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Key Points:
- First measurements of OH and HO2 + RO2 made in Antarctica outside of summer show dependence (concentration and ratio) on sea ice contact
- Using a 0-D model, we are able to reproduce OH concentrations and HO, partitioning by including bromine chemistry
- This influence of sea ice-derived halogens is another factor to be accounted for when considering impacts of changing polar sea ice

Supporting Information:
- Supporting Information S1
- Data Set S1
- Data Set S2
- Data Set S3

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Influence of Sea Ice-Derived Halogens on Atmospheric HOx as Observed in Springtime Coastal Antarctica

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Abstract
We present first observations of OH and (HO2 + RO2) carried out in Antarctica outside the summer season. Measurements were made over 23 days in spring at the coastal Antarctic station Halley. Increases in concentrations were evident during the measurement period due to rapidly increasing solar irradiance, and clear diurnal cycles were present throughout. There were also notable differences in air mass composition depending on wind direction. Air masses that had traversed the sea ice zone had both higher concentrations of OH and a larger OH/(HO2 + RO2) ratio. We use steady state kinetic arguments and a 0-D box model to probe the chemical drivers. We find that differences in bromine chemistry, previously measured at Halley, are sufficient to account for the observed differences in OH concentration as well as the ratio. There is some evidence also that chlorine chemistry is influencing concentrations of RO2.

Plain Language Summary
The chemistry that goes on in the air is very sensitive to the presence of reactive trace gases, known as OH and the sum of HO2 + RO2. We have made the first measurements of these gases during the Antarctic spring, at the British Antarctic Survey station, Halley, in coastal Antarctica. We show that their concentrations vary regularly over the course of a day but generally increase over the 23 days of measurements as the Sun rises after the Antarctic winter. We also show that the concentrations of OH varied considerably from one day to the next, depending on the prevailing wind direction. At Halley, the wind tends to arrive at the station either after it has traveled over the continental snowpack (to the east of the station) or from over the sea ice zone (to the west/southwest of the station). When air has traveled over the sea ice zone, we know that it carries higher concentrations of halogen gases. We show that the higher concentrations of OH in air that has traversed the sea ice zone can be accounted for by the presence of bromine chemistry.

1. Introduction
Evidence for active HOx (OH + HO2 + RO2) chemistry during summertime in the polar regions is clear from previous field campaigns. Outstandingly high concentrations of HOx have been observed at Antarctic Plateau stations. At South Pole station, of the order 2 x 10^6 molec/cm^3 for OH were reported by Mauldin et al. (2001) and 7 x 10^7 molec/cm^3 for the sum of HO2 + RO2 (Mauldin et al., 2004). At Concordia station, daily median values of 3.1 x 10^6 molec/cm^3 for OH and 9.9 x 10^7 molec/cm^3 for HO2 + RO2 have been reported (Kukui et al., 2014). The high concentrations are driven predominantly by photochemical emissions of precursor gases (H2O2, HCHO, and potentially also HONO) from the extensive polar snowpack (Chen et al., 2004; Kukui et al., 2014); HOx repartitioning reactions involving NOx, which also has a snowpack source (Jones et al., 2000; Jones et al., 2001), further enhance OH concentrations. The effect of snowpack emissions is amplified by a number of factors including the high altitude (and thus solar irradiance) and tendency for the existence of shallow stable boundary layers (Anderson & Neff, 2008). At coastal stations, while HOx concentrations are more moderate, the presence (Bloss et al., 2007; Kukui et al., 2012) or absence (Jefferson et al., 1998) of snowpack emissions remains a key driver of summertime HOx concentrations.

With its very short lifetime, OH concentrations are sensitive both to local sources and radical cycling reactions, and indeed, a tight coupling between HOx, NOx, and halogen chemistry has been demonstrated for summertime conditions in Antarctica, albeit a time of year when halogen concentrations are relatively low (Bauguitte et al., 2012; Bloss et al., 2007; Bloss et al., 2010; Kukui et al., 2014). HO2 and RO2 are produced by oxidation of organic compounds, including by chlorine radicals (e.g., Monks, 2005), as well as from formaldehyde, by photolysis or via reaction with bromine radicals.
Here we present first observations of OH and HO\textsubscript{2} + RO\textsubscript{2} carried out in Antarctica outside the summer season. We focus on the springtime, a time when ambient temperatures, water vapor, and NO\textsubscript{x} concentrations are low, solar irradiance is limited, but halogen chemistry is at its annual maximum. Specifically, we present observations from 22 September 2007 to 13 October 2007.

2. Experimental

2.1. Measurement location

The measurements were carried out at the British Antarctic Survey’s Halley V research station (75°35’S, 26°39’W), in coastal Antarctica. Boundary layer chemistry and meteorology at Halley are documented through a series of field campaigns. Springtime surface ozone depletion events are regularly observed (Jones et al., 2006; Jones et al., 2009; Roscoe & Roscoe, 2006), and active halogen chemistry has been reported (Buys et al., 2013; Saiz-Lopez et al., 2007, 2008). A key characteristic of Halley is the bimodal nature of the prevailing wind direction; for much of the time air arrives at Halley from the east, having been exposed to extensive fetch of surface snowpack across the continent. In contrast, air arriving from the west/south west has traversed the sea ice zone, with its associated enhanced salinity, which brings a chemical composition with elevated concentrations of halogens, including bromine compounds (e.g., Buys et al., 2013). Examples of this bimodal behavior, as demonstrated in the first 5 days of our measurements, is given in Figure S1 in the supporting information. This switch in wind regimes enables the assessment of air masses with different embedded characteristics. In this study, we use this knowledge of air mass characteristics to probe the target HO\textsubscript{x} data. Note that at Halley, local noon occurs at 13:44 pm.

2.2. Chemical Ionization Mass Spectrometer

Throughout 2007, a Chemical Ionization Mass Spectrometer (CIMS) was deployed at Halley to measure a range of trace gases. To measure inorganic bromine compounds the instrument was operated at “low pressure”; the “high pressure” operation enabled detection of OH and HO\textsubscript{2} + RO\textsubscript{2}, which we report here. Details of instrument operation are given in the supporting information. Switching between high- and low-pressure modes takes of the order several days; the CIMS therefore measured bromine compounds from 12 August 2007 to 17 September 2007 (Buys et al., 2013), and HO\textsubscript{x} chemistry from 22 September 2007 to 13 October 2007. Further details of the CIMS, and other, instrumentation, are given in the supporting information.

3. Results and Discussion

3.1. Overall Time series

The suite of measurements discussed in this paper are presented in Figure 1. The measurement period covers 23 days, during which considerable variation in environmental parameters was experienced. Solar zenith angle varied from a daily minimum (maximum) of 77° (105°) at the start of the measurement period to 68° (96°) at the end. Noon photolysis rates for J(O\textsubscript{1}D) (J (NO\textsubscript{2})) increased from 1.32 × 10\textsuperscript{−5} s\textsuperscript{−1} (8.9 × 10\textsuperscript{−3} s\textsuperscript{−1}) to 4.33 × 10\textsuperscript{−5} s\textsuperscript{−1} (1.4 × 10\textsuperscript{−2} s\textsuperscript{−1}) throughout the period of measurements. Wind speeds ranged from quiescent periods to storm of over 25 ms\textsuperscript{−1}. Wind direction was predominantly easterly, with air arriving at Halley from across the continent, but with two extended periods of south westerly flow, with air masses traversing the sea ice zone. The lowest panel in Figure 1 shows there was considerable variability in surface ozone during the observation period, with various periods with surface ozone depletion events, both partial and total. NO mixing ratios are low throughout the measurement period (<1.56 ± 1.41 pptv), with early signs of diurnal variation in NO, but not substantial at this stage.

Very clear diurnal variability was, however, evident in both OH and HO\textsubscript{2} + RO\textsubscript{2} at this time, superimposed on variable, but generally increasing concentrations during the 23 day period of measurements. Throughout, daily minima were around instrument detection limits for both OH and HO\textsubscript{2} + RO\textsubscript{2}. Maxima at local noon, under equivalent conditions (i.e., easterly air flow and wind speeds ~15 ms\textsuperscript{−1}) increased, for OH (HO\textsubscript{2} + RO\textsubscript{2}), from 1.5 × 10\textsuperscript{7} molec/cm\textsuperscript{3} (0.8 × 10\textsuperscript{8} molec/cm\textsuperscript{3}) on 24 September to 1.6 × 10\textsuperscript{8} molec/cm\textsuperscript{3} (2.4 × 10\textsuperscript{8} molec/cm\textsuperscript{3}) on 11 October. During the period of measurements the mean OH (HO\textsubscript{2} + RO\textsubscript{2}) was 2.4 × 10\textsuperscript{8} molec/cm\textsuperscript{3} (5.8 × 10\textsuperscript{7} molec/cm\textsuperscript{3}) and median OH (HO\textsubscript{2} + RO\textsubscript{2}) was 1.1 × 10\textsuperscript{8} molec/cm\textsuperscript{3} (4.4 × 10\textsuperscript{7} molec/cm\textsuperscript{3}). These values can be compared with observations from Summit, Greenland, made during spring 2007 (Liao et al., 2011). Their mean OH (HO\textsubscript{2} + RO\textsubscript{2}) was 3.1 × 10\textsuperscript{8} molecule cm\textsuperscript{−3} (3.3 × 10\textsuperscript{8} molec/cm\textsuperscript{3}) and
median OH (HO₂ + RO₂) was 3.0 × 10⁶ molec/cm³ (2.7 × 10⁸ molec/cm³). J(O¹D), temperature, and O₃ were key controls on HOˣ production at Summit. While the range of J(O¹D) was similar to that during the Halley experiment, temperature and O₃ concentrations were both higher, factors that will contribute to the higher HOˣ concentrations observed at Summit.

In addition to the diurnal variability, a further influence is apparent in the OH data. By comparing concentrations of OH according to wind direction, it is clear that during periods of sustained airflow, OH concentrations are consistently higher in air masses arriving from the west of Halley than from the east. The switch from “low OH” to “high OH” is rapid, varying from one day to the next. For example, on 23 September, with air arriving from the west of Halley, hourly averaged OH, centered at local noon, was 6.9 × 10⁵ molec/cm³, while the following day, with air flow from the east, OH was a factor ~4 less, at 1.8 × 10⁵ molec/cm³; at local noon on 4 October, with air arriving from the west, hourly averaged OH concentration was 7.2 × 10⁵ molec/cm³, while the following day, with airflow from the east, OH concentration at local noon had dropped by a factor of 1.7, to 4.2 × 10⁵ molec/cm³. This behavior suggests either rapid changes in environmental variables that influence radical chemistry, changes in HOˣ recycling or sink reactions, or emissions of short-lived HOˣ precursor species that would not retain a signature from day to day. We examine this behavior in greater detail below and probe the factors responsible for these differences.

3.2. Averaged Diurnal Cycles

Figure 2 shows averaged diurnal cycles calculated for OH and the sum of HO₂ + RO₂ for the period of measurements from 22 to 26 September (inclusive). The diurnal cycles are derived from data partitioned according to local wind direction—easterly defined as 60° to 120°, westerly defined as 220° to 280°. This period was chosen because it includes unbroken measurements of both OH and HO₂ + RO₂ and encompasses periods with sustained flow from both east and west.

For the sum of HO₂ + RO₂, the diurnal cycle is relatively unaffected by air mass origin, other than in the early morning, when air masses arriving at Halley from across the sea ice zone display a significantly higher concentration of HO₂ + RO₂ than air masses arriving from across the continent. We return to this below.

For OH, the overall behavior shows the characteristic diurnal cycle, with nighttime minimum and daytime maximum. However, during easterly airflow, the maximum is of the order 3 × 10⁵ molec/cm³, while under
westerly flow this increases to $7 \times 10^5$ molec/cm$^3$. Further, during westerly flow, OH concentrations rise earlier, and extend later, than they do during easterly flow. The question clearly follows: what is causing these differences?

Under low-temperature background atmospheric conditions, concentrations of OH as well as OH:HO$_2$ partitioning are controlled, to a first approximation, by concentrations of water vapor and CO, according to the following equations:

$$\text{O}_3 + \text{hv} \rightarrow \text{O}^1\text{D} + \text{O}_2 \quad \text{(J1)}$$

$$\text{O}^1\text{D} + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad \text{(R2)}$$

$$\text{OH} + \text{CO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}_2 \quad \text{(R3)}$$

$$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \quad \text{(R4)}$$

We use a steady state analysis approach (see Supporting Information S1) to calculate concentrations of OH at noon on these days. As shown in Figure 2c, temperatures measured at Halley on 22/23 September, when air arrived from the west, were generally lower than when air arrived from the east. Correspondingly, concentrations of water vapor, derived using the Goff-Gratch parameterization, are significantly (up to a factor of 3) lower in the westerly air flow. Taking this into account, as well as the varying ozone levels, we estimate, via reactions (J1) and (R2), lower levels of HO$_x$ when air arrived at Halley from the west than when air arrived from the east (see supporting information Table S1). Using R3 and R4 to estimate the OH:HO$_2$ ratio, which

Figure 2. Average observed diurnal cycles for (a) HO$_2$ + RO$_2$, (b) OH, (c) surface O$_3$, (d) temperature, derived from 22 to 26 September, according to wind direction at Halley. Grey lines represent times when air arrived at Halley from across the sea ice zone to the west; blue lines represent times when air arrived from across the continent to the east. Blue/grey shading represent ±2σ errors. Local noon is 13:44. All data are 10-min averages other than temperature which is hourly averages.
also depends on ozone concentration, we find similar mean OH concentrations of $4.5 \times 10^5$ molec/cm$^3$ regardless of wind direction—counter to what is observed. This analysis suggests that other factors are controlling the observed east/west differences in OH.

Halogens have significant sources associated with the sea ice zone (see, e.g., reviews by Simpson et al., 2007, and Abbatt et al., 2012) and influence HO$_x$ ratios via the reaction HO$_2$ + XO $\rightarrow$ HOX + O$_2$ (where X = Br, Cl, or I). HOX may then undergo photolysis to release OH. In this way, halogens can increase OH concentrations on short timescales (Stone et al., 2018). A role for bromine chemistry has been proposed to explain HO$_x$ observations at Summit, Greenland (Liao et al., 2011; Sjostedt et al., 2007). Previous work has demonstrated high concentrations of BrO and IO during springtime at Halley (Saiz-Lopez et al., 2007) as well as the presence of chlorine chemistry (Read et al., 2007). Furthermore, the influence of air mass origin on the concentration of bromine compounds measured at Halley has been demonstrated (Buys et al., 2013), with highest concentrations in air masses arriving at Halley from the sea ice zone to the west/southwest.

### 3.3. Influence of Halogen Chemistry

We explore the potential for bromine chemistry to influence HO$_x$ chemistry at Halley, by considering the influence on the OH:(HO$_2$ + RO$_2$) ratio. Figure 3a shows a plot of observed HO$_2$ + RO$_2$ vs observed OH for the period of observations from 22 to 26 September (inclusive), partitioned according to wind direction.

For air masses approaching Halley from the east, the ratio OH:(HO$_2$ + RO$_2$) is 0.0018, whereas for air masses approaching Halley from the west, the ratio is a factor 3.06 higher, at 0.0055.

If we assume that the OH:(HO$_2$ + RO$_2$) ratio is determined by the following reactions:

\[
\begin{align*}
\text{OH} + \text{CO} & \rightarrow \text{HO}_2 + \text{CO}_2 \\
\text{BrO} + \text{HO}_2 & \rightarrow \text{HOBr}
\end{align*}
\]

then at steady state

\[
\frac{d[\text{HO}_2]}{dt} = k_5[\text{CO}][\text{OH}] - k_6[\text{HO}_2][\text{BrO}] = 0
\]

It therefore follows that

\[
\frac{[\text{OH}]}{[\text{HO}_2]} = \frac{k_6[\text{BrO}]}{k_5[\text{CO}]}
\]

To a first order, if CO is constant, then the ratio OH:(HO$_2$ + RO$_2$) is determined by the concentration of BrO. Observations at Halley show that concentrations of CO do not vary with wind direction during the spring. Concentrations of inorganic bromine compounds observed at Halley during spring (Buys et al., 2013) were consistently higher (roughly factor 3 to 5) in air masses with sea ice zone contact than in air arriving at Halley from over the continent. Figure 3b shows the diurnal cycle of BrO partitioned according to wind direction at Halley during spring 2007 (3 to 7 September westerly air flow; 10 to 15 September easterly air flow). Concentrations are roughly a factor of 3 higher when air masses approach Halley from across the sea ice zone to the west of the station than they are for air masses approaching Halley from the east. While we do not have coincident BrO and HO$_x$ measurements (as described in section 2.2, the CIMS could not observe halogens and HO$_x$ simultaneously), the BrO observations were made only slightly earlier in the same year and thus provide a reasonable indication of BrO differences occurring in air masses with different origin during the period of HO$_x$ observations. The factor 3 increase in BrO concentrations is in line with the factor 3 difference in OH:(HO$_2$ + RO$_2$) ratio, implying a controlling role for BrO in determining HO$_x$ chemistry. Indeed, this conclusion is consistent with observations of Sjostedt et al. (2007) who made measurements at Summit, Greenland, during summer and found particularly high OH concentrations (daily median 1.1 $\times 10^7$ mol/cm$^3$) on a warm day with strong advection from the marine boundary layer.

A further indication for the role of bromine chemistry comes from the fact that the OH peak shown in Figure 2b is broader when air masses arrived at Halley from the west than when air arrived from the east. This implies that air masses that had crossed the sea ice zone to the west of Halley included a source of
OH that was operative close to twilight; in contrast, the air masses arriving from the east did not include this additional OH source. Br2 photolyzes around 400 to 500 nm and provides a source of bromine radicals, which can react with O3 to produce BrO. Reaction of BrO with HO2 produces HOBr, which in turn photolyzes (also at wavelengths longer than for J1) to produce OH. The inclusion of bromine chemistry thus provides a mechanism for repartitioning HO2 to OH at high solar zenith angles, which can account for the additional OH observed in air masses arriving at Halley from the west during twilight hours.

As described above, the diurnal cycle of HO2 + RO2 is generally unaffected by air mass origin, other than the significantly higher concentration of HO2 + RO2 observed at Halley in the early morning, when air masses arrived from across the sea ice zone. A key source of RO2 is the oxidation of hydrocarbons by chlorine atoms, via RH + Cl → R + HCl followed by R + O2 → RO2. Cl atoms are ~103 times more reactive with hydrocarbons than OH (Monks, 2005) so even at low concentrations they are able to enhance hydrocarbon oxidation in the atmosphere. The enhanced HO2 + RO2 concentrations at Halley in the early morning, in air that has traversed the sea ice zone and is thus likely to be enhanced in halogens, suggest the presence of a photolabile chlorine compound that builds up during the night, and is photolyzed on the return of sunlight. There were no measurements of chlorine compounds at Halley during 2007, but in a previous study, Read et al. (2007) estimated chlorine atom concentrations from hydrocarbon variability to be in the range 1.7 × 103 to 3.4 × 104 atom/cm3 in early September. By putting CH3O2 into steady state by matching production via Cl + CH4 with loss via reaction with HO2, we estimate concentrations of CH3O2 between 1 × 107 and 3 × 108 molecule/cm3 from this channel. The difference in HO2 + RO2 concentrations observed between easterly and westerly air flow in the morning are of the order 4 × 107 molecule/cm3, so in line with a potential additional chlorine source.

We chose to investigate the role that halogens play by using a zero-dimensional model employing a simple representation of bromine release to the boundary layer. We used the BOXMOX modeling framework of Knote et al. (Knote et al., 2015), employing the UKCA "CHEST" whole atmosphere chemistry mechanism (Morgenstern et al., 2009; O'Connor et al., 2014) and photolysis rates derived from the Tropospheric Ultraviolet and Visible (TUV) radiation model (Madronich, 2002) scaled to match the observed JO1D and JNO2. We initialized the model with measured temperature and pressure, from which water vapor concentrations were derived using the Goff-Gratch parameterization, as well as observed levels of O3, NOx, and VOCs (Read et al., 2007), at midnight local time. The model was integrated forward in time for two days using a one-hour time step, and data from the two days were averaged.

To represent the presence of rapidly recycled short-lived halogenated species, we used a proxy in the form of daytime emission of molecular bromine into the boundary layer. In all, four integrations were performed for conditions appropriate to 22 to 25 September. Data for 22 and 23 September were aggregated to generate data appropriate to westerly flow, while data for 24 and 25 September represent easterly flow. The main effect of the bromine source is to rapidly generate BrO radicals on reaction with ozone. These BrO radicals couple to HO2 chemistry via reaction with HO2 and photolysis of the HOBr product to release OH, increasing the rate of conversion of HO2 to OH and the OH:HO2 ratio.
Figure 4 shows the modeled levels of OH, HO2 + RO2, plotted according to east/west wind direction. Good agreement can be seen for both OH and HO2 + RO2 with respect to observations. In these integrations the bromine source terms were $1.1 \times 10^5$ (west) and $1.3 \times 10^4$ (east) molec cm$^{-3}$ s$^{-1}$ giving mean noontime BrO mixing ratios of 3.75 and 1.25 pptv, respectively. The west/east ratio in modeled noontime BrO of 3:1 is very similar to that shown in Figure 3b and reported for observed BrO at Halley (Buys et al., 2013). The Br2 source terms used here can be compared with the $0.5 \times 10^5$ molec cm$^{-3}$ s$^{-1}$ and $5 \times 10^5$ to $0.04 \times 10^5$ molec cm$^{-3}$ s$^{-1}$ used, respectively, by Saiz-Lopez et al. (2008) and Buys et al. (2013) to model atmospheric bromine chemistry during spring in coastal Antarctica.

While we do not assert that the ratio of (HO2 + RO2):OH ratio is solely under the control of bromine chemistry, these calculations do show that the observations may reflect different halogen loading in the airmasses originating in different sectors, and the results are broadly compatible with the findings of earlier measurements of BrO as a function of wind direction. At this time of year, we expect biogenic iodine emissions to be low and the halogen chemistry to be dominated by inorganic sources, such as the sea ice zone.

4. Summary and Conclusions

We report the first observations of OH and HO2 + RO2 in Antarctica made outside the summer season, which were made during spring at Halley station in coastal Antarctica. Concentrations increased over the period of observations (22 September to 14 October) due to the rapidly increasing solar irradiance, with a clear diurnal variability evident throughout.

The bimodal nature of prevailing winds at Halley station enables the comparison of chemical composition of air masses with sea ice zone contact to those with predominantly continental origin. We find a significant difference in concentrations of OH as well as in the OH:(HO2 + RO2) ratio that depend on the air mass origin. We explore this difference using both steady state approaches as well as a 0-D model. We find that the differences can be accounted for by the presence of bromine compounds, which have previously been measured during the spring at Halley. We also find indication of active chlorine chemistry influencing concentrations of RO2.
Sea ice in the polar regions is undergoing considerable change (Intergovernmental Panel On Climate Change, 2013; Turner & Comiso, 2017). Our results suggest that changes in the characteristics and extent of the sea ice zone that lead to changes in abundance of atmospheric halogens will also result in a change in OH. For example, a shift toward more new sea ice formation, with its higher salinity over multiyear ice, would be expected to increase the abundance of halogens; conversely, reduction in sea ice extent would ultimately reduce abundance of halogens. OH radicals play a key role in oxidation reactions that remove pollutants from the atmosphere. Especially given anticipated expansion of industrial activities in the Arctic, this is a further factor to take into account when considering the wider impacts of sea ice loss.

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