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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_x 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 HO_x 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 HO_x (OH + HO₂ + RO₂) chemistry during summertime in the polar regions is clear from previous field campaigns. Outstandingly high concentrations of HO_x have been observed at Antarctic Plateau stations. At South Pole station, of the order 2×10^6 molec/cm³ for OH were reported by Mauldin et al. (2001) and 7×10^7 molec/cm³ for the sum of HO₂ + RO₂ (Mauldin et al., 2004). At Concordia station, daily median values of 3.1×10^6 molec/cm³ for OH and 9.9×10^7 molec/cm³ 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); HO_x repartitioning reactions involving NO_x, 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 HO_x 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 HO_x concentrations.

With its very short lifetime, OH concentrations are sensitive both to local sources and radical cycling reactions, and indeed, a tight coupling between HO_x, NO_x, 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.

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Here we present first observations of OH and HO₂ + RO₂ carried out in Antarctica outside the summer season. We focus on the springtime, a time when ambient temperatures, water vapor, and NO_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_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 HO₂ + RO₂, 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_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(O¹D) (J(NO₂)) increased from $1.32 \times 10^{-5} \text{ s}^{-1}$ ($8.9 \times 10^{-3} \text{ s}^{-1}$) to $4.33 \times 10^{-5} \text{ s}^{-1}$ ($1.4 \times 10^{-2} \text{ s}^{-1}$) throughout the period of measurements. Wind speeds ranged from quiescent periods to storm of over 25 ms^{-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 ($<1.56 \pm 1.41 \text{ pptv}$), 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 HO₂ + RO₂ 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 HO₂ + RO₂. Maxima at local noon, under equivalent conditions (i.e., easterly air flow and wind speeds $\sim 15 \text{ ms}^{-1}$) increased, for OH (HO₂ + RO₂), from $1.5 \times 10^5 \text{ molec/cm}^3$ ($0.8 \times 10^8 \text{ molec/cm}^3$) on 24 September to $1.6 \times 10^6 \text{ molec/cm}^3$ ($2.4 \times 10^8 \text{ molec/cm}^3$) on 11 October. During the period of measurements the mean OH (HO₂ + RO₂) was $2.4 \times 10^5 \text{ molec/cm}^3$ ($5.8 \times 10^7 \text{ molec/cm}^3$) and median OH (HO₂ + RO₂) was $1.1 \times 10^5 \text{ molec/cm}^3$ ($4.4 \times 10^7 \text{ molec/cm}^3$). These values can be compared with observations from Summit, Greenland, made during spring 2007 (Liao et al., 2011). Their mean OH (HO₂ + RO₂) was $3.1 \times 10^6 \text{ molecule cm}^{-3}$ ($3.3 \times 10^8 \text{ molec/cm}^3$) and

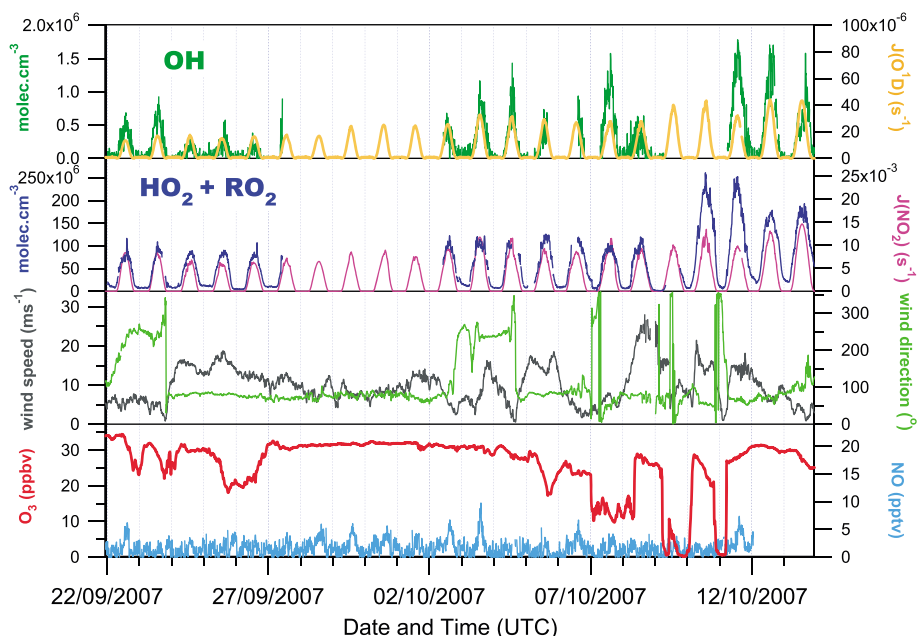


Figure 1. Time series of observations at Halley during the spring campaign, from 22 September to 14 October 2007. Data shown are 10-min averages.

median OH ($\text{HO}_2 + \text{RO}_2$) was 3.0×10^6 molec/cm³ (2.7×10^8 molec/cm³). $J(\text{O}^1\text{D})$, temperature, and O_3 were key controls on HO_x production at Summit. While the range of $J(\text{O}^1\text{D})$ was similar to that during the Halley experiment, temperature and O_3 concentrations were both higher, factors that will contribute to the higher HO_x 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 6.9×10^5 molec/cm³, while the following day, with air flow from the east, OH was a factor ~ 4 less, at 1.8×10^5 molec/cm³; at local noon on 4 October, with air arriving from the west, hourly averaged OH concentration was 7.2×10^5 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 4.2×10^5 molec/cm³. This behavior suggests either rapid changes in environmental variables that influence radical chemistry, changes in HO_x recycling or sink reactions, or emissions of short-lived HO_x 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 $\text{HO}_2 + \text{RO}_2$ 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 $\text{HO}_2 + \text{RO}_2$ and encompasses periods with sustained flow from both east and west.

For the sum of $\text{HO}_2 + \text{RO}_2$, 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 $\text{HO}_2 + \text{RO}_2$ 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 3×10^5 molec/cm³, while under

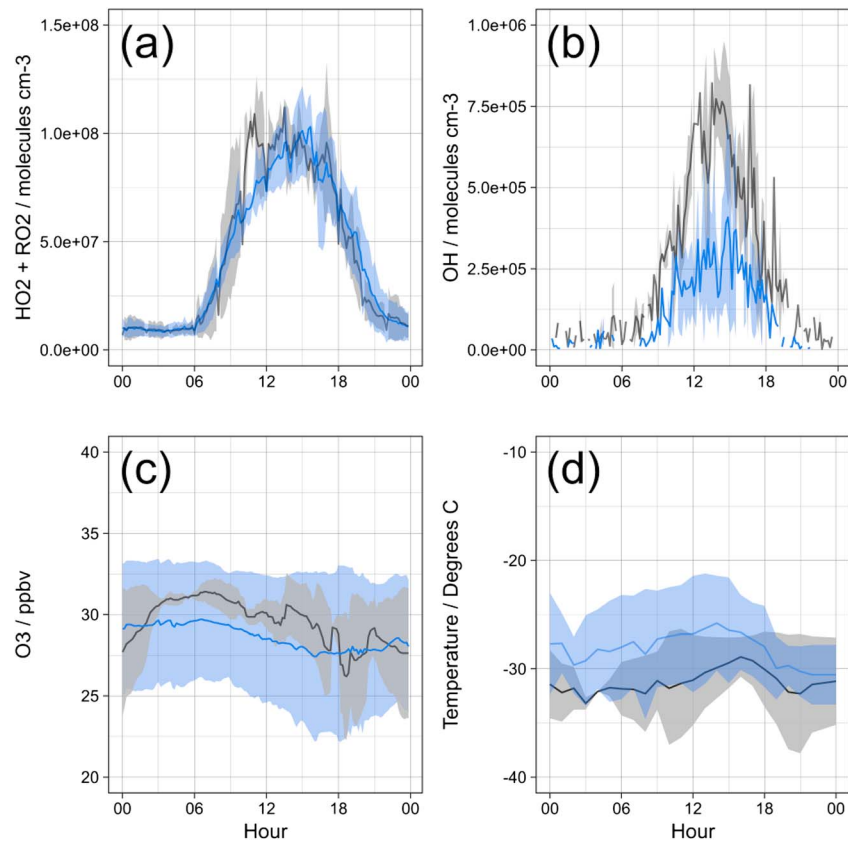


Figure 2. Average observed diurnal cycles for (a) HO₂ + RO₂, (b) OH, (c) surface O₃, (d) temperature, derived from 22 to 26 September, according to wind direction at Halley. Grey lines represent times when air arrived at Halley from across the sea ice zone to the west; blue lines represent times when air arrived from across the continent to the east. Blue/grey shading represent $\pm 2\sigma$ errors. Local noon is 13:44. All data are 10-min averages other than temperature which is hourly averages.

westerly flow this increases to 7×10^5 molec/cm³. 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:HO₂ partitioning are controlled, to a first approximation, by concentrations of water vapor and CO, according to the following equations:



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:HO₂ ratio, which

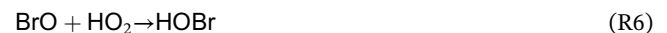
also depends on ozone concentration, we find similar mean OH concentrations of 4.5×10^5 molec/cm³ regardless of wind direction—counter to what is observed. This analysis suggests that other factors are controlling the observed east/west differences in OH.

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 HO₂ + XO → HOX + O₂ (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:(HO₂ + RO₂) ratio. Figure 3a shows a plot of observed HO₂ + RO₂ 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:(HO₂ + RO₂) 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:(HO₂ + RO₂) ratio is determined by the following reactions:



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:(HO₂ + RO₂) 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 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:(HO₂ + RO₂) 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 1.1×10^7 mol/cm³) 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

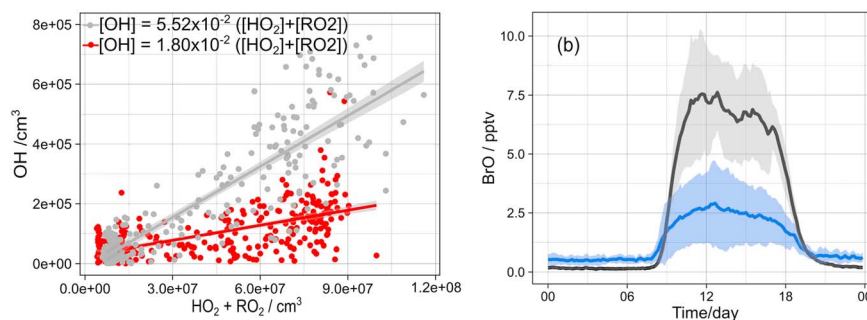


Figure 3. (a) Correlation plot of OH versus HO₂ + RO₂ from 22 September 2007 to 26 September 2007, partitioned by local wind direction (grey = winds from west; red = winds from east); (b) averaged BrO diurnal cycles BrO measured at Halley during first 2 weeks of September 2007, partitioned by local wind direction (grey = winds from west; blue = winds from east). Data shown as 10-min averages.

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, NO_x, 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 HO_x 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.

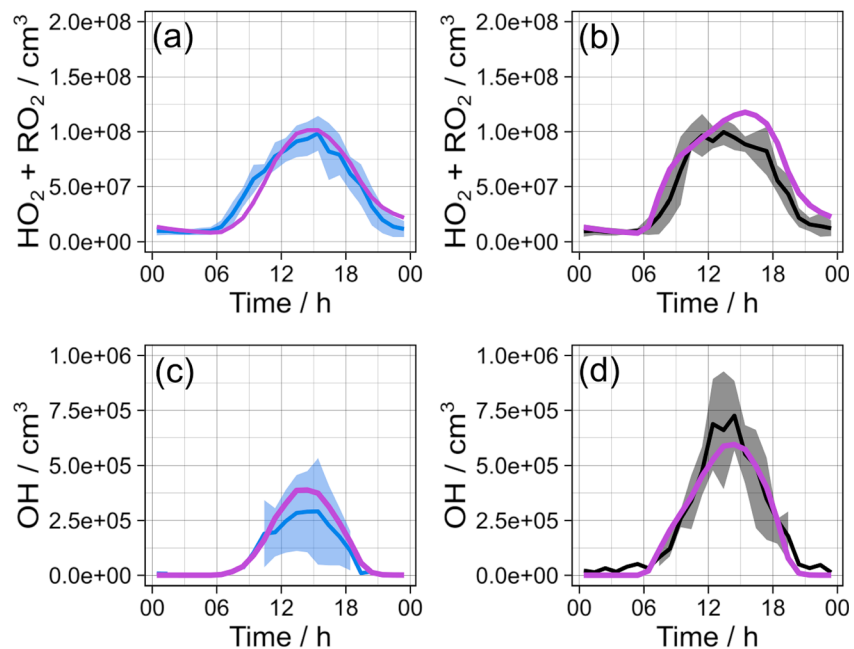


Figure 4. (a) Comparison between observed (blue: line = mean, shading = standard deviation) and modeled (magenta line) $[\text{HO}_2 + \text{RO}_2]$, throughout a diurnal cycle, for air masses arriving at Halley from the east (continental origin); (b) as for (a) but for air arriving from the west (sea ice zone origin); (c) as for (a) but for OH; (d) as for (b) but for OH. Observations shown as hourly averages to coincide with model output with a 1-hr time step.

Figure 4 shows the modeled levels of OH, $\text{HO}_2 + \text{RO}_2$, plotted according to east/west wind direction. Good agreement can be seen for both OH and $\text{HO}_2 + \text{RO}_2$ with respect to observations. In these integrations the bromine source terms were 1.1×10^5 (west) and 1.3×10^4 (east) $\text{molec cm}^{-3} \text{s}^{-1}$ 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 Br_2 source terms used here can be compared with the $0.5 \times 10^5 \text{ molec cm}^{-3} \text{s}^{-1}$ and 5×10^5 to $0.04 \times 10^5 \text{ molec cm}^{-3} \text{s}^{-1}$ 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 $(\text{HO}_2 + \text{RO}_2):\text{OH}$ ratio is solely under the control of bromine chemistry, these calculations do show that the observations may reflect different halogen loading in the air masses 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 $\text{HO}_2 + \text{RO}_2$ 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 $\text{OH}:(\text{HO}_2 + \text{RO}_2)$ 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 RO_2 .

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.

Acknowledgments

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