Direct Detection of Atmospheric Atomic Bromine Leading to Mercury & Ozone Depletion

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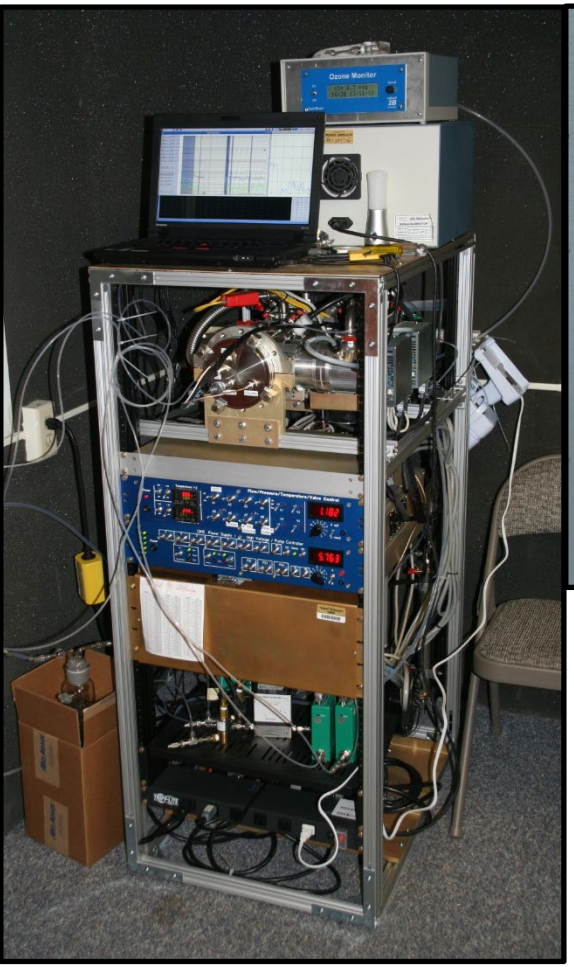
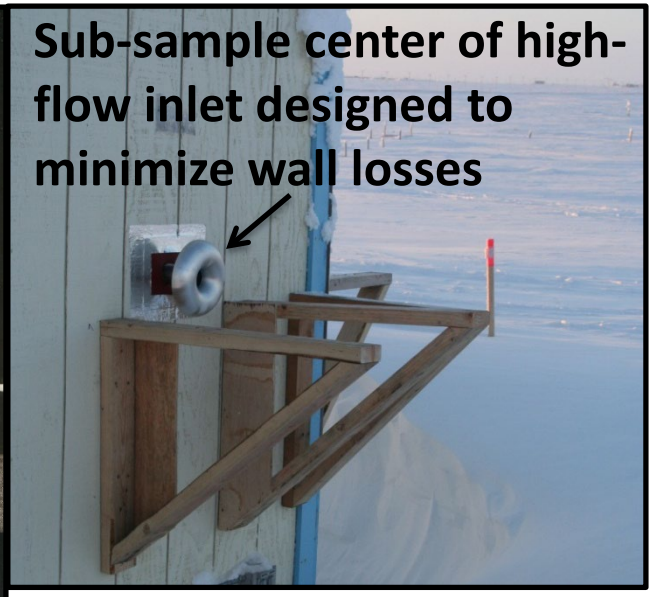
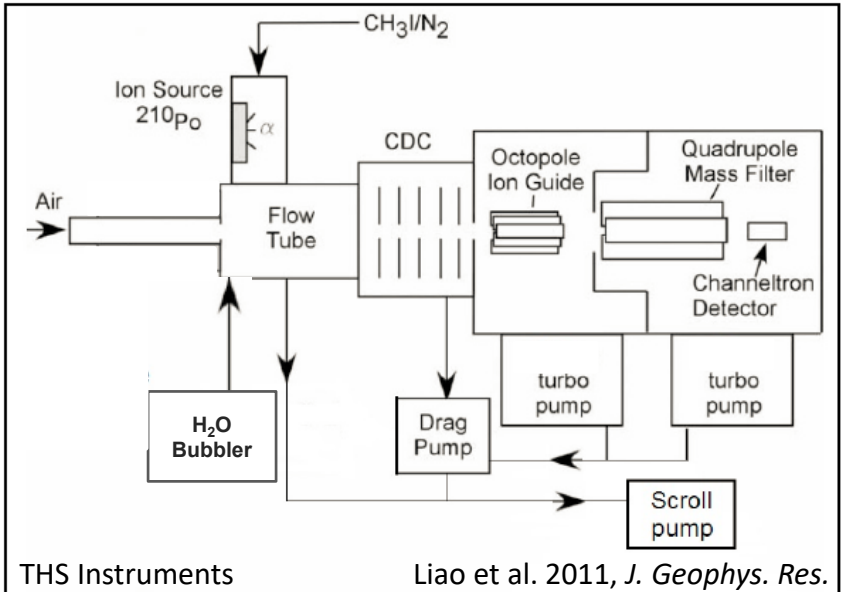
Chemical Ionization Mass Spectrometry (CIMS)

$$I(H_2O)_n^- + Br_2 \rightarrow IBr_2^- + H_2O$$





- **<1 ppt** limits of detection (LOD) for Br_2, $BrO^{\cdot}$, HOBr, Cl_2, BrCl, $ClNO_2$, N_2O_5, HO_2NO_2, **$ClO^{\cdot}$, $Br^{\cdot}$**
- <1 ppt LOD for **I_2** using SF_6^-
- Isotope ratios used to confirm ion identity, when possible



THS Instruments

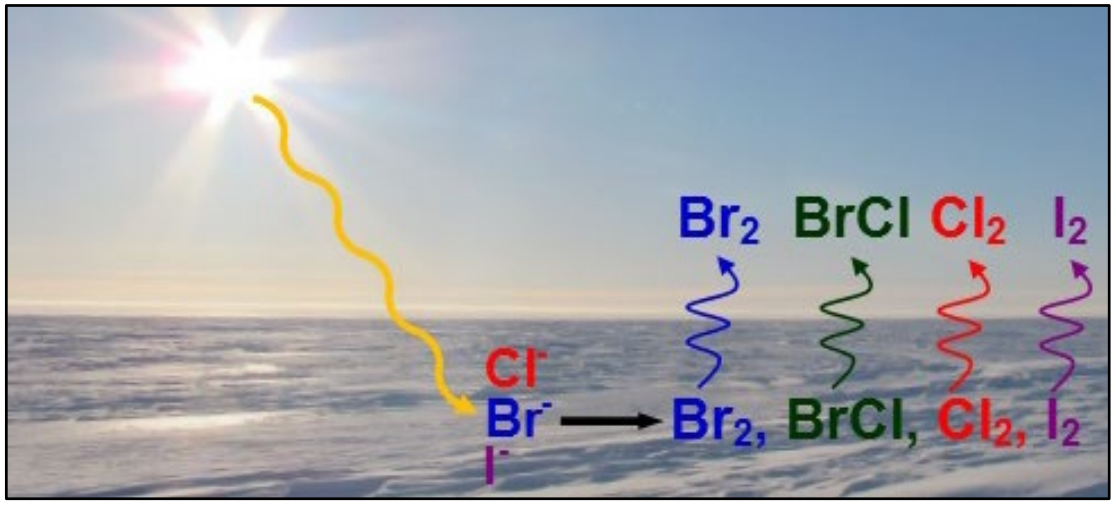
Liao et al. 2011, *J. Geophys. Res.*

- Automated field calibration using Br_2, Cl_2, and I_2 permeation sources

Arctic Measurements: Snowpack Photochemical Production of Br_2, BrCl, Cl_2, & I_2

Both natural sunlight & artificial light (solar simulator) snowpack experiments

Utqiaġvik, AK
Feb. 2014



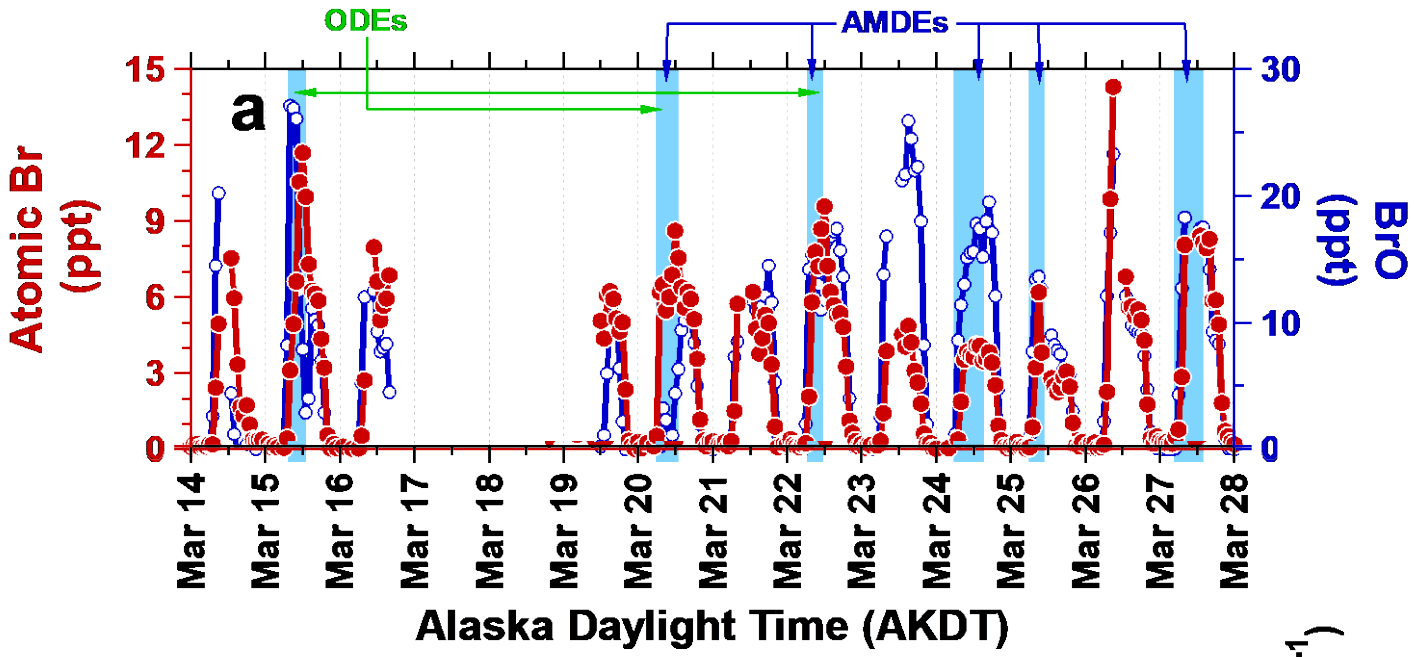
- **Upon irradiation, Arctic snowpack produces molecular halogens (Br_2, BrCl, Cl_2, and I_2)**
  - Consistent with previous Br_2 observations (Pratt et al., 2013, *Nature Geosc.*) and lab-based ice flow tube experiments (Halfacre et al., 2019, *ACP*)
- **Quantitation of Br_2 and Cl_2 snowpack production rates** (for model inputs) via above-snowpack, natural sunlight vertical profile measurements

Custard, Raso, Shepson, Staebler, & **Pratt***. 2017, *ACS Earth & Space Chem.*, 1(3), 142-151, https://doi.org/10.1021/acsearthspacechem.7b00014

Raso, Custard, May, Tanner, Newburn, Walker, Moore, Huey, Alexander, Shepson, & **Pratt***. 2017, *Proceed. Natl. Acad. Sci.*, 114(38), 10053-10058, https://doi.org/10.1073/pnas.1702803114

Direct Measurement of Ambient Atomic Br!

Utqiaġvik, AK, Mar. 2012

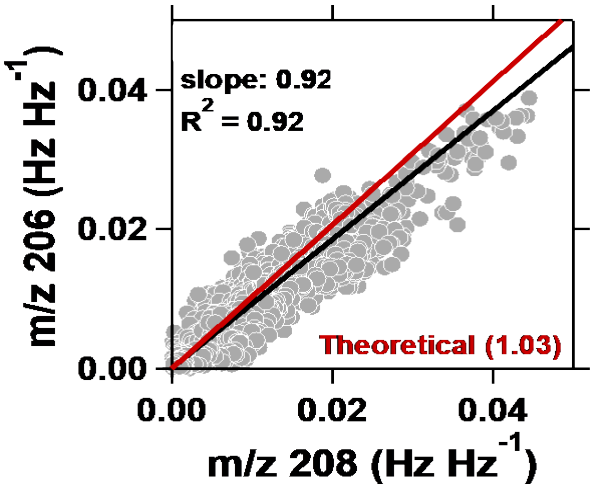


$$I(H_2O)_n^- + Br \rightarrow IBr^- + H_2O$$

First CIMS measurement of Br, monitored at *m/z* 206 ($I^{79}Br^-$):

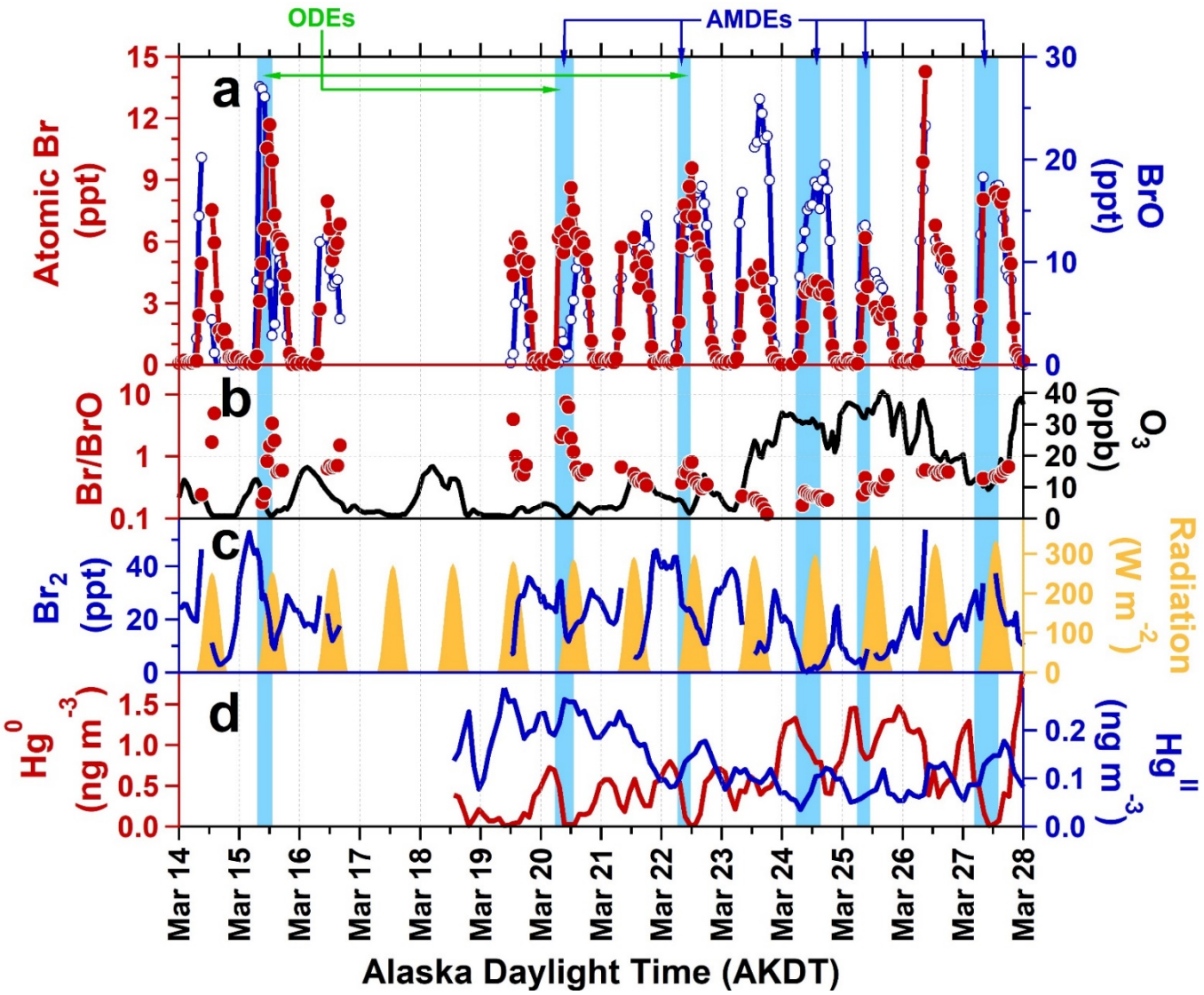
3σ LOD 2.5 ppt (1 min), 0.8 ppt (10 min)

Detailed calibrations & interference checks



Wang, McNamara, Moore, Obrist, Steffen, Shepson, Staebler, **Raso**, & **Pratt***. 2019, *Proc. Natl. Acad. Sci.*, 116(29), 14479-14484, https://doi.org/10.1073/pnas.1900613116

Comprehensive Suite of Bromine Measurements with Mercury and Ozone

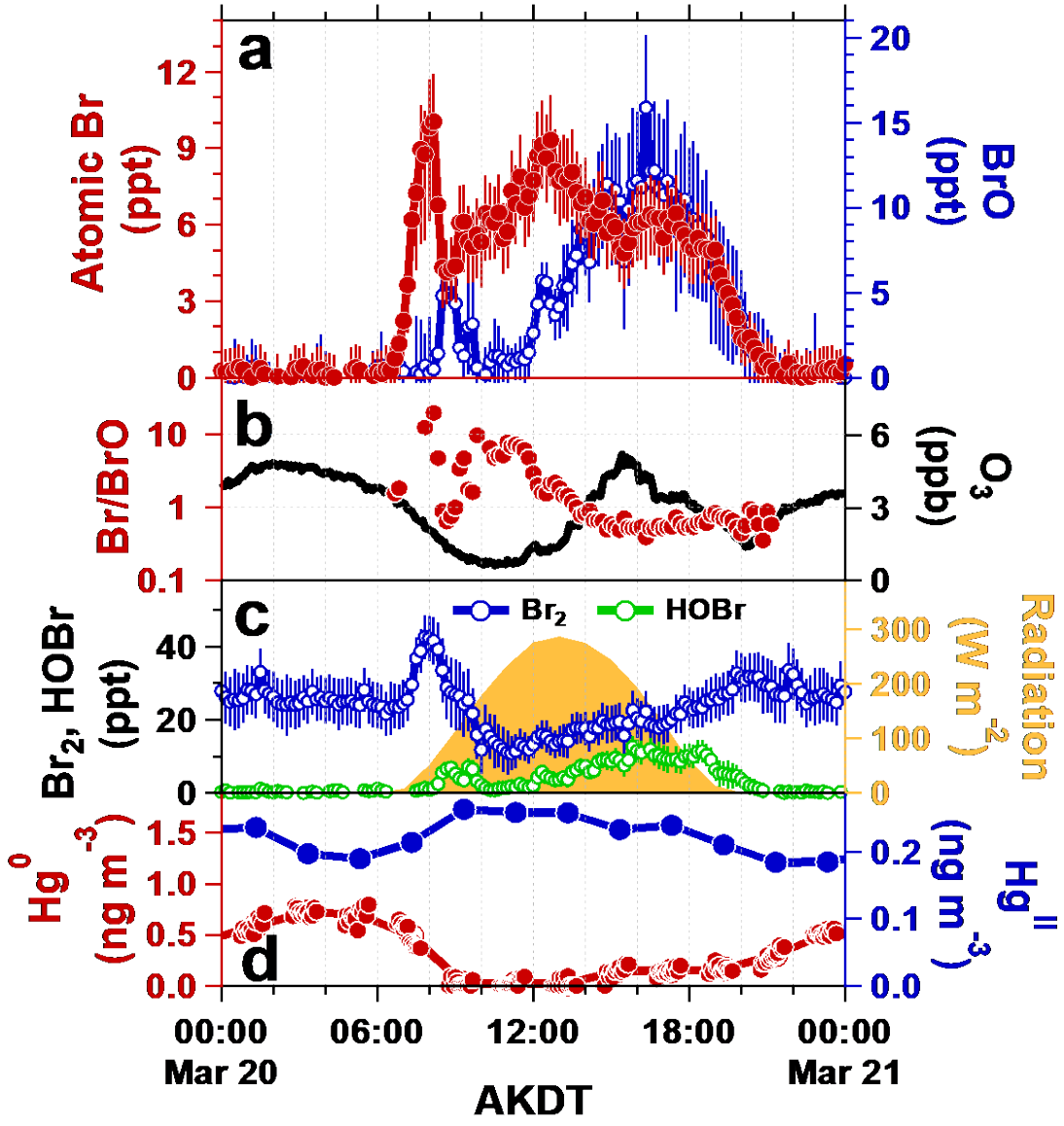


Br/BrO observed from 0.1-7.5, varying with $[O_3]$

Hg^0 depletion coincident with Hg^{II} production

Wang, McNamara, Moore, Obrist, Steffen, Shepson, Staebler, **Raso**, & **Pratt***. 2019, *Proc. Natl. Acad. Sci.*

Transition from Br → BrO

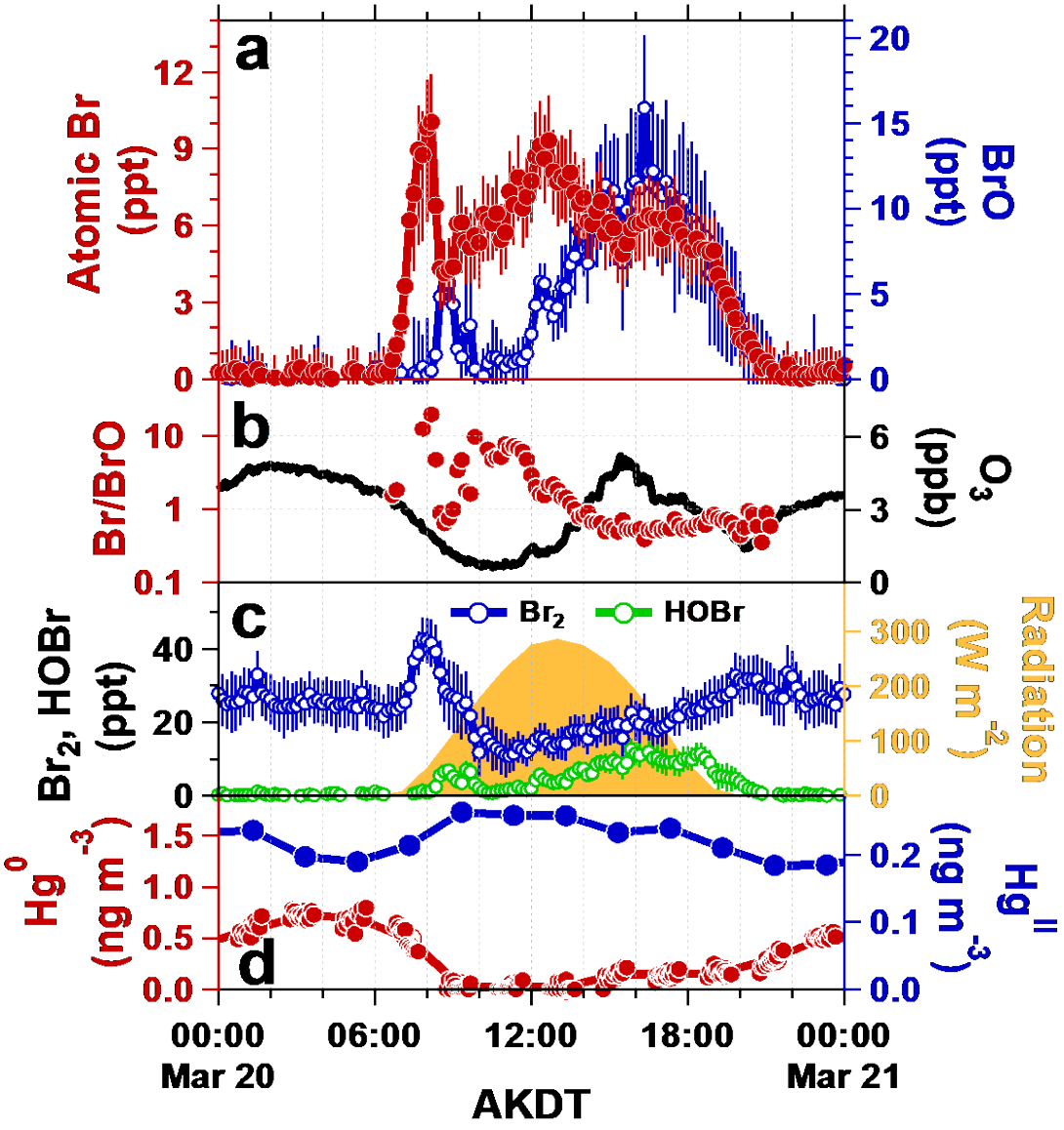


Diurnal profile of bromine chemistry:

- Snowpack Br_2 production upon sunrise
- Br_2 photolysis produces $Br^{\cdot}$, resulting in $\downarrow Hg^0$ and $\uparrow Hg^{II}$
- Increasing solar radiation reduces $[Br_2]$ via photolysis, despite ongoing snowpack production
- Afternoon mixing event increases $[O_3]$ and therefore $\uparrow$BrO and $\uparrow$HOBr

Wang, McNamara, Moore, Obrist, Steffen, Shepson, Staebler, **Raso**, & **Pratt***. 2019, *Proc. Natl. Acad. Sci.*

Transition from Br → BrO



Transition from Br → BrO with increase in O_3, due to increased vertical mixing in afternoon

Explanation of previous observation of Hg^0 depletion without BrO:

Br_2 recycling through $BrNO_2$ (rather than BrO & HOBr) from snowpack NO_2 emissions:

$Br + NO_2 \rightarrow BrNO_2$

$Br + BrNO_2 \rightarrow Br_2 + NO_2$

$BrNO_2 + Br^-_{(aq)} \rightarrow Br_2 + NO_2^-{}_{(aq)}$

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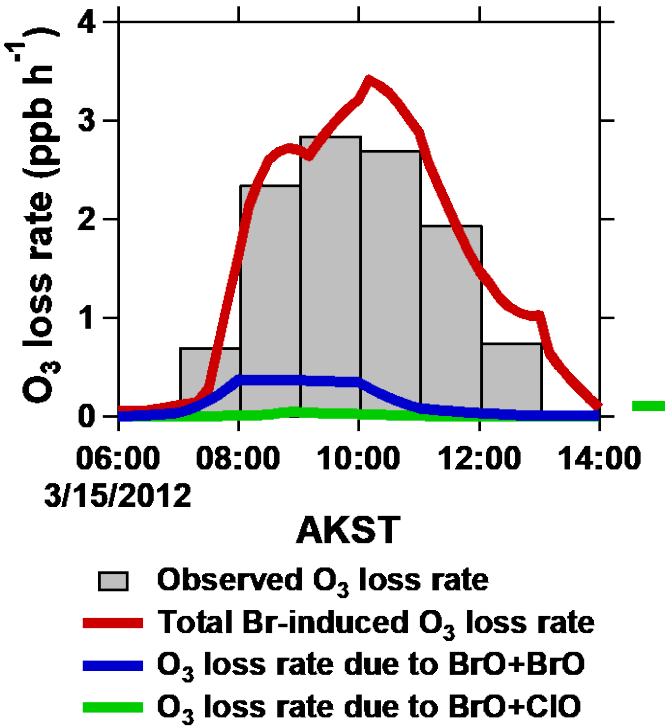
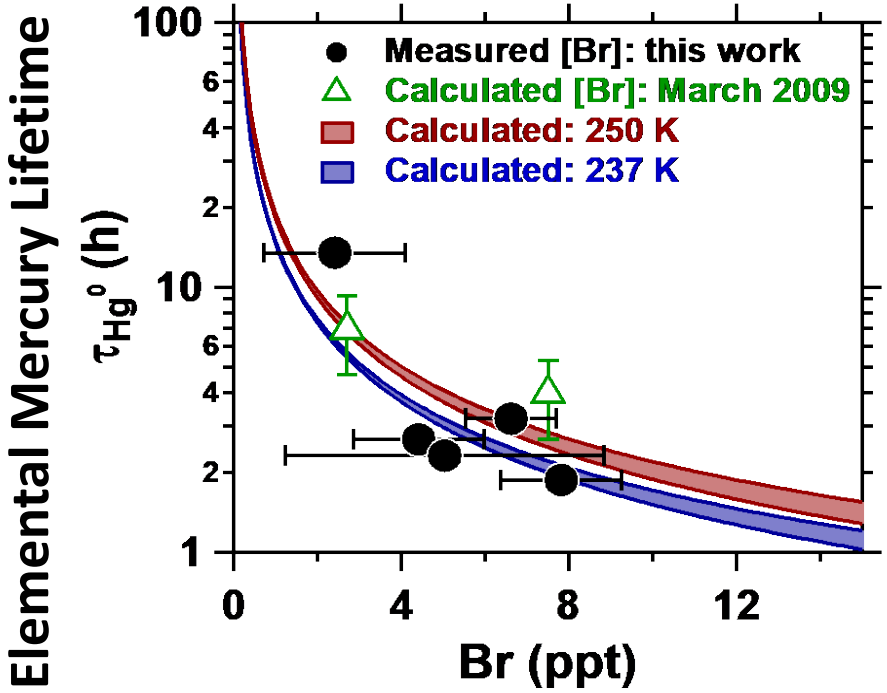
Quantitative Loss of O_3 and Hg^0

- Measured O_3 loss rate and Hg^0 lifetime in agreement with calculations using measured [$Br^{\cdot}$], proving $Br^{\cdot}$ as the main oxidant
- Snowpack Br_2 is needed for near-surface $Br^{\cdot}$ production; $Br^{\cdot}$ cannot be predicted based on $BrO^{\cdot}$ alone.
- Provides support for current laboratory-based knowledge of Hg^0 oxidation kinetics and global Hg modeling





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