Arctic Oxidation Chemistry

Connaught Summer Institute 2016

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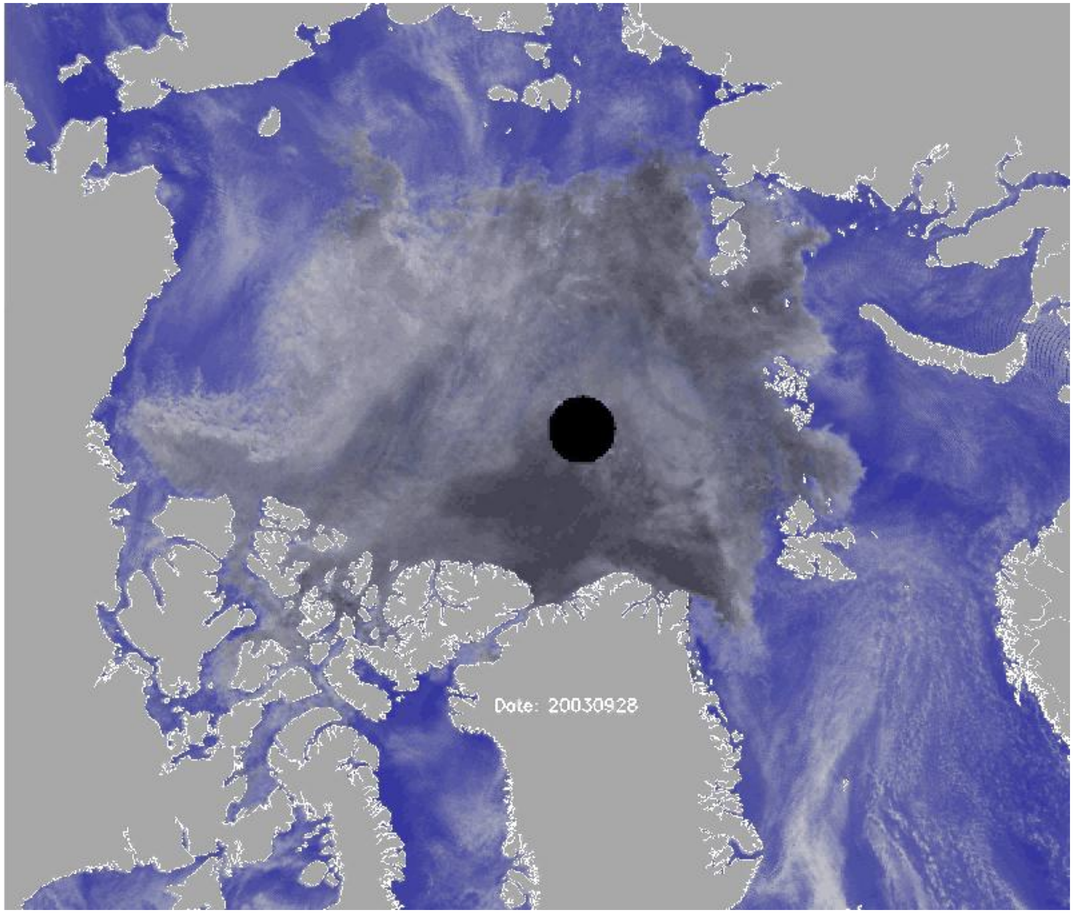
The Arctic from above



28 Sep 2003 – 10 May 2004 Credit: Ignatius Rigor (U. Wash.)

What did you see?

- Clouds
- Sea ice
- Motion

Not seen but affecting this animation

- Trace gases – oxidizers, greenhouse gases
- Aerosol particles – CCN and INP
- Water vapor
- Winds
- Currents

What I want to cover

- Ozone, oxidation capacity, and halogen gases
- How the Arctic processes chemicals differently than lower latitudes
- Greenhouse gases
- Big picture changes to the Arctic

Arctic atmospheric chemistry

- The Arctic is a unique region of the world
- Cold in winter -- ice and snow, but still alive
- Productive in summer -- green, sunny, and with many feeding species (whales, birds, etc.)
- Atmospheric chemistry affects the deposition of nutrients and pollutants to the Arctic
- However, the area's chemistry is not well understood nor has it been explored in vast spatial regions and seasons of the year.

Oxidation capacity

... is the ability of the atmosphere to clean itself by chemically oxidizing pollutants.

... globally controls methane lifetime.

... produces new particles.

... makes existing particles better CCN.

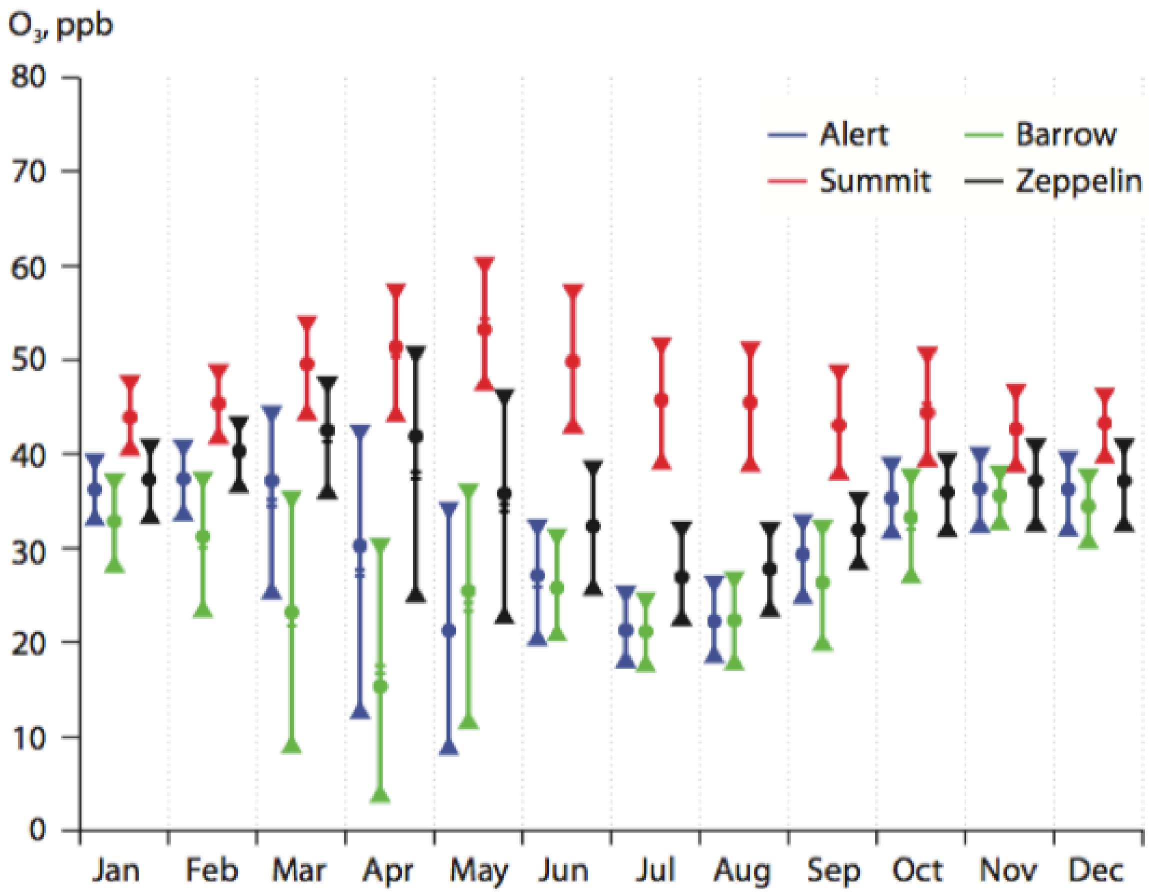
O_3 photochemistry produces OH radicals, the primary global oxidizer, thus **O_3 typically indicates oxidation capacity.**

Is the Arctic different?

- Most oxidation chemistry comes from ozone photochemistry. The Arctic is generally darker and sometimes has no ozone. Halogens (Br, Cl) often control oxidation instead of ozone.

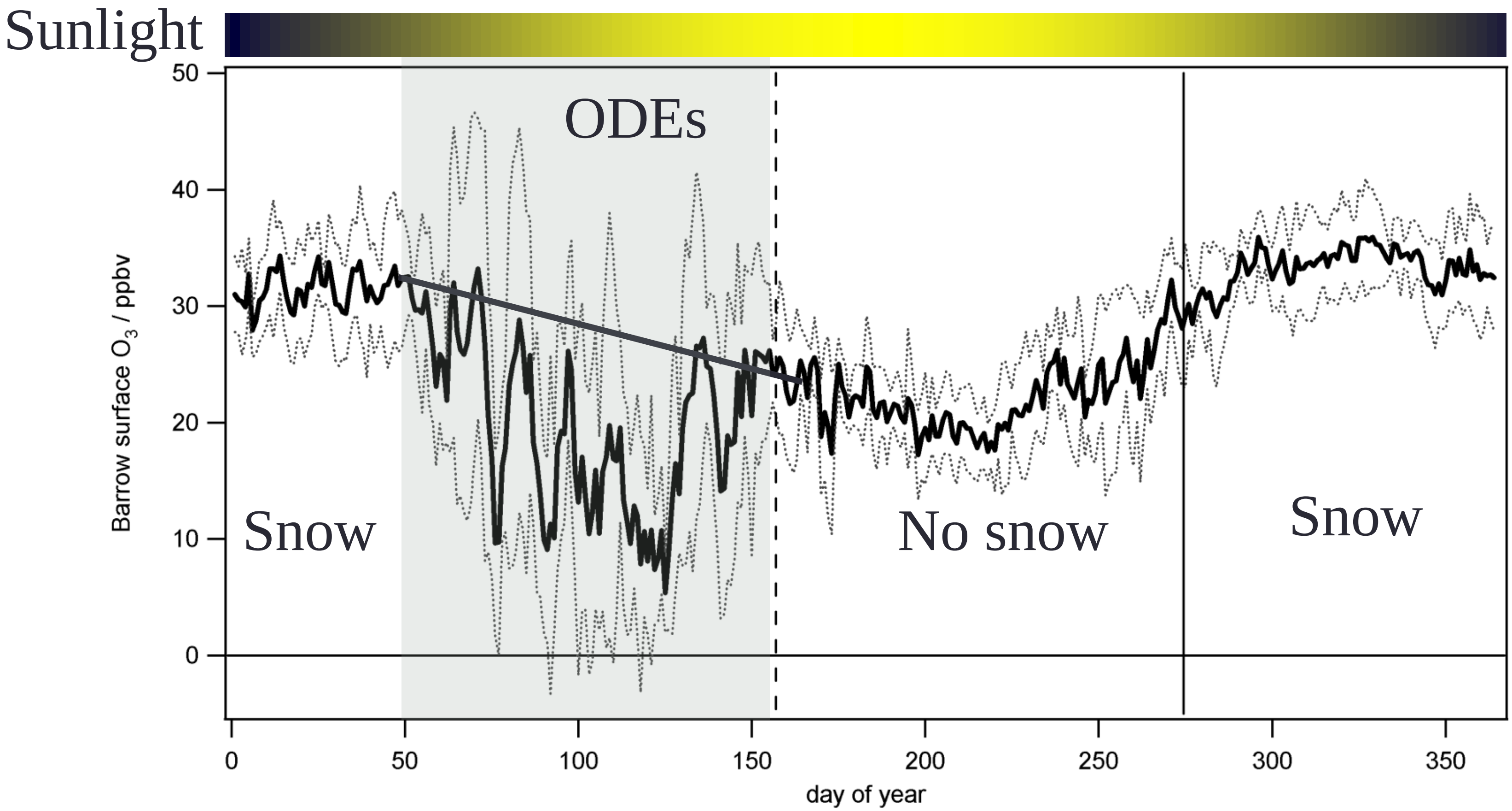
- There are generally low concentrations of cloud concentration nuclei (CCN) and ice nuclei (IN), and their chemistry is underexplored

Ozone Arctic Seasonal Cycle



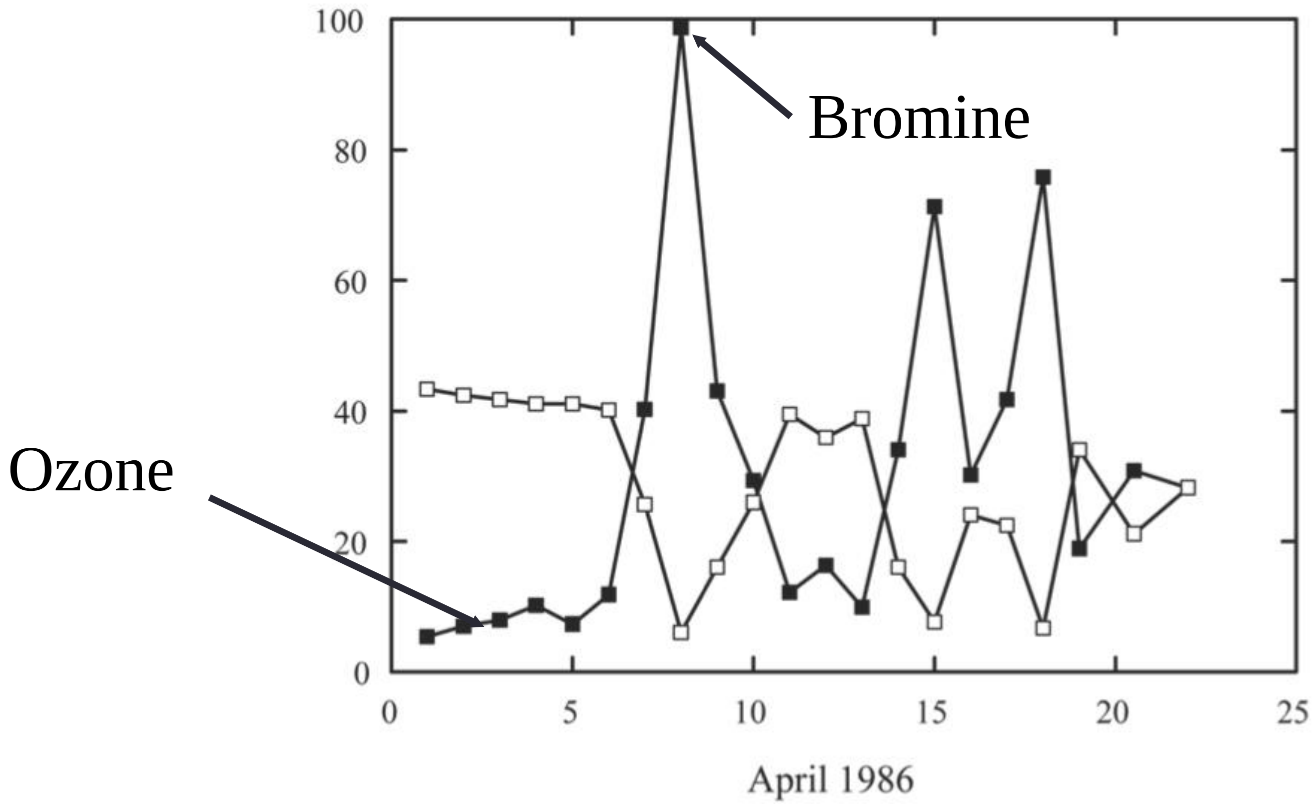
- AMAP report, original data from Hirdman et al. (2010)

Ozone depletion events (ODEs)



A 6-year average (Jan 1996 - Dec 2001) and +/- 1 standard deviation envelope

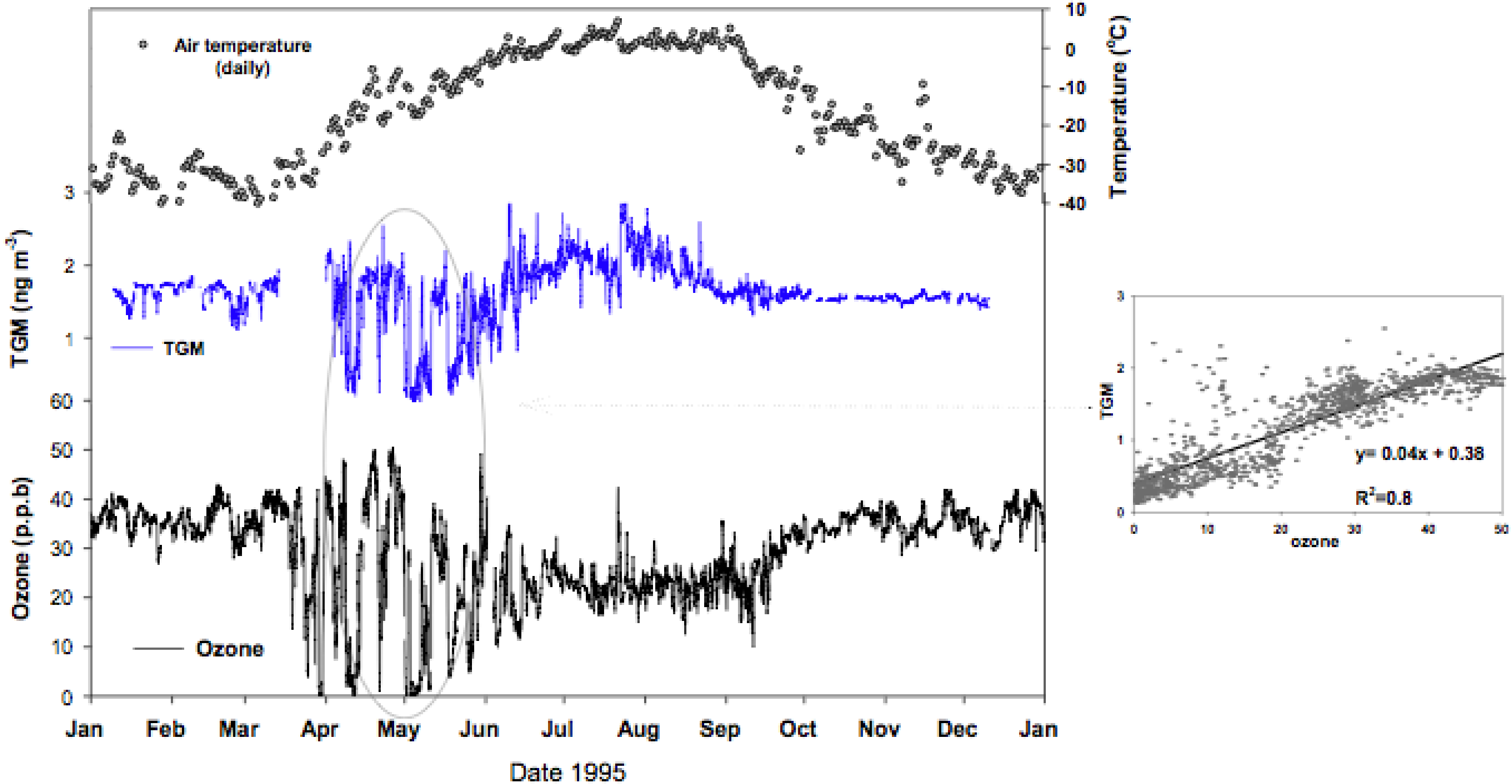
Bromine causes springtime O_3 losses



During the springtime, sea salts are converted to reactive gases that remove ozone and change the atmosphere's chemistry

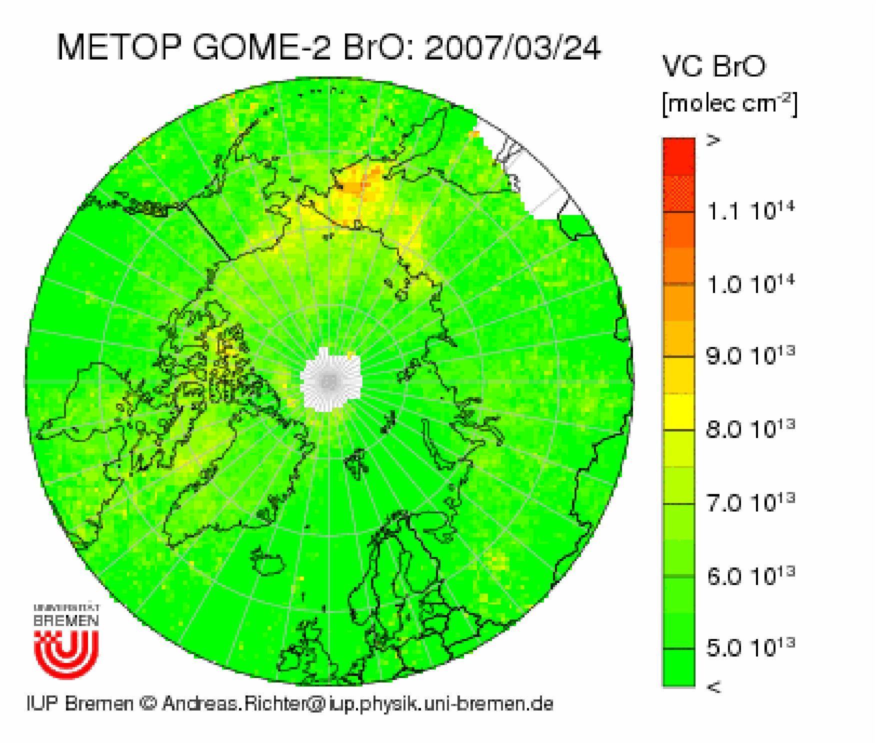
from Barrie et al., 1988

Springtime Chemistry Deposits Mercury



Halogens deplete ozone and scrub mercury from the air.
Schroeder et al. (1998), Nature.

BrO events observable from satellite

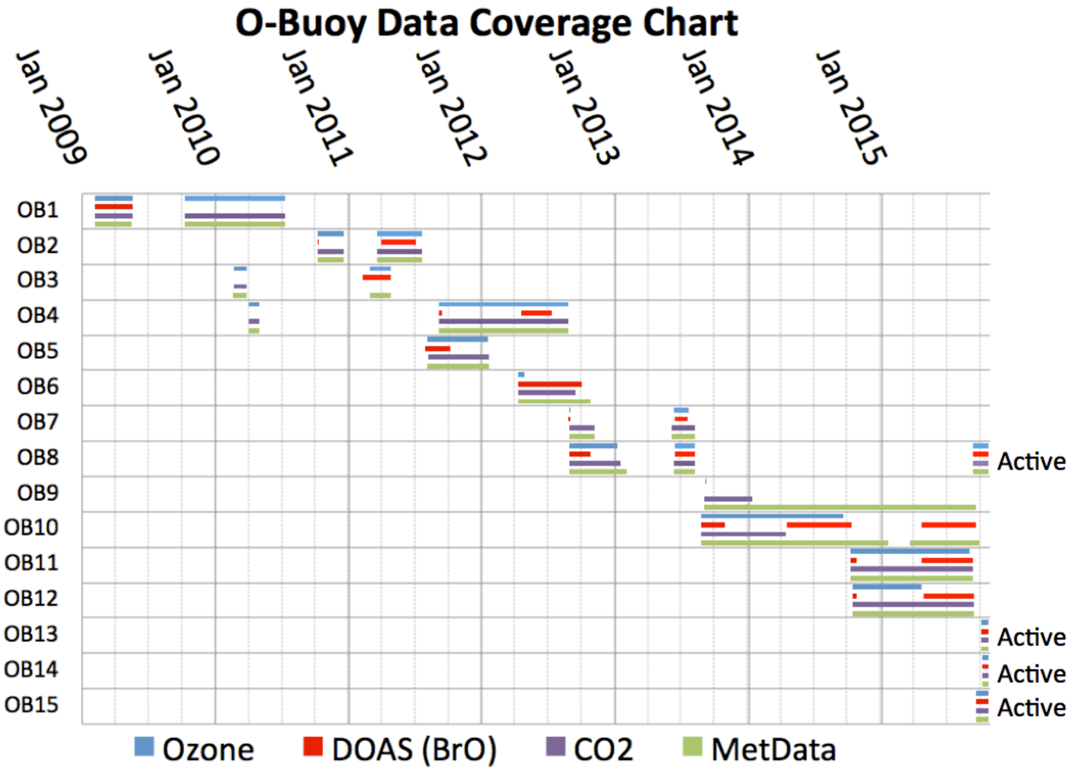


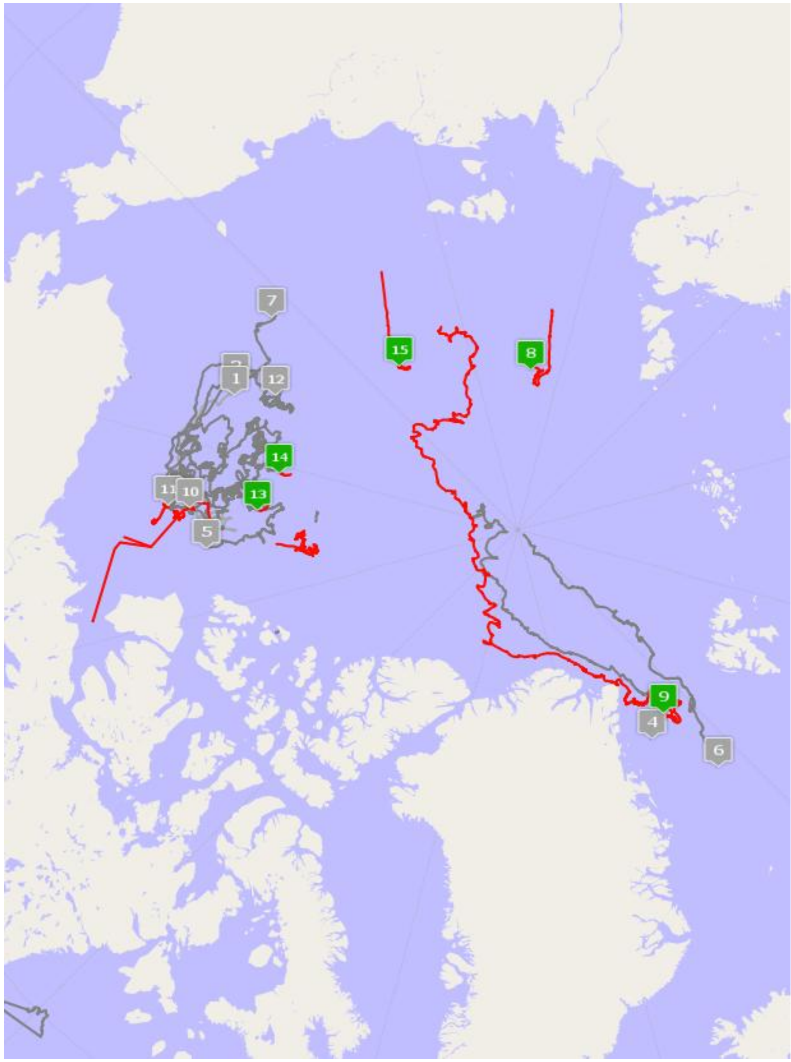
Observations of reactive halogens from space, courtesy of Andreas Richter, IUP Bremen, Germany.

O-Buoy sentinel species

- **CO_2** – Greenhouse gas, ocean exchange
- **O_3** – Indicates oxidation capacity
- **BrO** – Modifies oxidation capacity
- Meteorology and Time-lapse images

O-Buoy data covers the Arctic Ocean

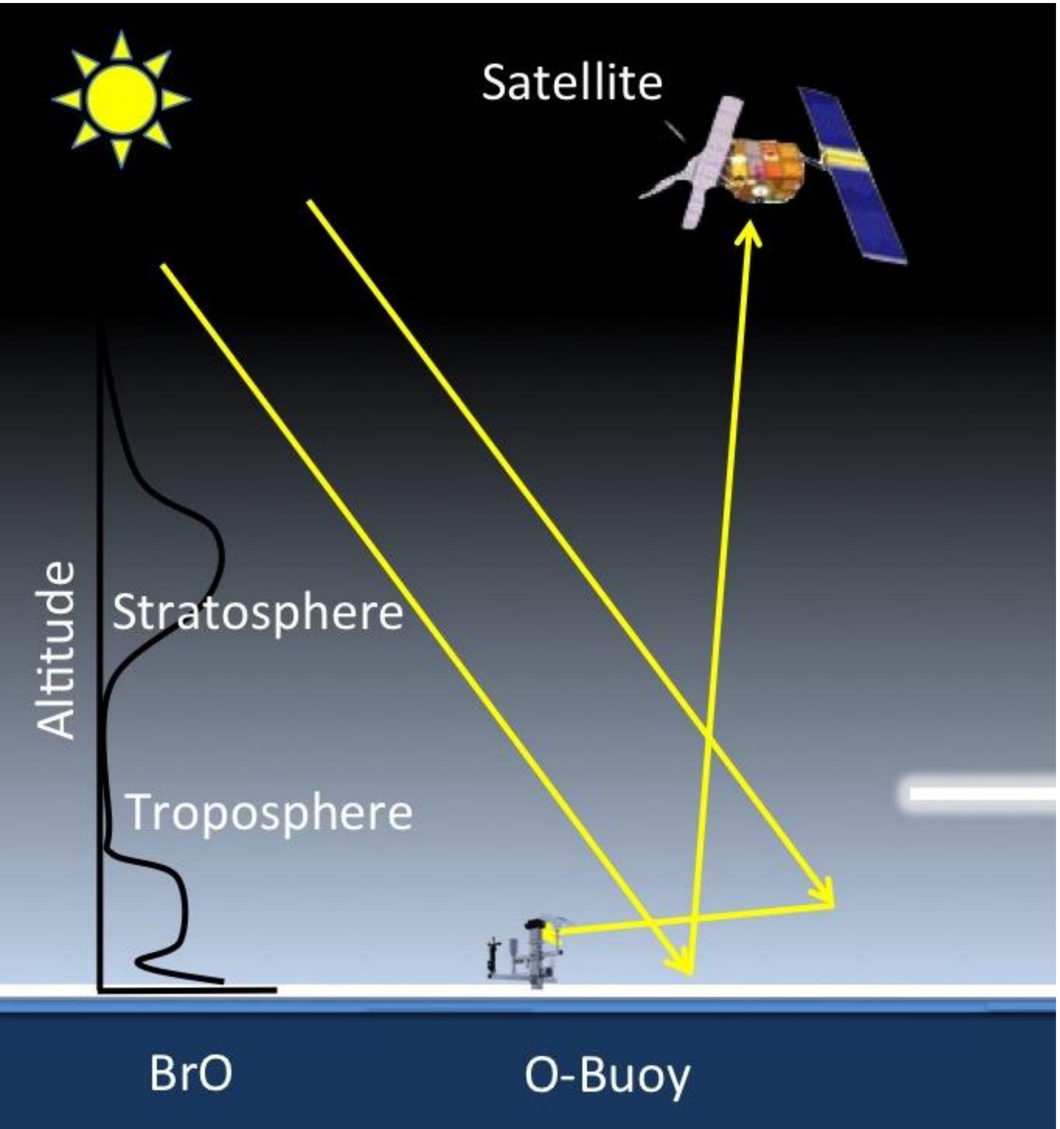




Data available at http://www.aoncadis.org

>400,000 spectra, 120,000 profiles

O-Buoy BrO observations

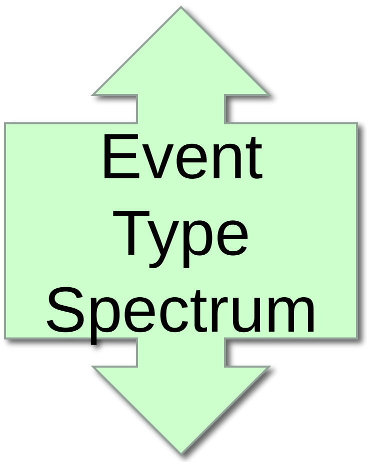


UV-Vis Spectrometer in O-Buoy measures scattered light

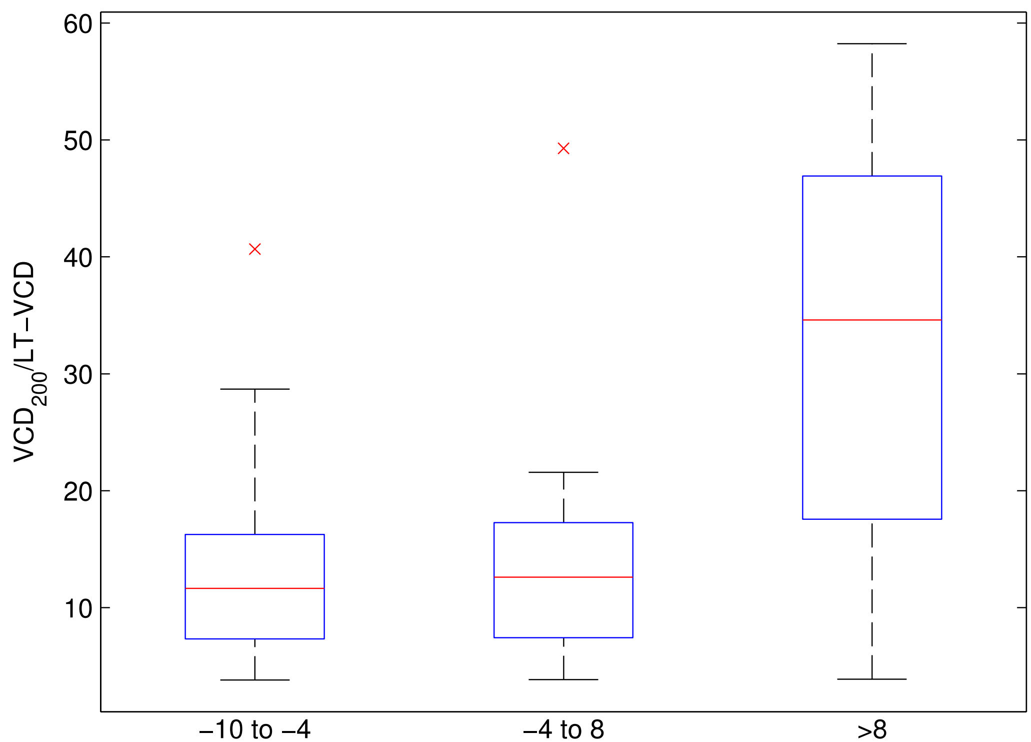
Tangent geometry isolates lower troposphere and measures BrO in lowest 200m and 2000m

Inversions control BrO profile

Shallow



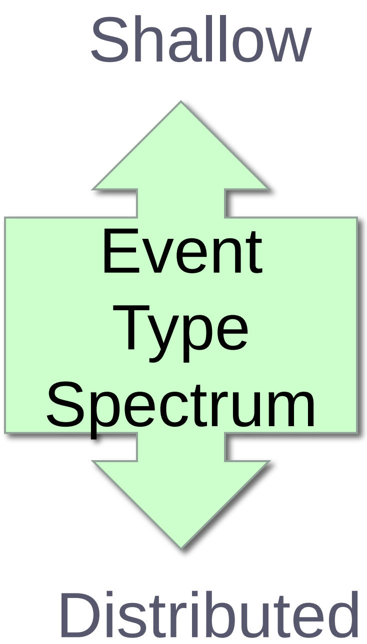
Distributed

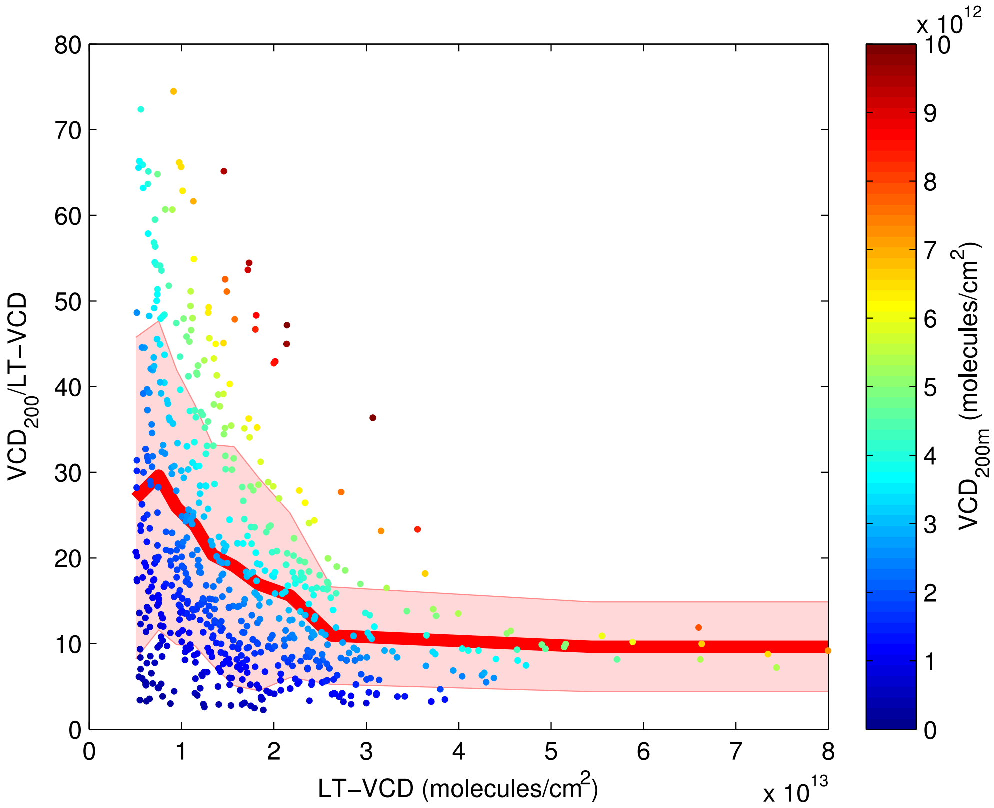


Neutral d*T*/d*z* Stable = Inversion

From Peterson et al. (2015) Atmos. Chem. Phys., **15**, 2119, doi:10.5194/acp-15-2119-2015

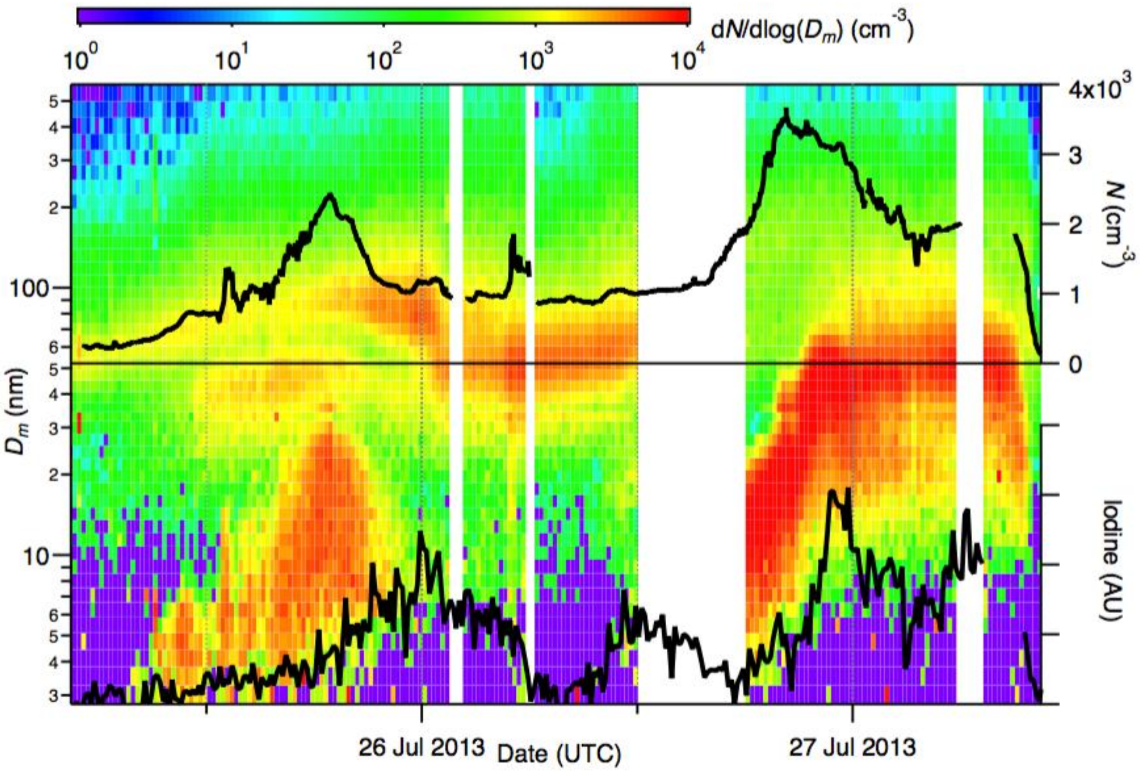
High BrO column events are mixed





High column events are “distributed”, while “shallower” events have less total BrO column.

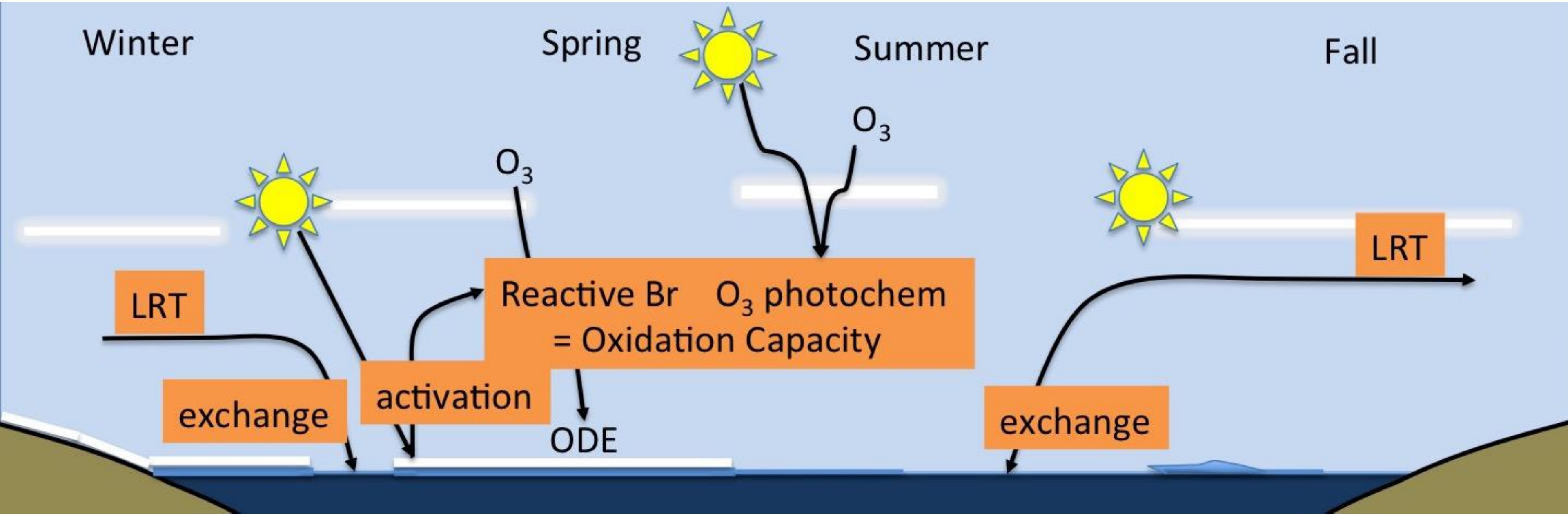
Iodine in new particle production



Allan and co-workers observed new particle production events in the Arctic and found iodine (another halogen) in the particles.

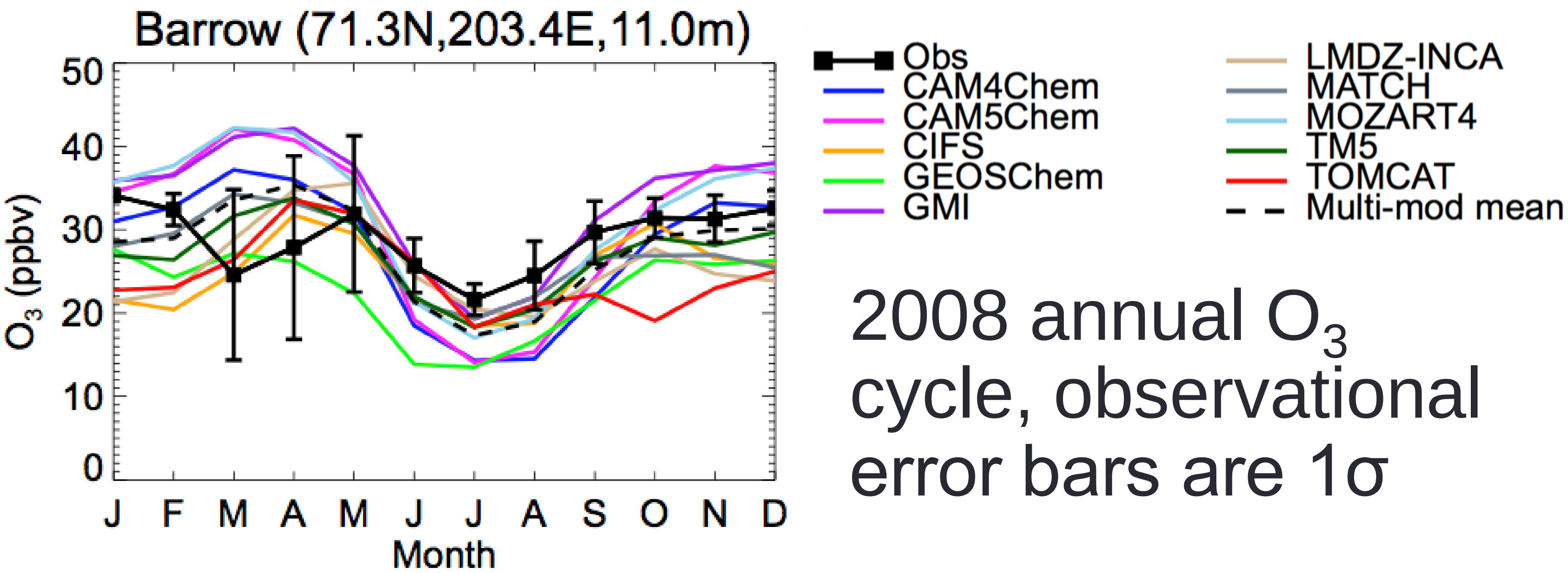
From Allan et al. (2015), Atmos. Chem. Phys., **15**, 5599, doi:10.5194/acp-15-5599-2015

Seasonal oxidation capacity



During springtime, photochemistry releases reactive bromine from sea ice, which depletes O_3. After snowmelt, halogens are gone and O_3 now controls oxidation capacity.

Models fail for O_3

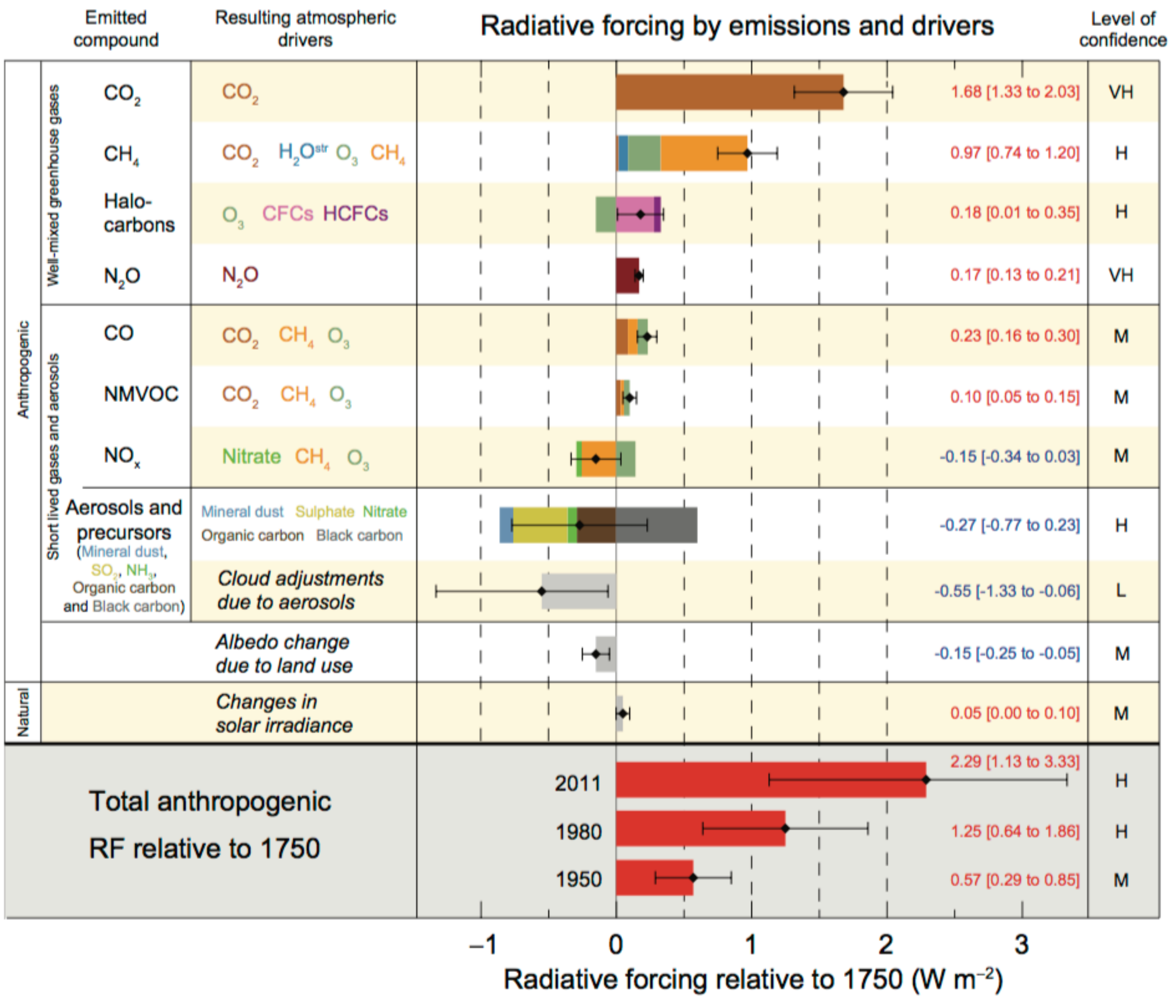


2008 annual O_3 cycle, observational error bars are 1σ

We do not understand or cannot model O_3 in the Arctic, esp. Spring + Summer. This impacts our understanding of Arctic oxidation capacity.

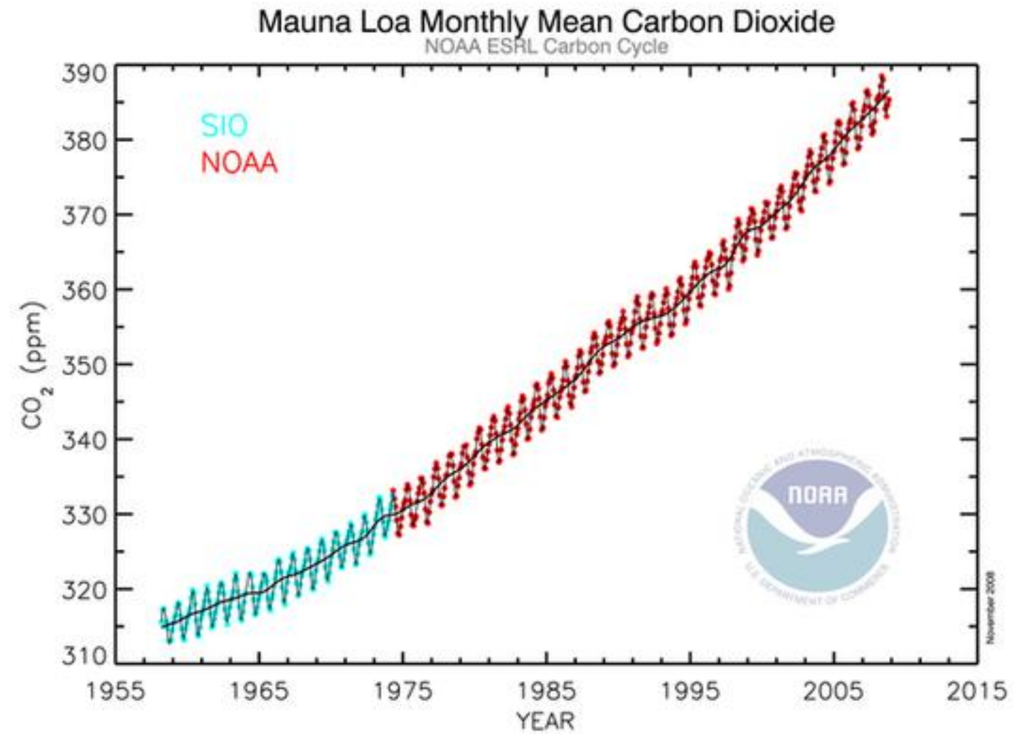
From Monks et al. (2015) Atmos. Chem. Phys., **15**, 3575, doi:10.5194/acp-15-3575-2015

IPCC report – Radiative forcing



IPCC report 2013

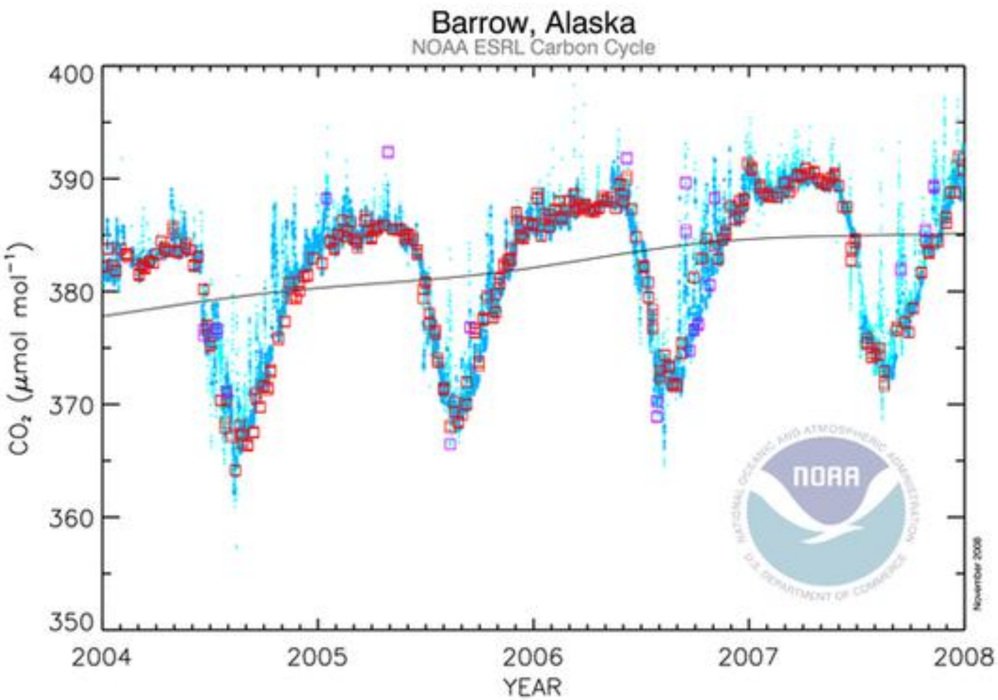
Carbon Dioxide (CO_2)



Atmospheric carbon dioxide monthly mean mixing ratios. Data prior to May 1974 are from the Scripps Institution of Oceanography (SIO, blue), data since May 1974 are from the National Oceanic and Atmospheric Administration (NOAA, red). A long-term trend curve is fitted to the monthly mean values. Contact: Dr. Pieter Tans, NOAA ESRL Carbon Cycle, Boulder, Colorado, (303) 497-6678, pieter.tans@noaa.gov, and Dr. Ralph Keeling, SIO GRD, La Jolla, California, (858) 534-7582, rkeeling@ucsd.edu.

Fossil fuel combustion has increased CO_2 markedly, but ~half of the fossil CO_2 that has been emitted has been taken up into the ocean and biosphere.

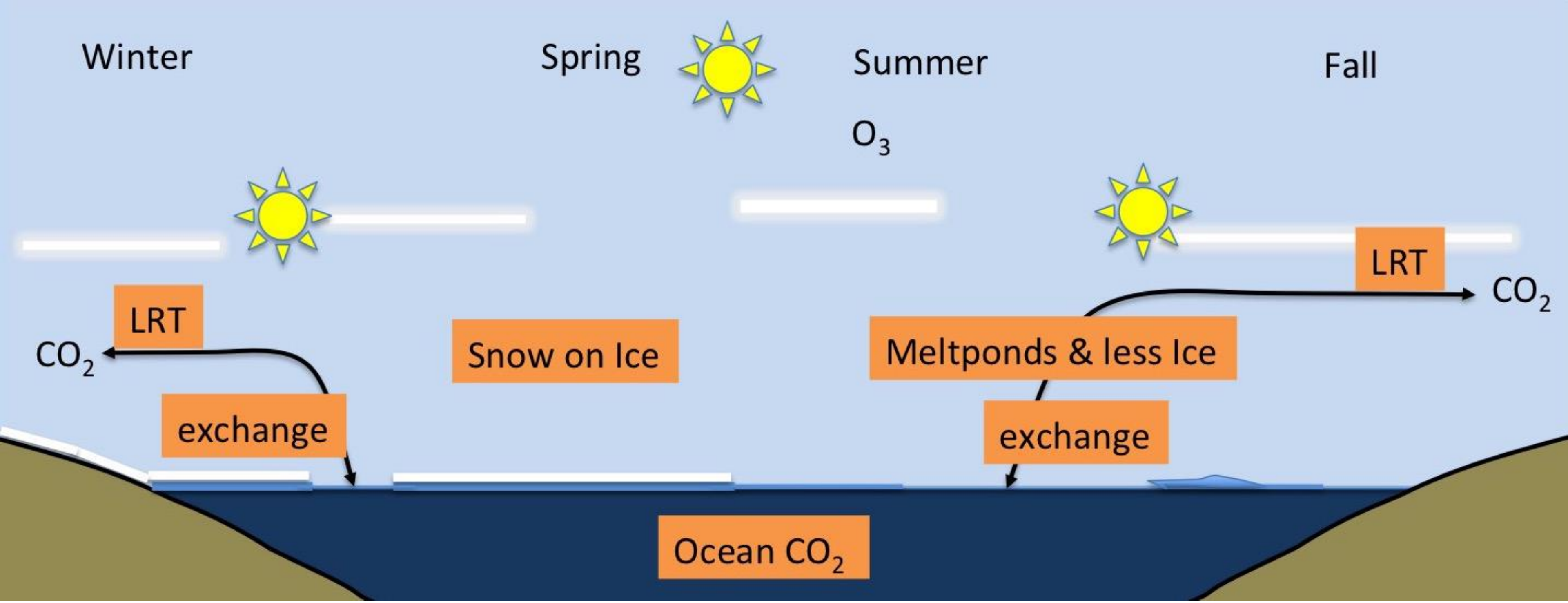
Carbon Dioxide (CO_2)



Time series showing measurements of atmospheric carbon dioxide using two independent methods. Hourly averaged values from the semi-continuous measurement system operating at the Barrow baseline observatory are shown in blue (plus). Measurements thought to be representative of baseline conditions are identified in dark blue (plus). Measurements thought to be locally influenced are shown in light blue (plus). Retained measurements from weekly air samples collected at the observatory but analyzed in Boulder, CO are shown in red (square). Weekly samples thought to be affected by local influences are shown in purple (square). Contact: Dr. Pieter Tans, (303) 497-6678, pieter.tans@noaa.gov, http://www.esrl.noaa.gov/gmd/ccgg/.

Carbon dioxide is breathed out by life and decay, and exhaust, and taken up by biological processes (plants). Huge summertime terrestrial sink (greenup).

Arctic Ocean CO_2 exchange



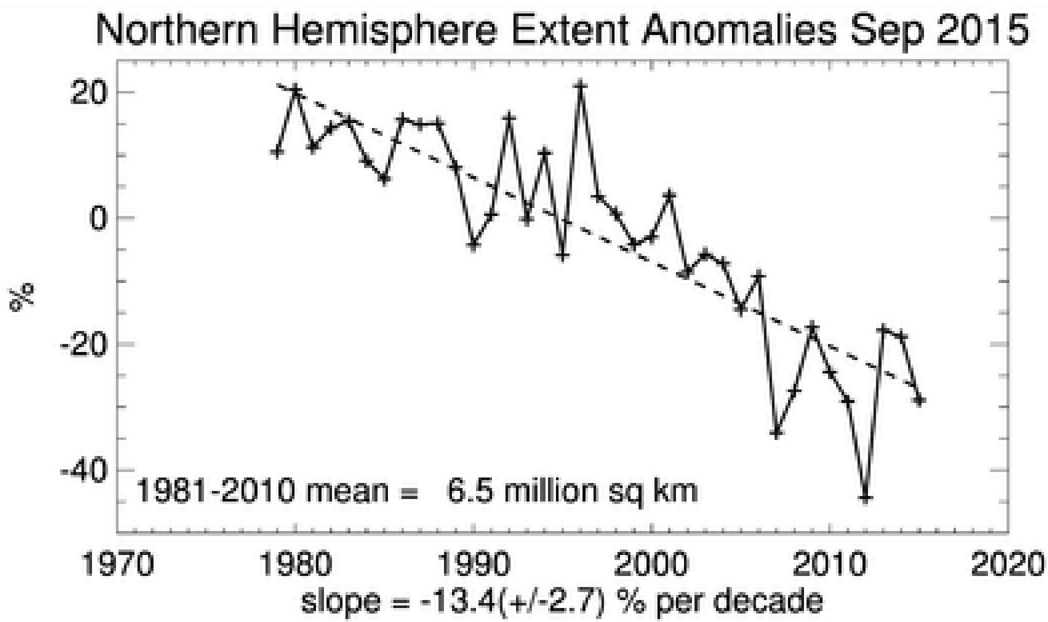
CO_2 is transported into and out of the Arctic and can exchange with the Arctic Ocean, possibly moderated by sea ice.

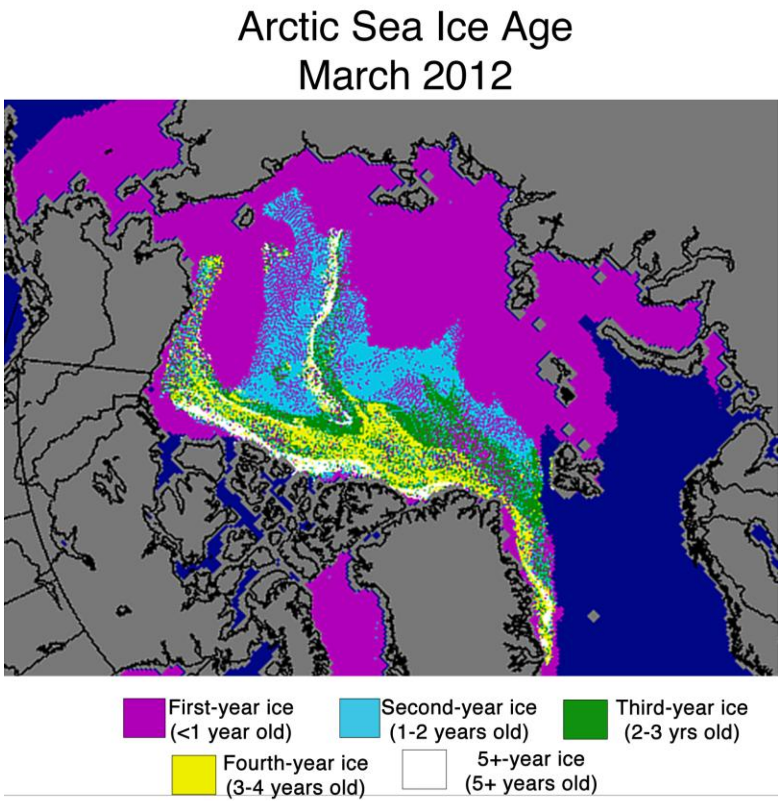
Seasonality of the Chemistry

- We know that in Springtime, the Arctic's chemistry enters a new regime with halogen chemistry, ozone depletion, and mercury deposition (at least at coastal sites).

- What about the rest of the year? What about on the ice cap?
- **Spring?** Some known at coastal sites. Limited on-ice obs.
- **Summer?** Ice breaker cruises (sporatic).
- **Fall?** Too Dangerous with broken ice conditions.
- **Winter?** Too Dark for most work

Sea ice is changing



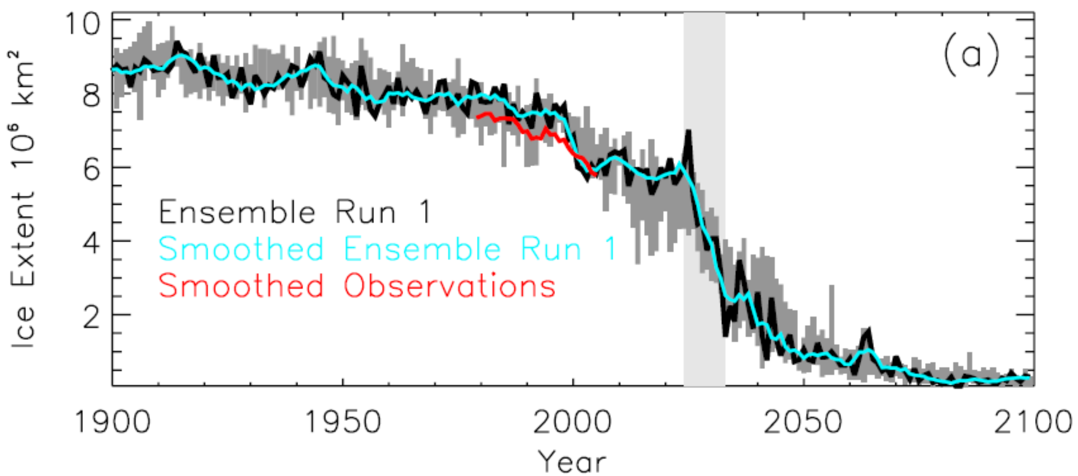


- Summer sea ice is declining.
- Winter sea ice is getting younger, saltier, more leads.
  How does this affect the air?

From NSIDC Arctic Sea Ice data. http://nsidc.org

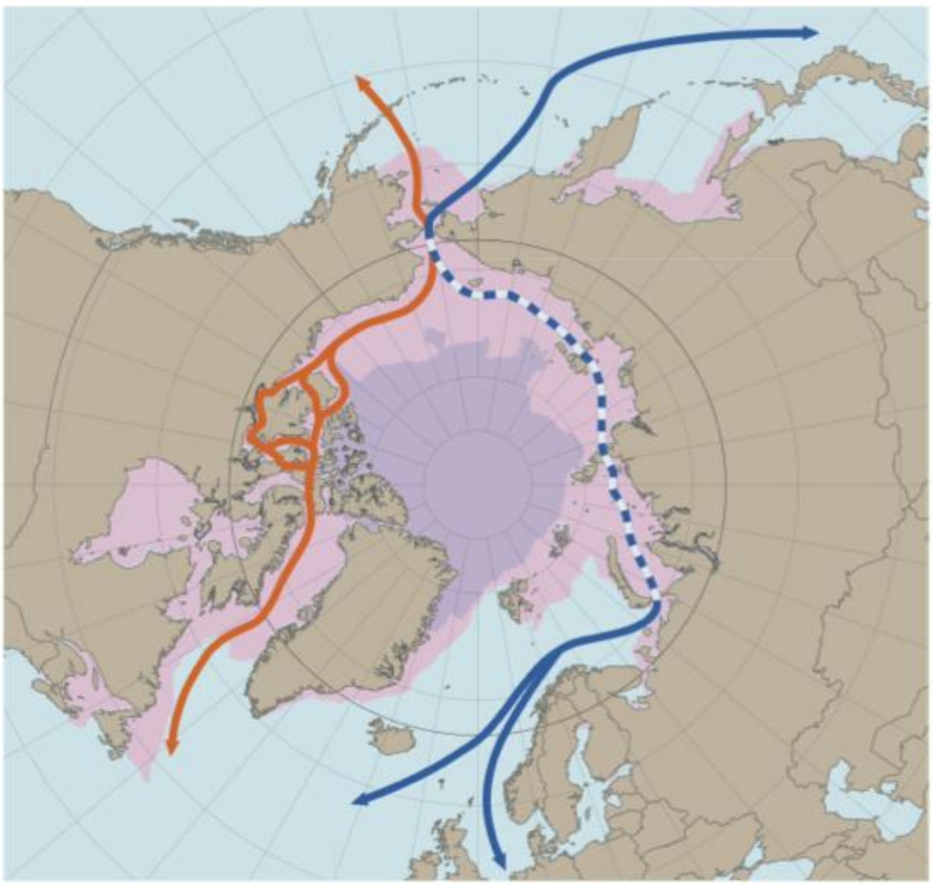
What will climate change do?

Changes in saltiness of sea ice may affect halogen / ozone / mercury chemistry in the springtime



Holland, M. M., C. M. Bitz, and B. Tremblay (2006), Future abrupt reductions in the summer Arctic sea ice, Geophys. Res. Lett., 33, L23503, doi:10.1029/2006GL028024.

Arctic shipping routes



Northwest Passage
Northeast Passage
Northern Sea Route

Sea-ice extent 2015
March
September

- Trans-Arctic shipping is increasing.
- This would lead to direct injection into the Arctic of BC, and ozone / aerosol precursors.

Big picture changes

- Dramatic changes in sea ice. Alters atmosphere, stability, potential to exchange gases with Arctic Ocean
- Dramatic warming. Will this change Arctic greenhouse gas emissions (e.g. CH_4, CO_2) or uptake (e.g. CO_2)
- Oceanic and terrestrial changes at surface. How do these change greenhouse gas exchanges as well as biogenic precursors to CCN and/or IN.
- Potential for Trans-Arctic shipping, increased oil/gas exploration. What effects?

Conclusions

- The Arctic needs better monitoring and better process-based modeling.
- Pollutant transformations and fate are different in the Arctic and need to be better understood.
- The Arctic atmosphere is highly stratified, complicating transport and chemistry, and with surface warming, this stratification may decrease.
- Sea ice changes are likely to change the Arctic atmosphere and climate in major ways.