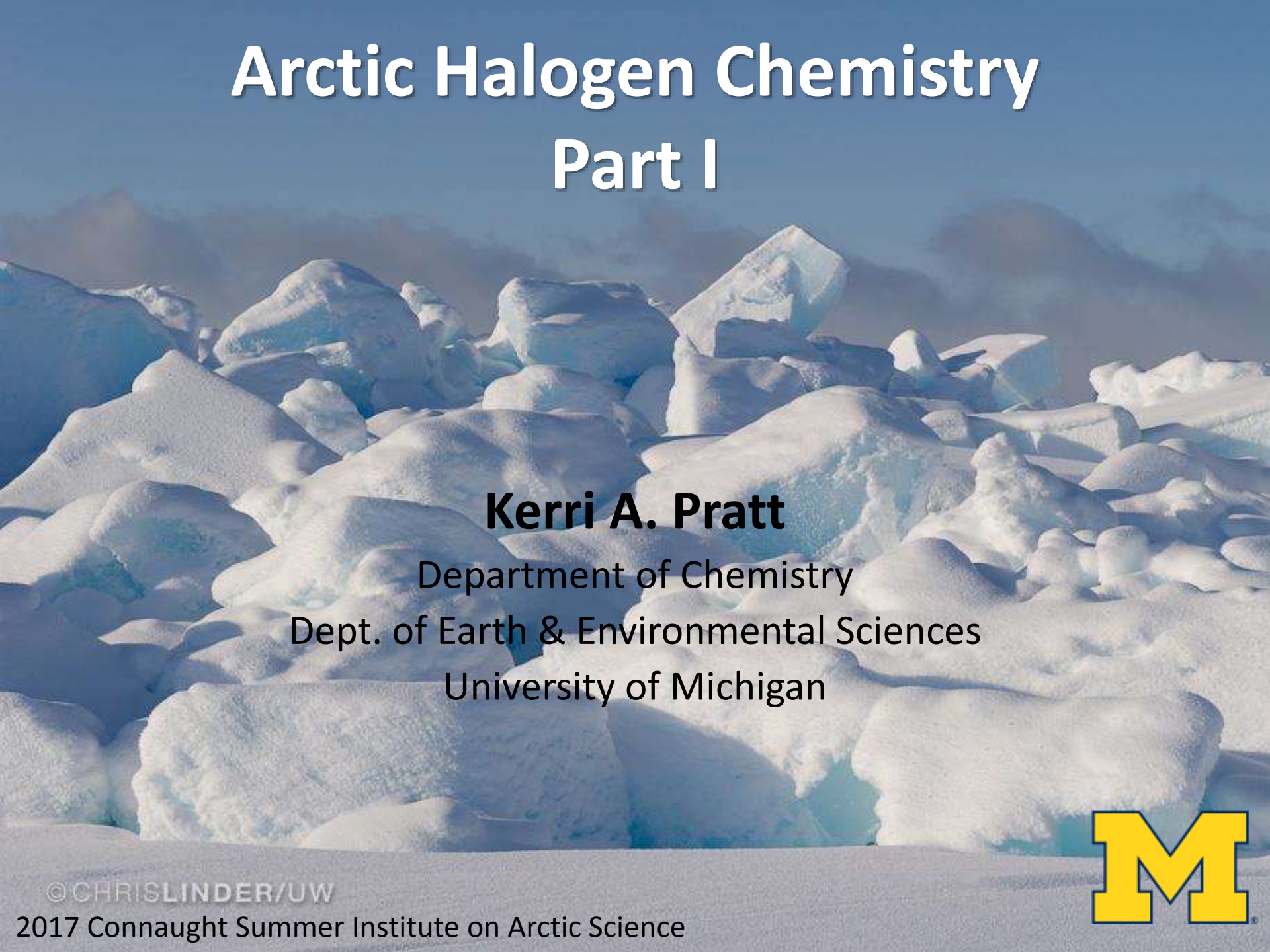
Arctic Halogen Chemistry
Part I



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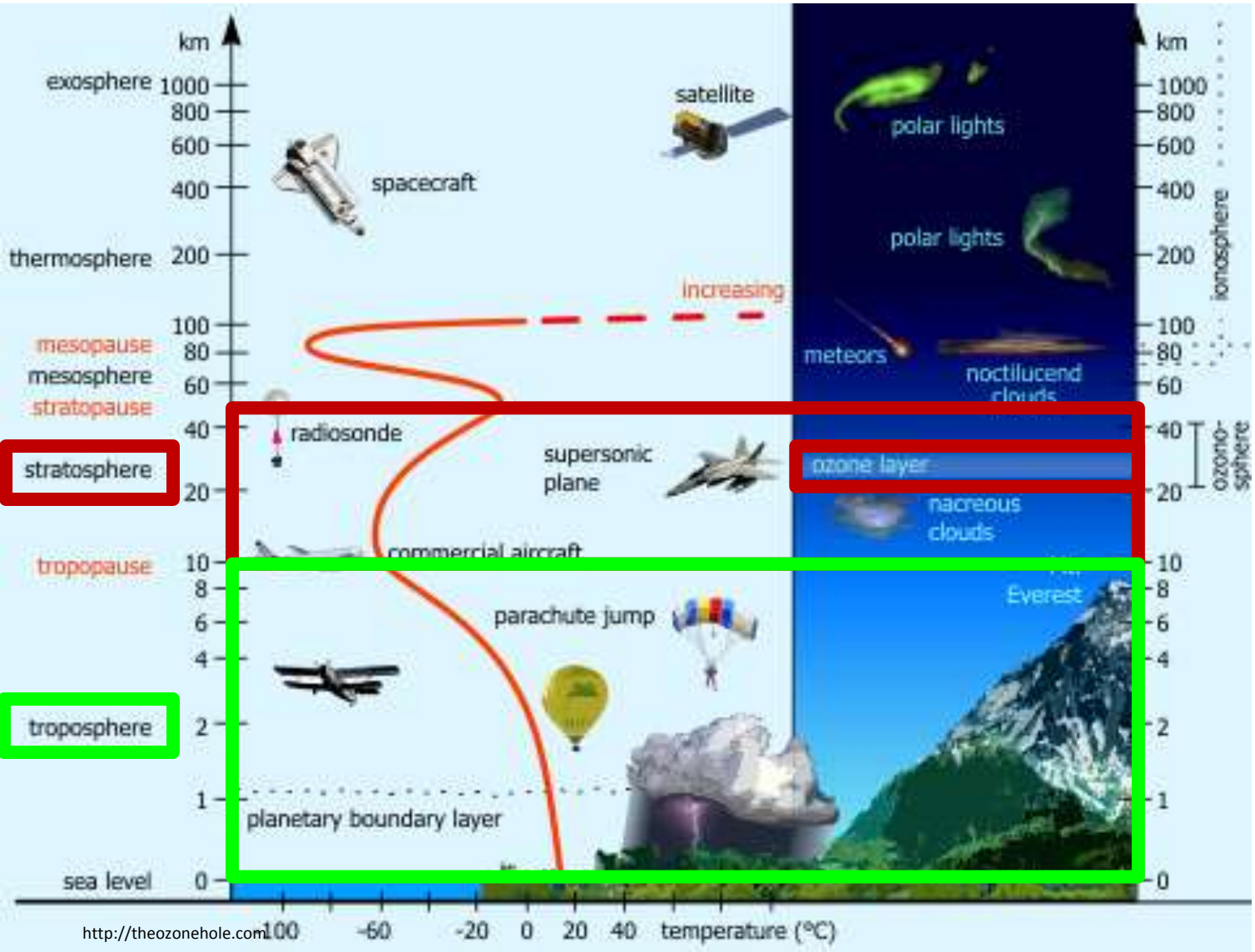
University of Michigan

2017 Connaught Summer Institute on Arctic Science

Layers of Earth's Atmosphere

We're going to talk about ozone chemistry in the troposphere – not to be confused with the ozone layer in the stratosphere!



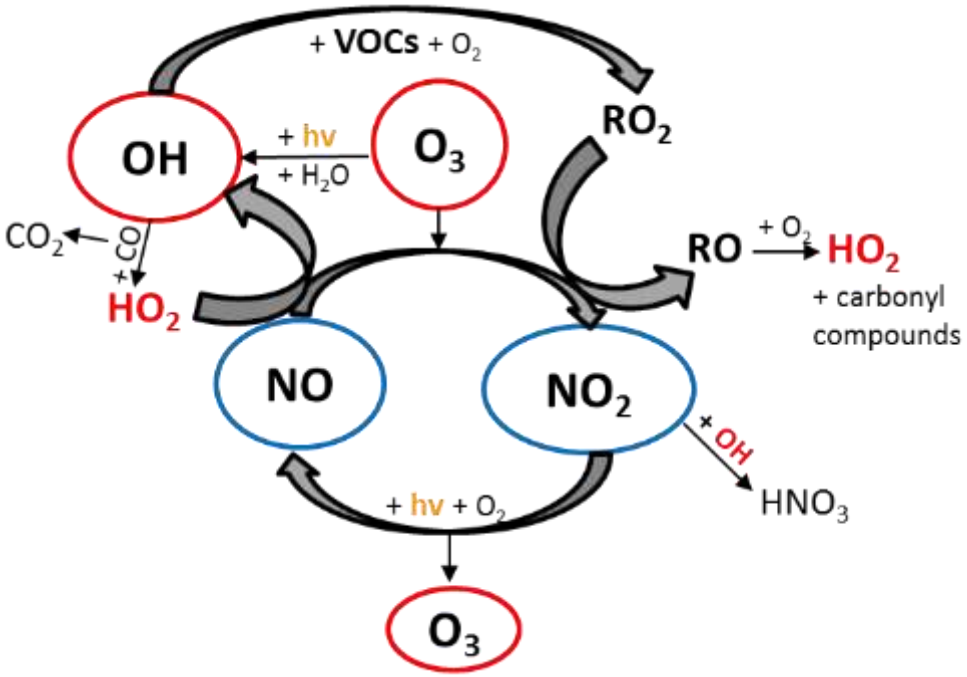
http://theozonehole.com

Atmospheric Oxidants

- Primary atmospheric oxidants: $OH^{\cdot}$, O_3, $NO_3^{\cdot}$
- **Oxidation capacity: the ability of the atmosphere to clean itself by chemically oxidizing (reacting with) pollutants.**
  - Globally controls methane (greenhouse gas) lifetime
  - Leads to new particle and secondary aerosol formation (impacting clouds (indirect effect) and precipitation (hydrological cycle))

- O_3 photochemistry produces OH radicals (primary global oxidant)
- Therefore, **O_3 is the typical indicator of oxidation capacity**

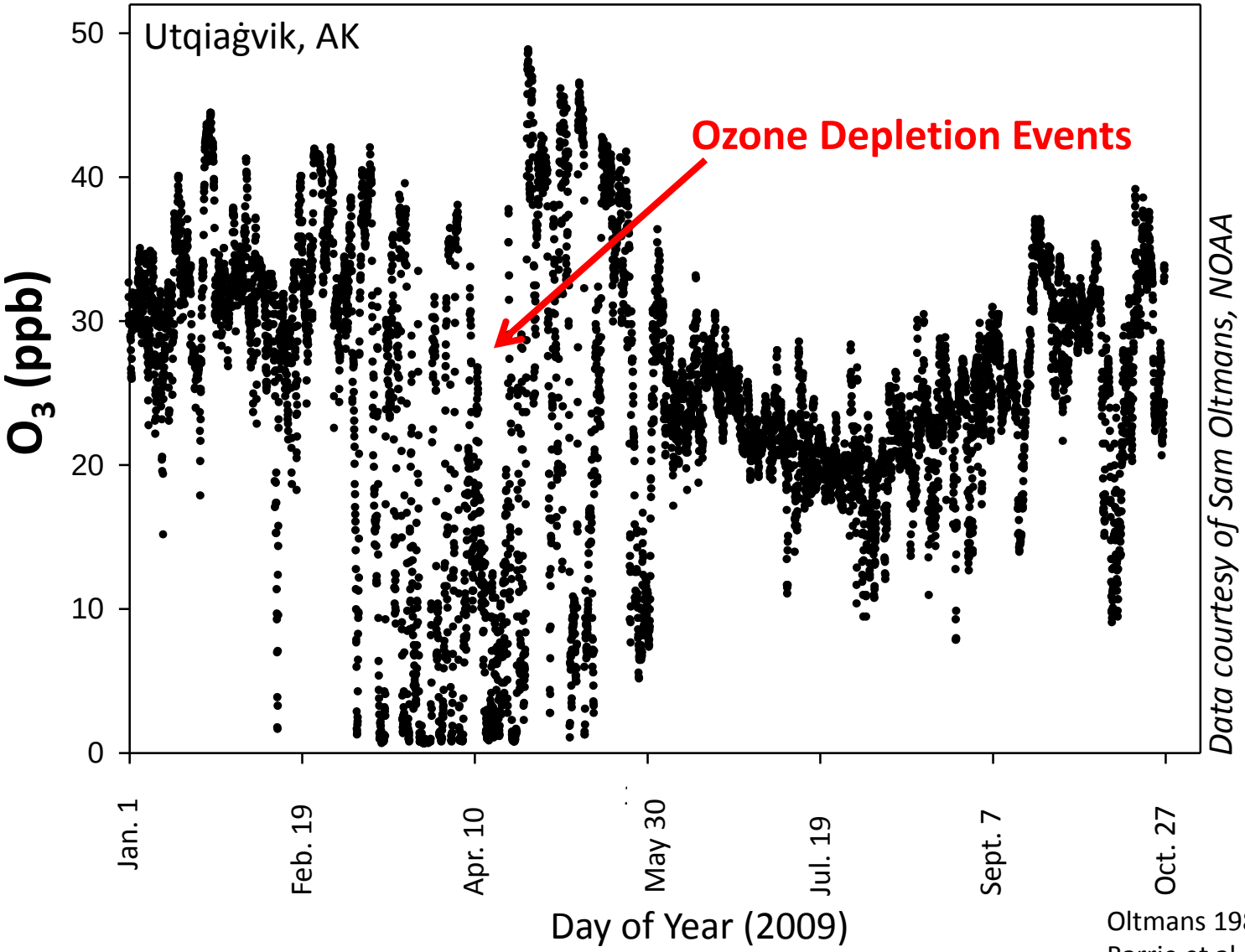
Tropospheric O_3 Cycle



Arctic Surface Ozone Depletion

Oxidative capacity of the atmosphere (removal of pollutants) is controlled by O_3.

Thompson 1992, *Science*



Oltmans 1981, *J. Geophys. Res.*;
Barrie et al. 1988, *Nature*

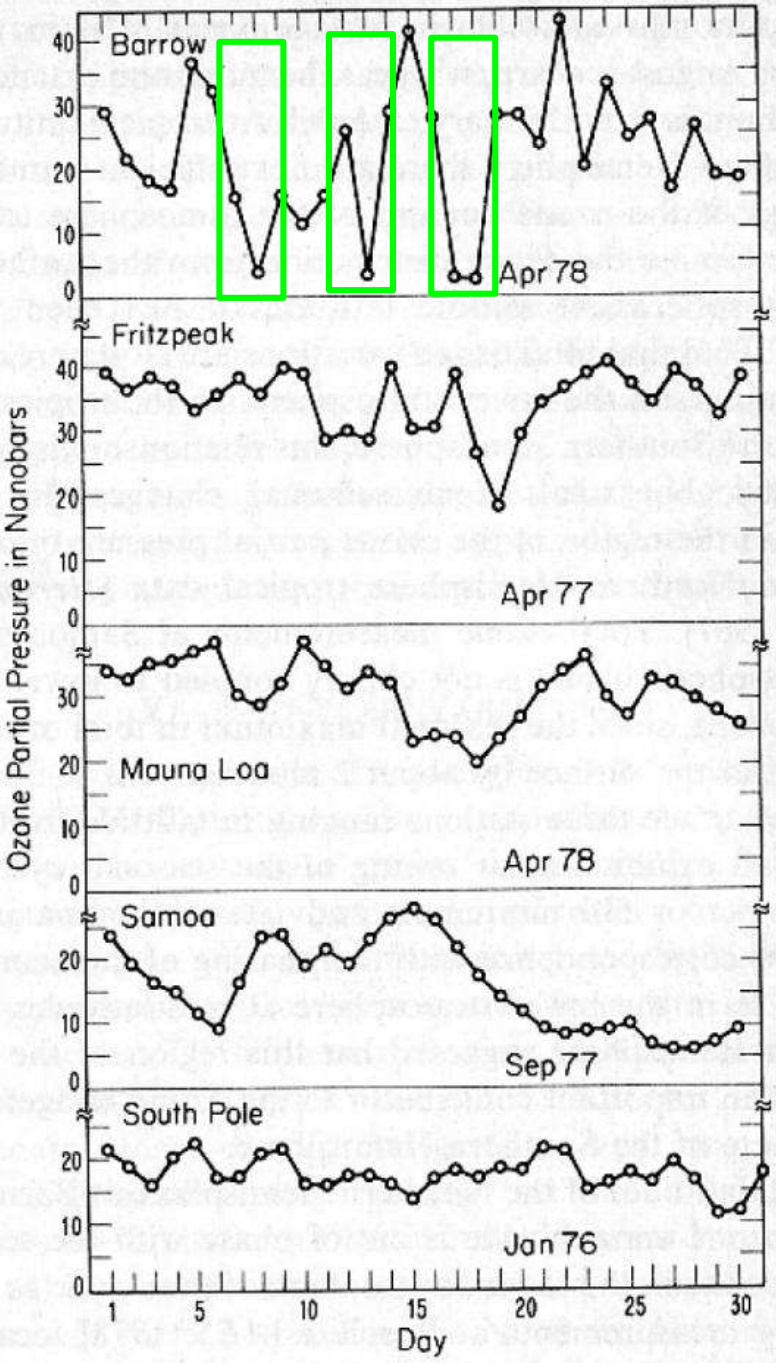
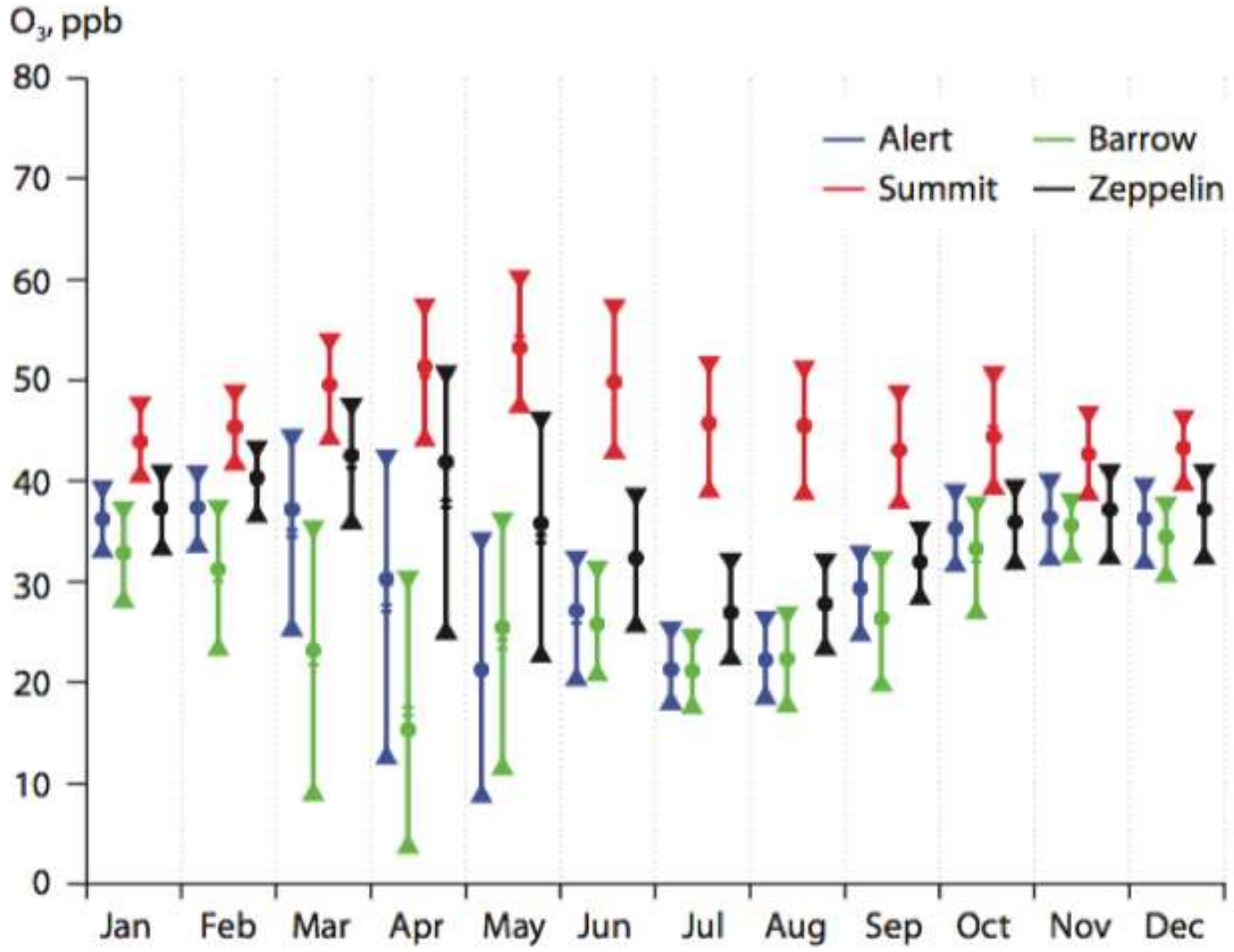


Fig. 4. Example of day-to-day variations of surface ozone.

Ozone Depletion Events (ODEs) are Unique to the Polar Regions *(and salt lakes)*

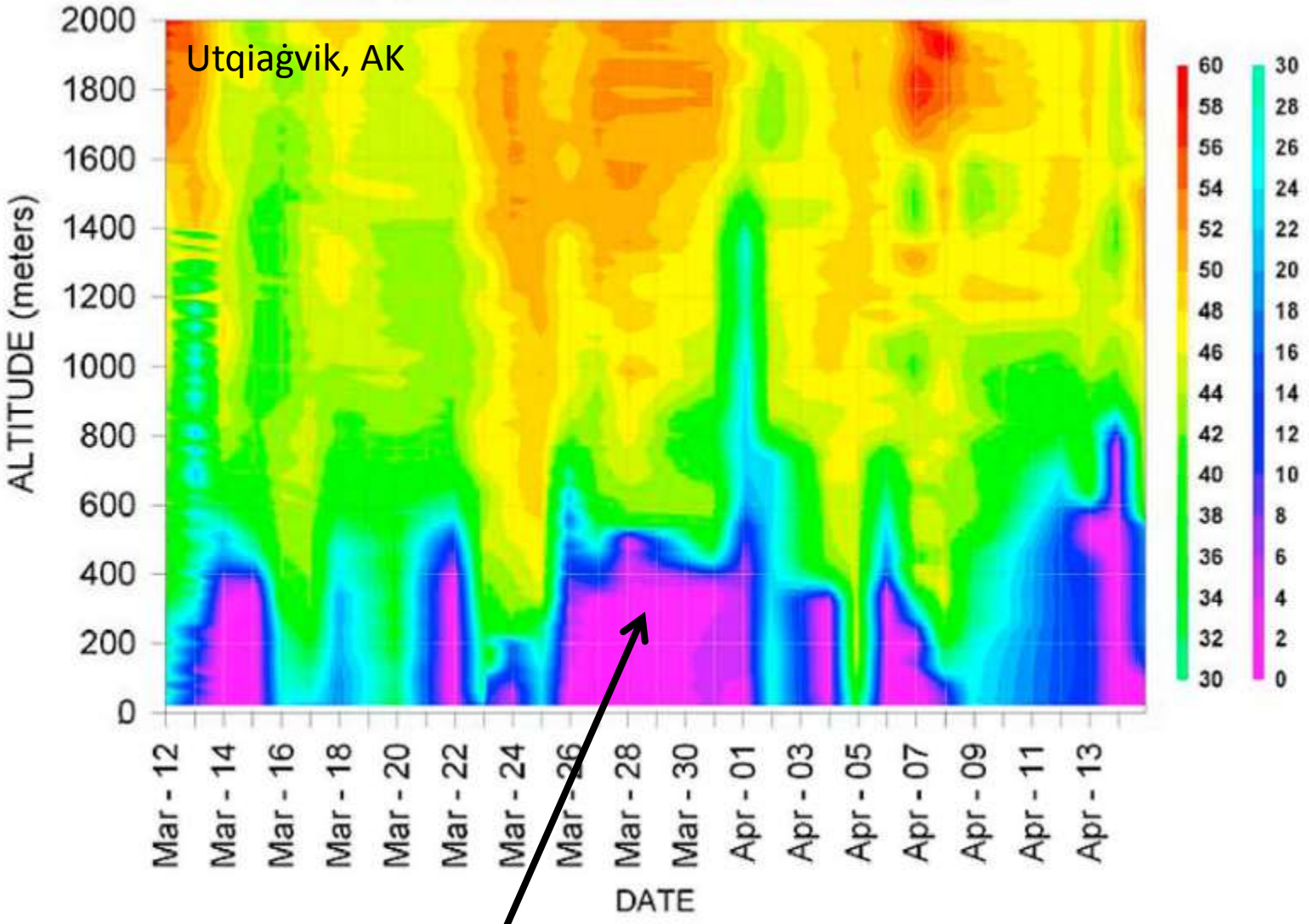
Oltmans 1981, *J. Geophys. Res.*

Arctic Ozone Seasonal Cycle



Hirdman et al 2010, ACP

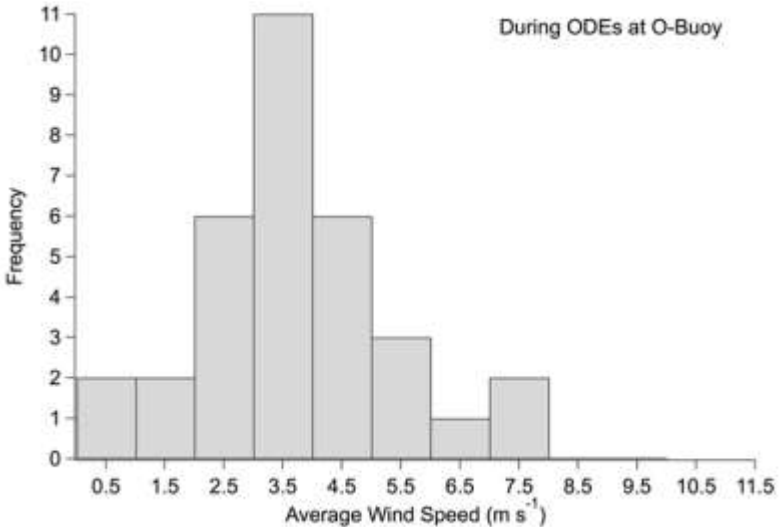
Ozone Depletion occurs near the Surface

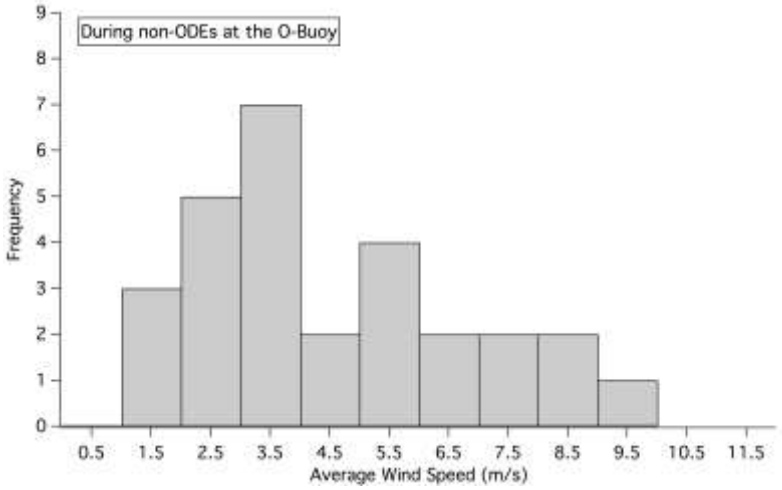


Oltmans et al. 2012, *JGR*

Arctic ODEs: Observed at Lower Wind Speeds; No Clear Dependence on Temperature

O-buoy deployments in Arctic sea ice





Halfacre et al, 2014, ACP

Ozone Recovery driven by Convective Mixing associated with Sea Ice Leads

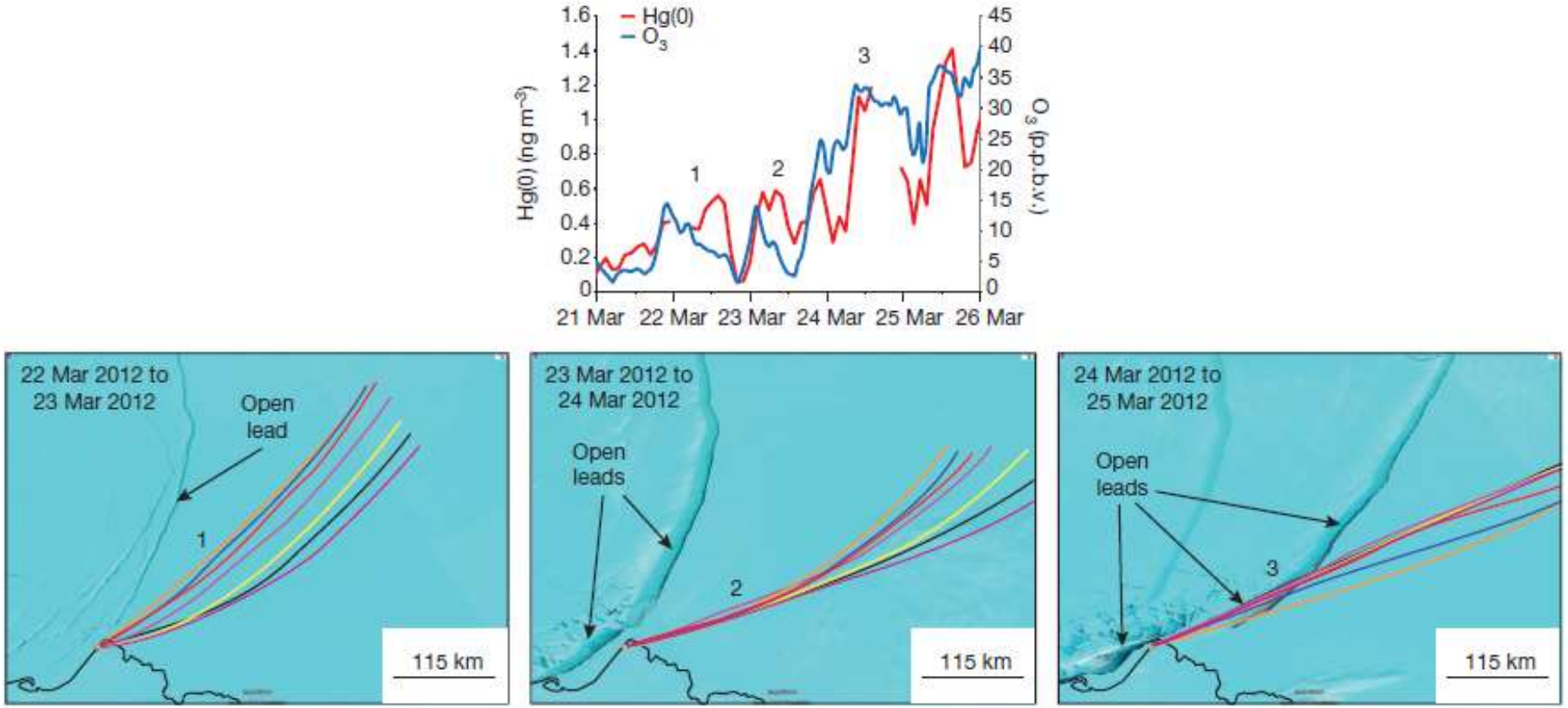
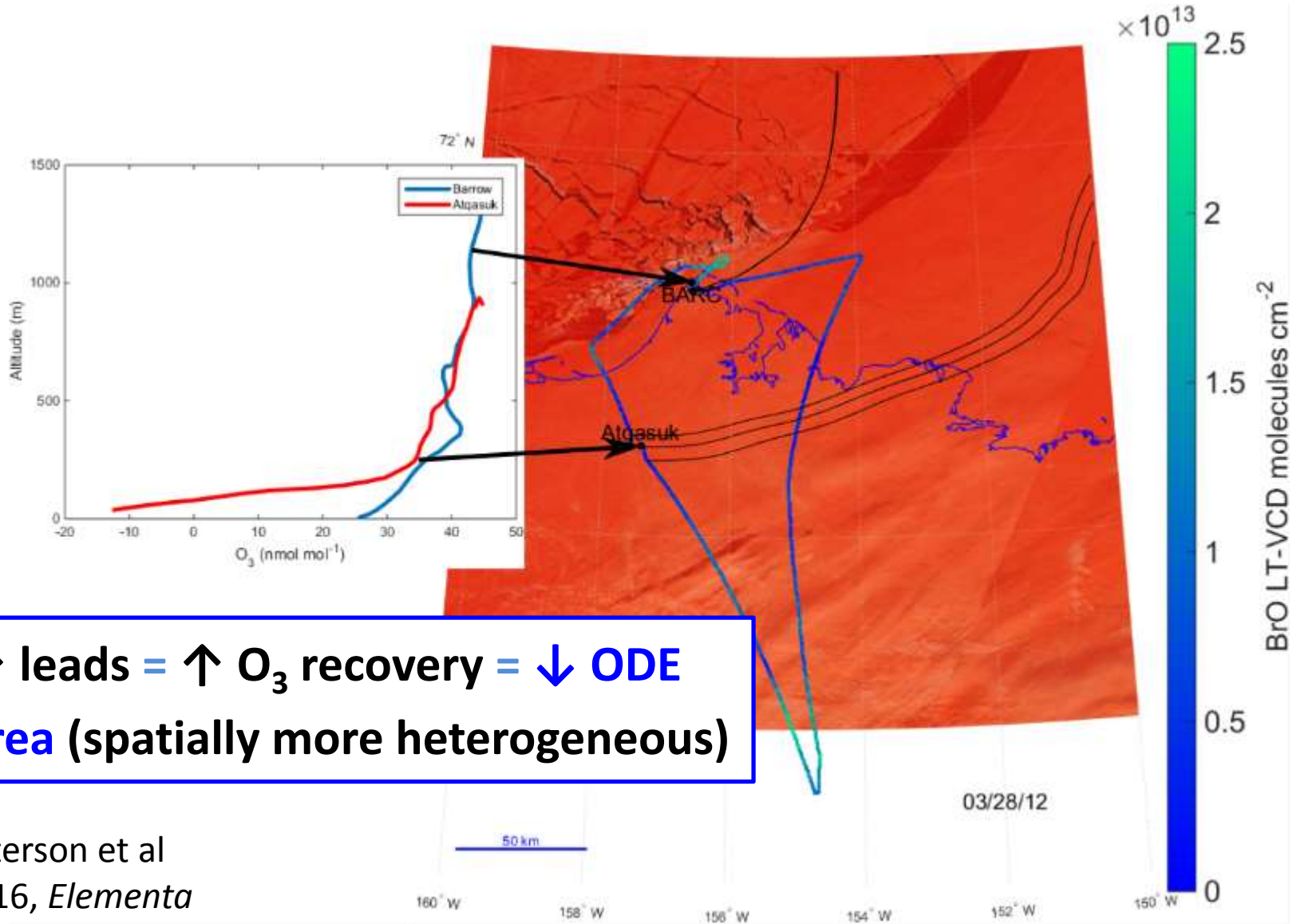


Figure 2 | Impact of sea-ice leads on Hg(0) and O_3 in 2012. Hg(0) and O_3 concentrations between 21 March 2012 and 26 March 2012. Bold numbers correspond to time periods as numbered on the corresponding satellite images. Satellite images were taken at approximately 16:00 UTC (Coordinated Universal Time) each day. Colours represent 24-hour HYSPLIT back-trajectory arrival times near Barrow: orange, 04:00 UTC; blue, 08:00 UTC; red, 12:00 UTC; pink, 16:00 UTC; yellow, 20:00 UTC; black, 00:00 UTC (the next day); and purple, 04:00 UTC (the next day). Original satellite images from Google Earth, Terrametrics.

Moore et al 2014, Nature

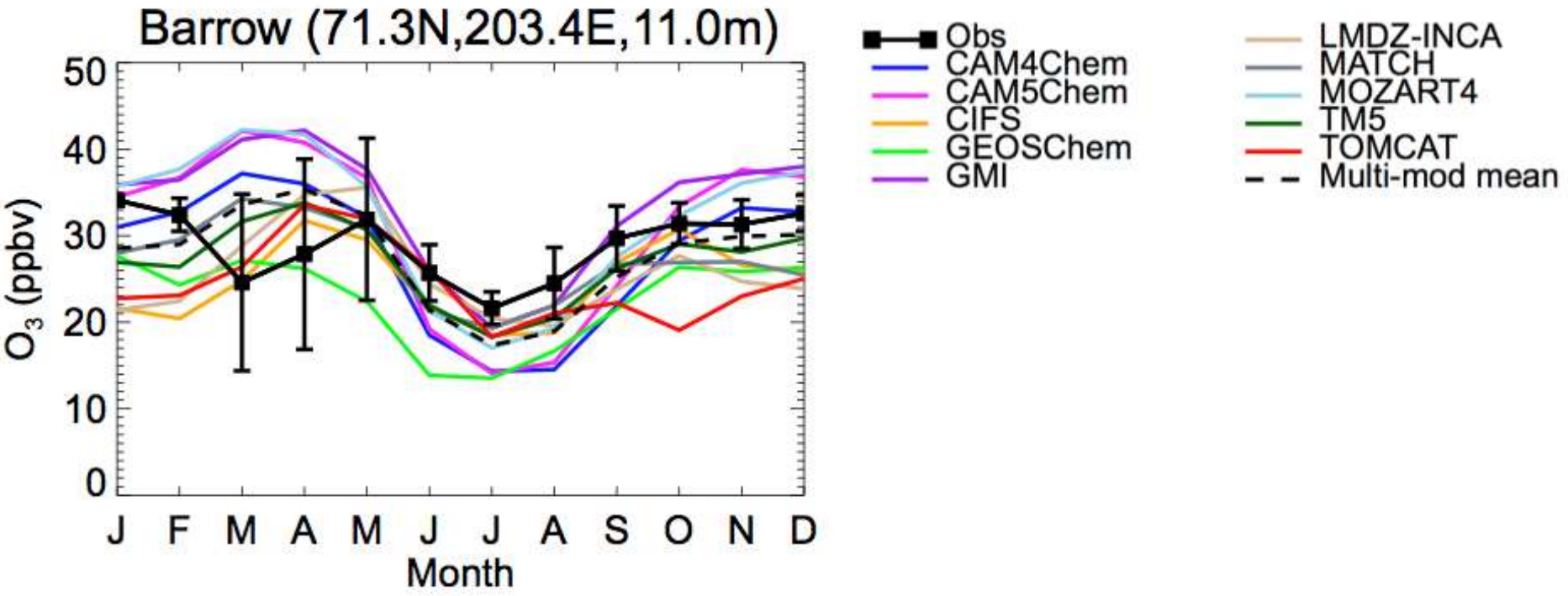
Inland Depletion of Ozone due to Transport & Lack of Lead Influence



↑ leads = ↑ O_3 recovery = ↓ ODE area (spatially more heterogeneous)

Peterson et al 2016, *Elementa*

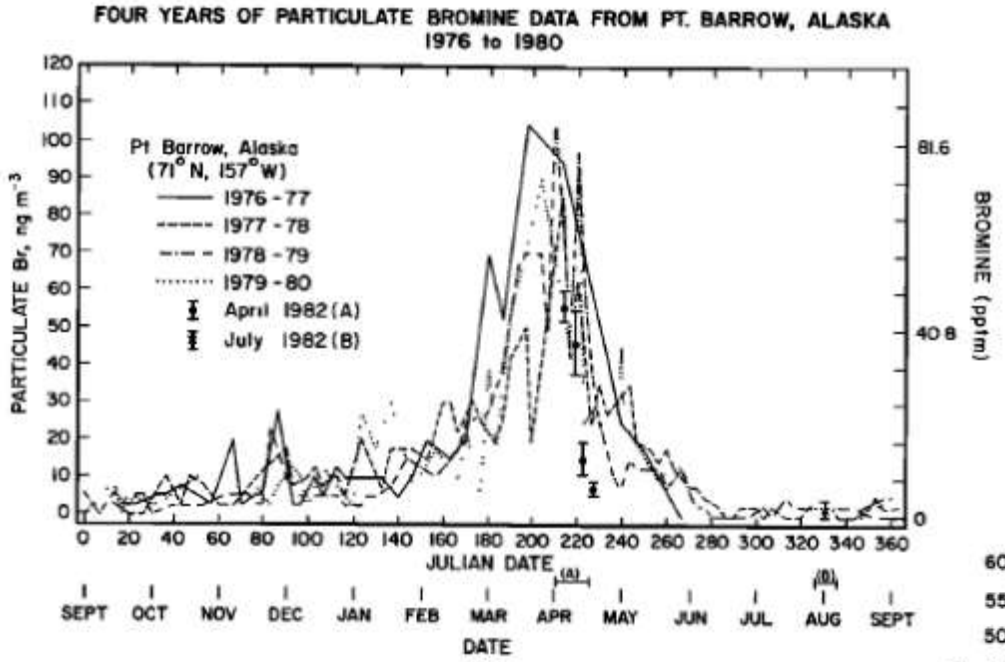
Global Models unable to Properly Simulate Polar Seasonal Ozone Cycle

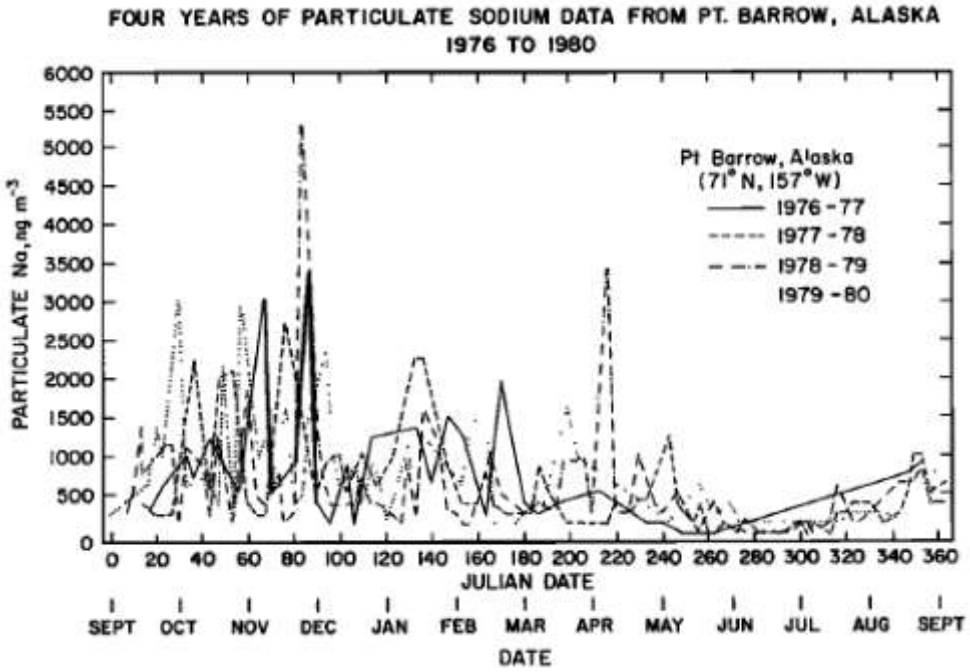


This illustrates our limited understanding and ability to simulate Arctic oxidation capacity.

Monks et al 2015, ACP

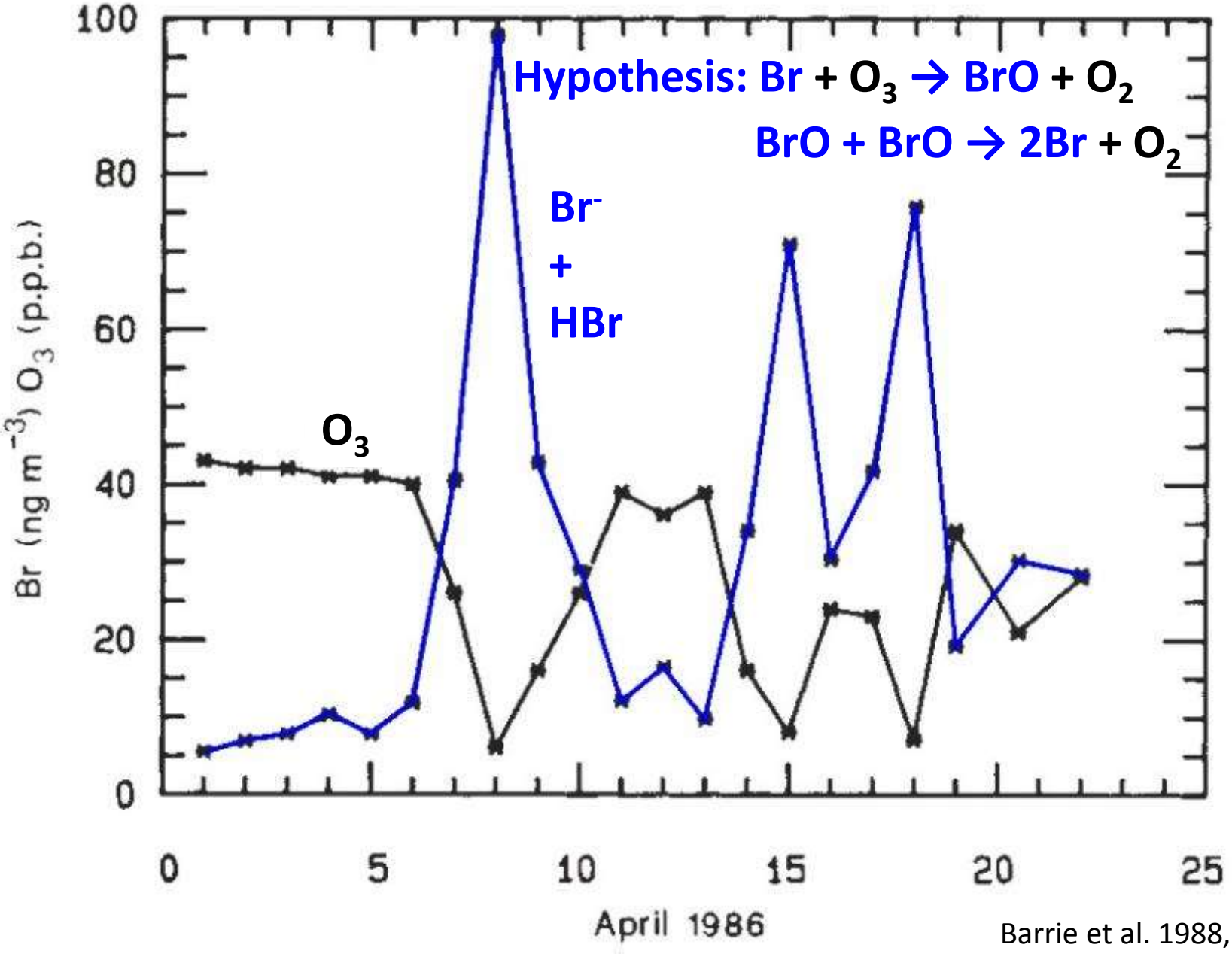
Springtime Maximum in Particulate Bromide (Br^-) – Not Correlated with Sea Spray Aerosol





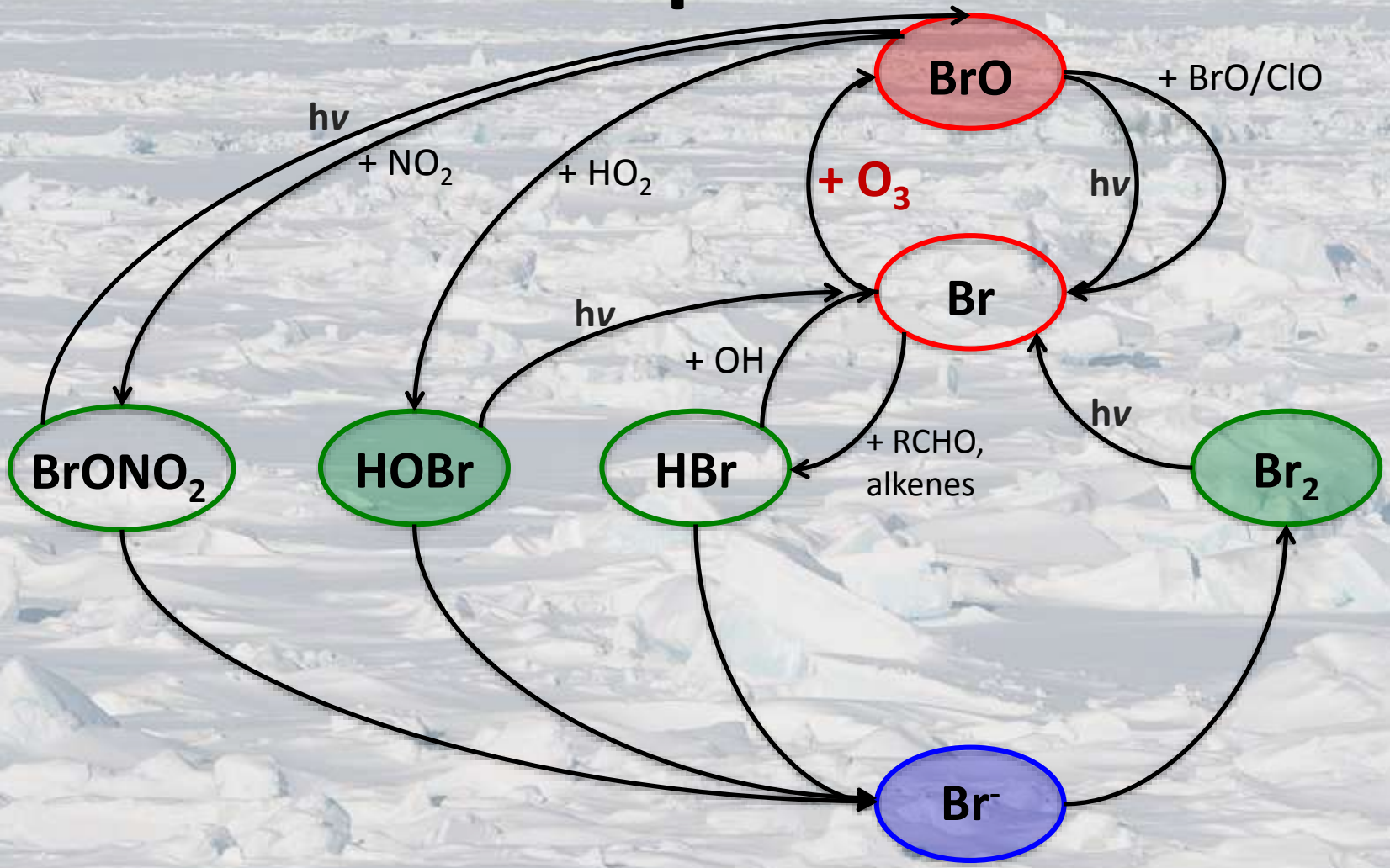
Berg et al 1983, JGR

Anti-correlation between Ozone and Bromine



Barrie et al. 1988, *Nature*

"Bromine Explosion" → Ozone Depletion Events

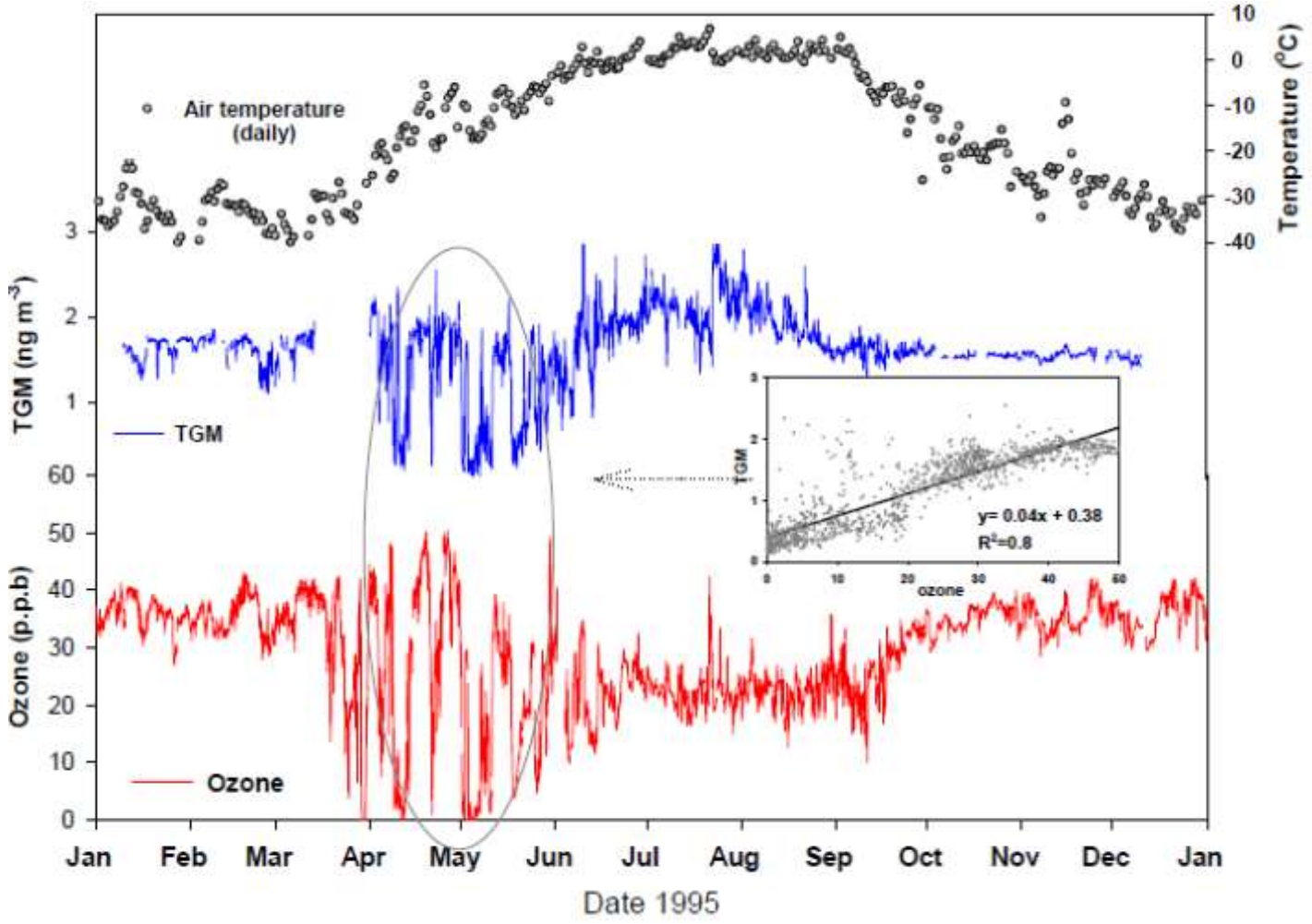


Barrie et al. 1988, *Nature*
Finlayson-Pitts et al. 1990, *Nature*
Fan & Jacob 1992, *Nature*

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

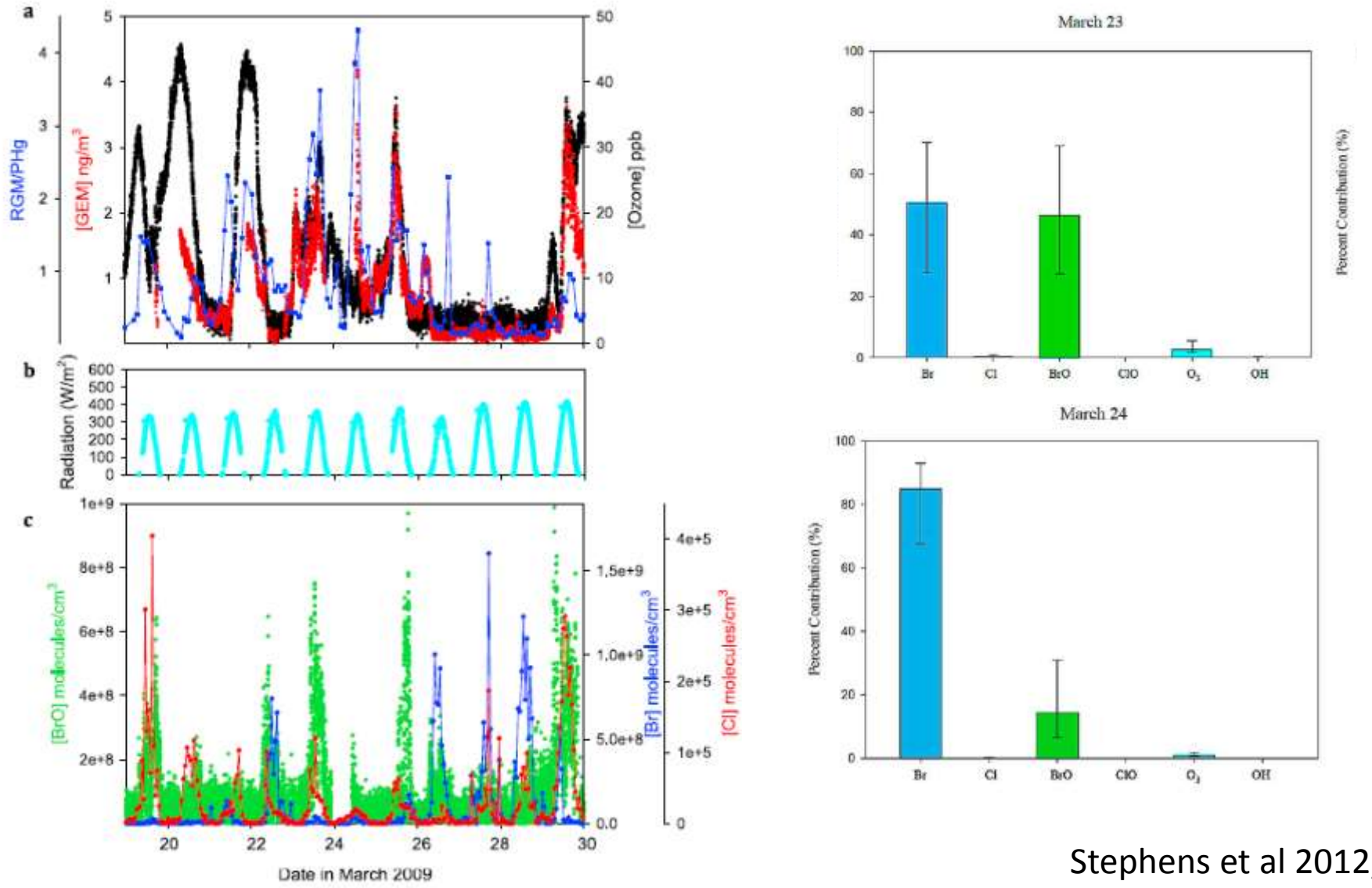
Atmospheric Mercury Depletion Events (AMDEs)

Hg(0) depletion correlated with O_3 loss



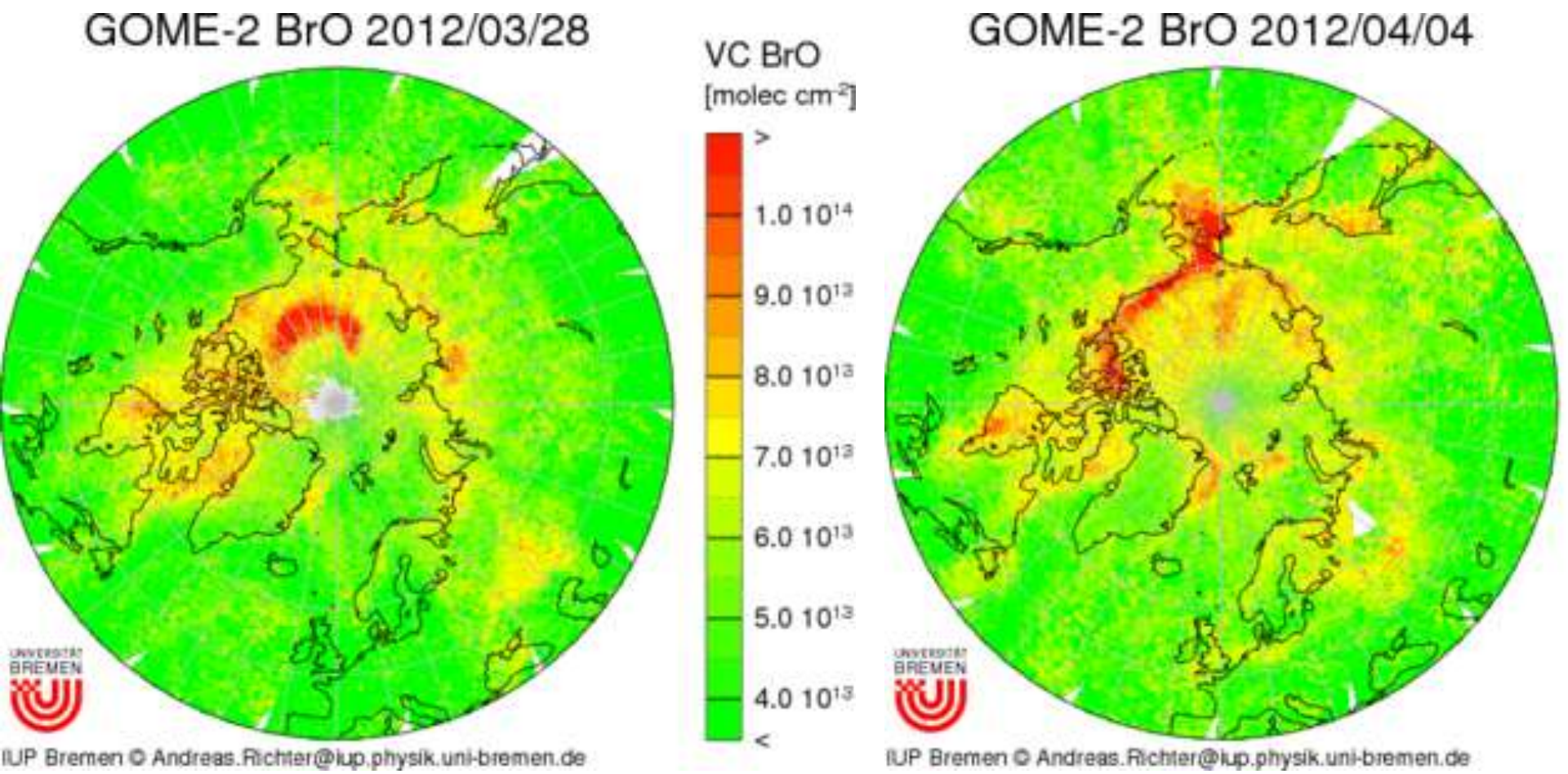
Schroeder et al 1998, *Nature*
Steffen et al 2008, *ACP*

Mercury Depletion driven by Bromine Chemistry



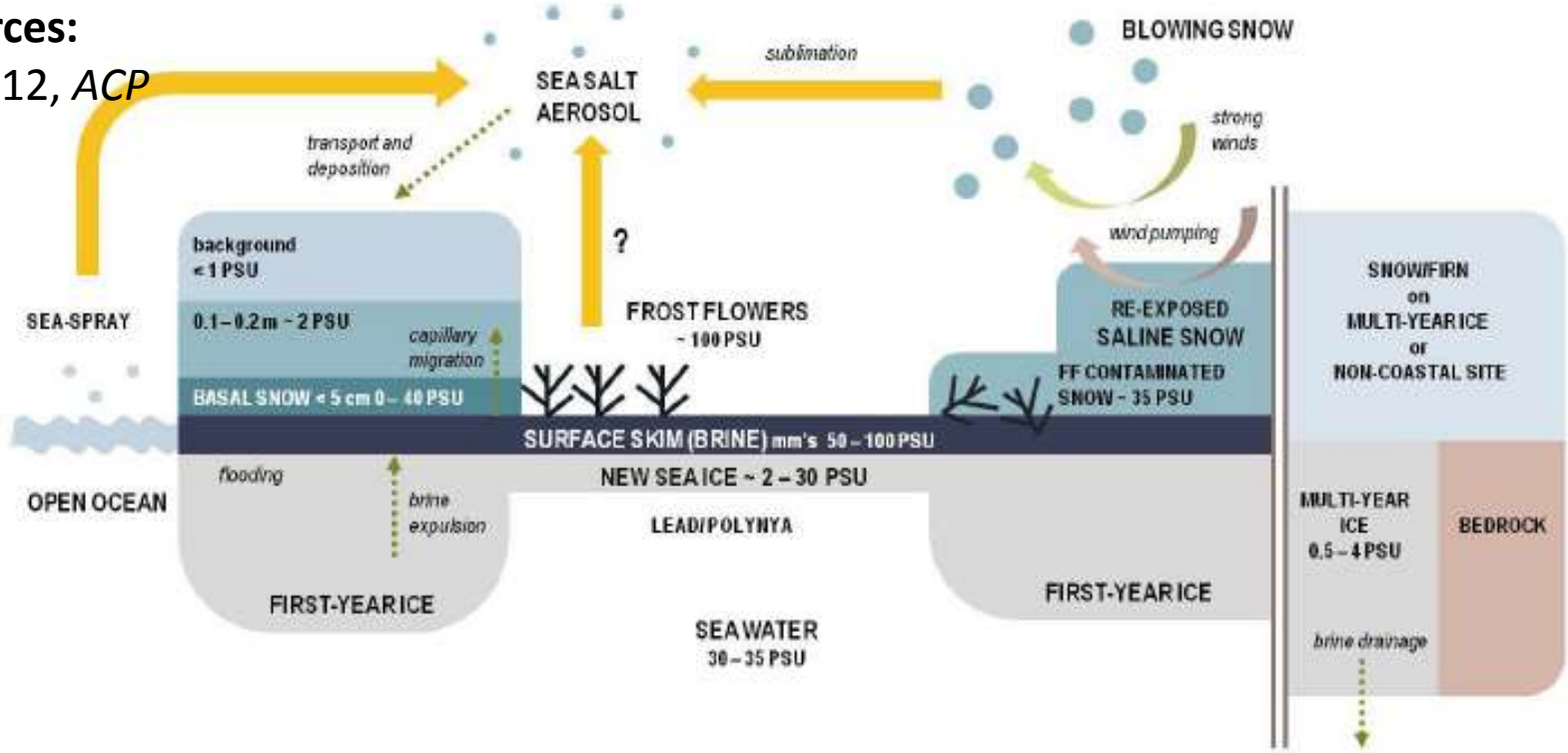
Stephens et al 2012, JGR

Satellite-Based BrO˙ Observations



Source(s) of Reactive Bromine?

Proposed Sources:
Abbatt et al 2012, *ACP*



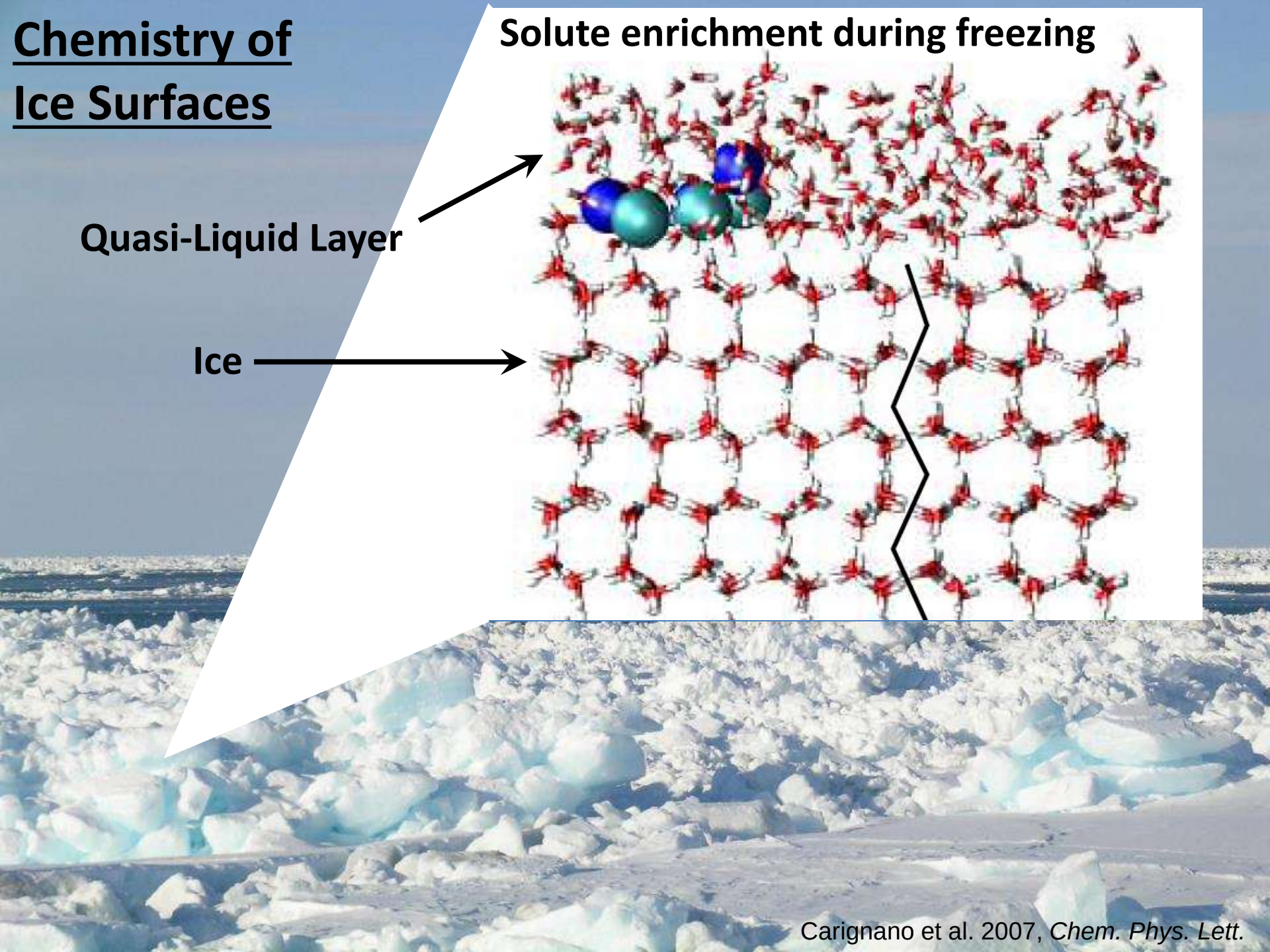
Atmos. Chem. Phys., 7, 621–627, 2007
www.atmos-chem-phys.net/7/621/2007/

Atmospheric Chemistry and Physics

First-year sea-ice contact predicts bromine monoxide (BrO) levels at Barrow, Alaska better than potential frost flower contact

W. R. Simpson[1], D. Carlson[1], G. Hönninger[1,2,†], T. A. Douglas[3], M. Sturm[3], D. Perovich[3], and U. Platt[2]

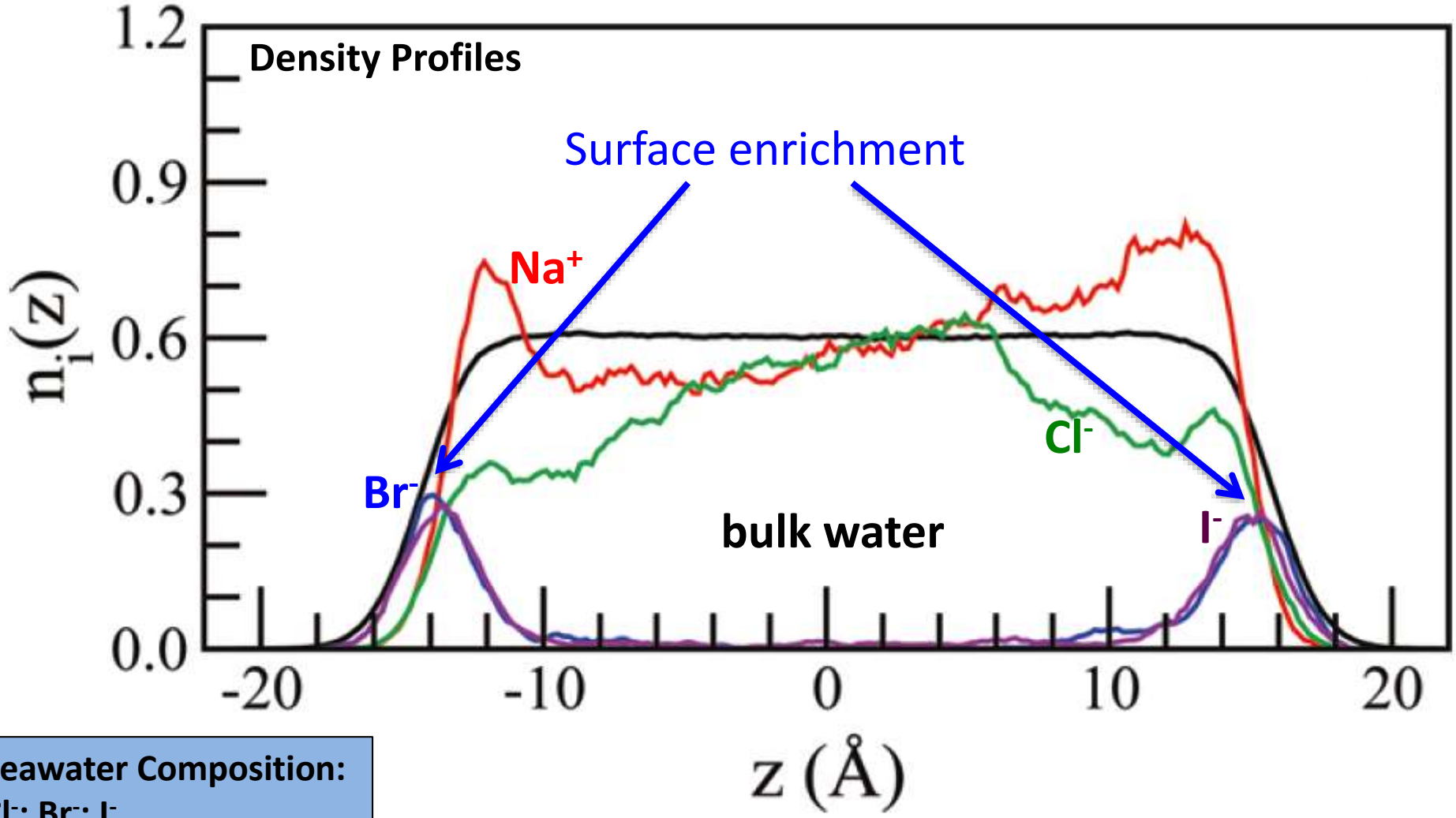
Chemistry of Ice Surfaces



Carignano et al. 2007, *Chem. Phys. Lett.*

Surface Enrichment of Bromide

Molecular dynamics simulation of aqueous mixture of Na^+, Cl^-, Br^-, and I^-



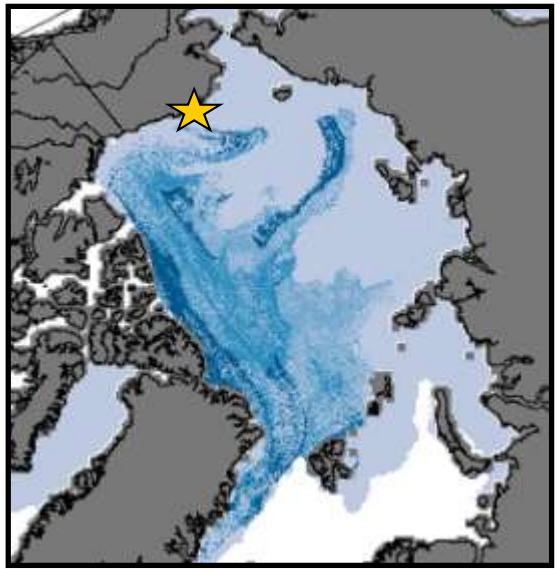
Seawater Composition:
Cl^-: Br^-: I^-
890,000: 1,300: 1

Gladich et al. 2011, *J. Phys. Chem. A*

Focus: Arctic molecular halogen production
Approach: Chemical Ionization Mass Spectrometry (CIMS)

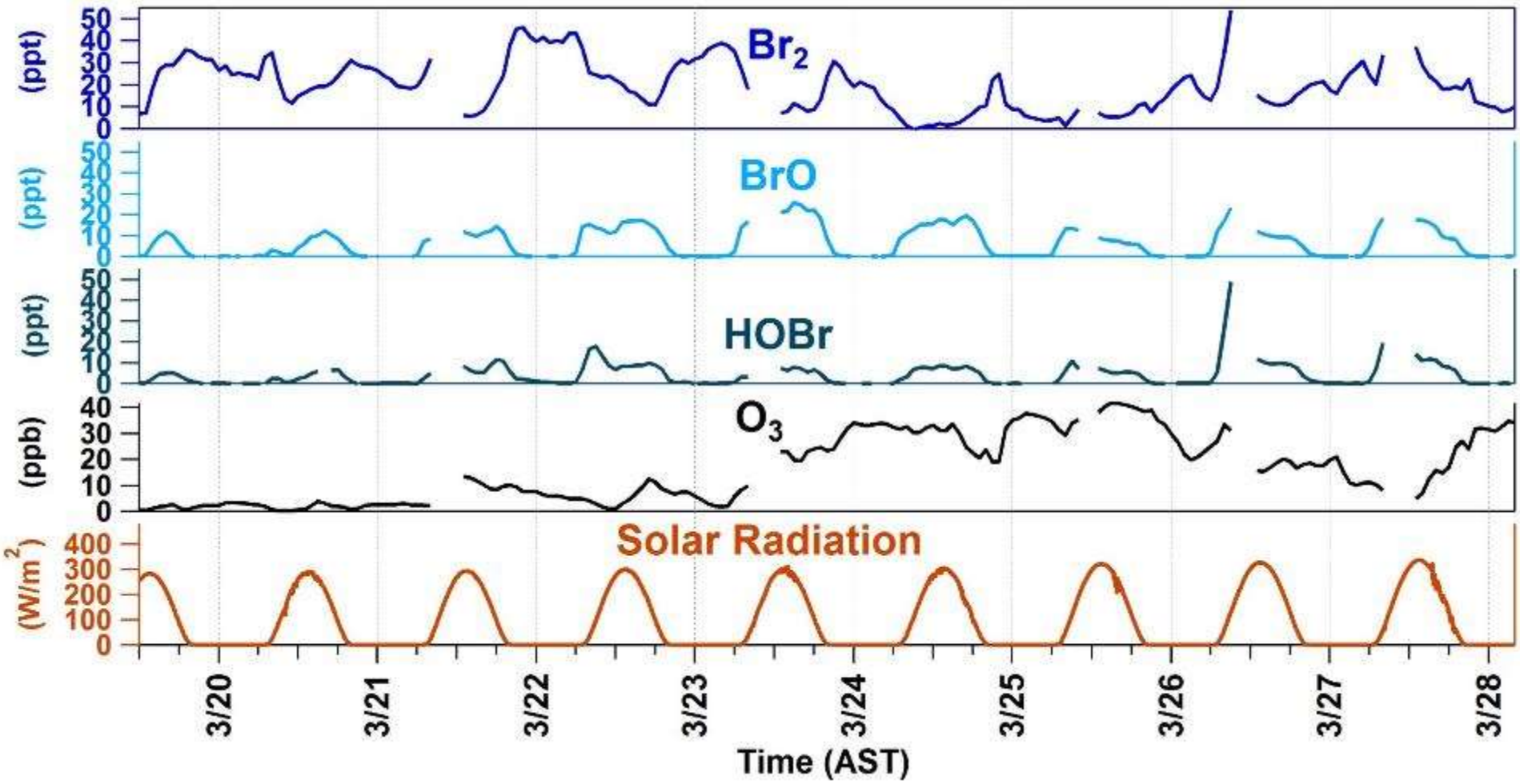
$$I(H_2O)_n^- + Br_2 \rightarrow IBr_2^- + H_2O$$

- **<1 ppt** limits of detection (LOD) for Br_2, BrO, HOBr, Cl_2, BrCl, **ClO**
- Automated field calibration using Br_2 and Cl_2 permeation sources
- Utqiaġvik (Barrow), AK – Mar. 2012, Feb. 2014, Mar. – May 2016



Liao et al. 2011, *JGR;*
Liao et al. 2012, *JGR;*
Custard et al. 2016, *ES&T;*
Custard et al. 2017, *ACS Earth & Space Chem.;*
Raso et al. 2017, *Submitted*

Bromine Chemistry Measurements



$Br_2 + h\nu \rightarrow 2Br^{\cdot}$

$Br^{\cdot} + O_3 \rightarrow BrO^{\cdot} + O_2$

$BrO^{\cdot} + HO_2^{\cdot} \rightarrow HOBr$

Pratt & Shepson

nature geoscience

LETTERS

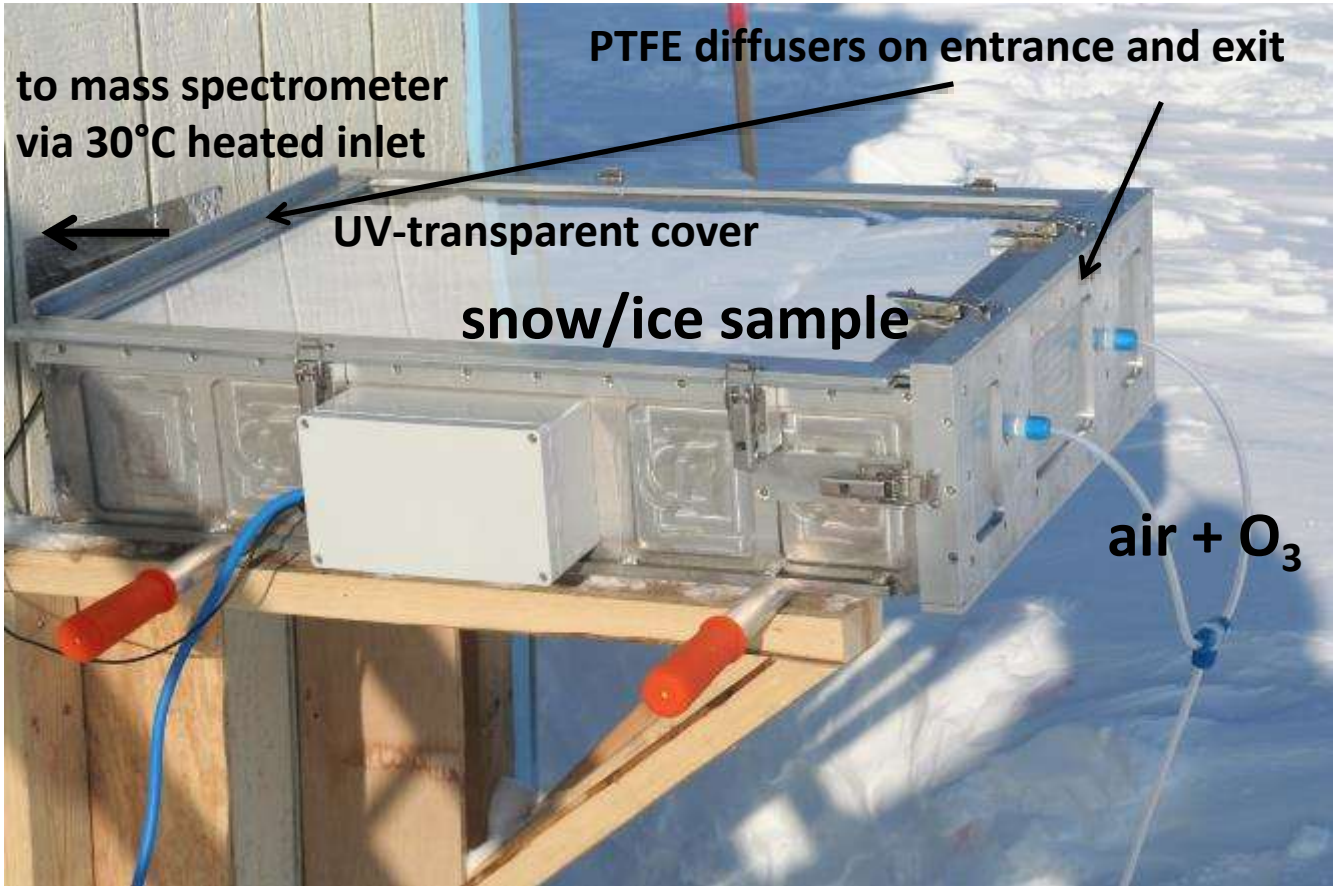
PUBLISHED ONLINE: 14 APRIL 2013 | DOI: 10.1038/NGEO1779

Photochemical production of molecular bromine in Arctic surface snowpacks

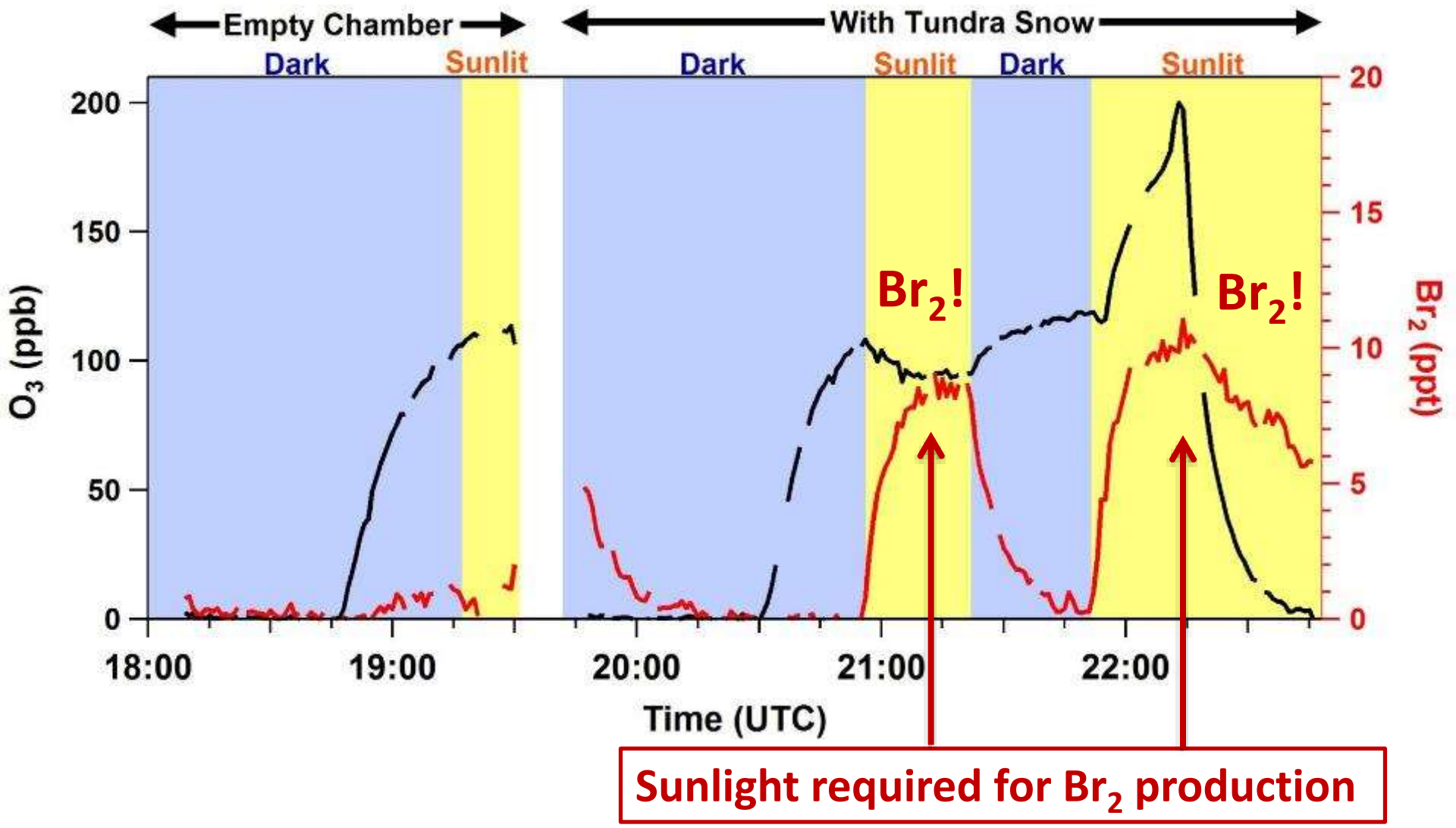
Kerri A. Pratt[1]*, Kyle D. Custard[1], Paul B. Shepson[1,2], Thomas A. Douglas[3], Denis Pöhler[4], Stephan General[4], Johannes Zielcke[4], William R. Simpson[5], Ulrich Platt[4], David J. Tanner[6], L. Gregory Huey[6], Mark Carlsen[1] and Brian H. Stirm[7]

What is the initial source of Br_2 to the Arctic troposphere?

Snow Chamber

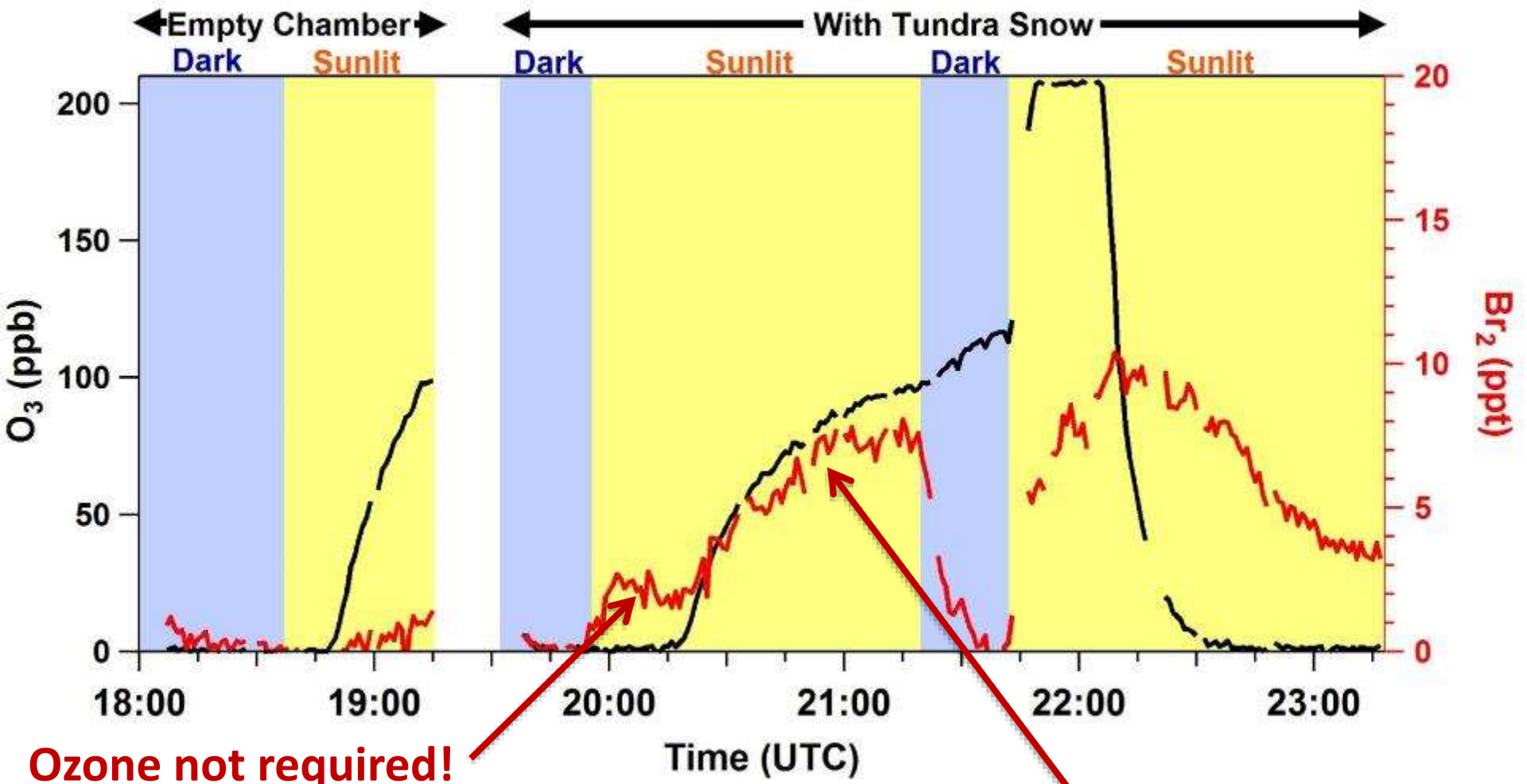


Photochemical Snowpack Production of Br_2



Pratt et al. 2013, *Nature Geoscience*

Bromine Activation: *In-situ* Oxidant



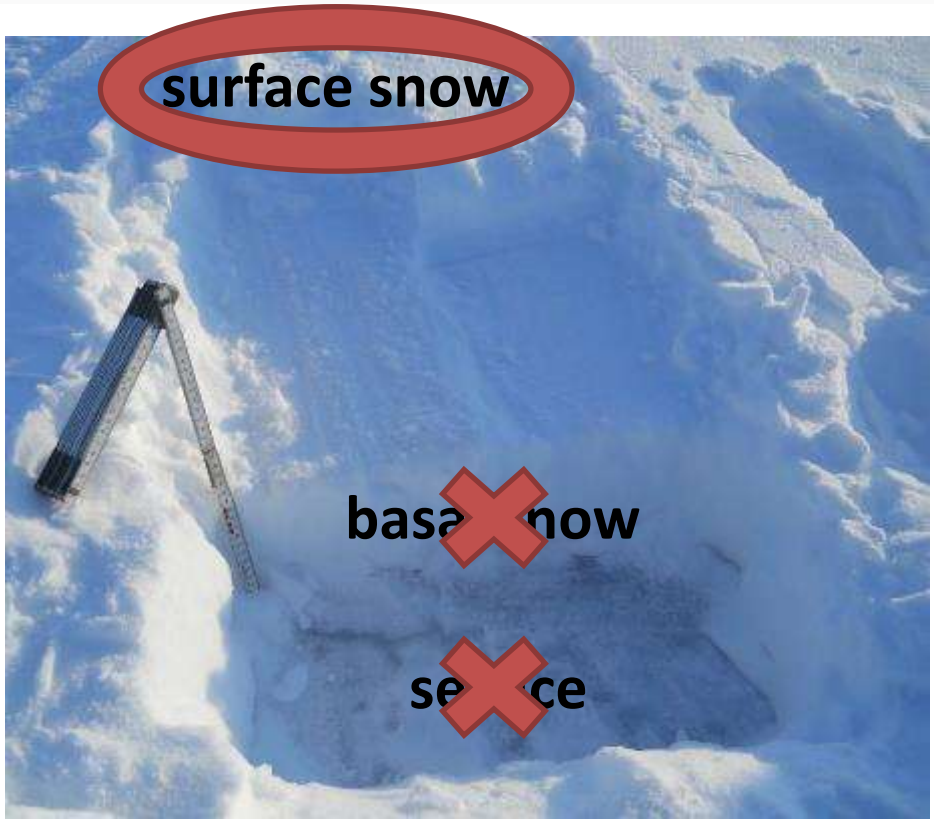
Ozone not required!

(*In-situ*, condensed-phase oxidant)

Br_2 enhanced with ozone addition

Pratt et al. 2013, *Nature Geoscience*

Br_2 Production: Acidic Snow Enriched in Bromide



10 snow/ice samples tested

- Bromine efficiently produced from ***both*** **tundra & FYI surface snow** with **pH <7 & $[Br^-]/[Cl^-] > 1/200$**
  (enriched in bromine compared to sea ice)
- Surface snow above multi-year sea ice not tested
- ***Not*** **first-year sea ice:** pH 7.3 , Br^-/Cl^- ~1/500

Pratt et al. 2013, *Nature Geoscience*