Influence of Sea Ice-Derived Halogens on Atmospheric HO$_X$ as Observed in Springtime Coastal Antarctica

Anna Jones[1], Neil Brough[1,*], and Paul Griffiths[2]

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

[2]NCAS-Climate and Centre for Atmospheric Science, Cambridge University, Cambridge, UK

*Now at NIWA, Wellington, New Zealand

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Abstract:

We present first observations of OH and (HO_2 + RO_2) 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:(HO_2 + RO_2) 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 RO_2.

Sea ice in the polar regions is undergoing considerable change. 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 towards more new sea ice formation, with its higher salinity over multi-year ice, would be expected to increase the abundance of halogens; conversely, overall 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.

Introduction:

Several studies have examined HO_x (OH + HO_2+RO_2) chemistry on the Antarctic Plateau. Outstandingly high concentrations have been reported, driven primarily by photochemical emissions of precursor gases (H_2O_2, HCHO, and potentially also HONO) from the extensive polar snowpack. HO_x repartitioning reactions involving NO_x, which also has a snowpack source, 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.

Fewer studies had considered HO_x chemistry at coastal stations, especially outside the summer season. Existing studies had shown that, at coastal sites, HO_x concentrations are more moderate, and the presence or absence 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 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.

To explore links to halogen chemistry, we present observations of OH and HO_2+ RO_2 in coastal Antarctica during spring. **We focus on the springtime, as ambient temperatures, water vapour, and NO_x concentrations are low, solar irradiance is limited but increasing, and halogen chemistry is at its annual maximum.**

Location:

The Halley Clean Air Sector Laboratory where the measurements were made
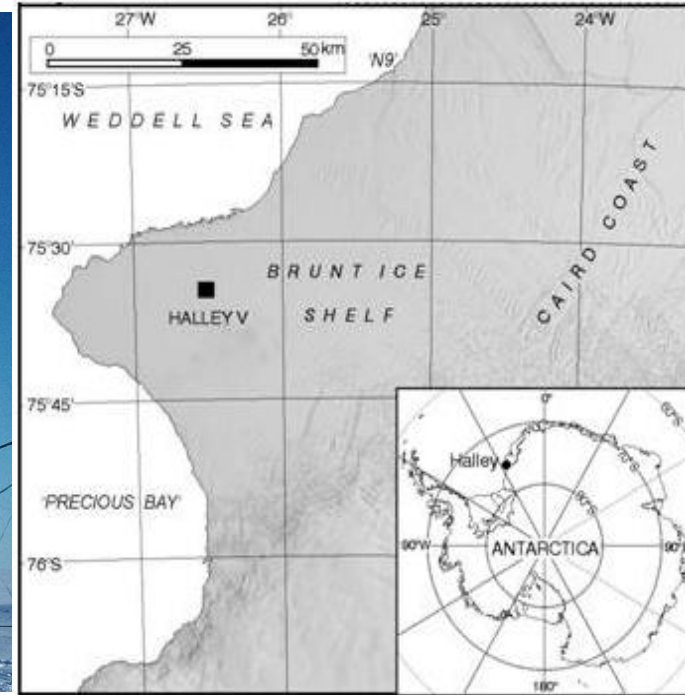
The measurements were carried out at the British Antarctic Survey's Halley V research station (75°35'S, 26°39'W), in coastal Antarctica, where active halogen chemistry has been previously reported. **A key characteristic of Halley is the bimodal nature of the prevailing wind direction:** for much of 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. Comparing air with these different origins proved effective for assessing the influence of halogens on HO_x chemistry.

Instrumentation:

OH and HO_2+RO_2; and halogens
- Chemical ionisation mass spectrometer (high pressure mode for OH and HO_2+RO_2; low pressure mode for halogens – therefore HO_x and halogen measurements were not coincident in time).
    - Measurement uncertainty ~30% for OH and ~35% for HO_2 + RO_2.
    - Limit of detection for OH ~1.3×10^5 molecule cm^{-3} for a 10-min integration period, estimated from the standard deviation of the background measurement (3 σ)

Surface ozone
- Thermo Environmental Instruments Inc. model 49 U.V. Photometric Ozone Analyser (detection limit 1 ppbv; linearity 2%)

Photolysis rates of JO^1D and JNO_2
- Meteorologieconsult GmbH single monochromator with a diode array detector, measuring over 2-π, used to measure downwelling actinic fluxes. The flux ratio method described in Jones et al. (2008) (based on sequential downwelling/upwelling observations and varying solar zenith angle), used to derive photolysis rates of JO^1D and JNO_2
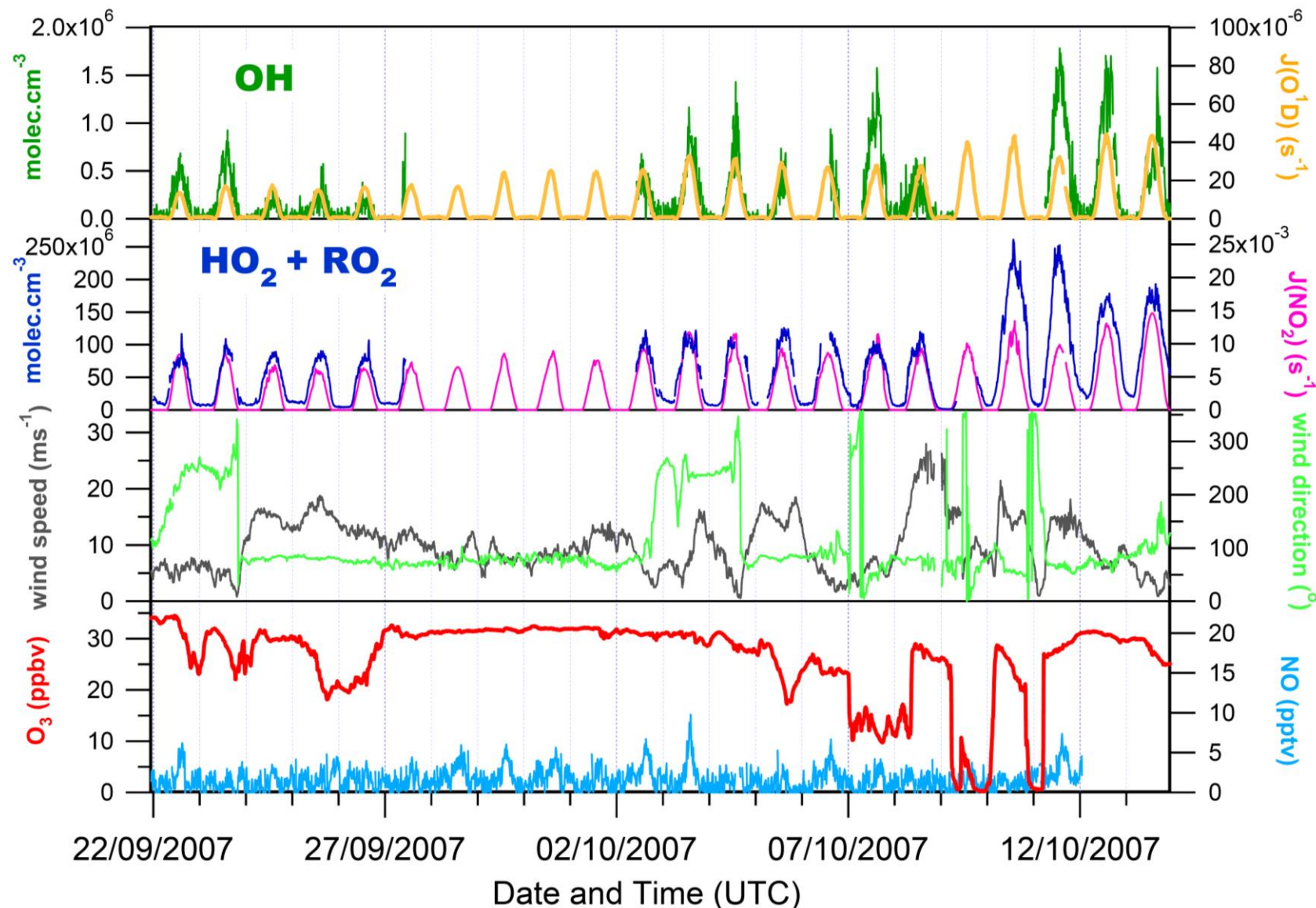
NO
- dual channel chemiluminescence analyser (Sonoma Tech.) with detection limit (2 sigma) for NO of 2 pptv (1-min mean) and < 1.0 pptv (10-min mean)

Results (1): Overall timeseries

Overall timeseries shows:

- Steady increasing diurnal variation in JO^1D and JNO_2

- Low concentrations of NO

- Periods of ozone depletion events

- Gradually increasing concentrations of OH, but...

- Diurnal variation in OH that does not follow evolving photolysis rates, but shows apparent link to wind direction

Figure 1) overall time series for the period of springtime measurements

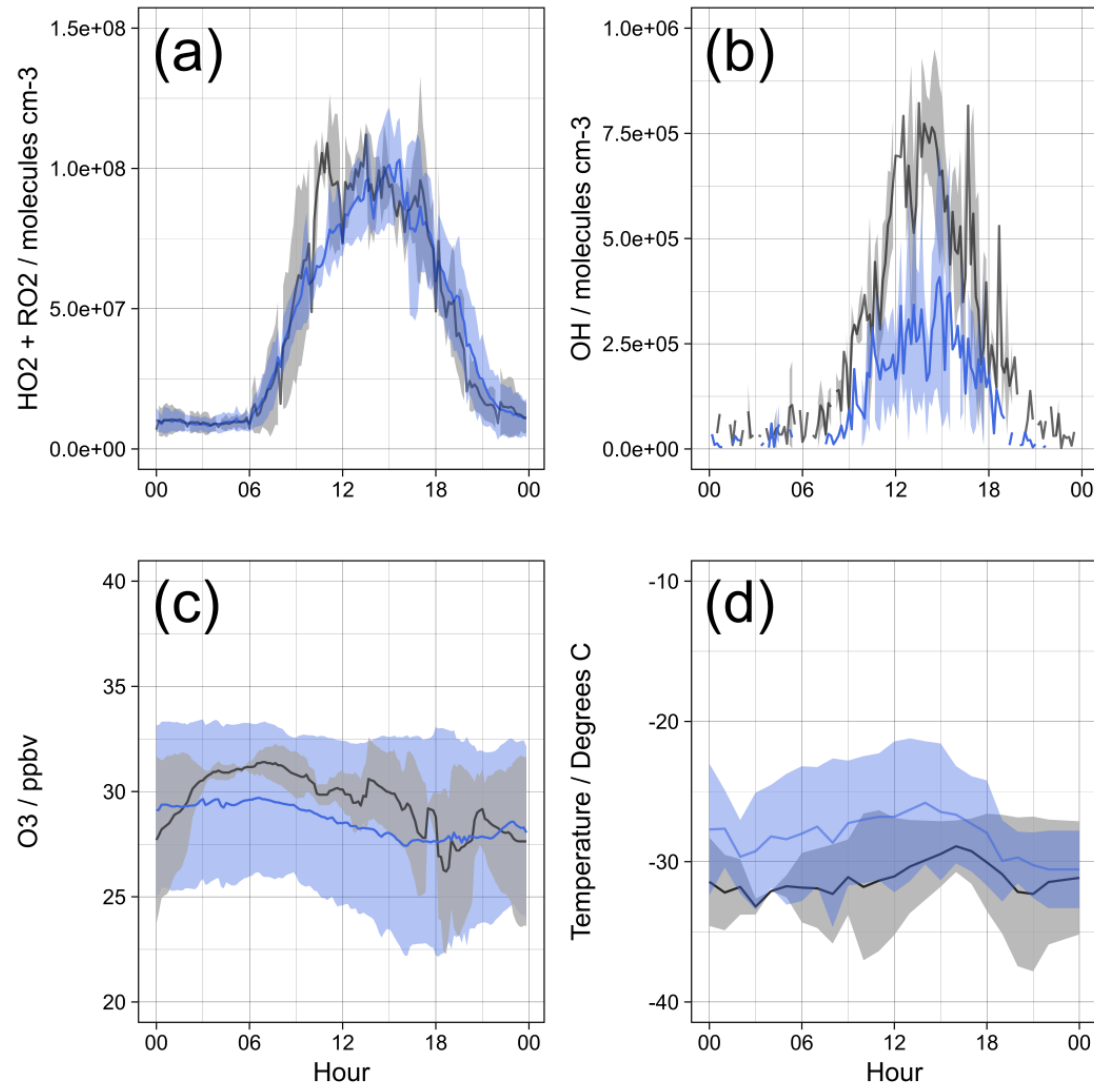# Results (2): Influence of wind direction on diurnal variation

Figure 2) average observed diurnal cycles partitioned according to wind direction, for (a) $HO_2 + RO_2$, (b) OH, (c) surface O_3, (d) temperature, derived from 22 to 26 September.
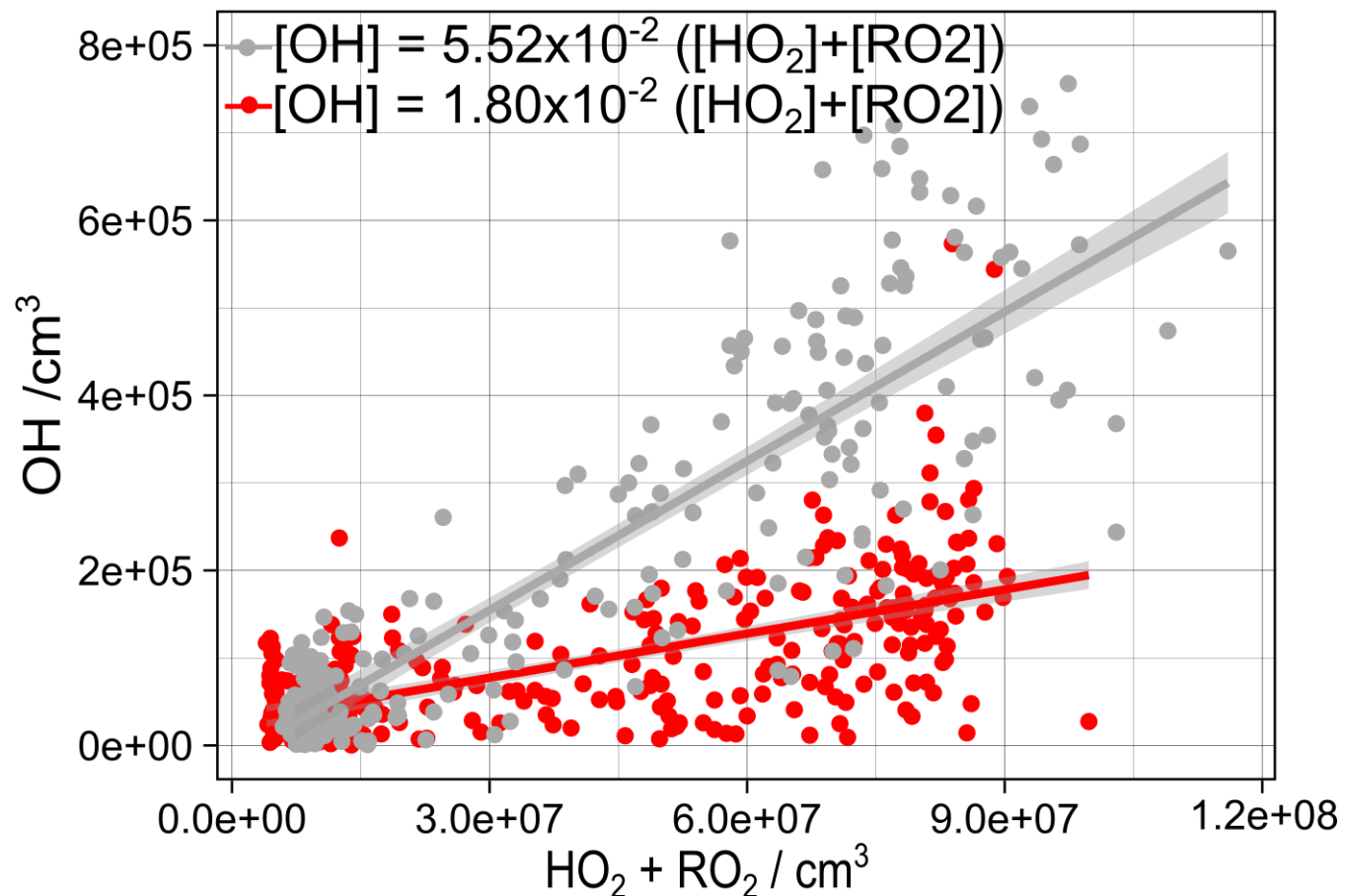***Grey lines*** *represent times when air arrived at Halley from across the sea ice zone to the west (220° to 280°);* ***blue lines*** *represent times when air arrived from across the continent to the east (60° to 120°).*
Blue/grey shading *represent ±2σ errors. Local noon is 13:44. All data are 10-min averages other than temperature which are hourly averages.*

Averaged diurnal cycles show:

- Small influence of air mass origin on HO_2+RO_2 in early morning only, when concentrations in air with sea ice zone contact were higher;

- Clear influence of air mass origin on concentrations of OH, with considerably greater concentrations when air arrived at Halley from across the sea ice zone.

Results (3): Influence of wind direction on ratio OH : (HO$_2$+RO$_2$)

Legend in plot:
$[OH] = 5.52 \times 10^{-2} ([HO_2] + [RO2])$
$[OH] = 1.80 \times 10^{-2} ([HO_2] + [RO2])$

Axis labels:
OH /cm^3
HO$_2$ + RO$_2$ / cm^3

**Partitioning the ratio according to wind direction shows:**

- for air masses approaching Halley from the east, the ratio OH:(HO$_2$+RO$_2$) is 0.0018

- for air masses approaching Halley from the west, the ratio is 0.0055

- i.e. in air masses arriving at Halley from across the sea ice zone, the ratio OH:(HO$_2$+RO$_2$) is a factor 3.06 higher.

Figure 3) Correlation plot of OH versus HO$_2$+RO$_2$ from 22 September 2007 to 26 September 2007, partitioned by local wind direction (grey = winds from west; red = winds from east).

If we assume that the OH:$(HO_2 + RO_2)$ ratio is determined by the following reactions:

$$OH + CO \rightarrow HO_2 + CO_2 \qquad (R1)$$
$$BrO + HO_2 \rightarrow HOBr \qquad (R2)$$
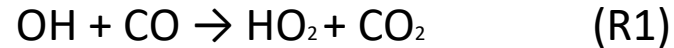
then at steady state: $\dfrac{d[HO2]}{dt}$ = k1[CO][OH]−k2[HO$_2$][BrO] = 0

It therefore follows that: $\dfrac{[OH]}{[HO2]} = \dfrac{k2[BrO]}{k1[CO]}$

This analysis suggests:

- To a first order, if CO is constant, then the ratio OH:(HO_2+RO_2) is determined by the concentration of BrO.

At Halley during spring, [CO] does not vary with wind direction

We therefore anticipate that at Halley during spring, [BrO] is instrumental in determining OH:(HO_2+RO_2)

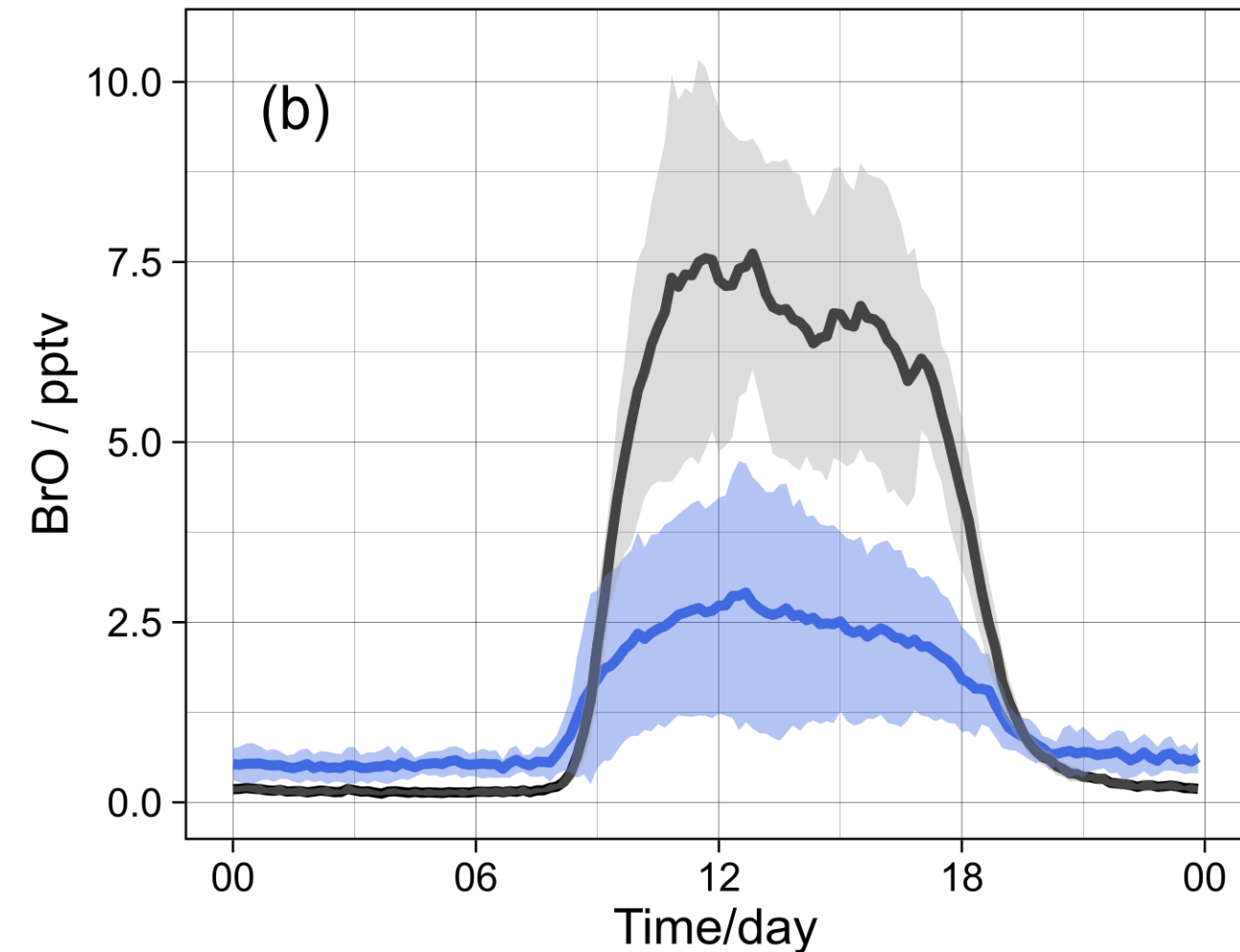# Results (5): Influence of wind direction on diurnal cycle of BrO

Figure 4) *Averaged BrO diurnal cycles, derived from BrO measured at Halley from 3rd to 15th September 2007, partitioned by local wind direction (grey = winds from west; blue = winds from east). Data shown as 10-min averages.*

BrO was measured at Halley during the first 2 weeks of September 2007. Partitioning BrO according to wind direction shows:

- Concentrations of BrO are roughly a factor of 3 higher when air masses approach Halley from across the sea ice zone to the west than they are for air masses approaching from the east.

- The factor 3 increase in BrO concentrations is in line with the factor 3 difference in OH:$(HO_2 + RO_2)$ ratio derived when partitioning according to wind direction

- **This result implies a controlling role for BrO in determining HO_x chemistry at Halley during spring.**
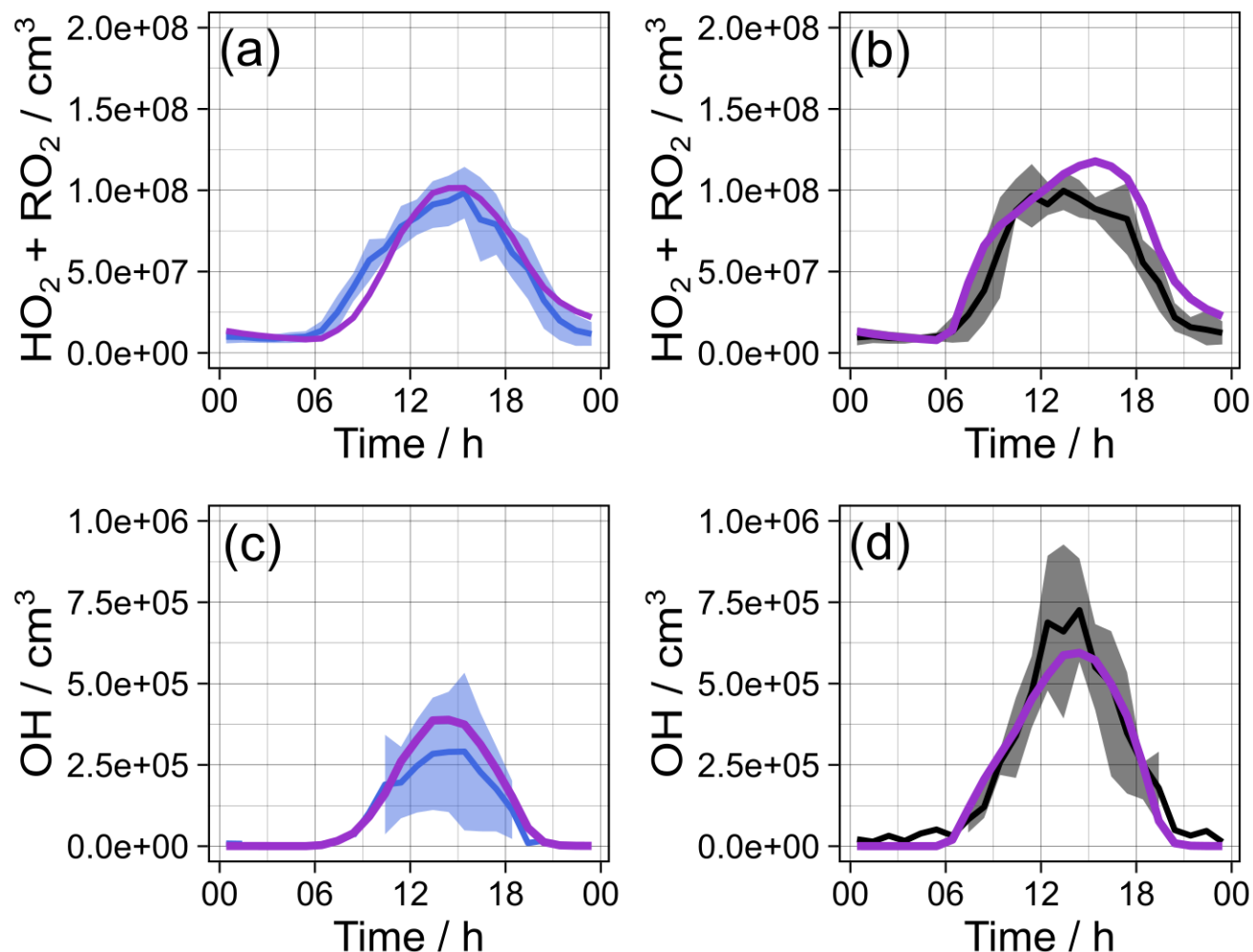
Modelling (1): The approach

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 modelling 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 JO^1D and JNO_2. We initialized the model with measured temperature and pressure, from which water vapour concentrations were derived using the Goff-Gratch parameterization, as well as observed levels of O_3, 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 HOx chemistry via reaction with HO_2 and photolysis of the HOBr product to release OH, increasing the rate of conversion of HO_2 to OH and the OH:HO_2 ratio.**

Modelling (2): Modelled vs observed HO_x chemistry according to wind direction

Figure 5) (a) Comparison between observed (blue: line = mean, shading = standard deviation) and modelled (magenta line) [HO2 + RO2], 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.

Comparing modelled and observed (HO_2+RO_2) and OH shows:

- The model is able to capture the shape of the observed diurnal profiles, as well as the magnitude of the peaks

- The model shows little change in (HO_2+RO_2), in line with the observations

- The model shows significant difference in [OH] depending on wind direction (and thus bromine loading) in line with observations

Conclusions

- We have presented the first observations of OH and HO_2+RO_2 in Antarctica carried out outside the summer season;

- Concentrations increased over the period of observations and clear diurnal cycles were evident;

- The bimodal nature of prevailing winds at Halley enables the comparison of chemical composition of air masses that have had contact with the sea ice zone, to those that have not;

- We find significant difference in concentration of OH depending on air mass origin, with some difference in HO_2+RO_2 in the early morning;

- We explore the difference using both steady state approaches and a 0-D model: we find that the differences can be accounted for by the presence of bromine compounds, which have been previously measured at Halley;

- There is some indication (not discussed here) of chlorine chemistry influencing concentrations of RO_2 in the early morning.

Outlook

- Sea ice in the polar regions is undergoing considerable change. 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 towards 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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