

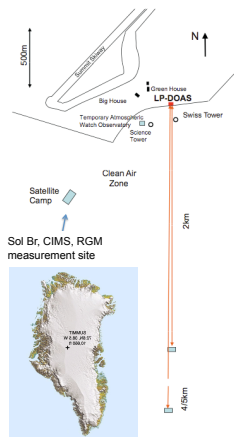


Greenland Summit HOx/Halogen Experiment: 2007 and 2008

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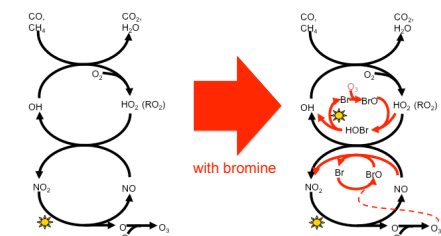
Introduction



The layout of the measurements during the GSHOX campaign at Summit, Greenland.

Reactive halogens in Arctic regions and their impact on ozone levels have been a subject of extensive research since the mid 1980s. In particular, studies have focused on coastal regions close to first-year sea ice. Less is known about halogens in more remote regions, such as the Greenland ice sheet. Motivated by indirect evidence of halogen chemistry, two field campaigns have been conducted at Summit, Greenland (latitude 32 km, latitude = 72.55°N), in May/June 2007 and June/July 2008. The purpose of these studies was to measure air and snow properties with a particular focus on halogen and HO_x chemistry at Summit. Measurements of gas phase soluble bromide as well as Differential Optical Absorption Spectroscopy (DOAS) and Chemical Ionization Mass Spectrometer (CIMS) confirm the presence of gas phase reactive bromine at Summit. The most likely source of gas phase bromine is activation of Br⁻ in the snow followed by release of active Br⁻ to the overlying air, despite the relatively small concentrations of Br⁻ compared to the coastal Arctic. Mixing ratios of soluble bromide and BrO above the snow were also found to be small (with maxima of ~4 ppt). This amount of bromine can oxidize and contribute to deposition of long-lived gaseous elemental mercury and may perturb HO_x partitioning. A complete description of the experimental set up including the micrometeorological situation at Summit during the campaigns will be presented. In order to understand the chemical and physical processes occurring during these field experiments we have also developed a 1D model for snow physics and chemistry, coupled to the boundary layer model MISTRA. The model indicates that the observed bromine can be explained by photochemical release from the snow pack.

Reactive bromine impacts atmospheric radical cycles

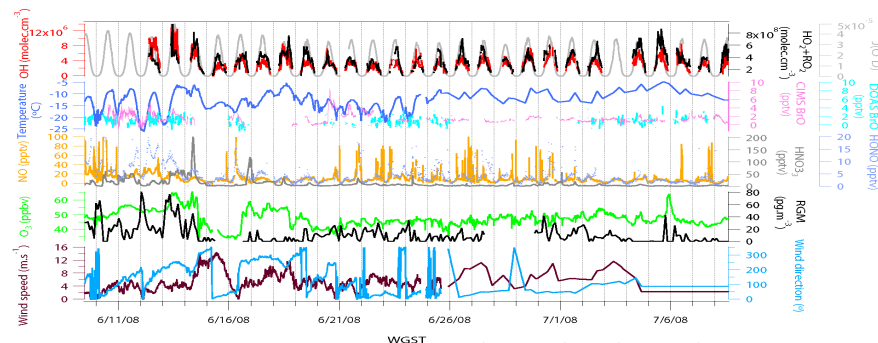


Summary of Measurements

Species and parameters	Instrument	Uncertainty	Institution	Reference
O ₃	UV absorption ozone analyzer	< ±5%	Ga. Tech	
NO	Chemiluminescent gas analyzer	±10%	Ga. Tech	Fryerson et al. (2000)
CO	Canister/GC	< ±4%	UCI	Swanson et al. (2002)
CH ₄	Canister/GC	< ±5%	UCI	Swanson et al. (2002)
NMHC	Canister/GC	< ±5%	UCI	Swanson et al. (2002)
OH	CIMS	±30%	Ga. Tech	Sjostedt et al. (2007)
HO ₂ + RO ₂	CIMS	±35%	Ga. Tech	Sjostedt et al. (2007)
BrO	CIMS	±30%–36%	Ga. Tech	Liao et al. (2011a)
Br	DOAS	±10%	UCLA	Stutz et al. (2011)
SMPS-N	SMPS/CPC	±10%	UNH	Ziemia et al. (2010)
SMPS-S	SMPS/CPC	±10%	UNH	Ziemia et al. (2010)
GEM	Tekran	±2%	NOAA	Brooks et al. (2011)
RGM	Tekran	±5%	NOAA	Brooks et al. (2011)
PFM	Tekran	±5%	NOAA	Brooks et al. (2011)
HNO ₃	Mist Chamber	±15%–20%	UNH	Dibb et al. (1998)
Soluble Bromine	Mist Chamber	±15%–20%	UNH	Dibb et al. (1998)
HONO	Mist Chamber	±15%–20%	UNH	Dibb et al. (1998)
Actinic Flux	SAFS	±10%	U. Houston	Shetter et al. (1999)
Temperature	F-Thermocouples	±0.5 °C	U. Houston	Haman et al. (2011)
WS/WD	AWSD/digital compass		U. Houston	Haman et al. (2011)

See Liao et al. ACPD, 2011 for a complete summary of the measurements.

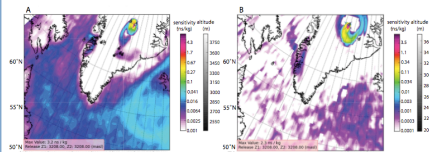
Time Series of Measurements in 2008



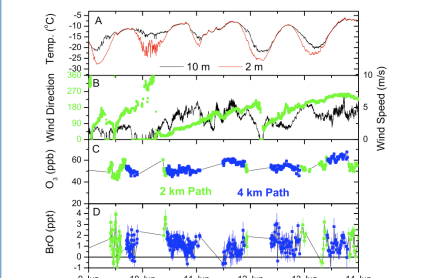
See Liao et al. ACPD, 2011 for a summary of both 2007 and 2008

- Diurnal profiles of OH and HO₂ + RO₂ largely followed the patterns of J (O¹D) with a maximum at local noon, consistent with the behaviors of short-lived photochemically active species
- The median midday values of HO₂ + RO₂ and OH concentrations observed by chemical ionization mass spectrometry (CIMS) were 2.7 × 10⁹ molec cm⁻³ and 3.0 × 10⁸ molec cm⁻³ in spring 2007, and 4.2 × 10⁹ molec cm⁻³ and 4.1 × 10⁸ molec cm⁻³ in summer 2008
- In summer 2008 [BrO]_{mean} measured by CIMS was 1.5 pptv
- LP-DOAS BrO mixing ratios in May 2007 and June 2008 were typically between 1–3 pptv, with maxima of up to 5 pptv
- The BrO concentrations at Summit were often near detection limits of both instruments
- A basic photochemical O-D box model highly constrained by observations of H₂O, O₃, CO, CH₄, NO, and J values predicted HO₂ + RO₂ reasonably well and under predicted OH

Local Air Masses

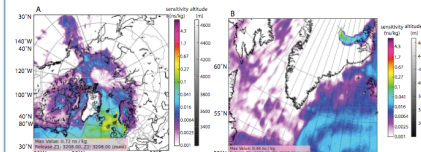


Footprint emissions sensitivity for the period of 10 (A) and 12 (B) June 2008, 00:00–03:00 UTC, using the nested model output (0.5°). The release location (Summit Station) is marked with an "X". The retroplume centroid locations for each day back are shown as colored circles, where the color is scaled to elevation. On 10 June 2008, days 1, 2, and 3 are clearly located over the Greenland ice sheet. On 12 June 2008 only days 1 and 2 are visible, with day 3 being further north over the Greenland ice sheet. Note the enhanced sensitivity in the lowest model layer recirculating around Summit.

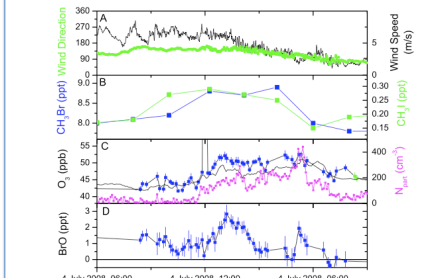


Period of local air masses during the beginning of the 2008 GSHOX experiment. Strong temperature gradients between 2m and 10m altitude (A) and low wind speeds (B) were observed at night during this period. Ozone mixing ratios (C) showed little variability, while DOAS BrO (D) varied between 0–5ppt. The gaps in LP-DOAS data at night are due to the reduced visibility in the presence of ground fog. (See Stutz et al. ACPD, 2011)

Marine Air Masses

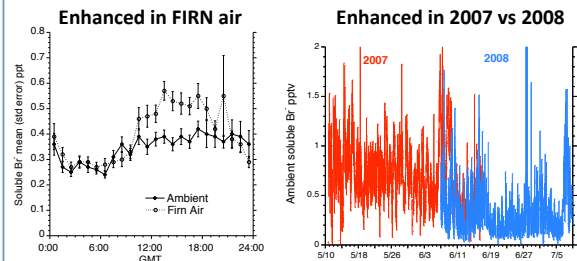


FLEXPART Footprint emissions sensitivity for 4 July 2008, 12:00–15:00 UTC using the global model output (1°). The release location (Summit Station) is marked with an "X". The retroplume centroid locations for each day back are shown as colored circles, where the color is scaled to elevation. Air arriving at Summit Station during this period clearly originated from the North Atlantic and was at the Greenland coast less than 24h earlier.



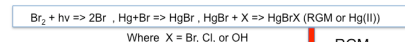
Example case of a marine air mass, as indicated by the FLEXPART retroplume, arriving at Summit at 12:00 UTC on 4 July 2008. Wind direction and speed (A) showed a slow turn from 120 to 80 and a slow decrease, respectively. CH₃Br and CH₃I (B) as well as particle number and ozone (C) were increased from noon to 18:00 UTC compared to their morning levels. DOAS BrO mixing ratios (D) showed a simultaneous increase from 0–1ppt in the morning to a maximum of 2.8±0.6ppt at 13:12 UTC. (See Stutz et al. ACPD, 2011)

Soluble Bromide



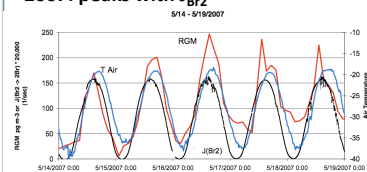
The soluble bromide measurements confirm that photochemical activation of Br⁻ in the snow causes release of active Br to the overlying air despite trace concentrations of Br⁻ in the snow (means 15 and 8 nmol Br⁻ kg⁻¹ of snow in 2007 and 2008). (See Dibb et al., ACP, 2010)

Reactive Gaseous Mercury



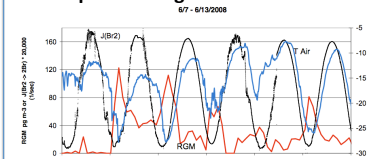
RGM Deposition

2007: peaks with J_{Br2}



Significant levels of BrO (1–5 pptv) in the near surface air were often accompanied by depletions of gaseous elemental mercury (GEM) below background levels, and in-situ production of reactive gaseous mercury (RGM). GEM reacts to form the mercury-X radical (HgX·, X=OH,Cl,Br), which is further oxidized to stable RGM (HgBr₂, HgBrOH, HgBrCl, etc.), or thermal decomposition. These are controlled by the availability of Br, OH, Cl, etc. to produce RGM (Hg(II)), versus the lifetime of HgX by thermal dissociation.

2008: peaks at night



At Summit, the availability of Br appears to be controlled by J(Br₂), requiring a sun angle of > 5 degrees, while the formation of RGM is dependent on temperature. The majority of the deposited RGM is readily photoreduced and re-emitted to the air as GEM. However, a small fraction becomes buried at depth. Extrapolating to the entire Greenland ice sheet, we calculate an estimated net annual sequestration of ~13 metric tons Hg per year, buried long-term under the sunlit photoreduction zone. (See Brooks et al. ACPD, 2010)

Summary

- LP-DOAS and CIMS confirm the presence of BrO at Summit, Greenland.
- LP-DOAS measurements combined with FLEXPART analysis show that air masses of marine origin have elevated BrO, but these transport events are rare. Local influence of snow on the composition of the boundary layer is more frequent and a case study shows that these air masses also contain elevated BrO.
- A related OD box model (results not shown) suggests that OH is under predicted, even when constrained to measured Br (See Liao et al. ACPD, 2011).
- Measurements of Hg show that bromine is involved in oxidation of mercury at Summit, however temperature effect may also impact RGM concentrations.
- Both soluble bromide and a 1D model of snow photochemistry suggest that bromine is released from the snow pack to the boundary layer.
- We have also developed a 1D model for snow photochemistry (MISTRA-SNOW) which will be presented in a related talk during the workshop.

Acknowledgements

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