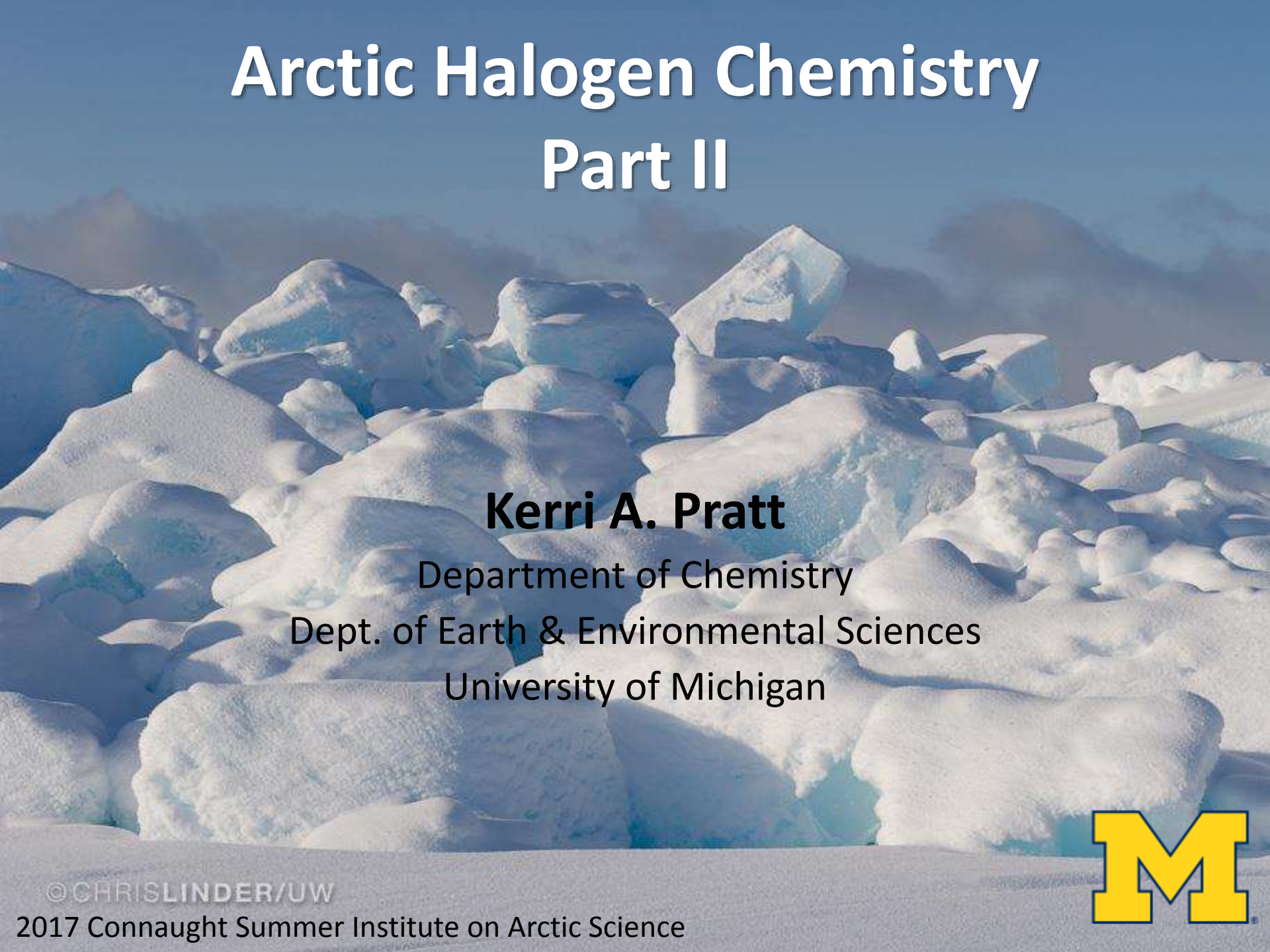
Arctic Halogen Chemistry
Part II



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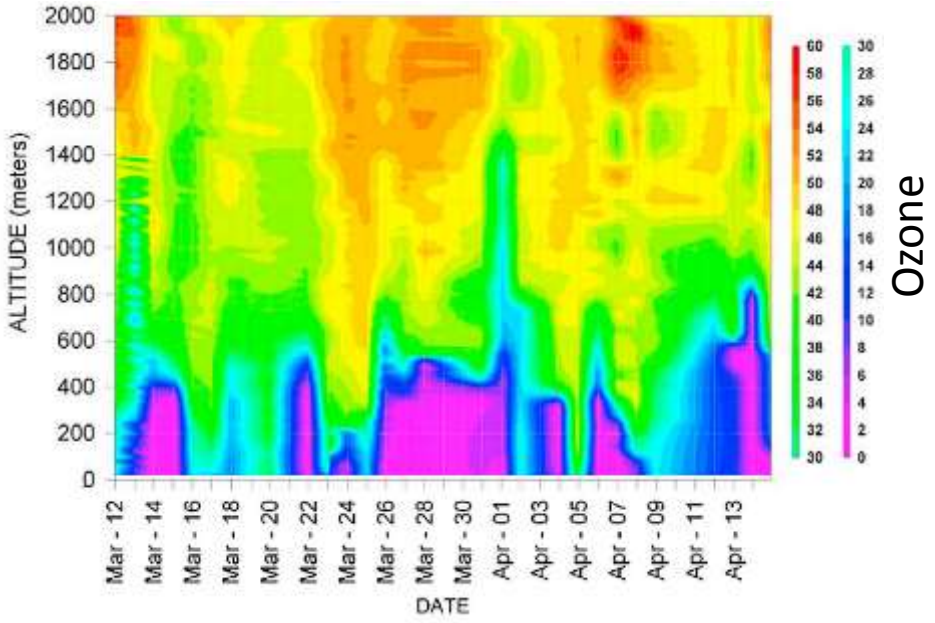
2017 Connaught Summer Institute on Arctic Science

Reminders from Yesterday!

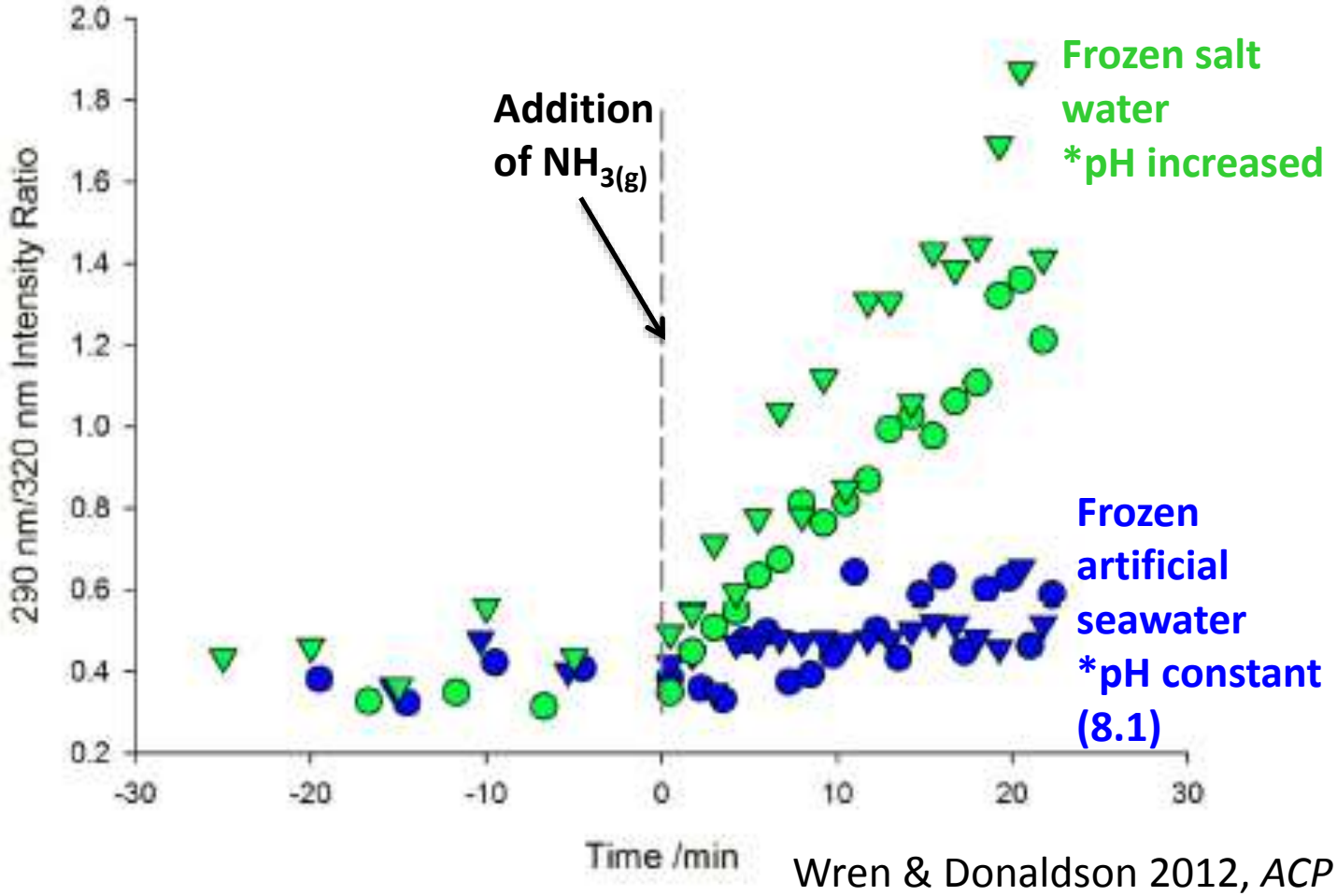
- Ozone (O_3) is important for pollutant removal from the atmosphere.
- Near-surface O_3 is often depleted in the springtime in the Arctic.
- Reactions of Br atoms with ozone cause O_3 depletion
- Br_2 is produced from sunlit Arctic surface snow!



Sea Ice does not Produce Br_2 (Pratt et al. 2013)

→ Sea Ice is Buffered Against pH Change

Lab Study: Frozen seawater surface buffered against pH change from gas deposition



Glancing-angle laser induced fluorescence with surface-active, pH-sensitive fluorescent dye (harmine)

Wren & Donaldson 2012, *ACP*

Frost Flowers – Br_2 Production Not Expected

Br^-/Cl^-: ~1/900 - 1/700 (too low)

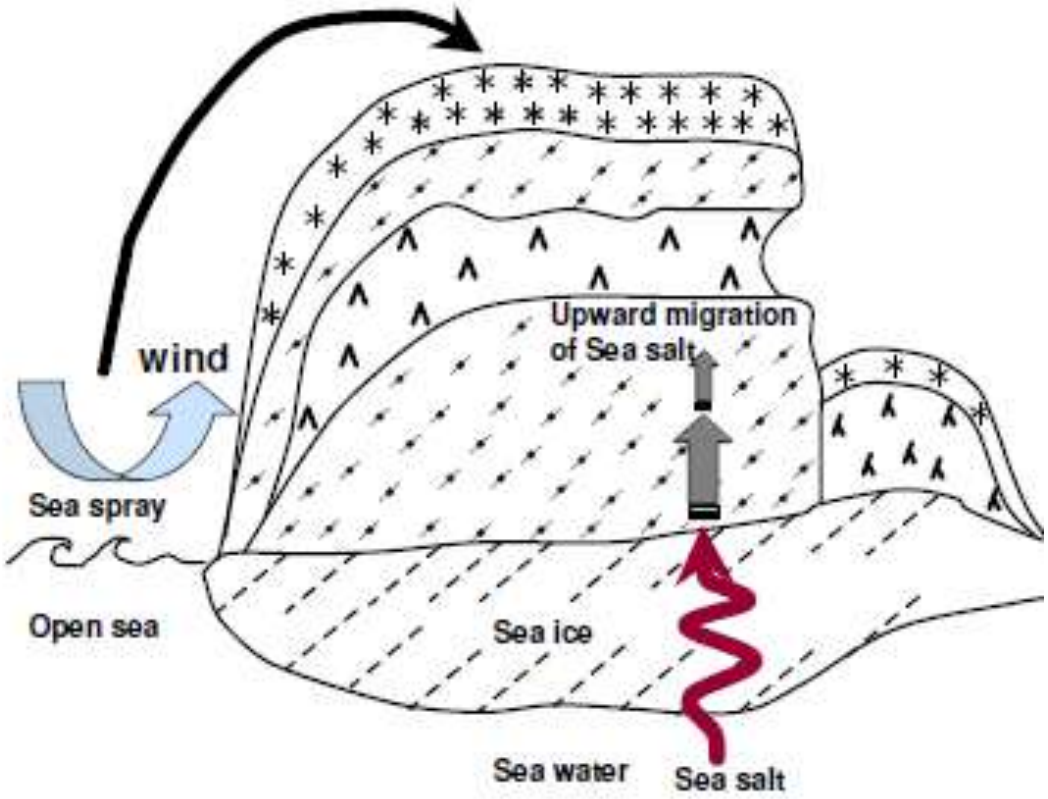
pH: 7.4-8.7 (too high)

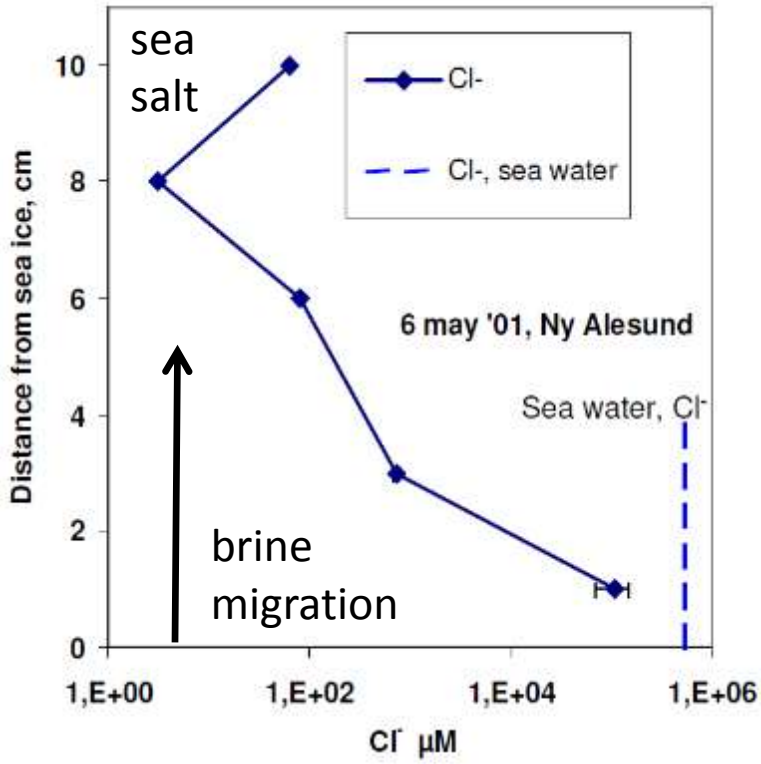
(Douglas et al 2012, *JGR*)

"Frost flowers are unlikely to be a direct source of atmospheric bromine [due to pH]." (Kalnajs & Avallone 2006, *GRL*)

Wind + frost flowers does not produce aerosols in the lab (Roscoe et al 2011, JGR; Yang et al 2017, ACP).

Sea Spray Deposition to Surface Snowpack





Domine et al. 2004, *ACP*

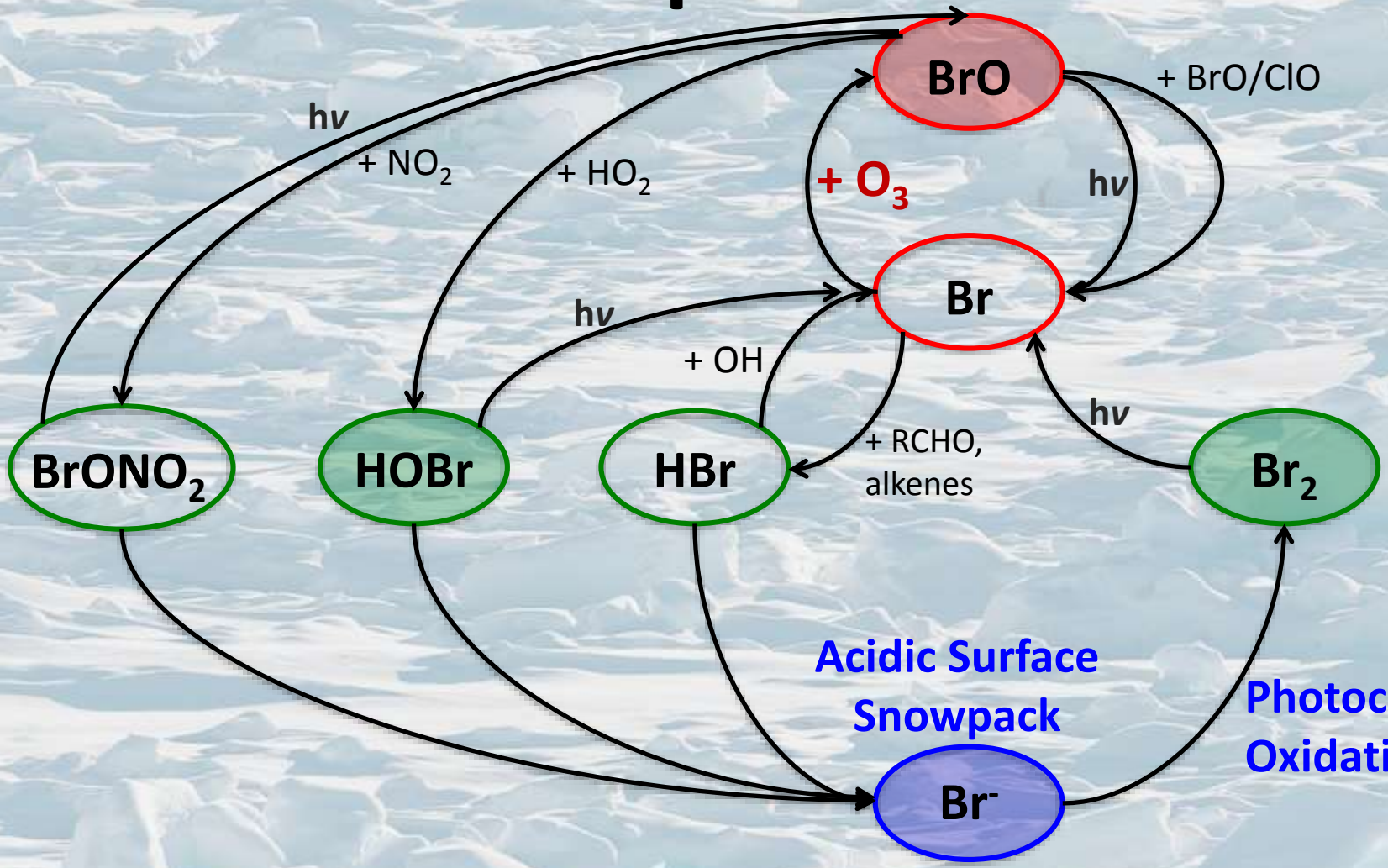
Arctic first-year sea ice covered by ~29 cm (average) of snow in springtime (Kwok et al. 2011, *JGR*)

Atmospheric deposition determines chemistry of surface snow

→ impacts $[Br^-]/[Cl^-]$ & pH

→ bromine activation

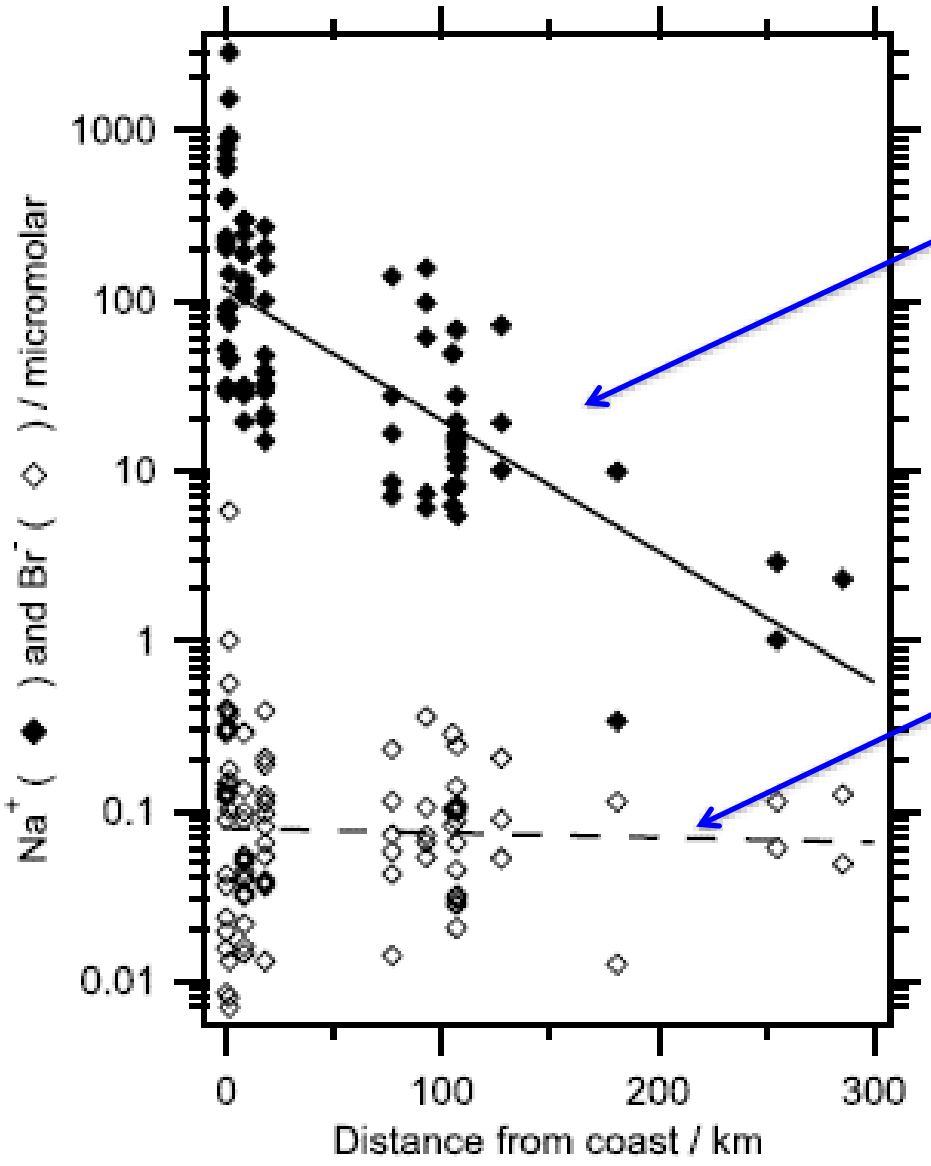
"Bromine Explosion" → Ozone Depletion Events



Barrie et al. 1988, *Nature*
Finlayson-Pitts et al. 1990, *Nature*
Fan & Jacob 1992, *Nature*

McConnell et al. 1992, *Nature*
Abbatt et al. 2012, *Atmos. Chem. Phys.*
Pratt et al. 2013, *Nature Geoscience*

Inland Tundra Snow as Bromine Source



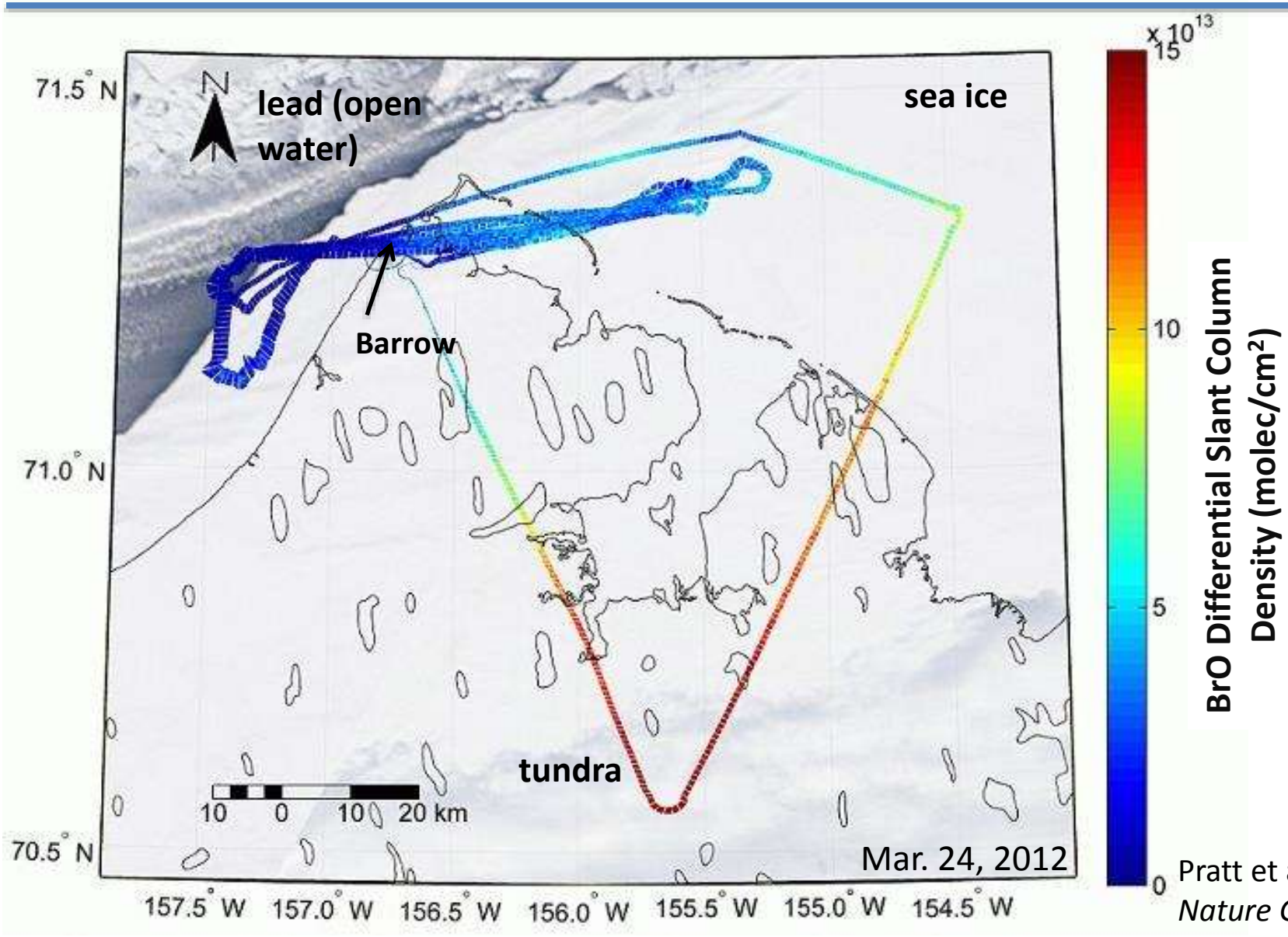
Decreasing Na^+ inland due to increased deposition of sea spray aerosol

Transport and inland deposition of trace bromine gases (e.g., HOBr, HBr, $BrNO_2$)

- 75-90% of deposited bromine is estimated to be re-emitted as Br_2/BrCl

Simpson et al 2005, *GRL*
Piot & von Glasow 2008, *ACP*

BrO Enhanced Near Surface over Snow-Covered Tundra



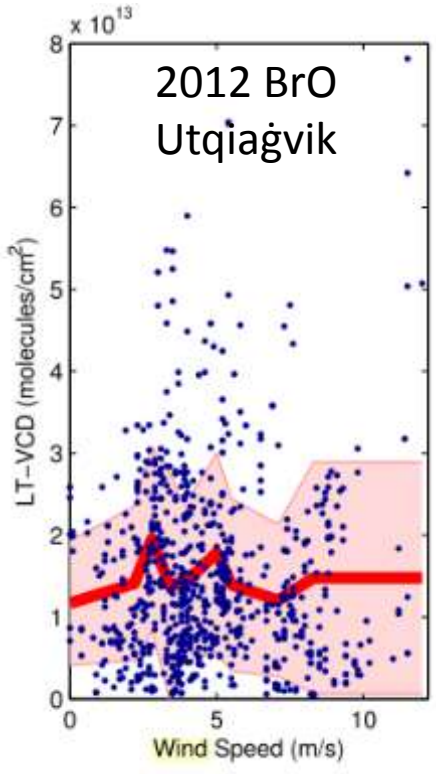
Pratt et al. 2013, *Nature Geoscience*

Additional Arctic Br_2 Sources?

? **Surface snow above MYI** *(likely)*

– Similar pH, [Br^-], and [Cl^-] as tundra snow near Utqiaġvik (Krnavek et al 2012, *Atmos. Environ.* & P. Peterson, Pratt Lab)

? **Blowing Snow** (Antarctic model – Yang et al 2008, *GRL*)

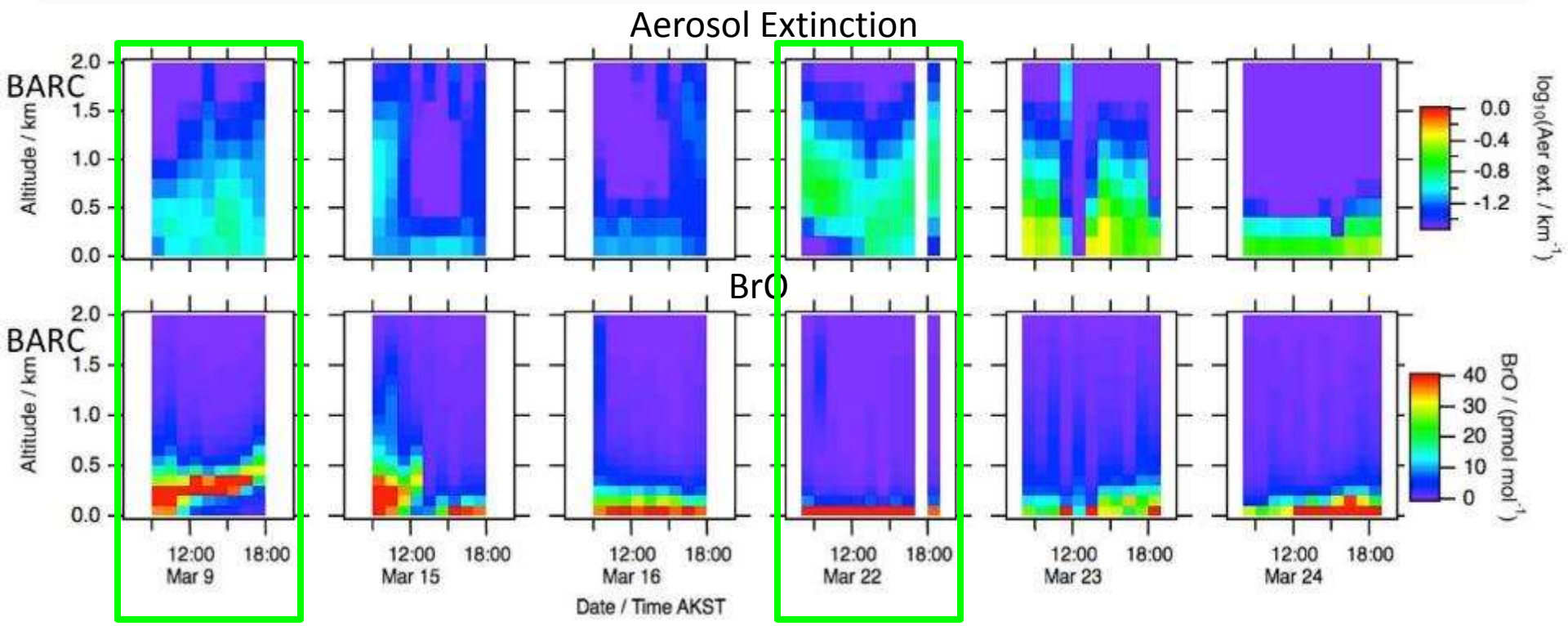


Peterson et al. 2015, *ACP*

- *Hypothesis:* wind-driven snow lofting, followed by snow sublimation & sea salt aerosol production, followed by reactions on particle surfaces to produce reactive bromine
- *Need experimental tests:* simultaneous measurements of surface snow, lofted snow grains, aerosols (size & chemistry), and reactive bromine (BrO, Br_2) to connect the proposed full cycle

- In Utqiaġvik, increased wind (increased atmospheric mixing) typically is accompanied by increased O_3.

Enhanced Aerosol ≠ BrO Vertical Propagation



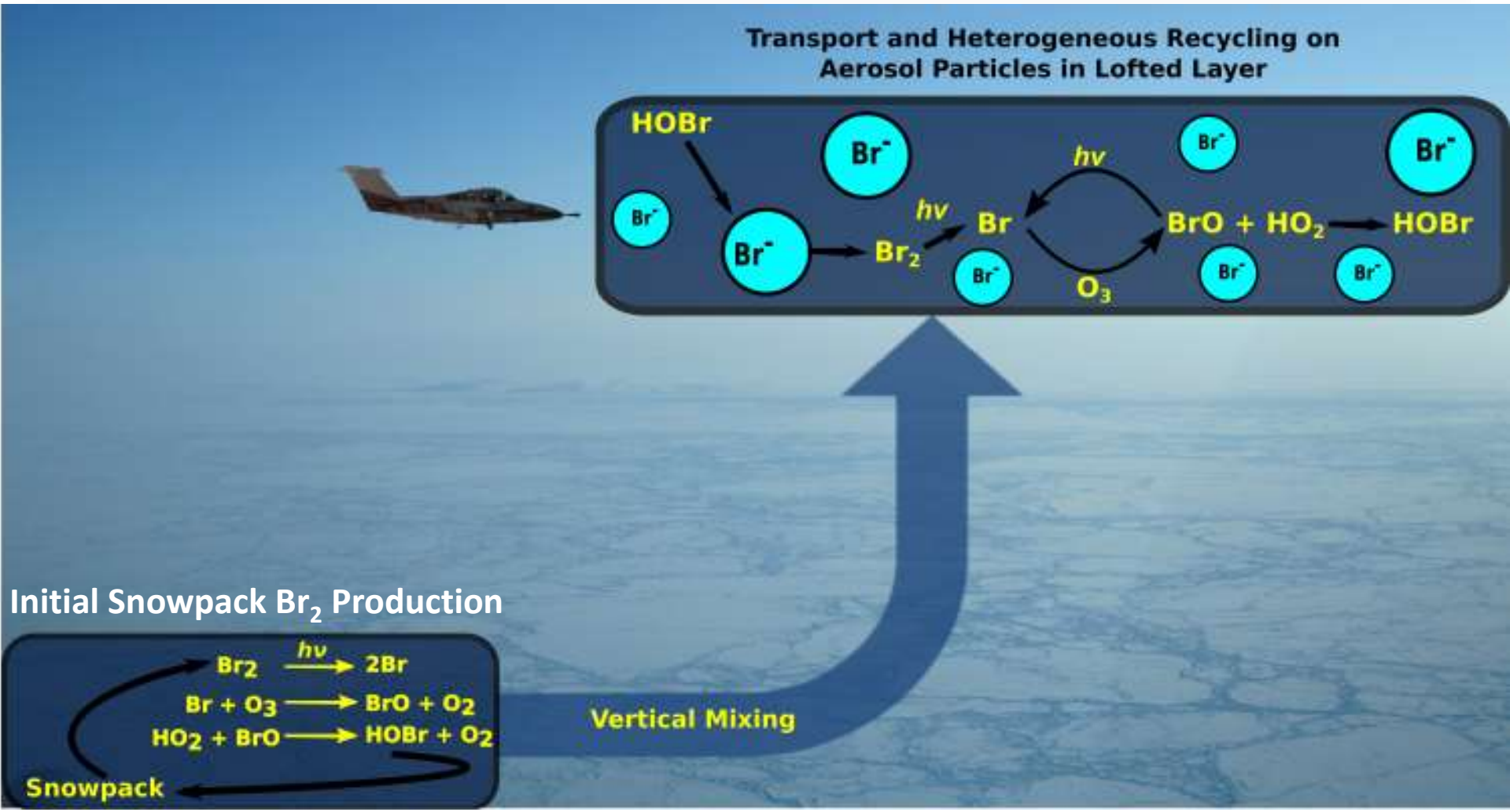
"Aerosol aloft is necessary for BrO to be present aloft, but it is not sufficient to always cause BrO to propagate vertically when aerosol extinction is present."

Important factors:

- Meteorology (Peterson et al 2015, *ACP*)
- Aerosol chemical composition (sea spray aerosol: aerosol Br^-)

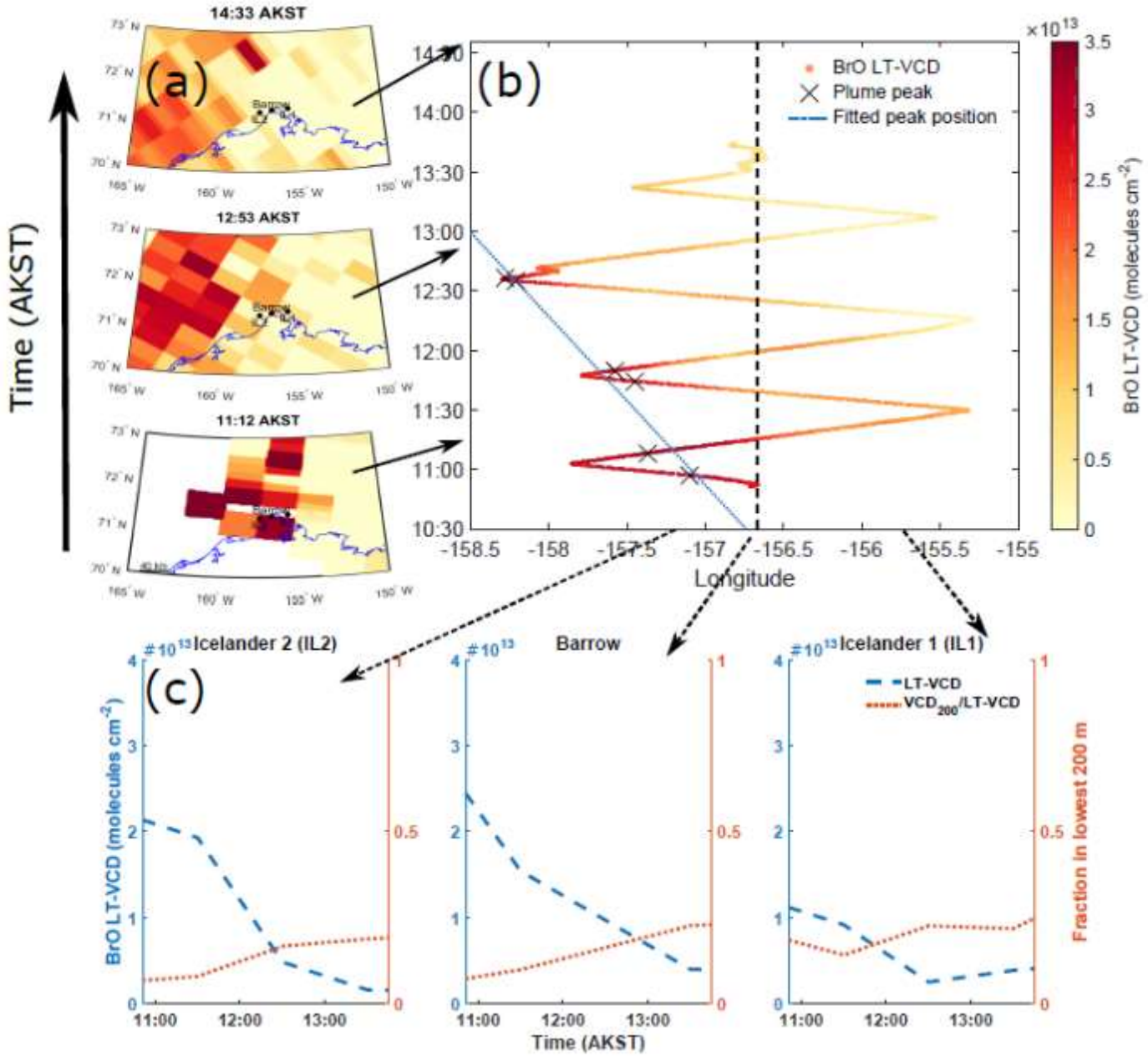
Simpson et al 2017, *ACP*

Lofted Bromine Chemistry Sustained by Recycling Reactions on Aerosols



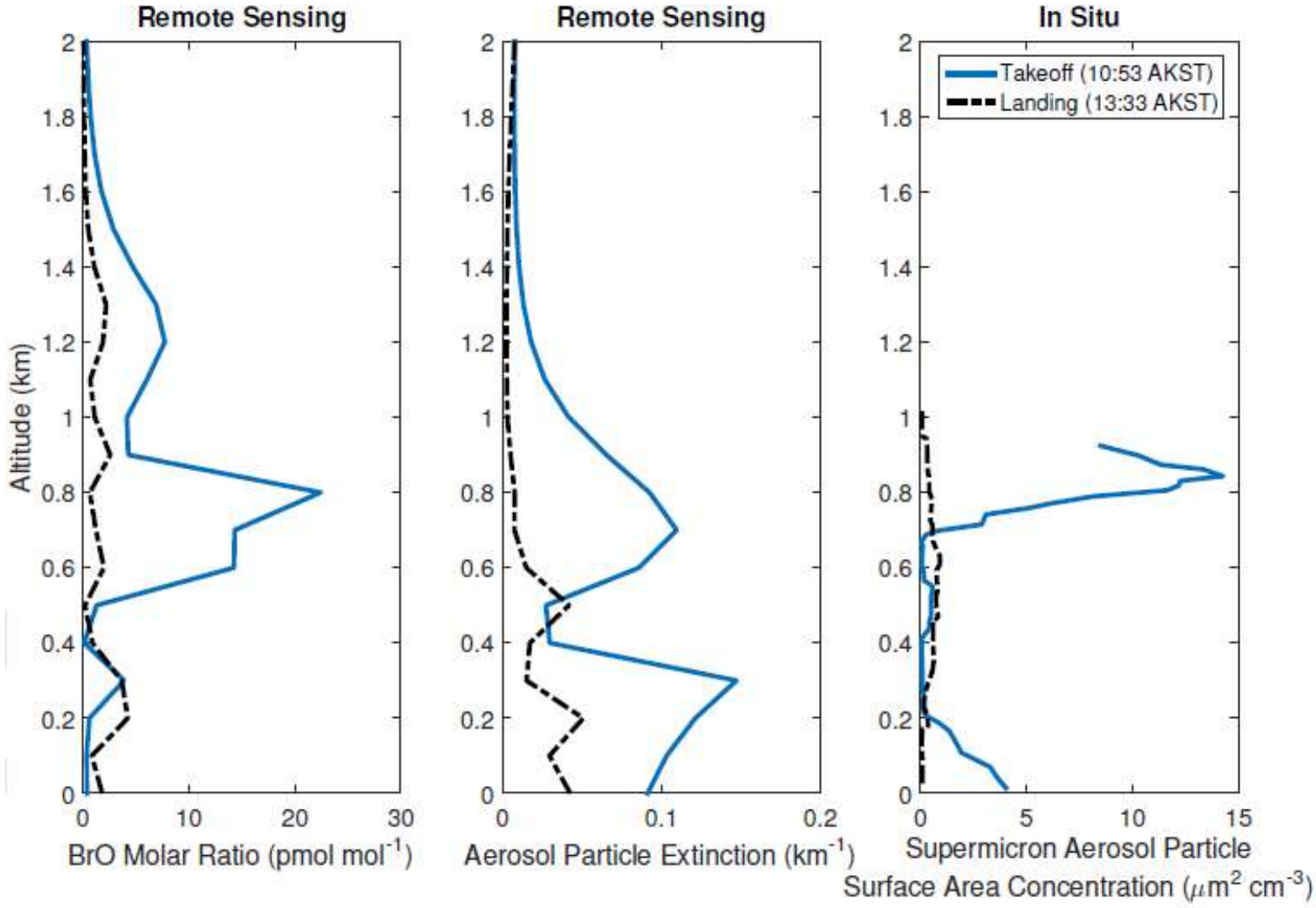
Peterson et al. 2017, *ACP*

BrO Plume moving at Speed of Air Mass



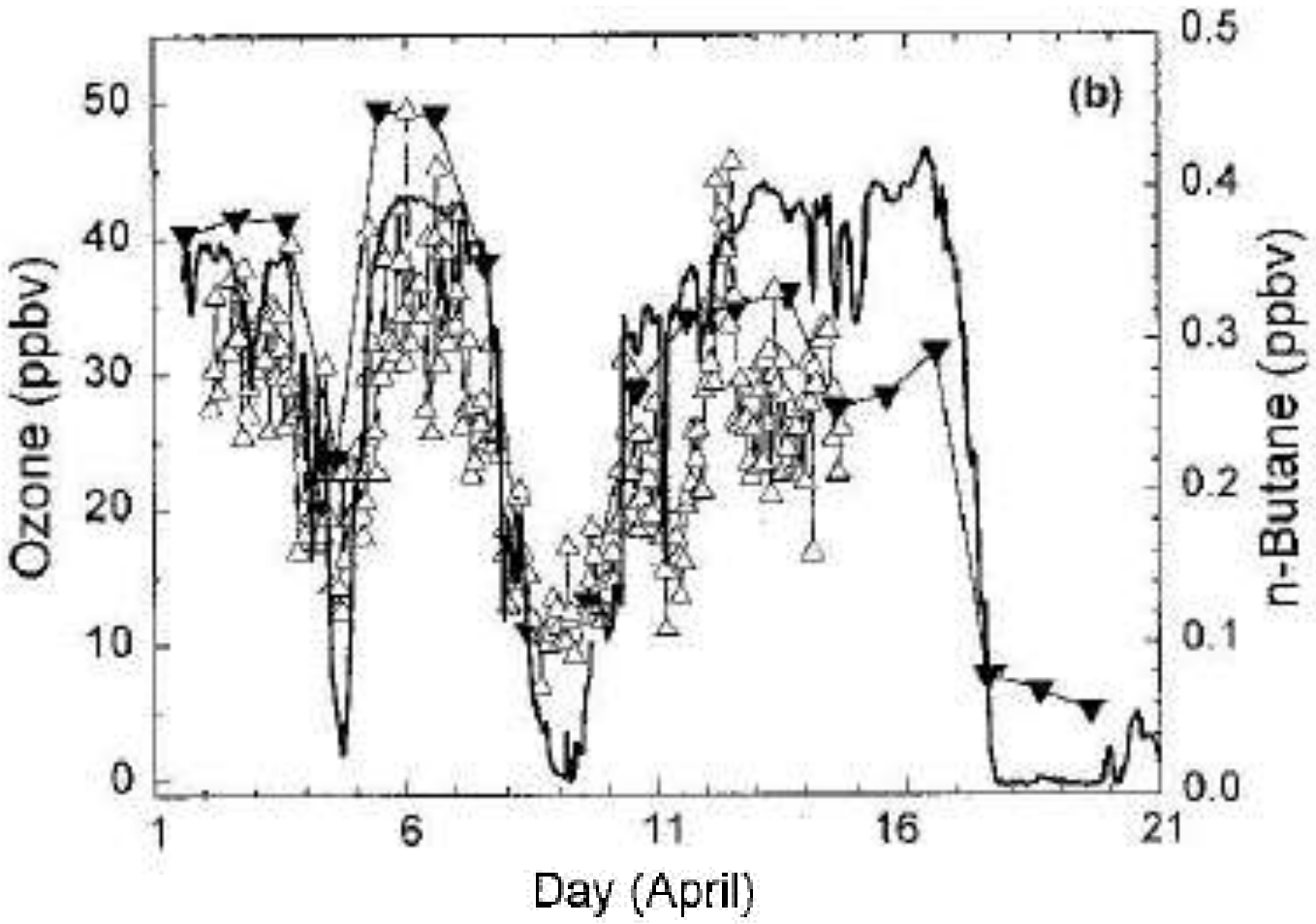
Peterson et al. 2017, *ACP*

Lofted BrO Co-located with Enhanced Supermicron Aerosol



Peterson et al. 2017, *ACP*

Evidence of Cl Atom Reactions with Hydrocarbons



Examples: k_{Cl} ~100x k_{OH} for n-butane

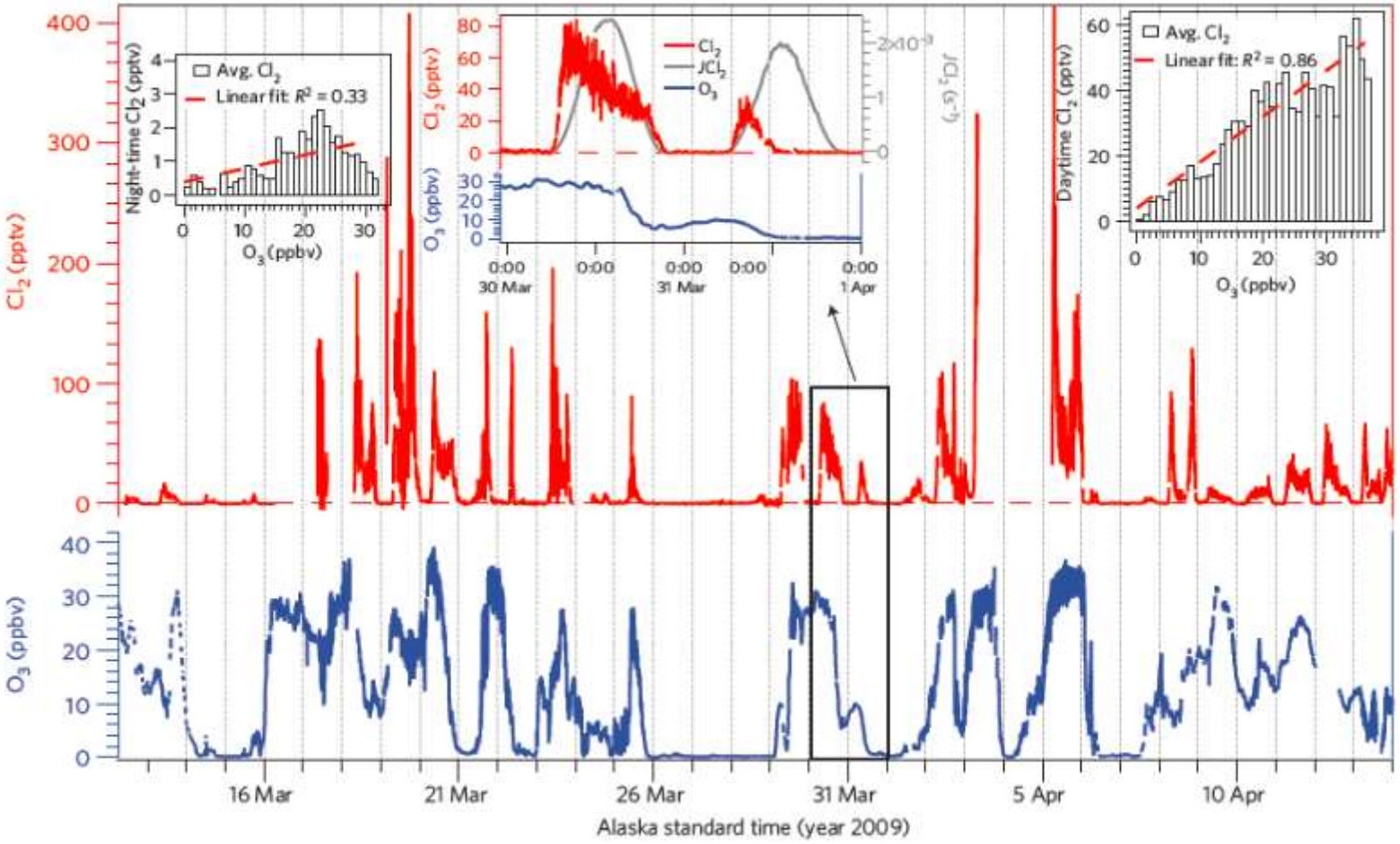
k_{Cl} ~20x k_{OH} for methane

Jobson et al 1994, *JGR*

nature geoscience
LETTERS
PUBLISHED ONLINE: 12 JANUARY 2014 | DOI: 10.1038/NGEO2046

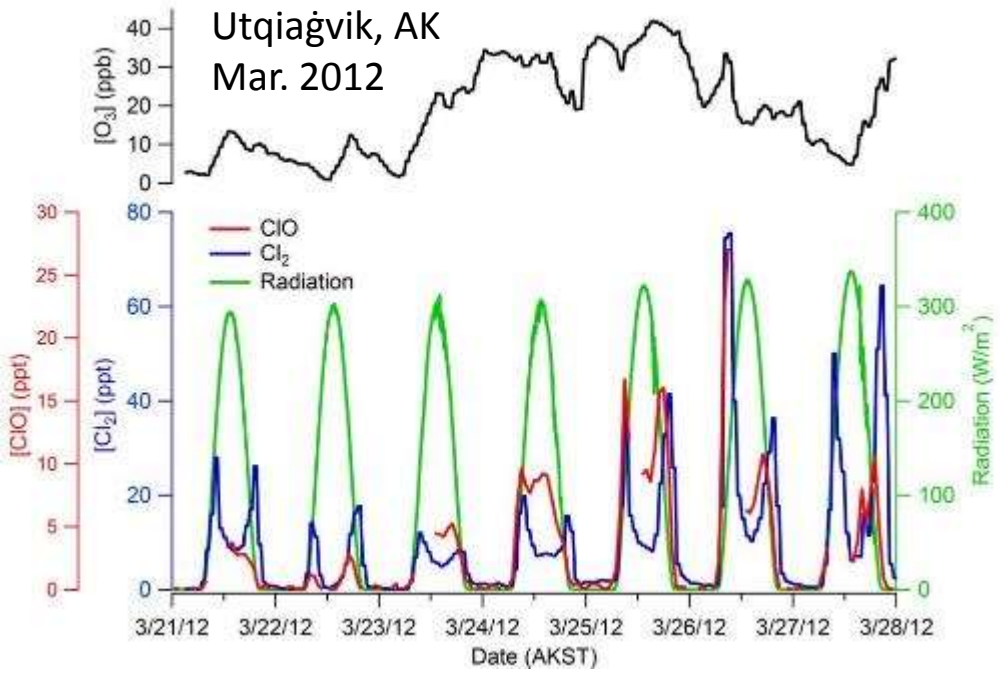
High levels of molecular chlorine in the Arctic atmosphere

Jin Liao[1,2,3], L. Gregory Huey[1]*, Zhen Liu[1,4], David J. Tanner[1], Chris A. Cantrell[5,6], John J. Orlando[5], Frank M. Flocke[5], Paul B. Shepson[7], Andrew J. Weinheimer[5], Samuel R. Hall[5], Kirk Ullmann[5], Harry J. Beine[8], Yuhang Wang[1], Ellery D. Ingall[1], Chelsea R. Stephens[7], Rebecca S. Hornbrook[5], Eric C. Apel[5], Daniel Riemer[5], Alan Fried[5], Roy L. Mauldin III[5,6,9], James N. Smith[5], Ralf M. Staebler[10], J. Andrew Neuman[2,3] and John B. Nowak[2,3]



Cl_2 correlated with O_3 and radiation

ClO Measurement – Constraint on [Cl]

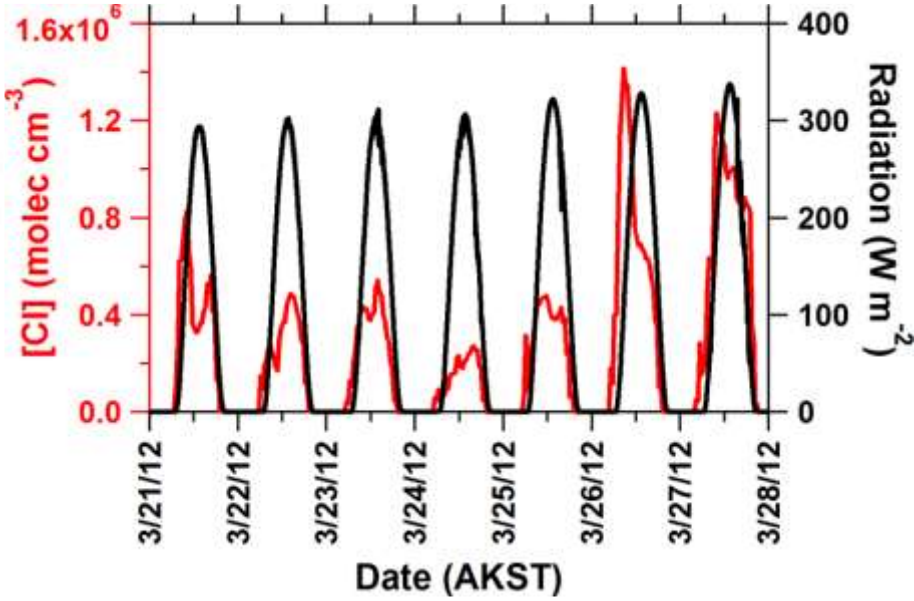


First CIMS measurement of ClO:

3σ LOD 2.6 ppt (1 min), 0.3 ppt (1 h)

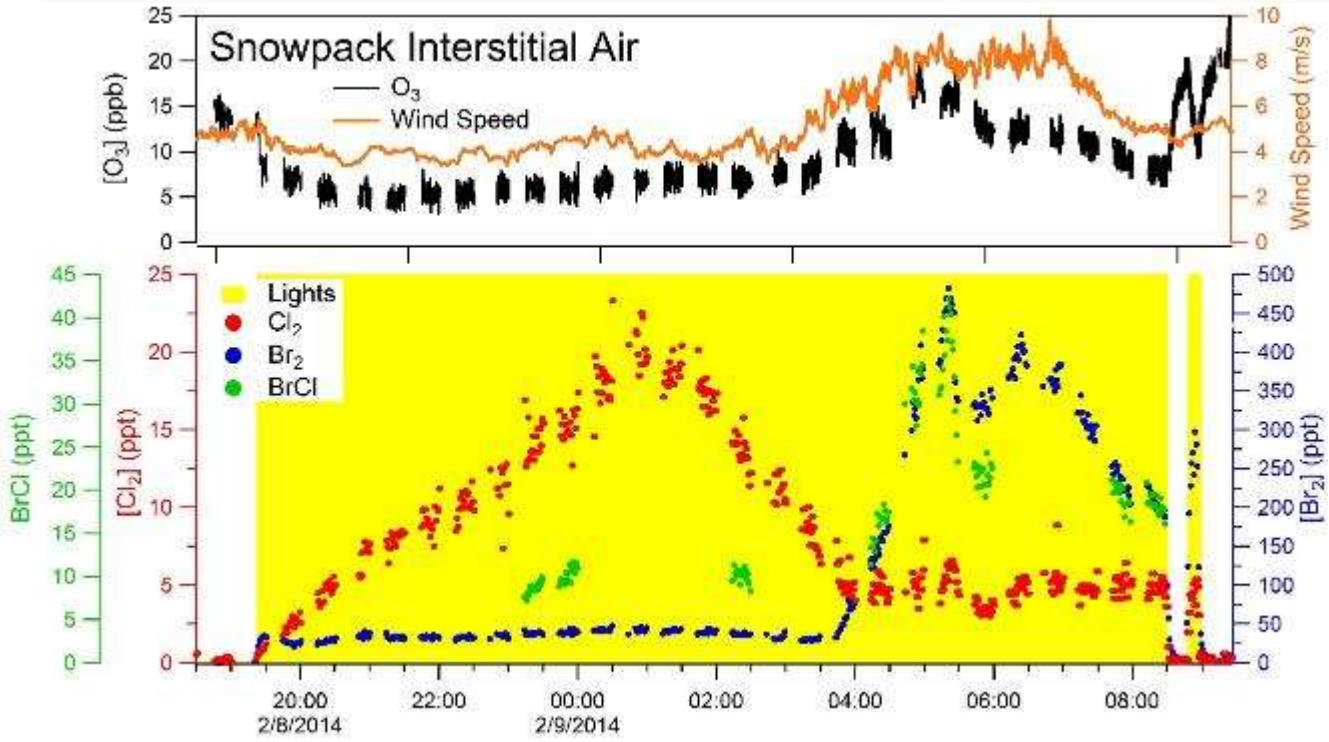
Custard et al 2016, *ES&T*

0-D model constrained by measured $[Cl_2]$ simulates [ClO] within measurement uncertainty, providing an improved constraint on [Cl]

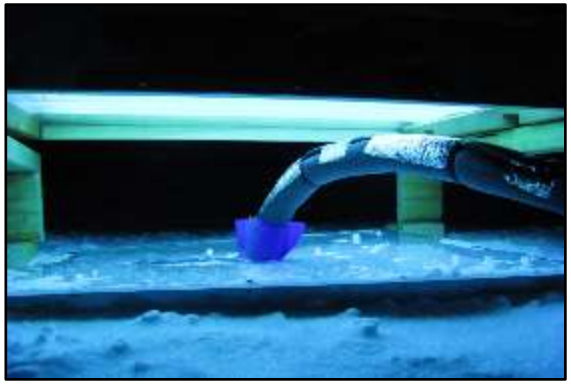


Modeled [Cl] suggest that previous calculations, based on hydrocarbon levels, are underestimates due to the longer lifetimes of the hydrocarbons

Photochemical Snowpack Cl_2 and BrCl Production



Artificially irradiated snowpack
Utqiaġvik, AK
Feb. 2014

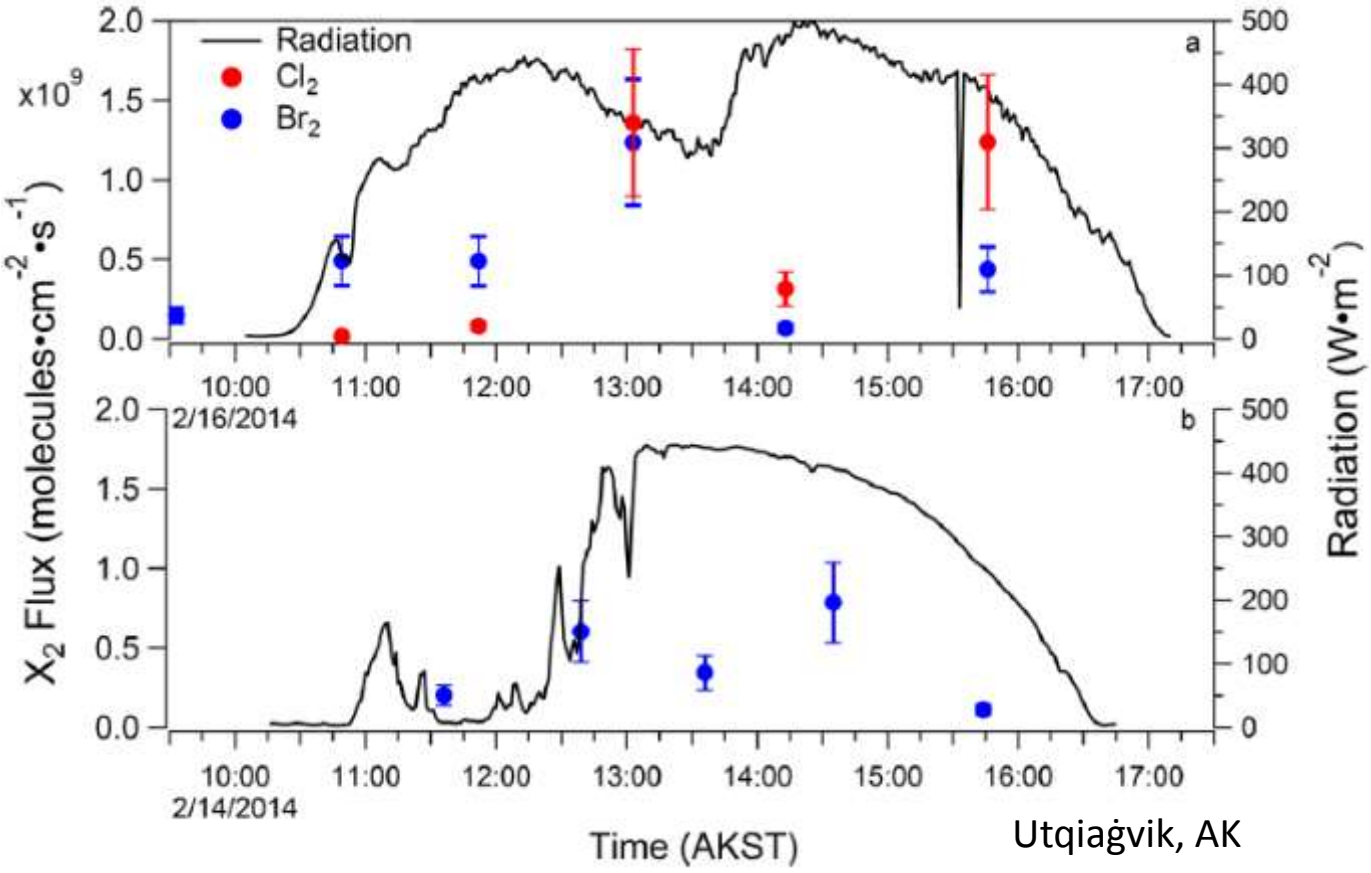


- Upon illumination, Arctic snowpack produces molecular halogens (first observations of snowpack Cl_2 and BrCl production)
- Br_2 and BrCl followed similar trends, with production *enhanced* by the addition of O_3 and at air temperatures below which $NaCl{\cdot}2H_2O$ precipitates
- Cl_2 production *limited* at <10 ppb O_3 and temperatures below which $NaCl{\cdot}2H_2O$ precipitates (consistent with previous lab studies - Sjostedt & Abbatt 2008, *ERL*)

Custard et al. 2017, *ACS Earth & Space Chem.*

Snowpack Br_2 and Cl_2 Fluxes

First Br_2 and Cl_2 snowpack fluxes calculated based on vertical concentration gradients above sunlit snowpack

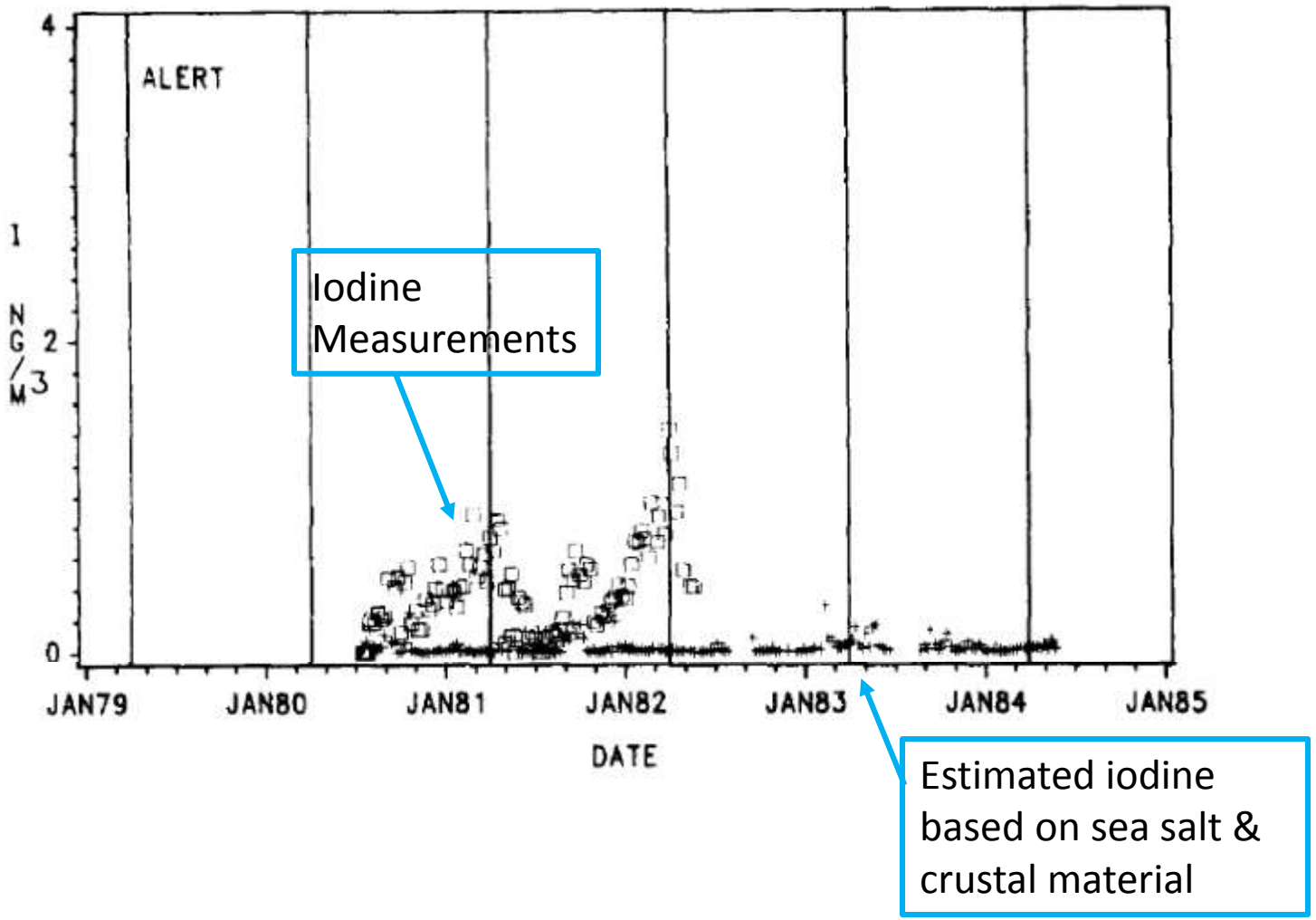


Consistent with previous modeling studies estimating Br_2 fluxes: 9.0 x 10^7 to 2.7 x 10^9 molecules cm^{-2} s^{-1}

Custard et al. 2017, *ACS Earth & Space Chem.*

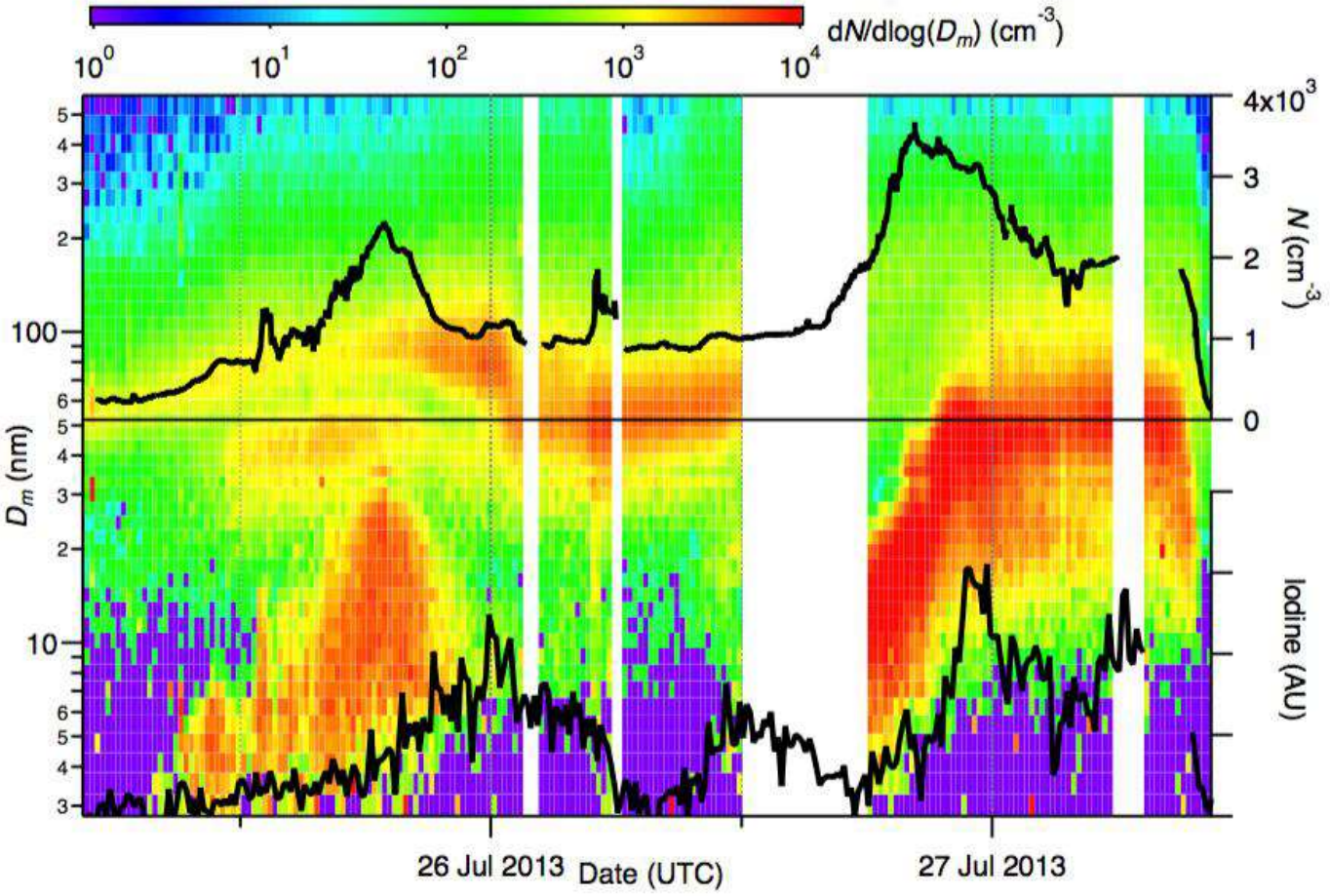
Evidence of Arctic Iodine Chemistry

Particulate Iodine



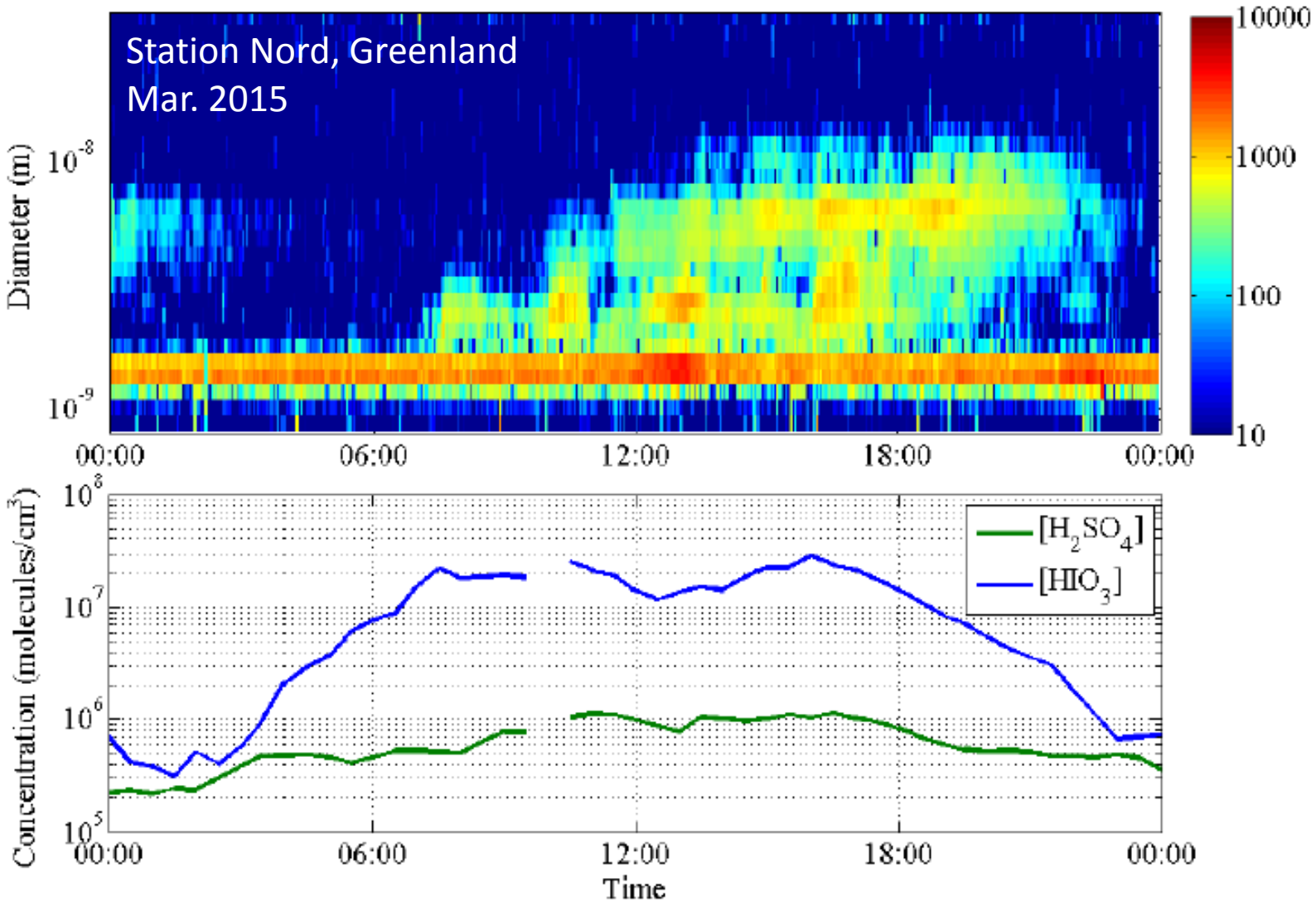
Sturges & Barrie 1988, Atmos. Environ.

Aerosol Iodine Associated with New Particle Formation and Growth



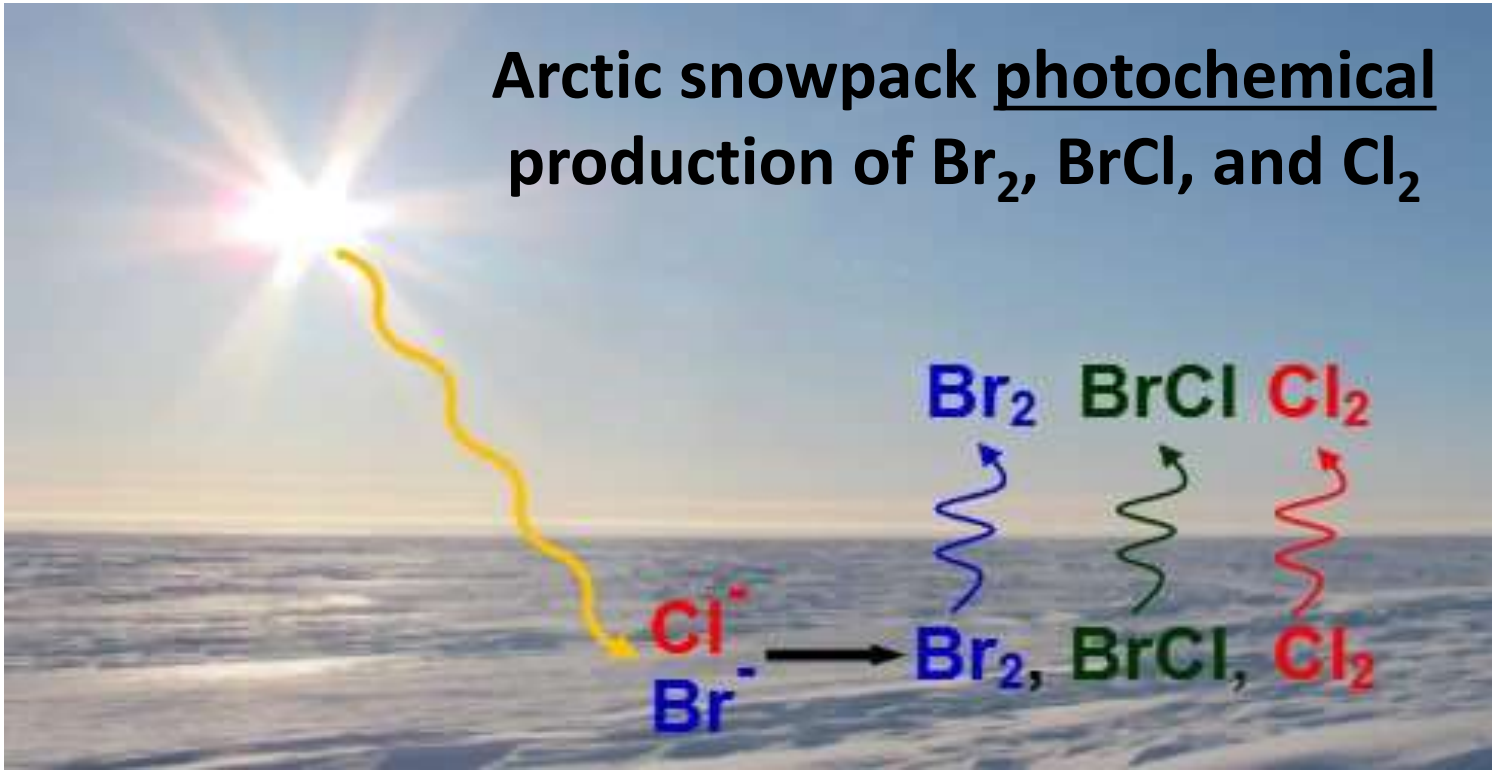
Allan et al 2015, ACP

Iodic acid (HIO_3) Clusters Associated with New Particle Formation



Sipilä et al 2016, *Nature*

Snowpack Molecular Halogen Production



- Relative amounts of Br_2, BrCl, and Cl_2 may be related to snowpack temperature & precipitation of $NaCl \cdot 2H_2O$
- Constraint on [Cl] provided by simultaneous Cl_2 and ClO CIMS measurements

Custard et al. 2016, *ES&T*
Custard et al. 2017, *ACS Earth & Space Chem.*