, 2004.
- Wesely, M. L.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, *Atmos. Environ.*, 23, 1293–1304, 1989.
- Wessel, S., Aoki, S., Winkler, P., Weller, R., Herber, A., Gernandt, H., and Schrems, O.: Tropospheric ozone depletion in polar regions – A comparison of observations in the Arctic and Antarctic, *Tellus B – Chem. Phys. Meteorol.*, 50, 34–50, 1998.
- Wolff, E. W., Rankin, A. M., and Rothlisberger, R.: An ice core indicator of Antarctic sea ice production?, *Geophys. Res. Lett.*, 30, 2158, doi:10.1029/2003gl018454, 2003.

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Yang, X., Pyle, J. A., and Cox, R. A.: Sea salt aerosol production and bromine release: Role of snow on sea ice, *Geophys. Res. Lett.*, 35, L16815, doi:10.1029/2008gl034536, 2008.

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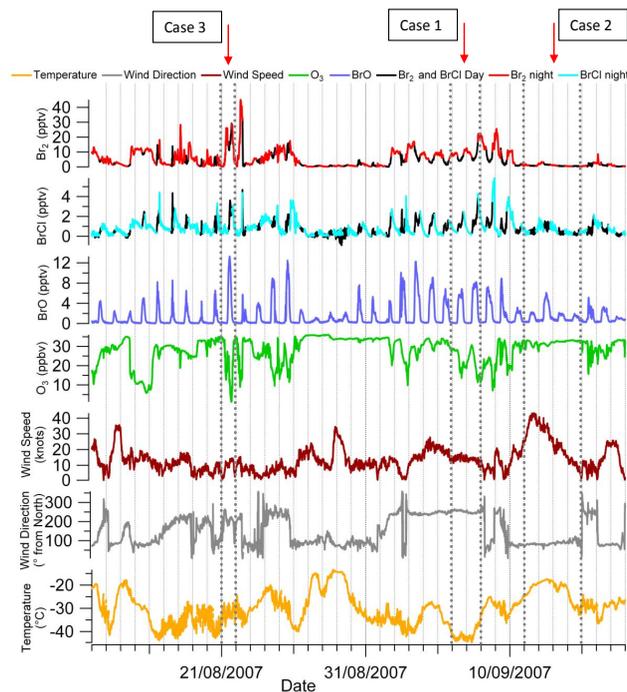
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**Table 1.** Calculated sensitivity and LOD for BrO, Br<sub>2</sub> and BrCl for the measurement period 12 August 2007–18 September 2007. Details of measurements (max, mean, and standard deviation) for Br<sub>2</sub> and BrCl are based on night observations only – see Sect. 3.2. Minimum values were below detection limits for all three species.

	BrO	Br <sub>2</sub>	BrCl
Sensitivity Hz.ppt <sup>-1</sup>	4.9	4.9	4.9
2σ detection limit for 10 min averages (pptv)	0.1	0.1	0.1
Maximum observed (pptv)	13.3	45	5.9
Mean night-time observation (pptv)	–	5.8	1.0
Standard deviation of 10 min averages (pptv)	2.2	6.0	1.0

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**Fig. 1.** Overview of measurements at Halley from 12 August to 18 September 2007. Br<sub>2</sub>, BrCl and BrO are shown as 10 min averages; for Br<sub>2</sub> and BrCl, day time observations are coloured black. Also shown are surface O<sub>3</sub> (10 min averages), local wind speed and direction, and local temperature.

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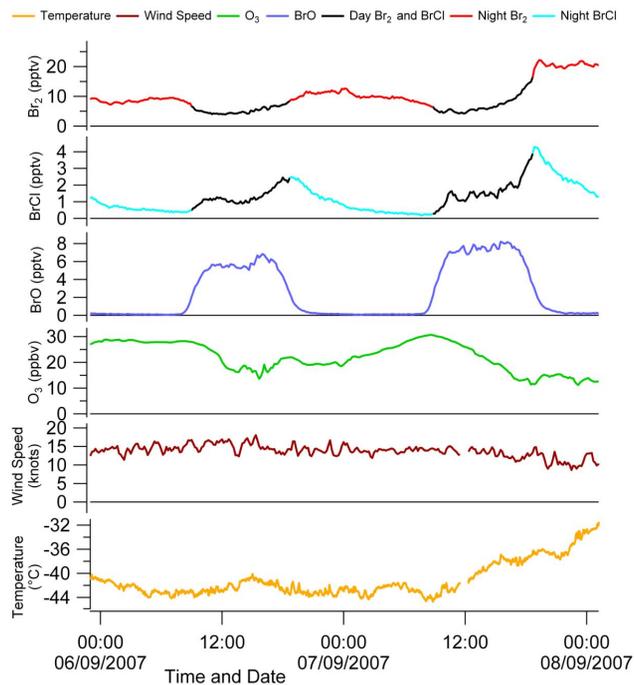
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**Fig. 2.** Wind speed, temperature, surface O<sub>3</sub>, and CIMS Br<sub>2</sub>, BrCl and BrO measurements from Halley on 6–7 August 2007. Br<sub>2</sub> and BrCl day time measurements are coloured black.

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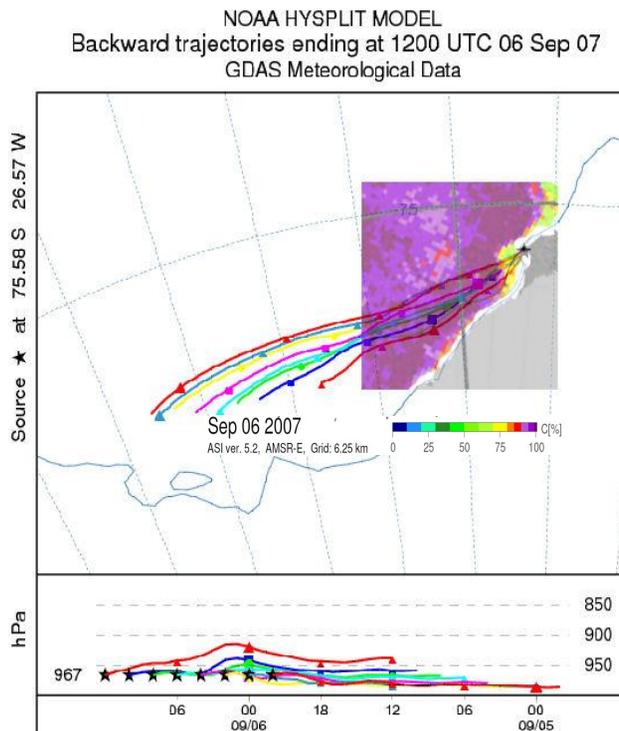
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**Fig. 3.** 2-day back trajectory showing air parcel history (location and atmospheric pressure) prior to arrival at Halley on 6 September 2007 overlaid on an AMSR-E image of percentage sea-ice cover. The star marks the position of Halley, and the triangles mark 6-hourly intervals.

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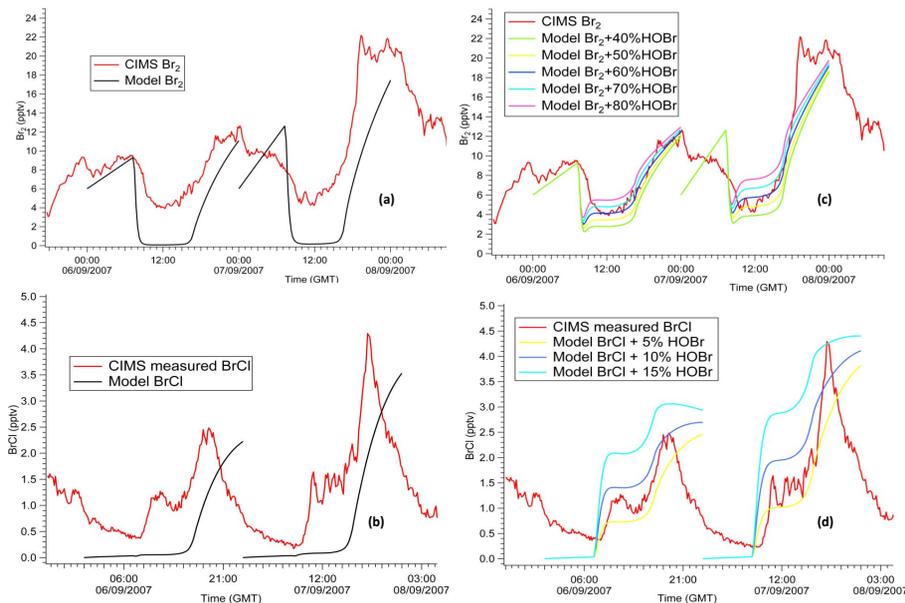
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**Fig. 4.** (a) comparison between measured (with CIMS) and modelled Br<sub>2</sub> for the 6 and 7 September 2007; (b) as for (a) but this time showing BrCl; (c) 40%, 50%, 60%, 70%, and 80% of model HOBr added to model Br<sub>2</sub>; (d); 5%, 10% and 15% of model HOBr added to model BrCl.

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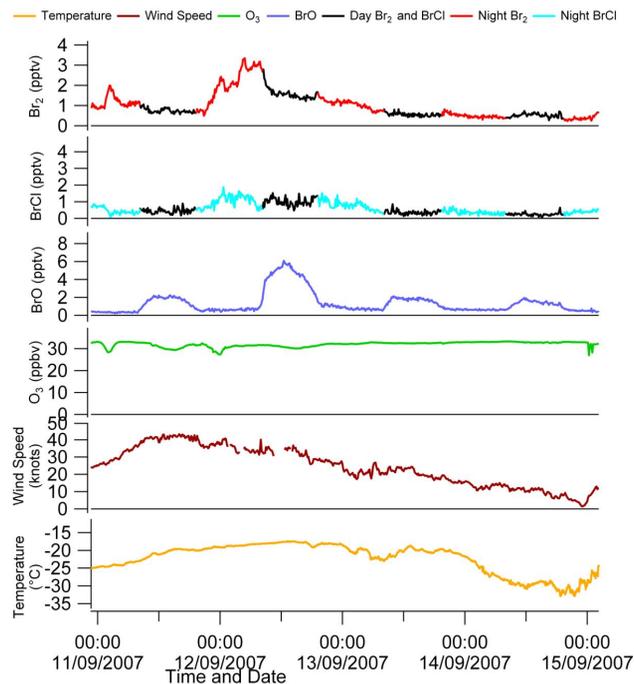
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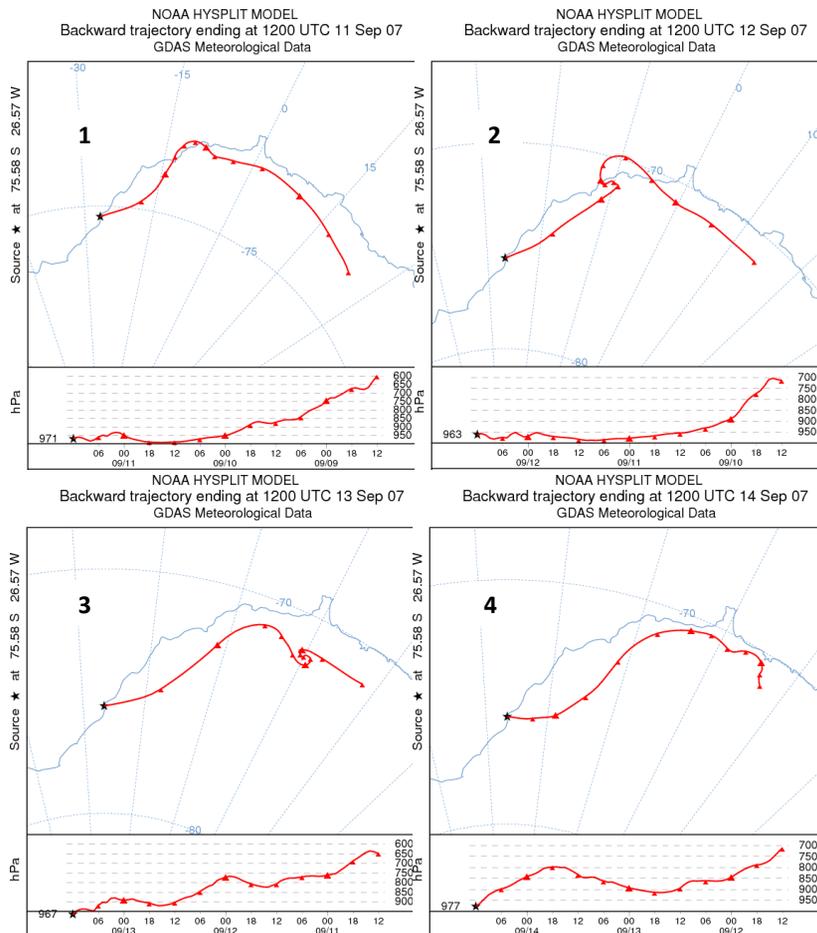


**Fig. 5.** Wind speed, temperature, surface O<sub>3</sub> and CIMS Br<sub>2</sub>, BrCl and BrO measurements from Halley on 11–14 September 2007.

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**Fig. 6.** HYSPLIT 3-day back trajectories from 1200hrs on 11–14 September 2007, with pressure as an indicator of height of the air mass.

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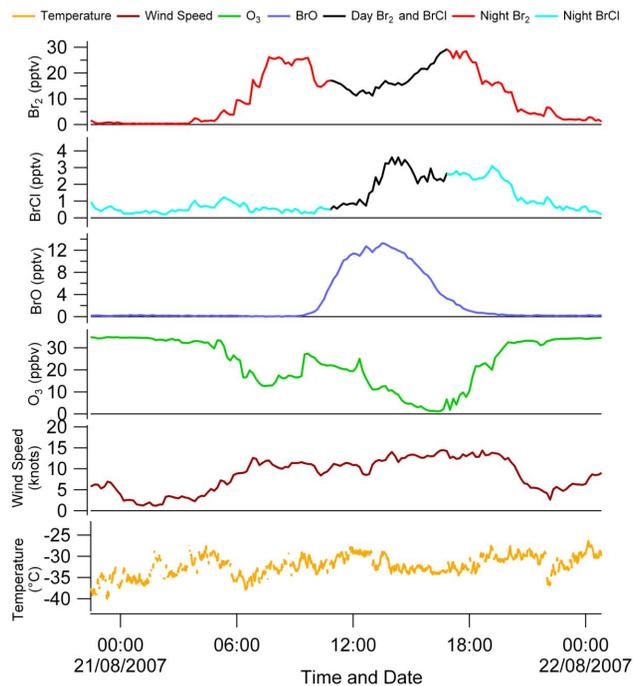
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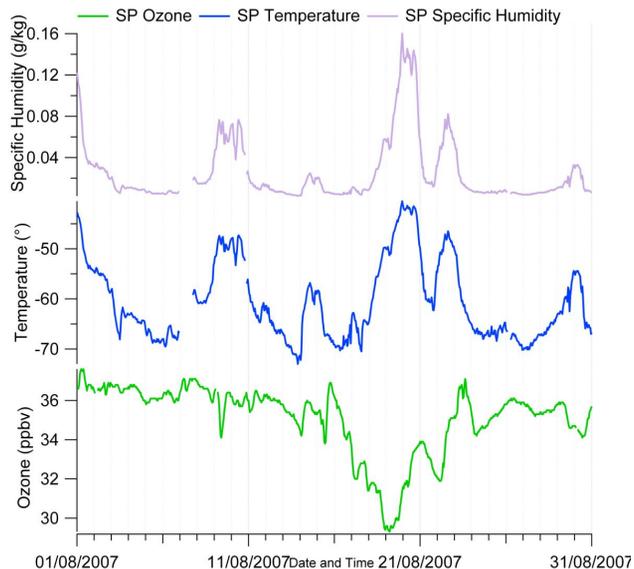
**Fig. 7.** Wind speed, temperature, surface O<sub>3</sub> and CIMS Br<sub>2</sub>, BrCl and BrO measurements from Halley on 21 August 2007.

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**Fig. 9.** South Pole surface ozone, temperature and specific humidity, from 1–31 August 2007.

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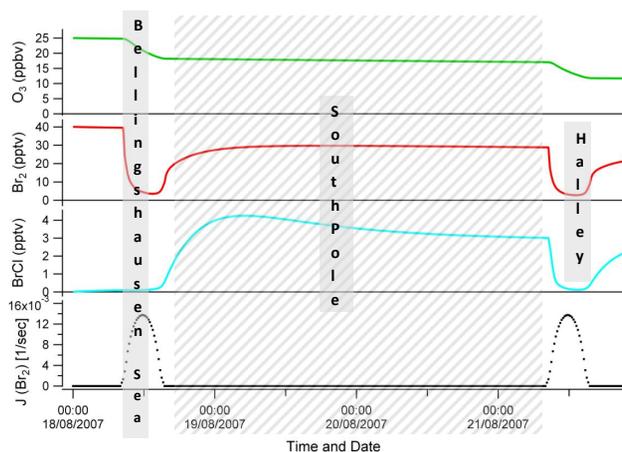
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**Fig. 10.** MISTRA 0-D run 4 days in length showing  $[Br_2]$ ,  $[BrCl]$ ,  $[O_3]$  and  $j$ rate  $Br_2$  model output. Only the first and last of those days under the influence of sunlight (darkness is highlighted with the gray box). Mixing ratio on the left axis, and time in hours since the start of the run along the bottom. The location of the air mass is highlighted at key stages of its transcontinental path.

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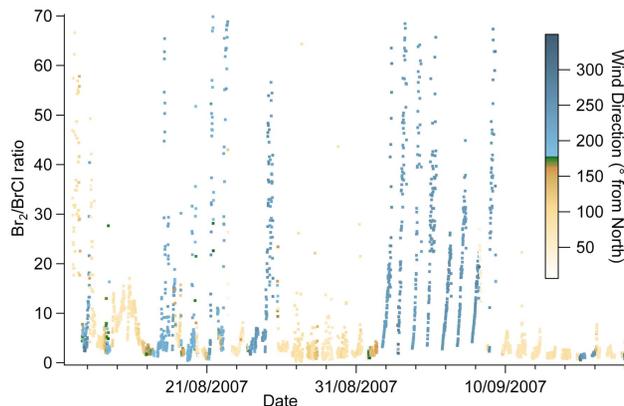
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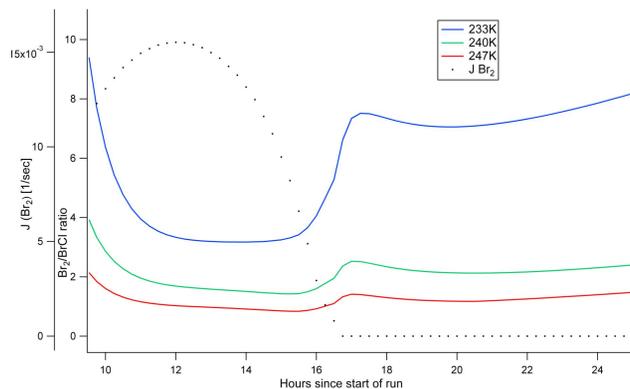


**Fig. 11.** Night time ratio of Br<sub>2</sub>:BrCl throughout the measurement period. The colour coding indicates local wind direction (browns indicate sea ice zone origin; greens indicate continental origin), emphasising the influence of air mass origin on the calculated ratio. At very low BrCl, the ratio is off the scale shown here.

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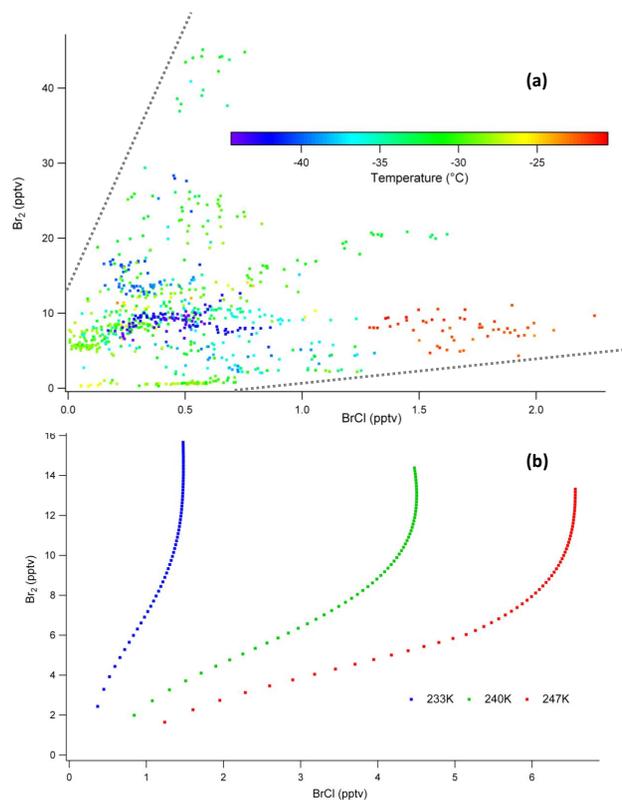
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**Fig. 12.** Modelled variation in  $\text{Br}_2:\text{BrCl}$  ratio at three temperatures relevant to polar spring. The black dots indicate  $J(\text{Br}_2)$ .

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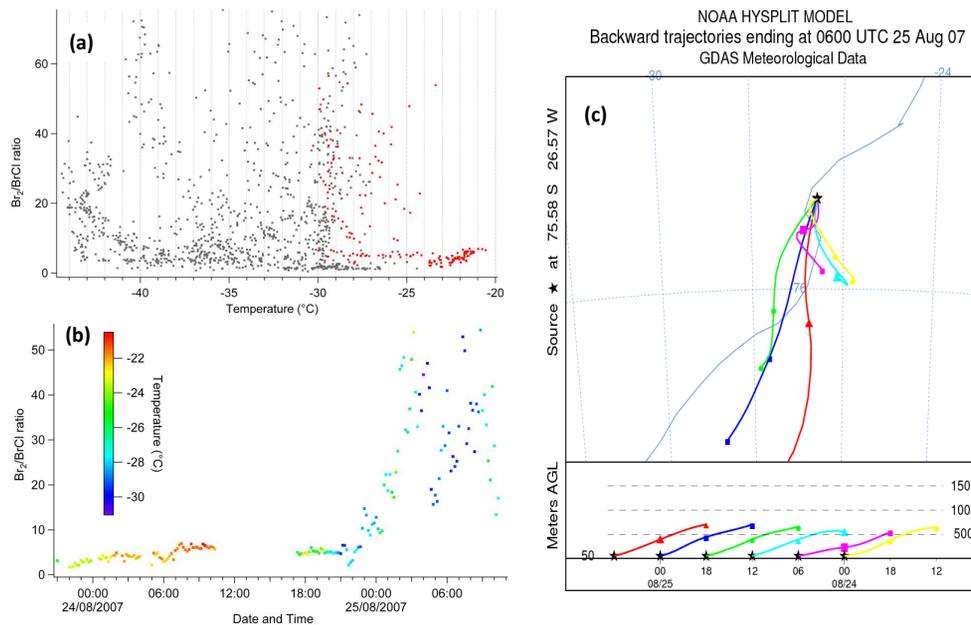


**Fig. 13. (a)** Observed Br<sub>2</sub> vs. BrCl, colour coded for temperature, for data arriving at Halley from directly across the sea ice zone (200°–300°) at night. **(b)** Modelled Br<sub>2</sub> vs. BrCl, colour coded for temperature.

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**Fig. 14.** (a) Measured Br<sub>2</sub>:BrCl ratio versus ambient temperature for observations filtered to include only air arriving directly from the sea ice zone (200° to 300°), and including only night time observations. The data in red are for a 2 day period (24–25 August) which is the only time in these filtered data when ambient temperatures were above −25 °C; (b) time series of Br<sub>2</sub>:BrCl ratio, colour coded for temperature, for the 24–25 August; (c) 12-h back trajectories arriving at Halley on 24–25 August. Air masses arriving at Halley during the early part of the period, when temperatures were ~−20 °C, had also passed over Precious Bay, the region of open water/newly forming sea ice, to the south west of Halley.