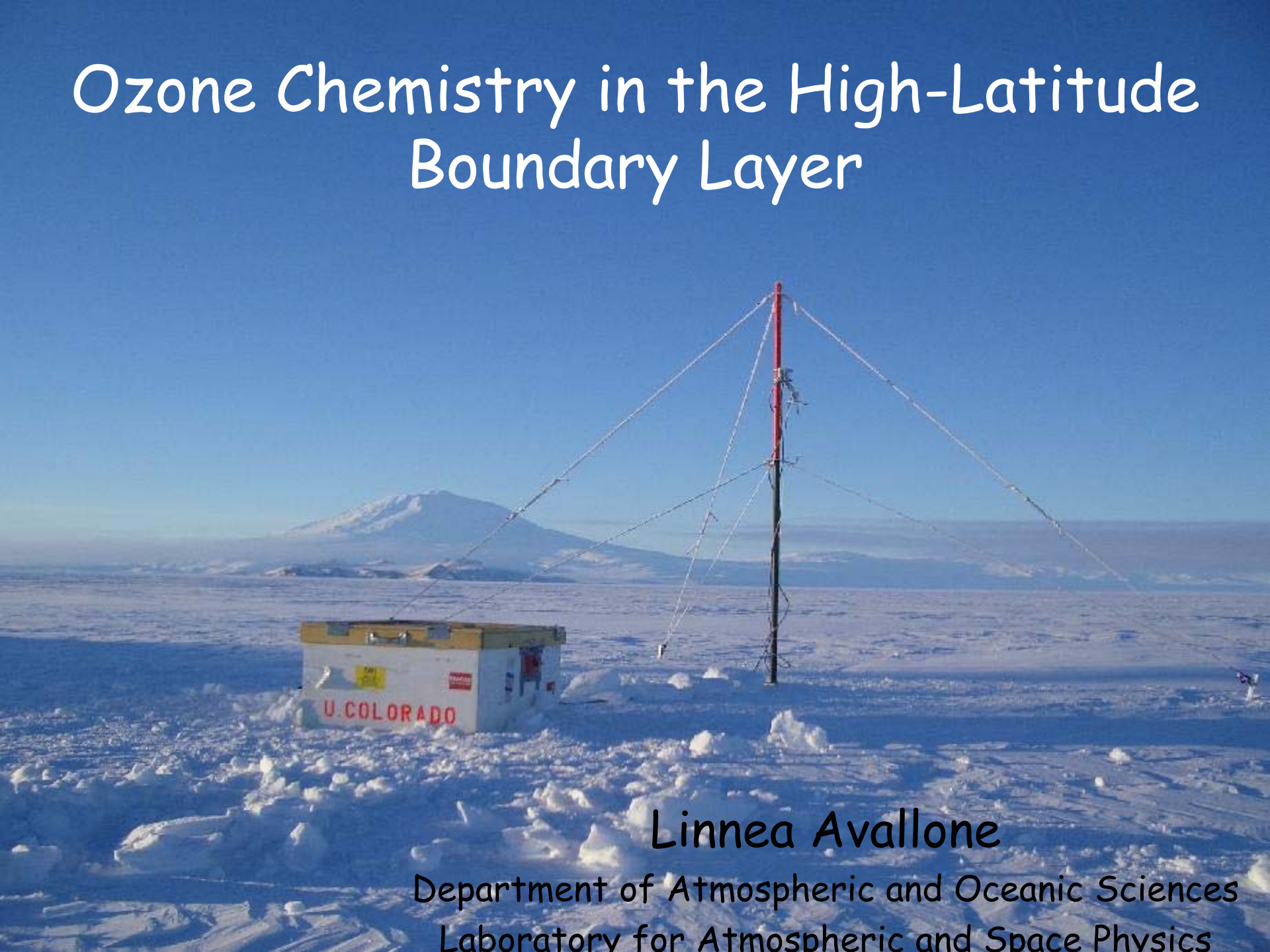
Ozone Chemistry in the High-Latitude Boundary Layer



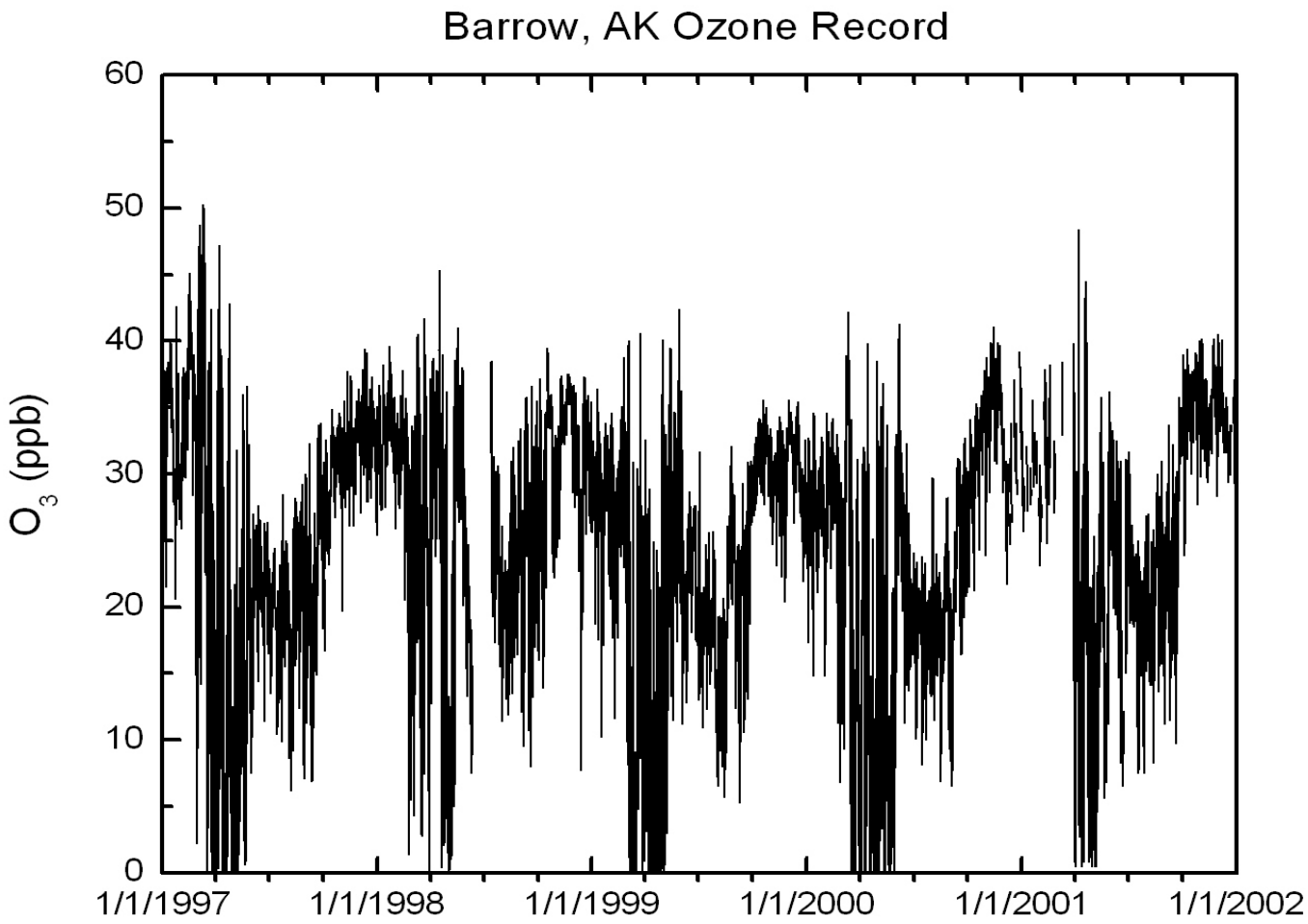
Linnea Avallone
Department of Atmospheric and Oceanic Sciences
Laboratory for Atmospheric and Space Physics

Outline

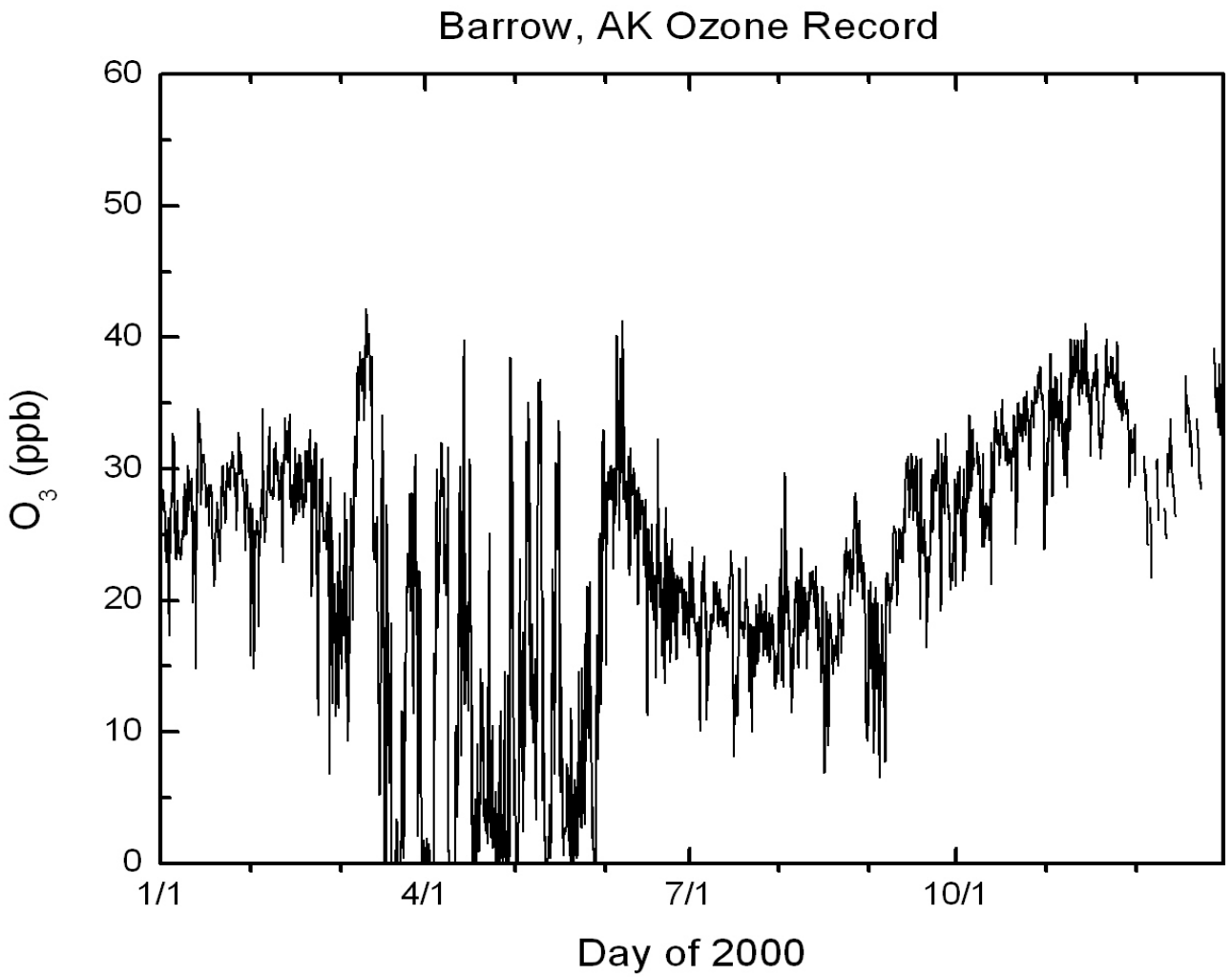
- Brief history of boundary layer ozone loss phenomenon
- In situ observations of BrO at Arctic sites
- Preliminary results from Antarctic experiments in 2002 and 2004

Brief History

- Springtime ozone loss observed at many sites around Arctic since 1970s



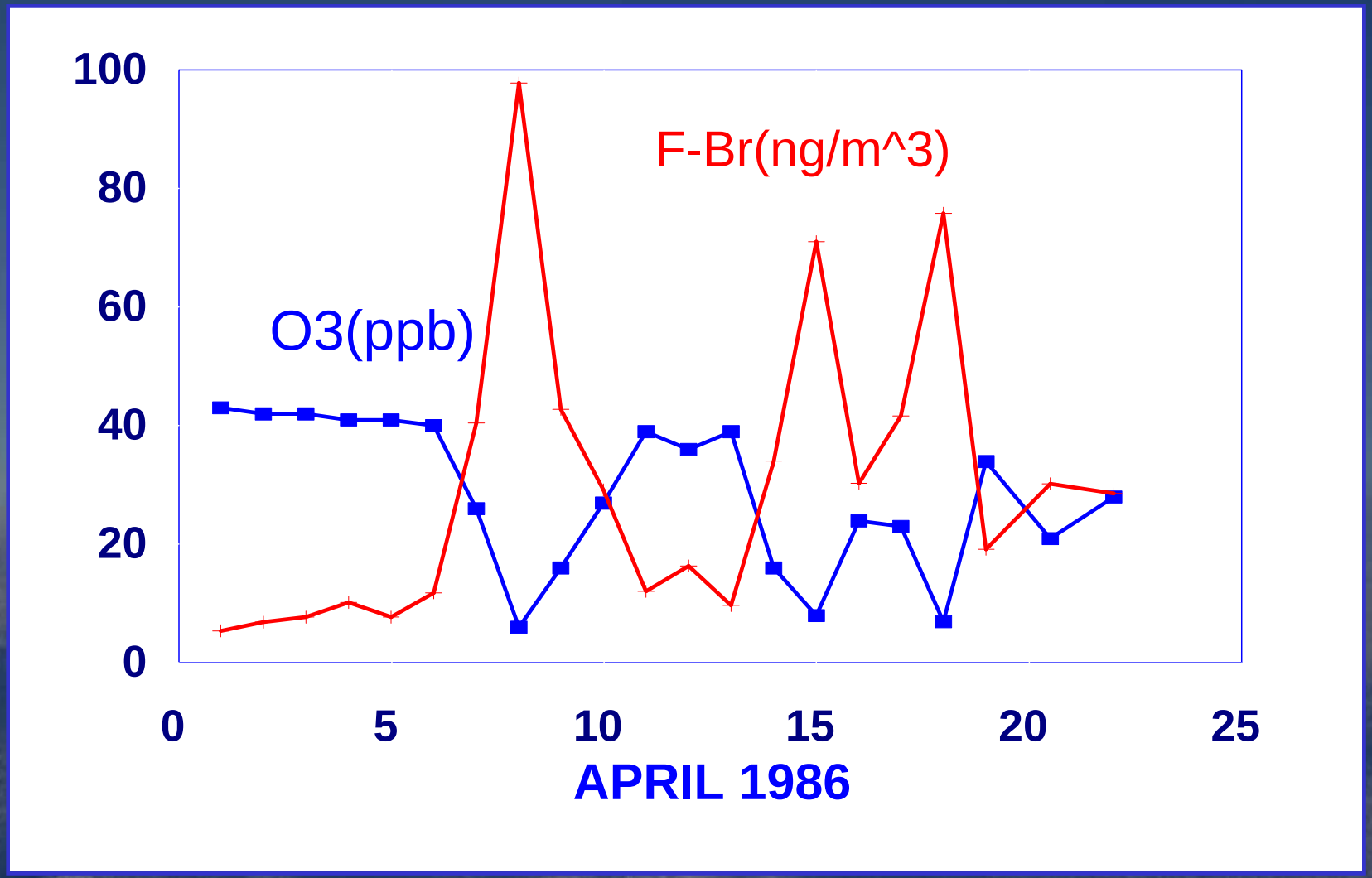
Data courtesy NOAA CMDL



Data courtesy NOAA CMDL

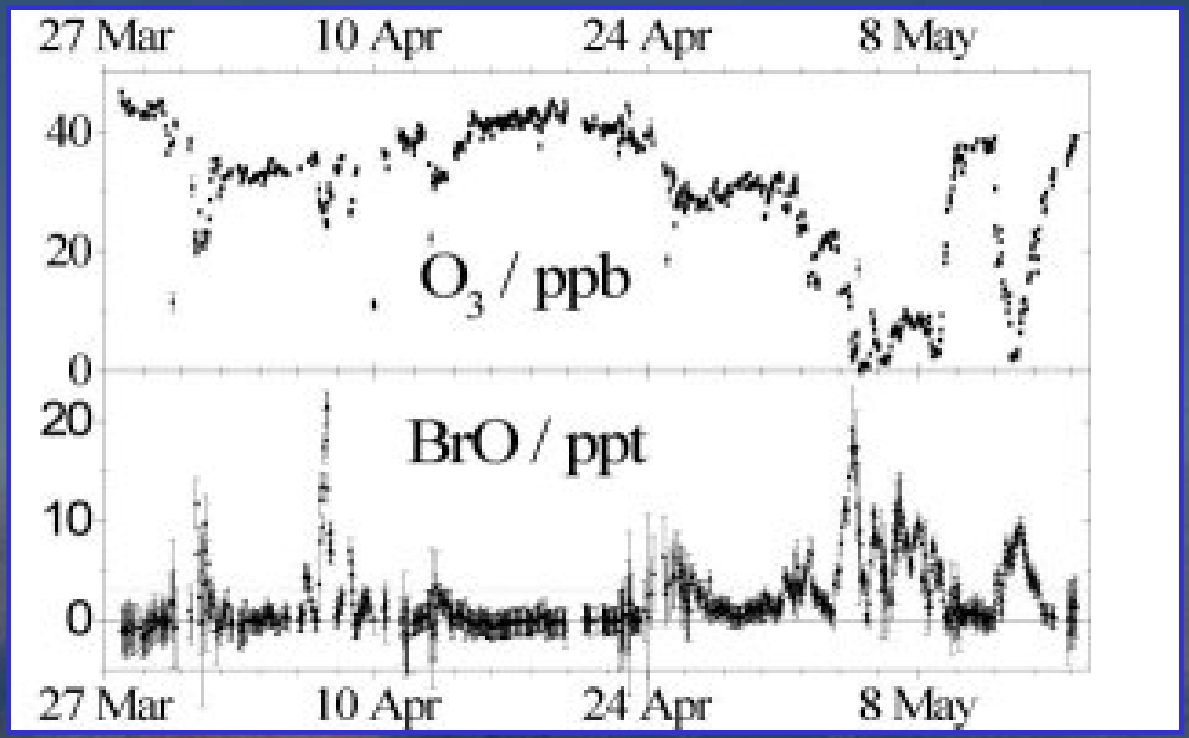
Brief History

- Springtime ozone loss observed at many sites since 1970s
- Early studies suggested link to "Arctic Haze" – pollution transported from Europe and Asia
- Filterable Br correlated with ozone loss



Barrie et al., *Nature*, 1988

Brief History



Tuckerman et al., *Tellus*, 1997

- Later studies show some correlation between ozone loss and presence of BrO

Ozone Loss in the Arctic

$$2\,(Br + O_3 \rightarrow BrO + O_2)$$

$$BrO + BrO \rightarrow 2Br + O_2$$

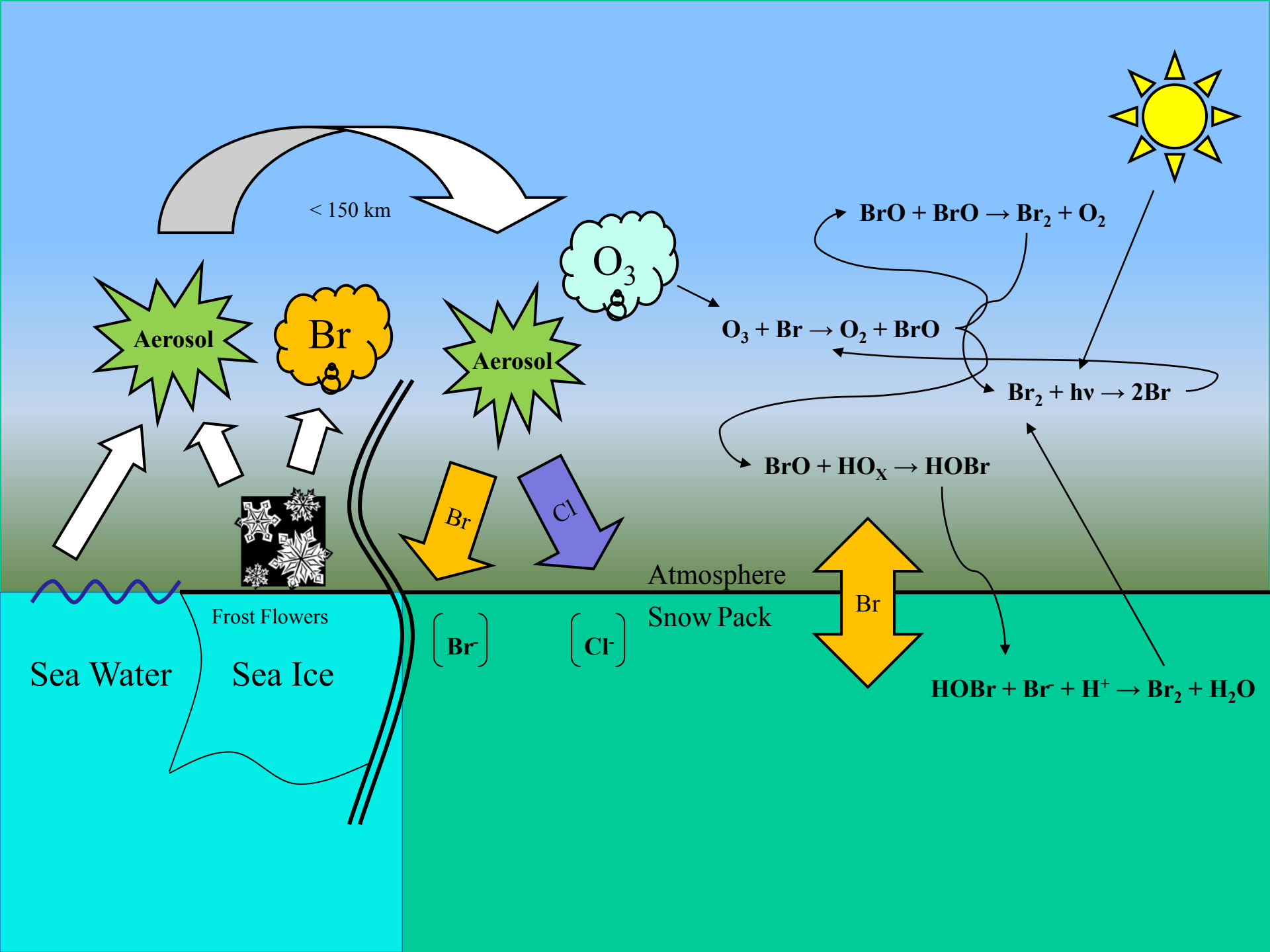
$$2\,O_3 \rightarrow 3\,O_2$$

- Natural chemistry in the Arctic caused by bromine episodically removes O_3 near the surface every spring
- Allows other gases to build up to unnaturally high levels, including mercury and certain hydrocarbons

Where does bromine come from?

"leads" spray deposits
salt on snowy surfaces

frost flowers
made of brine


< 150 km
Aerosol
Br
Aerosol
O_3
$O_3 + Br \rightarrow O_2 + BrO$
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$Br_2 + h\nu \rightarrow 2Br$
$BrO + HO_X \rightarrow HOBr$
$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$
Br
Cl
Atmosphere
Snow Pack
Br
Frost Flowers
Br^-
Cl^-
Sea Water
Sea Ice

"Bromine Explosion"

$$HOBr_{(aq)} + Br^-_{(aq)} + H^+_{(aq)} \rightarrow H_2O_{(aq)} + Br_{2(g)}$$

$$Br_2 + h\nu \rightarrow 2Br$$

$$Br + O_3 \rightarrow BrO + O_2$$

$$BrO + HO_2 \rightarrow HOBr + O_2$$

$$\text{Net: } H^+ + Br^- + HO_2 + O_3 \rightarrow Br + H_2O + 2O_2$$

[Fan and Jacob, 1992]

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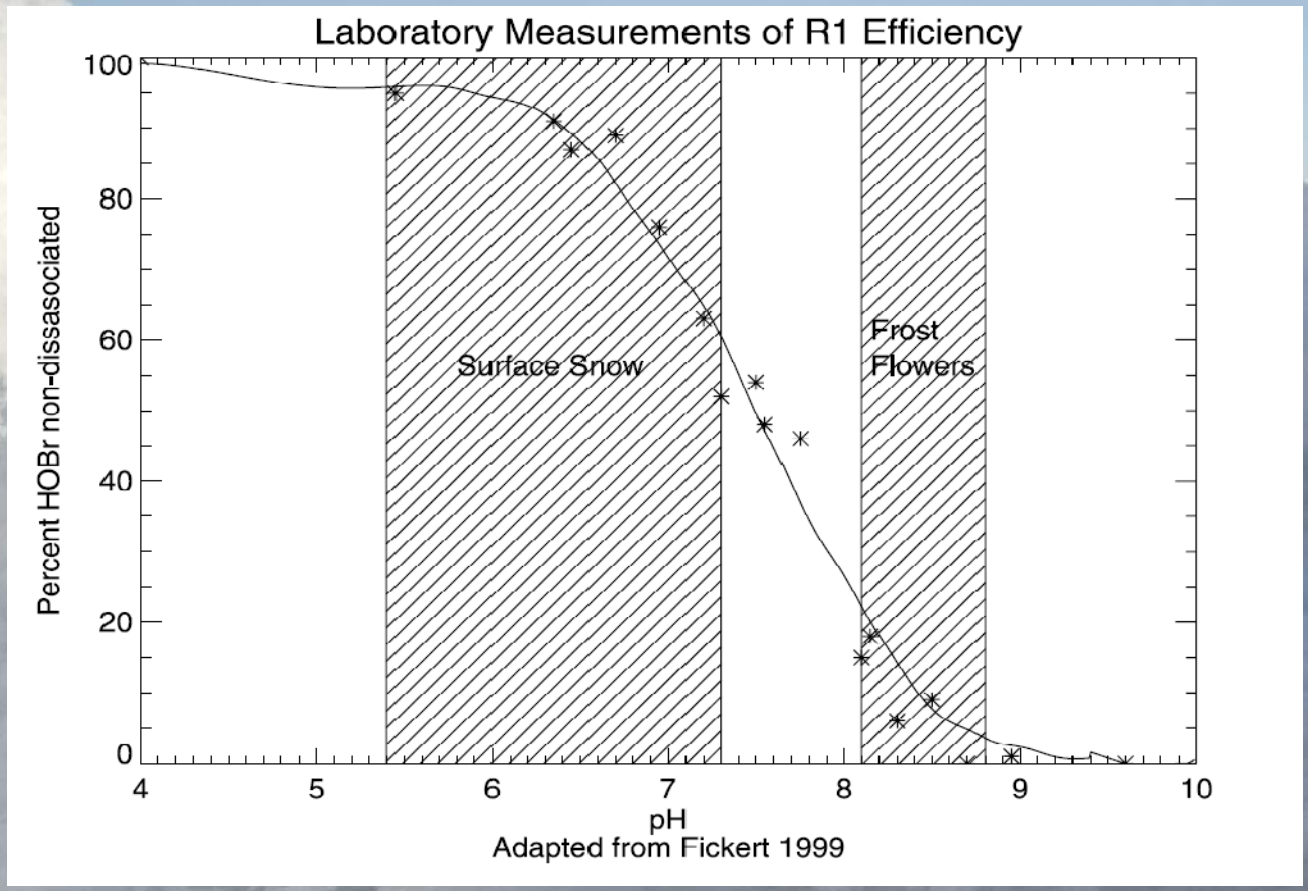
[Fan and Jacob, 1992]



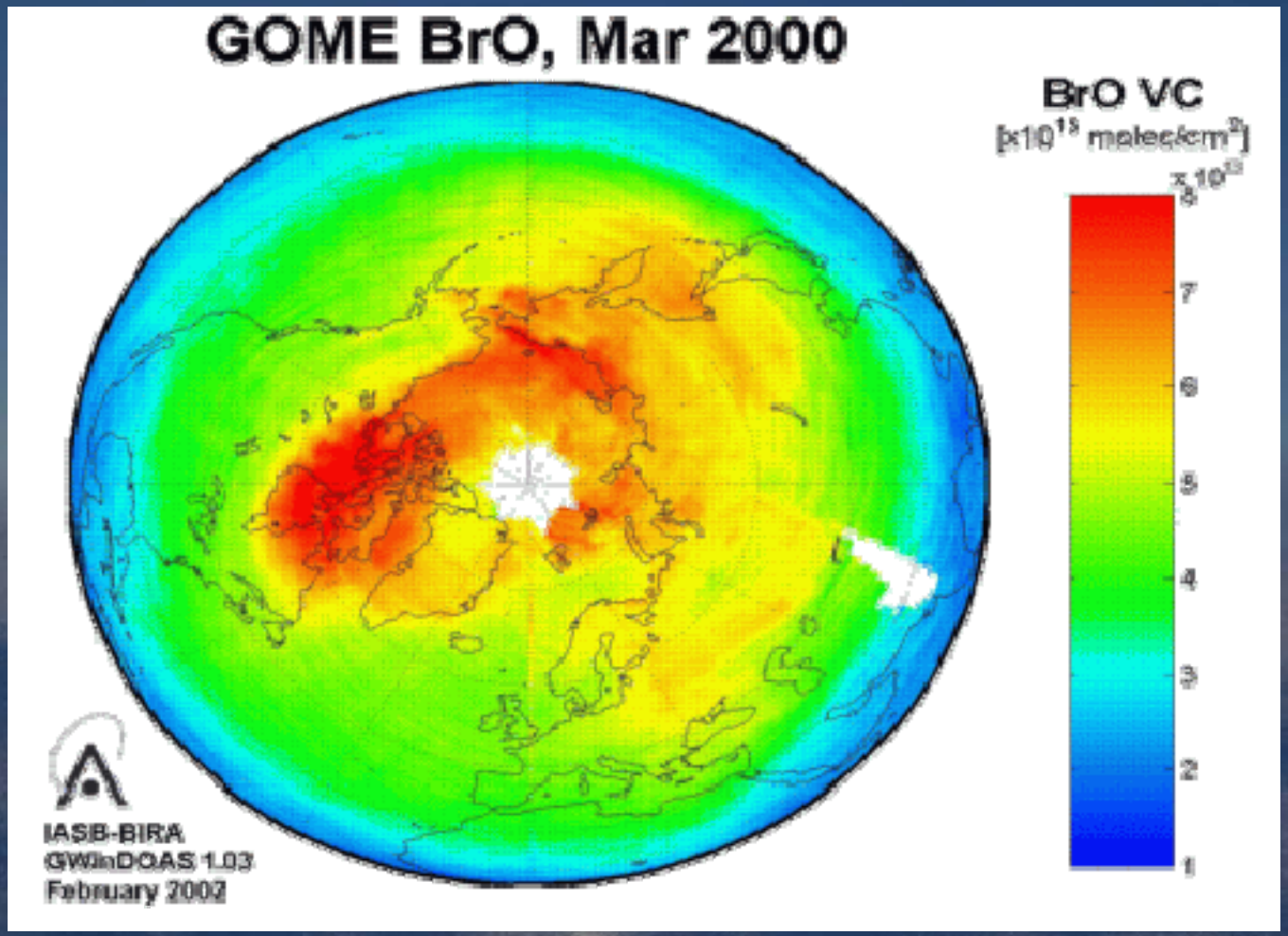
Source	pH	Cl/Br
Sea Water	7.6 - 8.2	650
Frost flowers, measured	8.1 – 8.7	269-367
Surface snow, measured	5.4 – 7.3	13-980

[*Kalnajs and Avallone 2006*]

Why should we care?

- Bromine activation is widespread

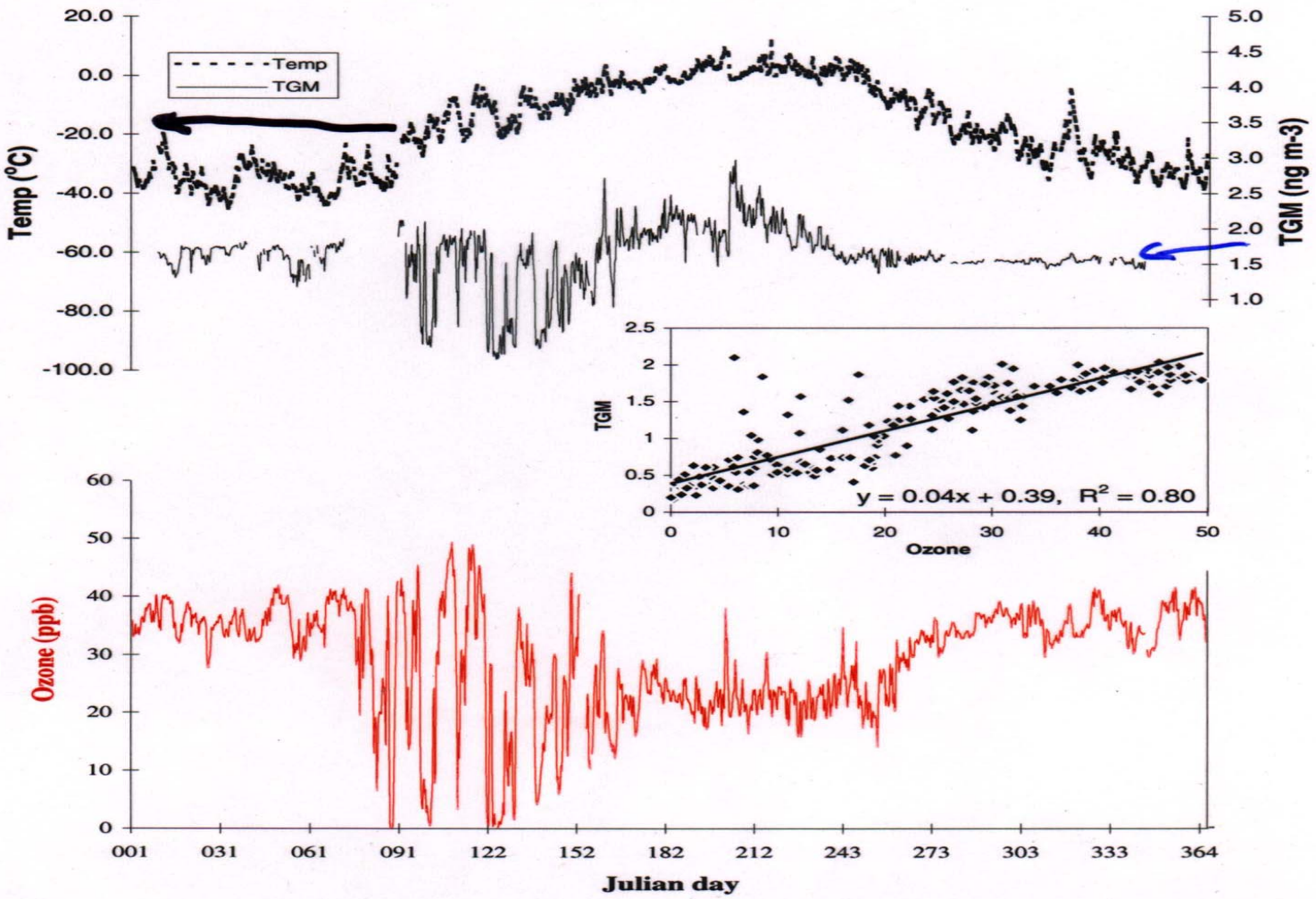
BrO is widespread



Why should we care?

- Bromine activation is widespread
- Bromine may react with gaseous mercury (Hg^0), converting it to forms that are deposited into ecosystems

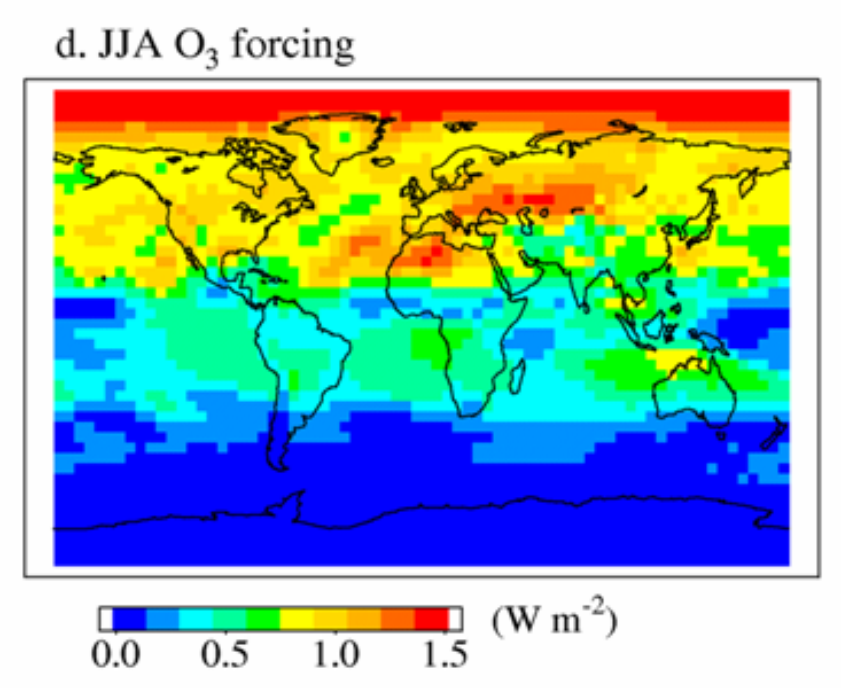
Correlation of Mercury with Ozone



Schroeder et al., *Nature*, 1998

Why should we care?

- Bromine activation is widespread
- Bromine may react with gaseous mercury (Hg^0), converting it to forms that are deposited into ecosystems
- Possible climate implications of boundary layer ozone loss



JJA tropospheric ozone forcing above pre-industrial levels [*L.J. Mickley 2001*]

- Tropospheric Ozone has significant climate forcing at poles
- ODEs affect arctic ozone budget
- Antarctic is cleaner than arctic → study non-anthropogenic contribution
- ODEs play a role in aerosol formation → ice core interpretation

In Situ Measurements of Halogens

- Prior to 1996, all observations of halogens had been made either by long-path spectroscopy (DOAS) or by collection and analysis of aerosols or air samples
- In situ measurements provide higher temporal resolution, and potentially higher spatial resolution

Measurement Sites

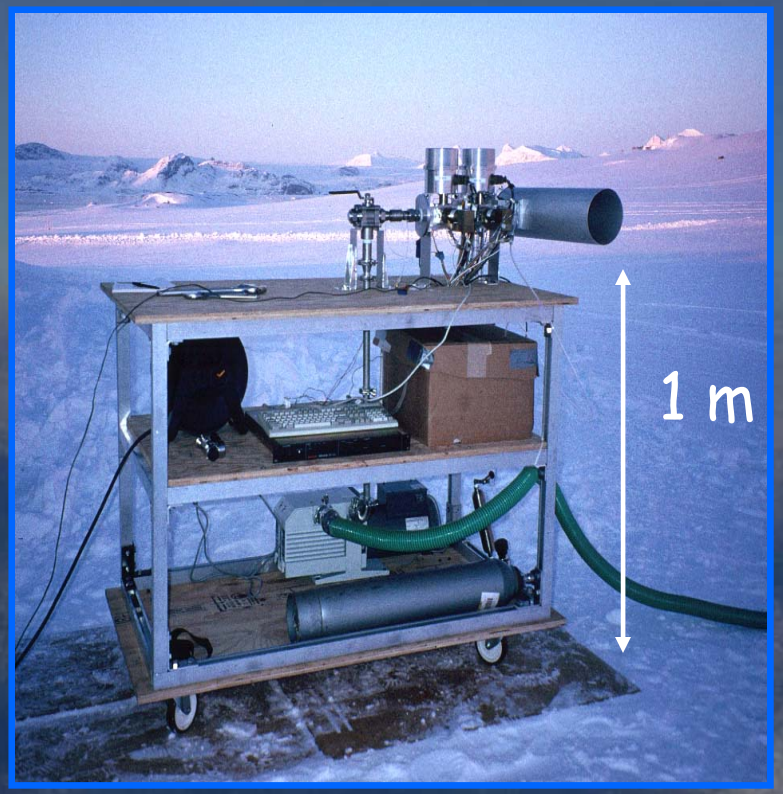
PSE 2000

ARCTOC

Instruments

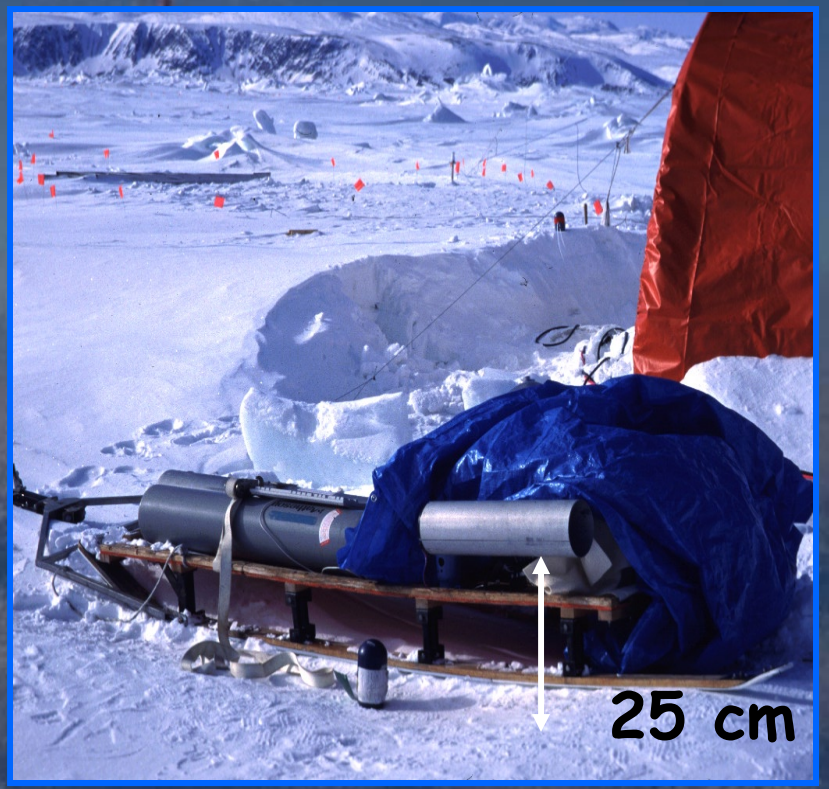
ARCTOC '96

Ny Ålesund, April-May

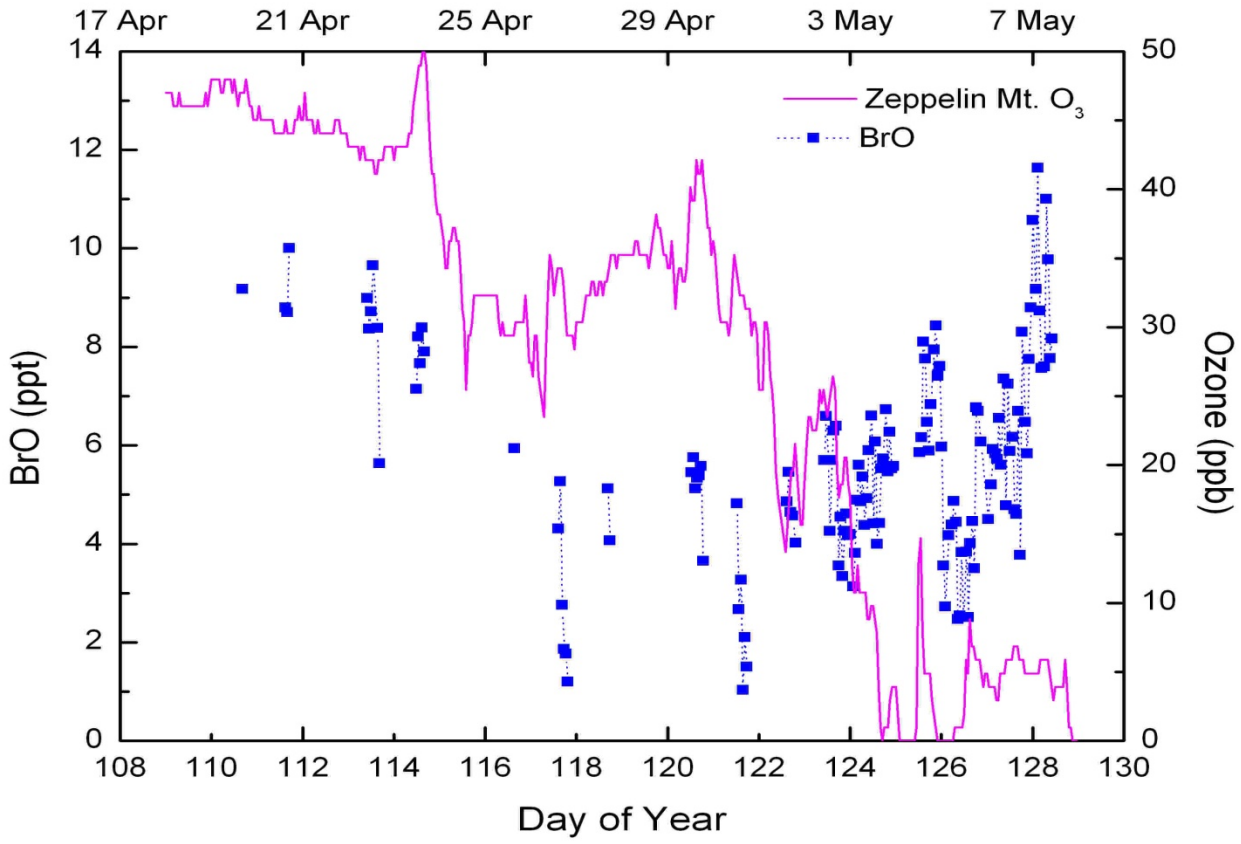


Polar Sunrise 2000

Alert, May



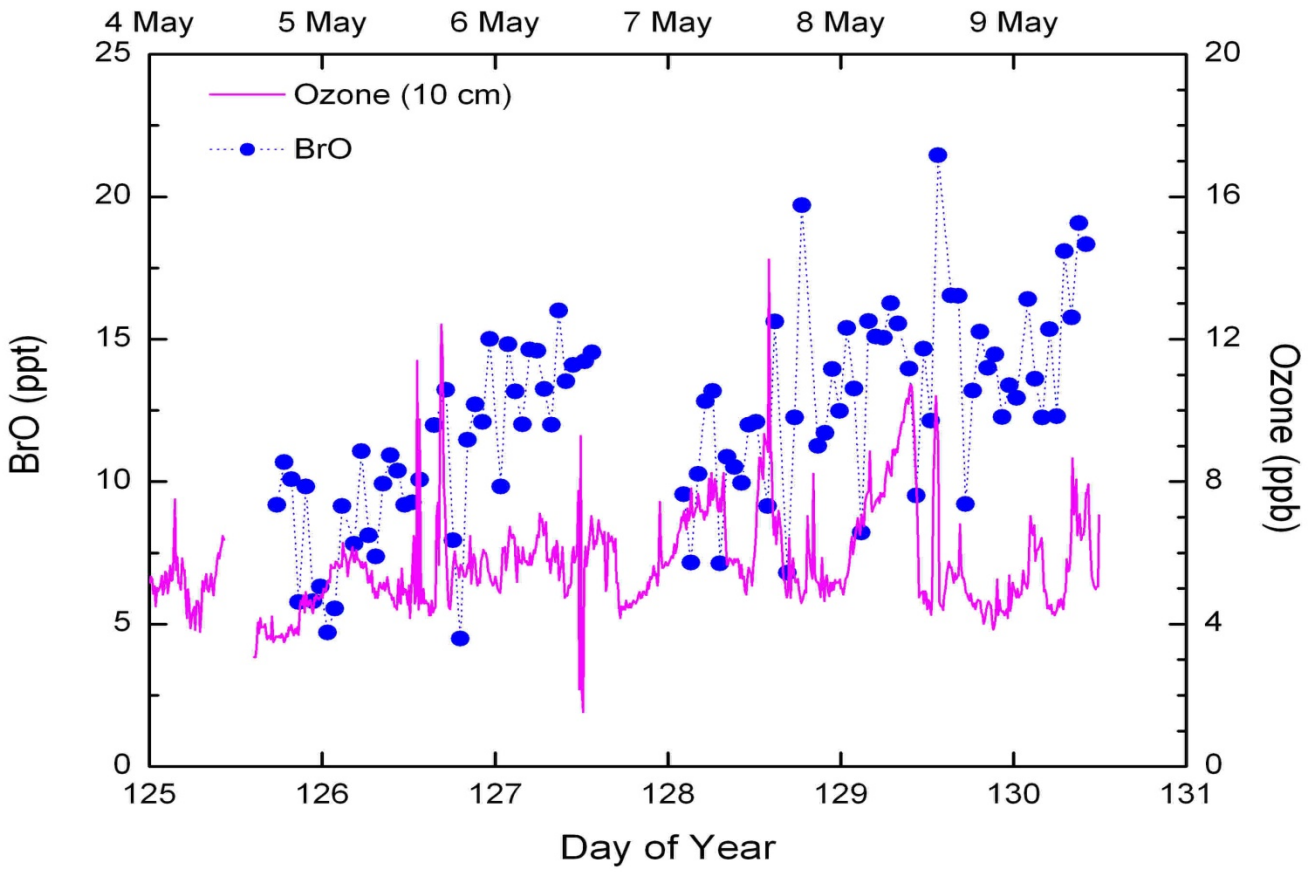
ARCTOC '96 BrO



Avallone et al., *JGR*, 2003

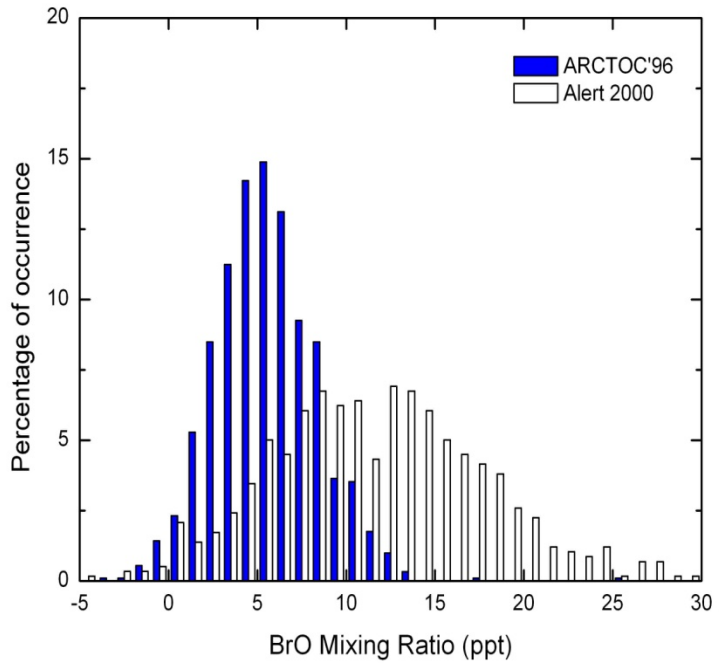
Alert 2000 Ice Camp

Alert 2000 BrO



Avallone et al., *JGR*, 2003

Lessons from in situ BrO measurements

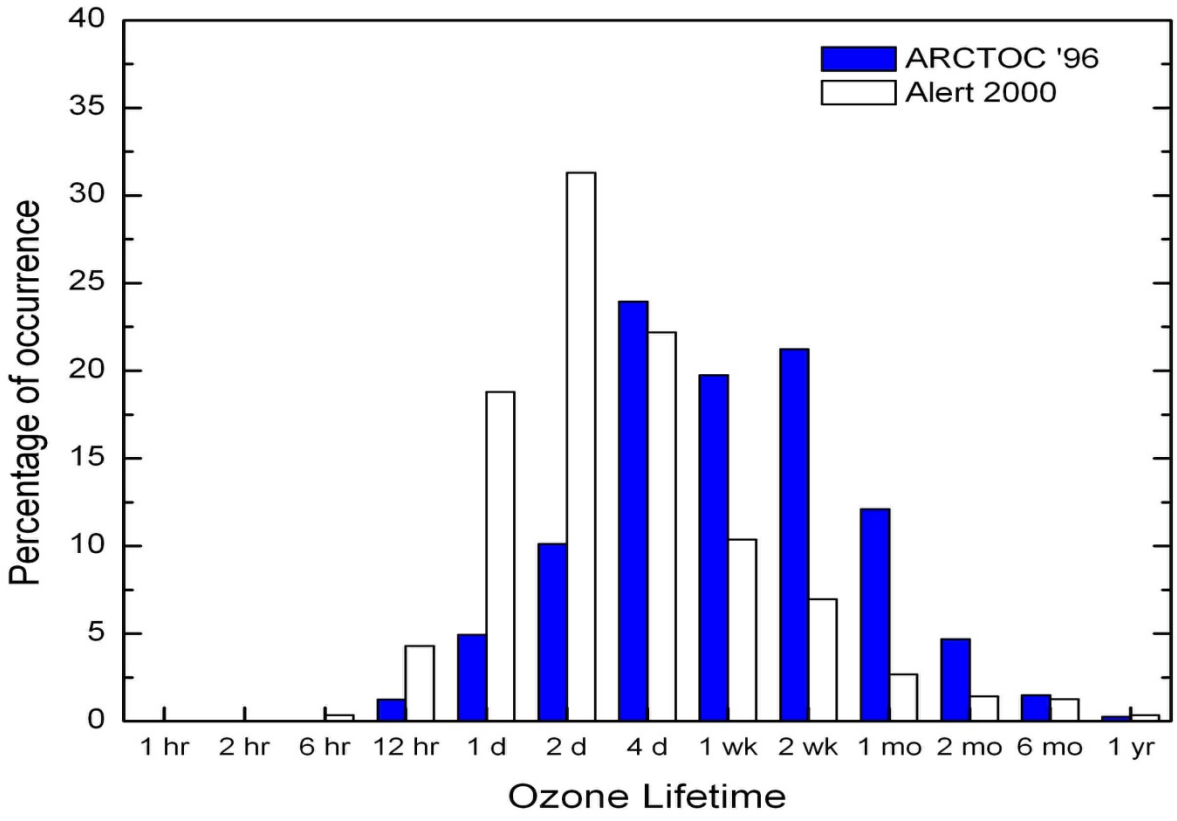


BrO + BrO,

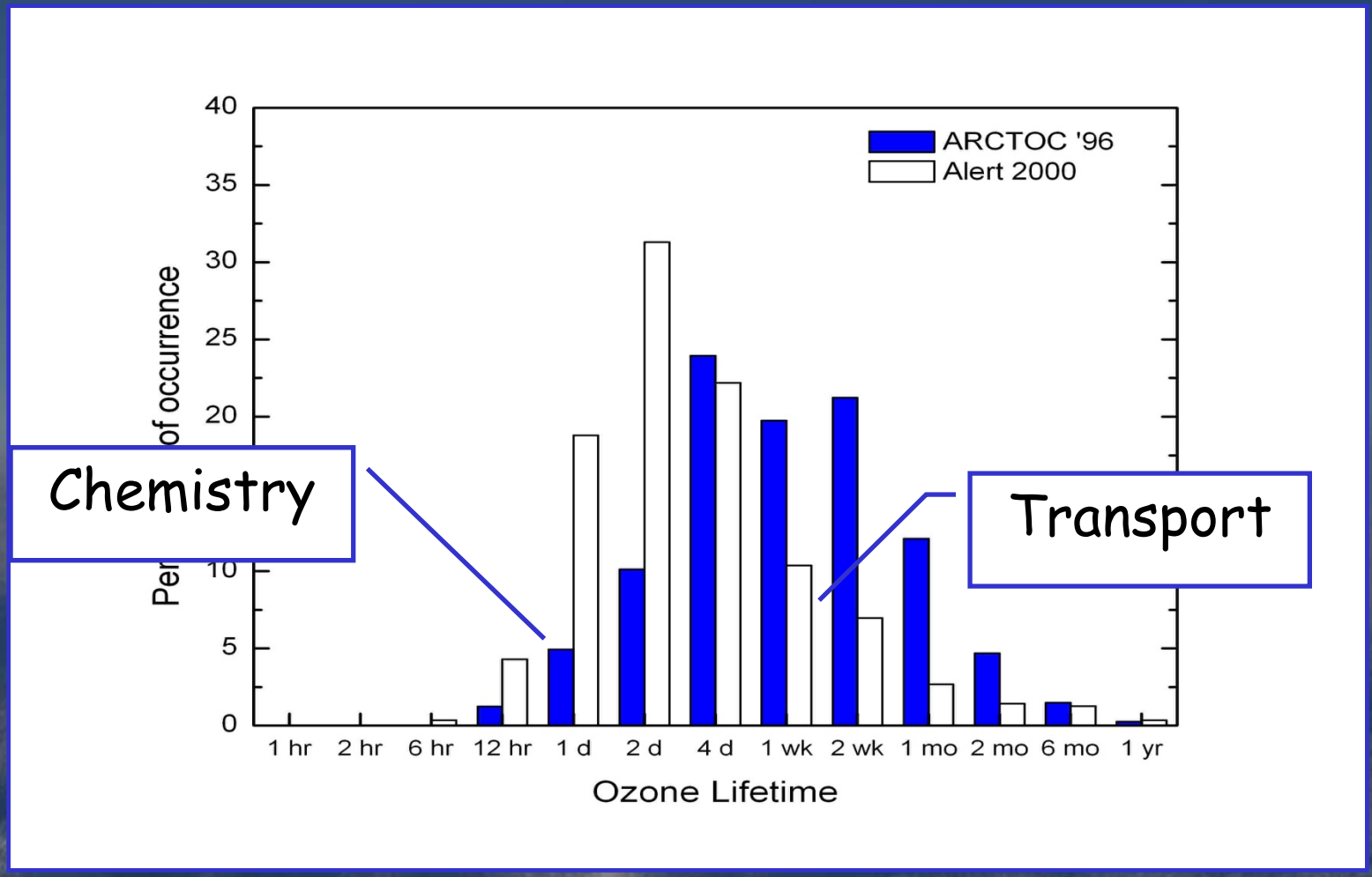
ClO + BrO

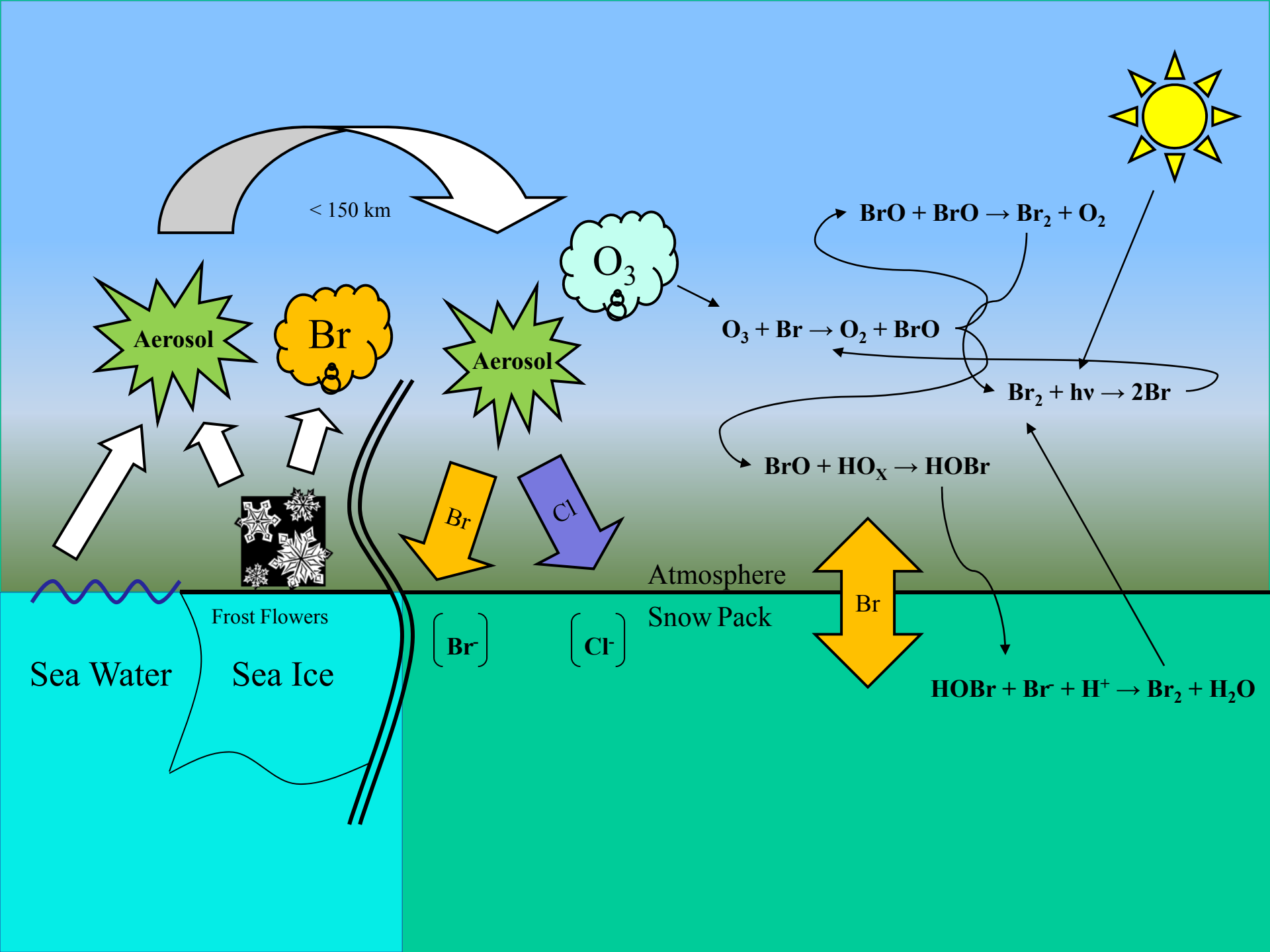
Ozone Lifetime

Ozone Lifetime



Ozone Lifetime

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Atmosphere
Snow Pack
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What about the Antarctic?

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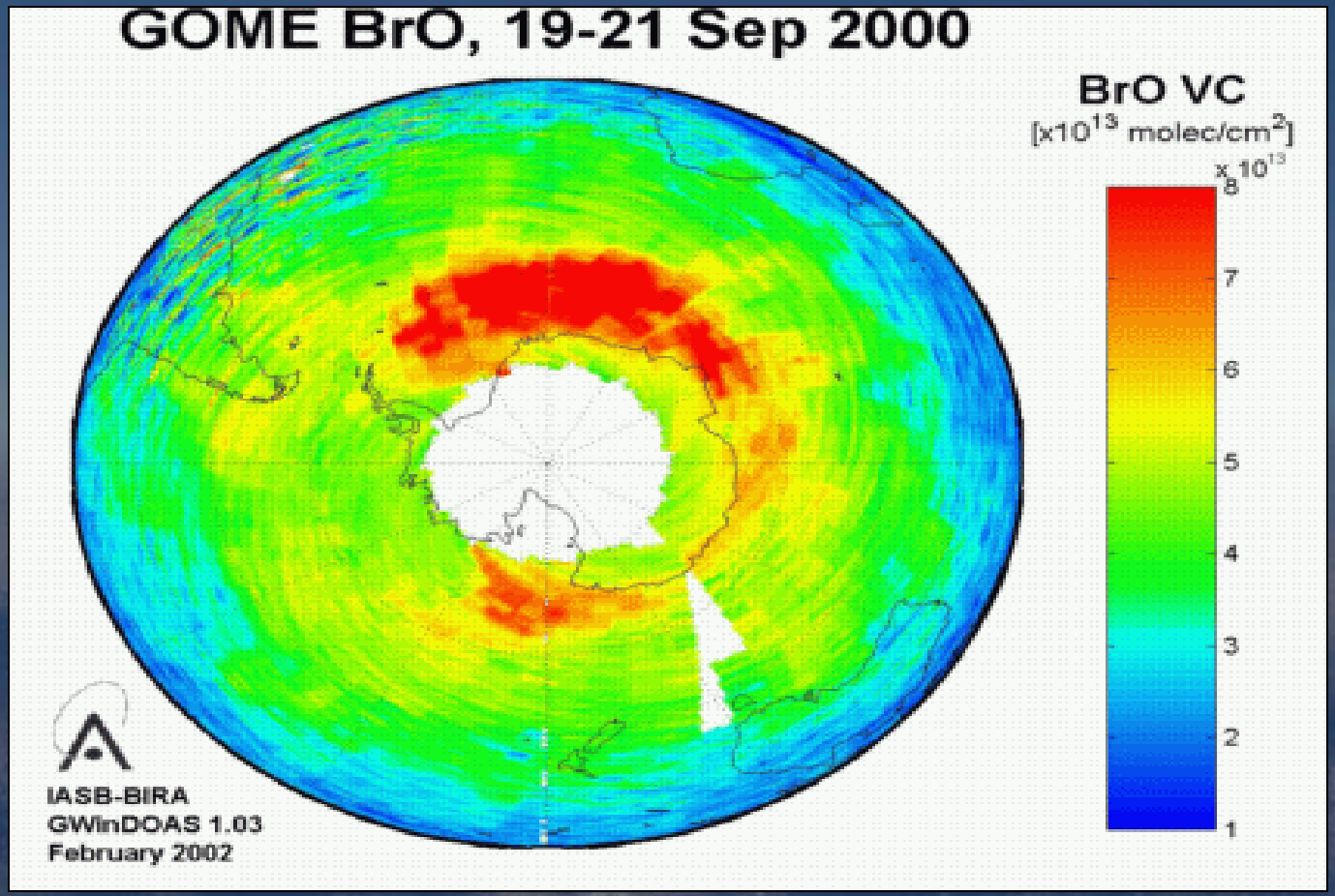
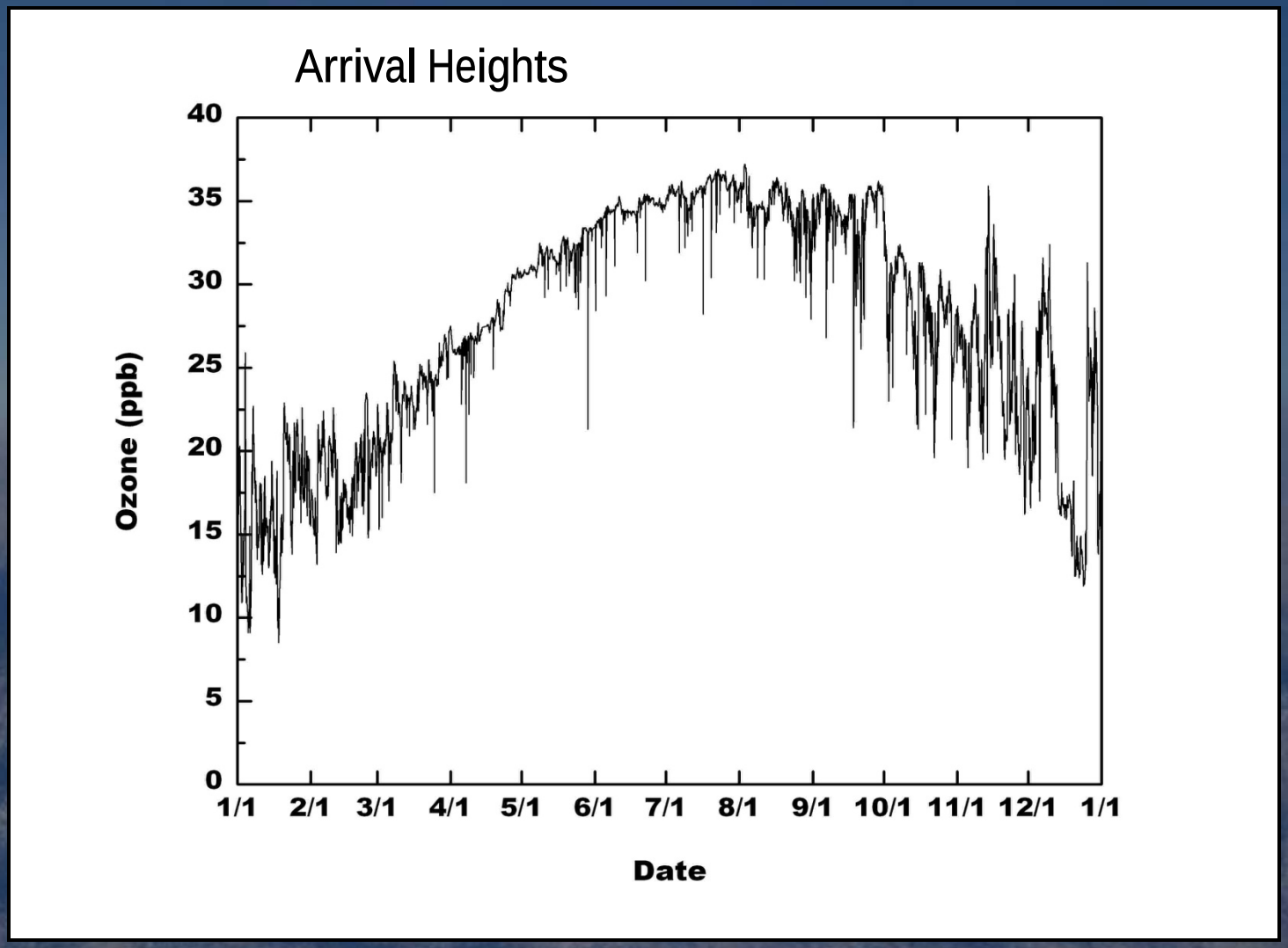


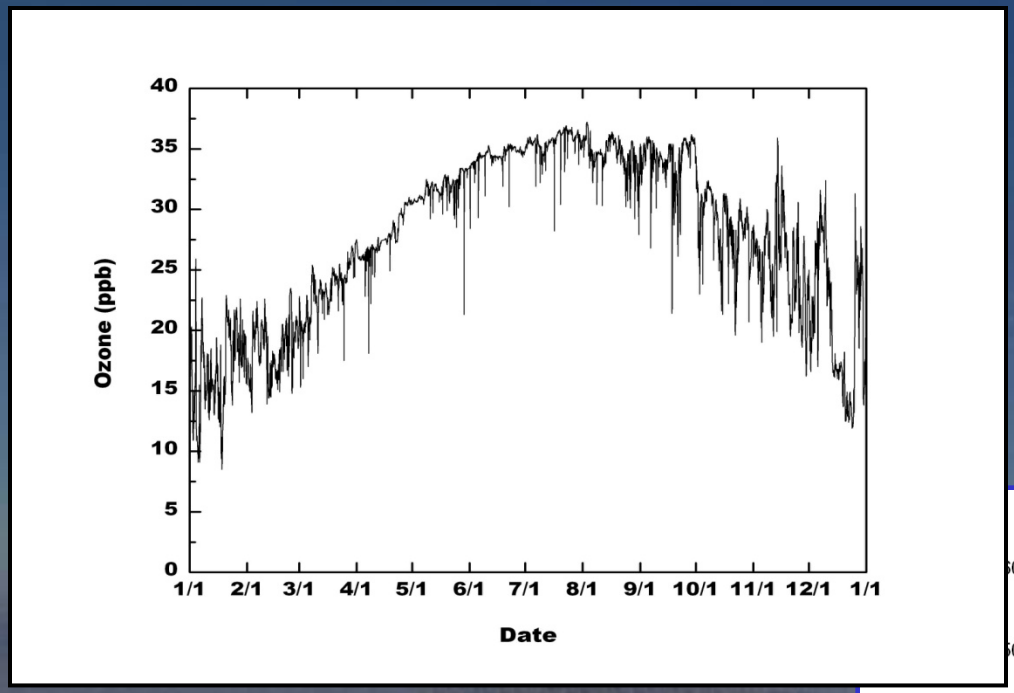
Questions about Antarctic boundary layer ozone

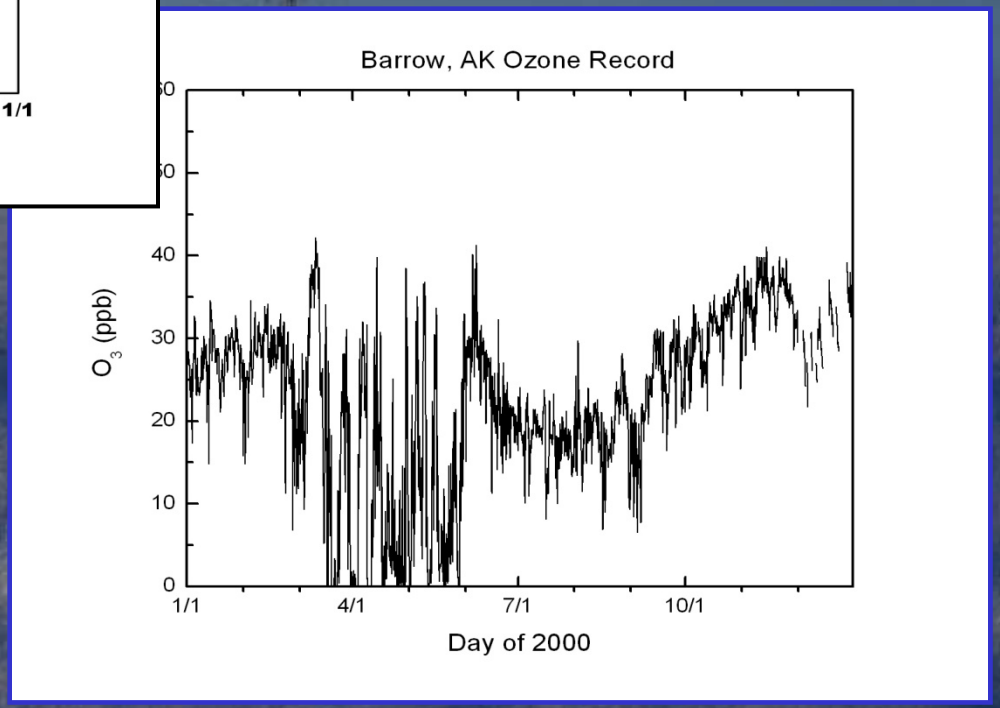
- Does surface ozone loss happen in the Antarctic?
- If so, can we explain it? Is it due to bromine?

Ozone loss in Antarctica?



Ozone loss in Antarctica? Yes, but…



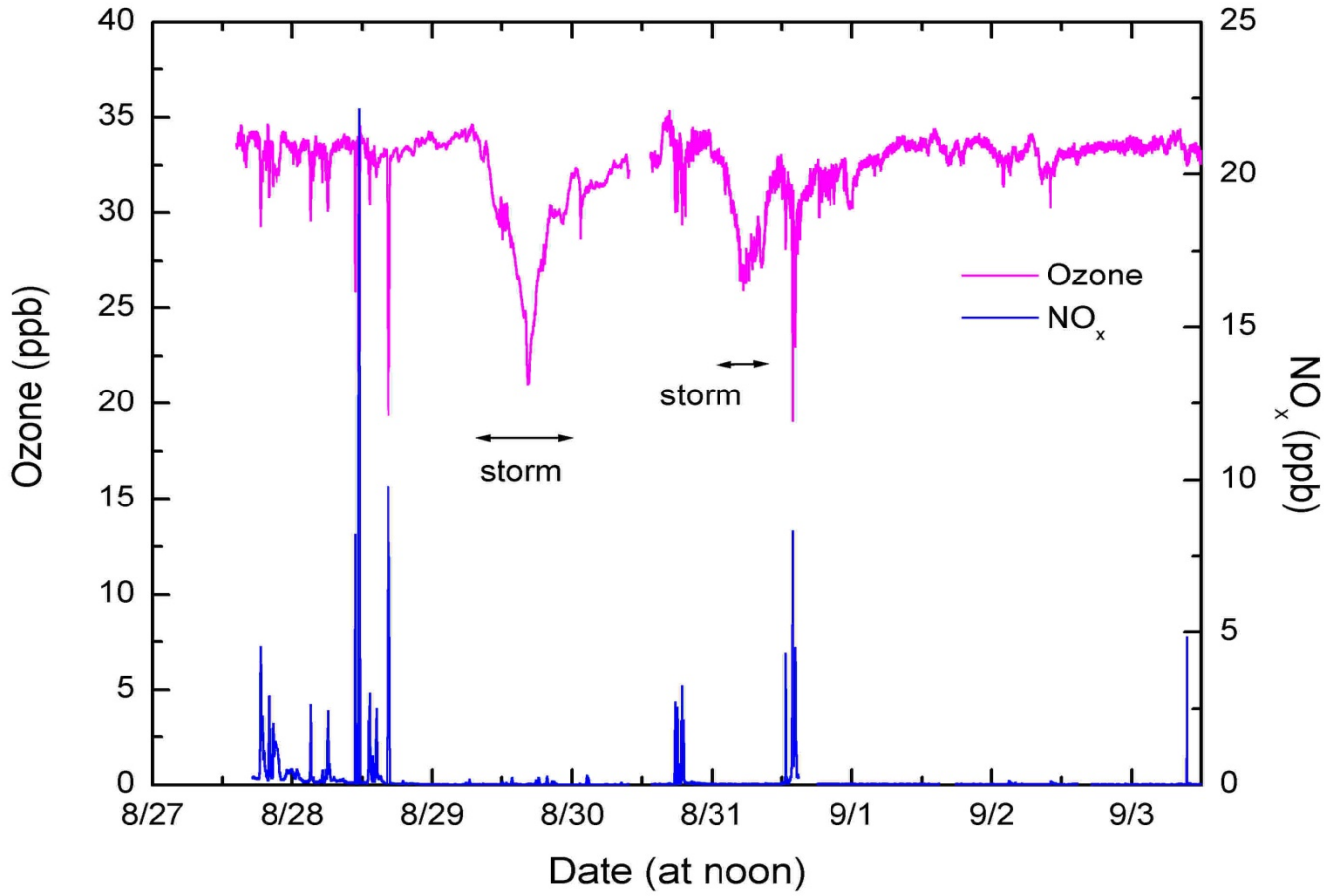


Not as deep or dramatic at McMurdo as in the Arctic

Measurements at Arrival Heights

Winfly 2002

First Results



Is there BrO at McMurdo?

Yes, but…

- There's something else present - not the form we expected

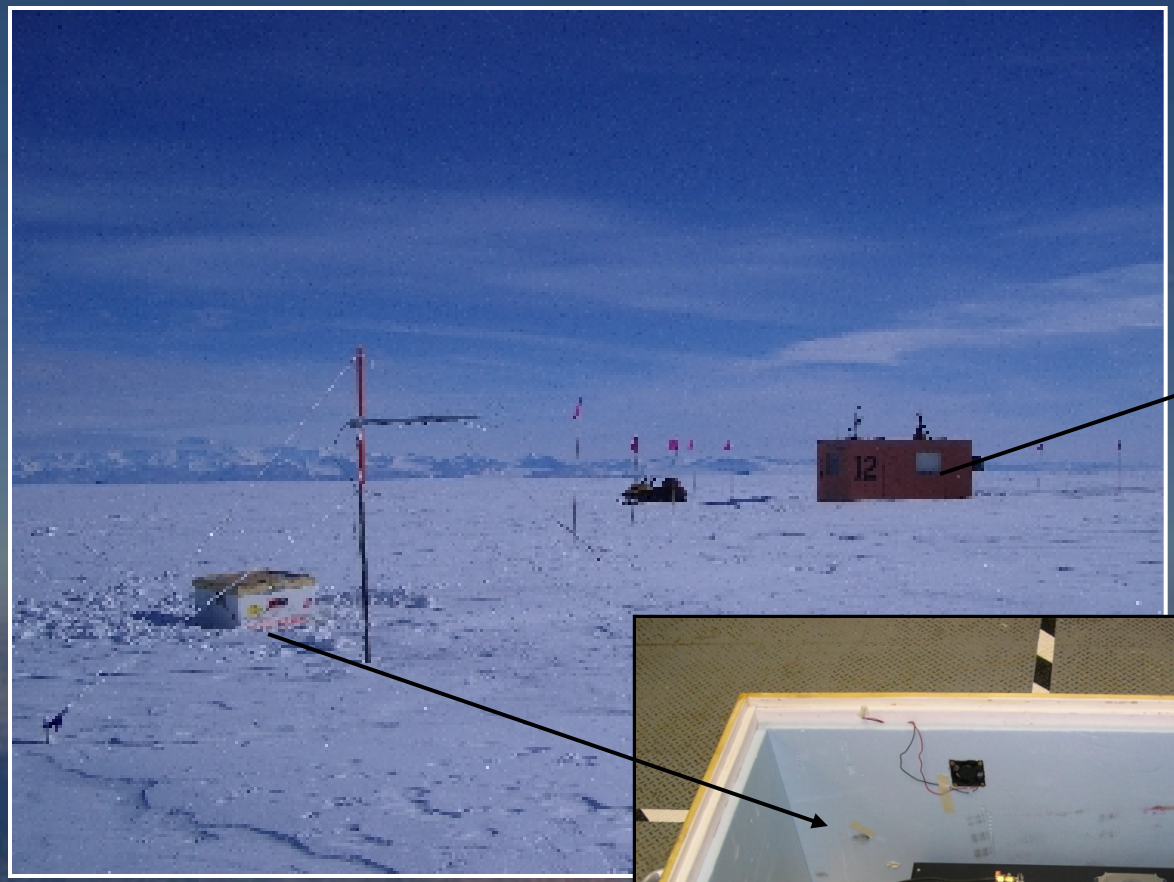
- Continuing data analysis and lab work

So for 2004 season….

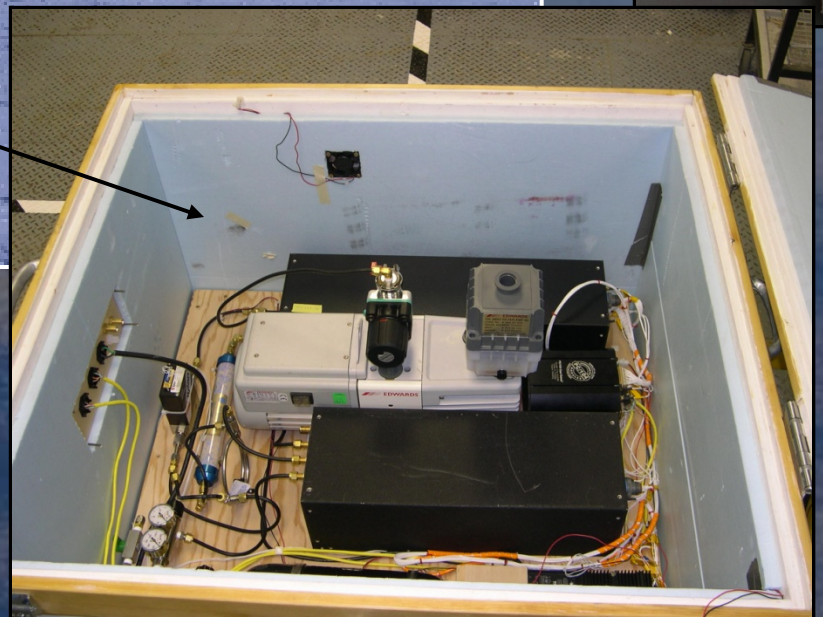
2004 Field Season Goals

- "Clean Air" site – near Pegasus runway
- Continue to monitor "pollution tracers"
- Measure ozone fluxes from/to snow surface
- Sample snow for chemical content

Field Site - Fish Hut #12

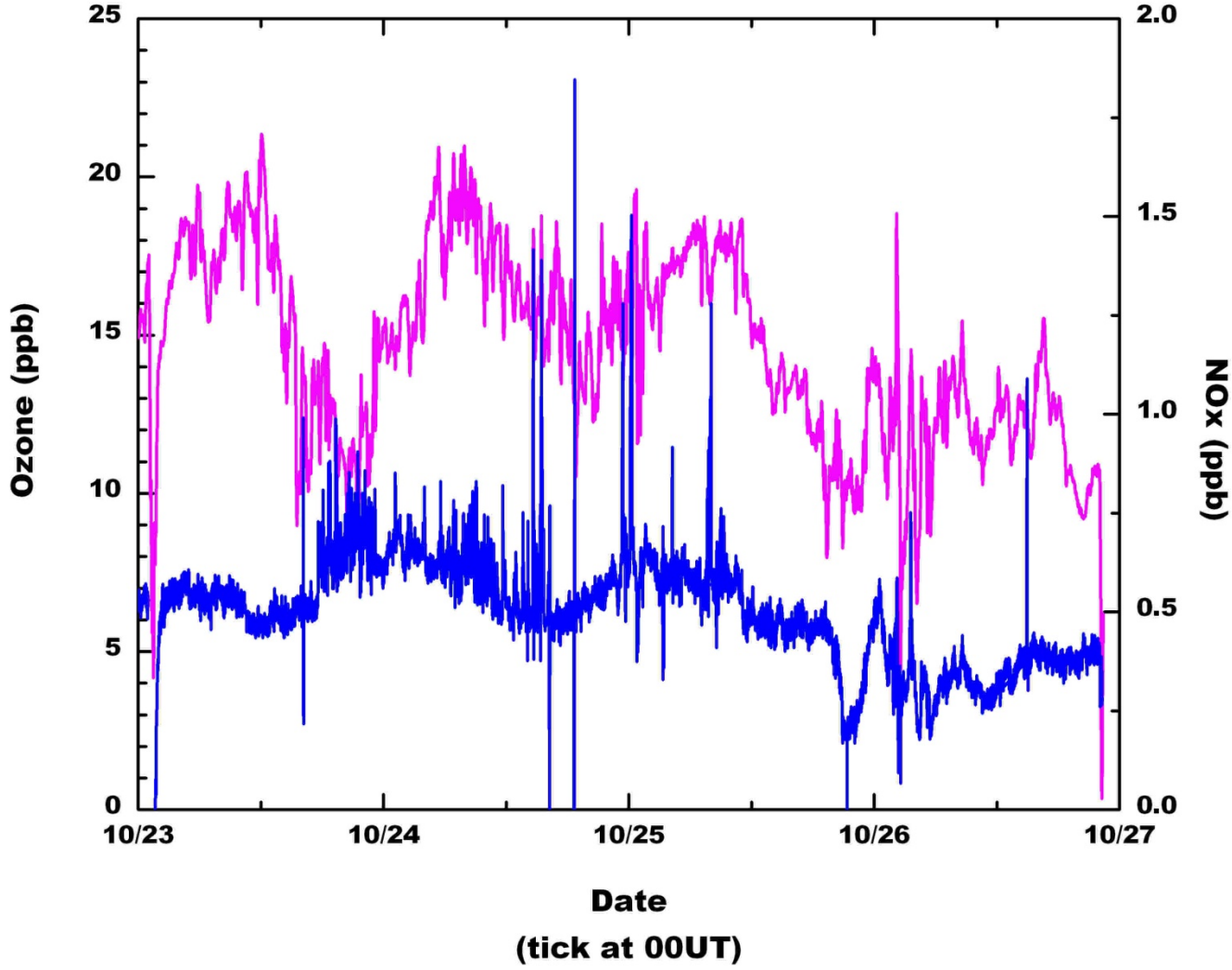


monitoring

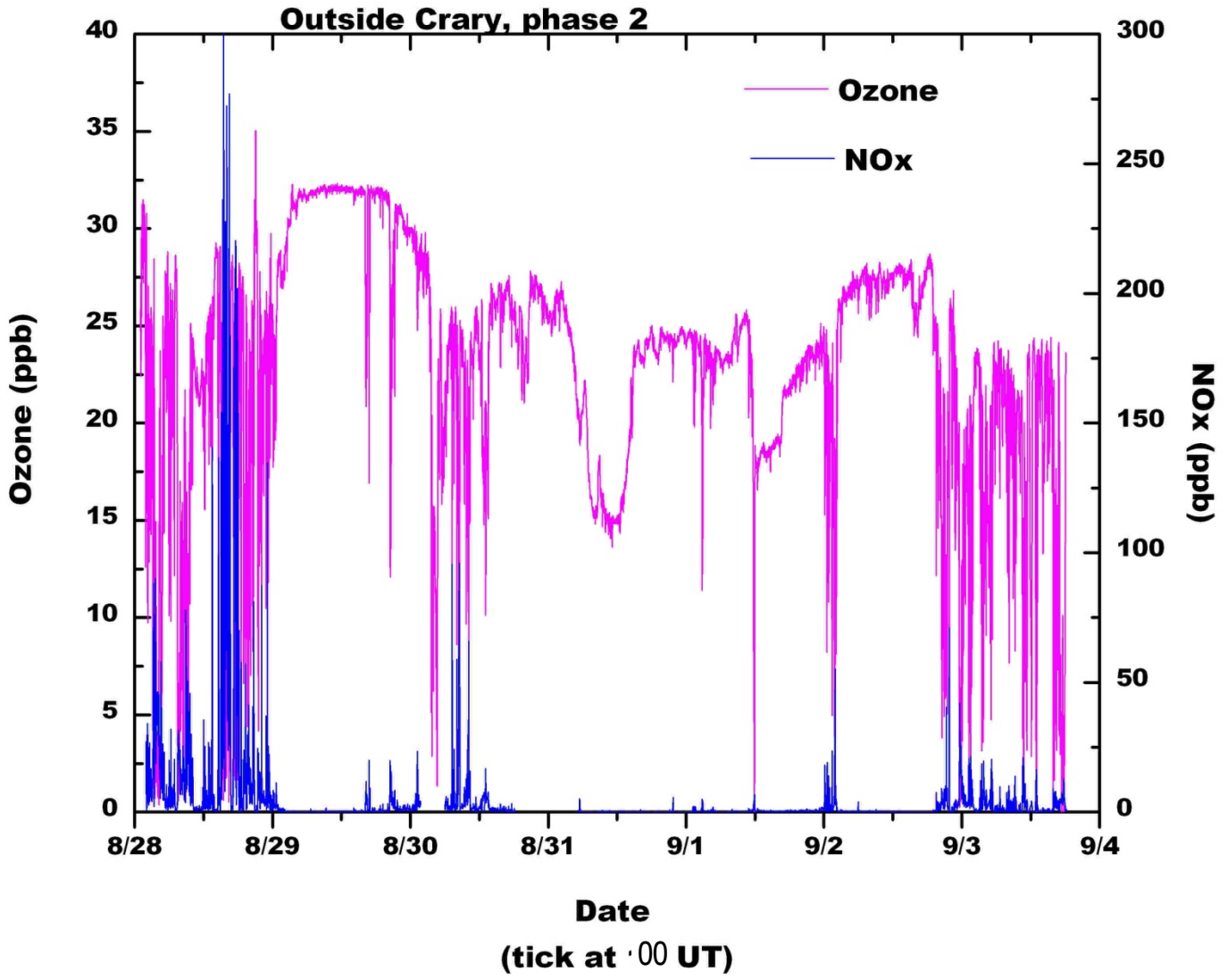


fluxes

Ozone Behavior

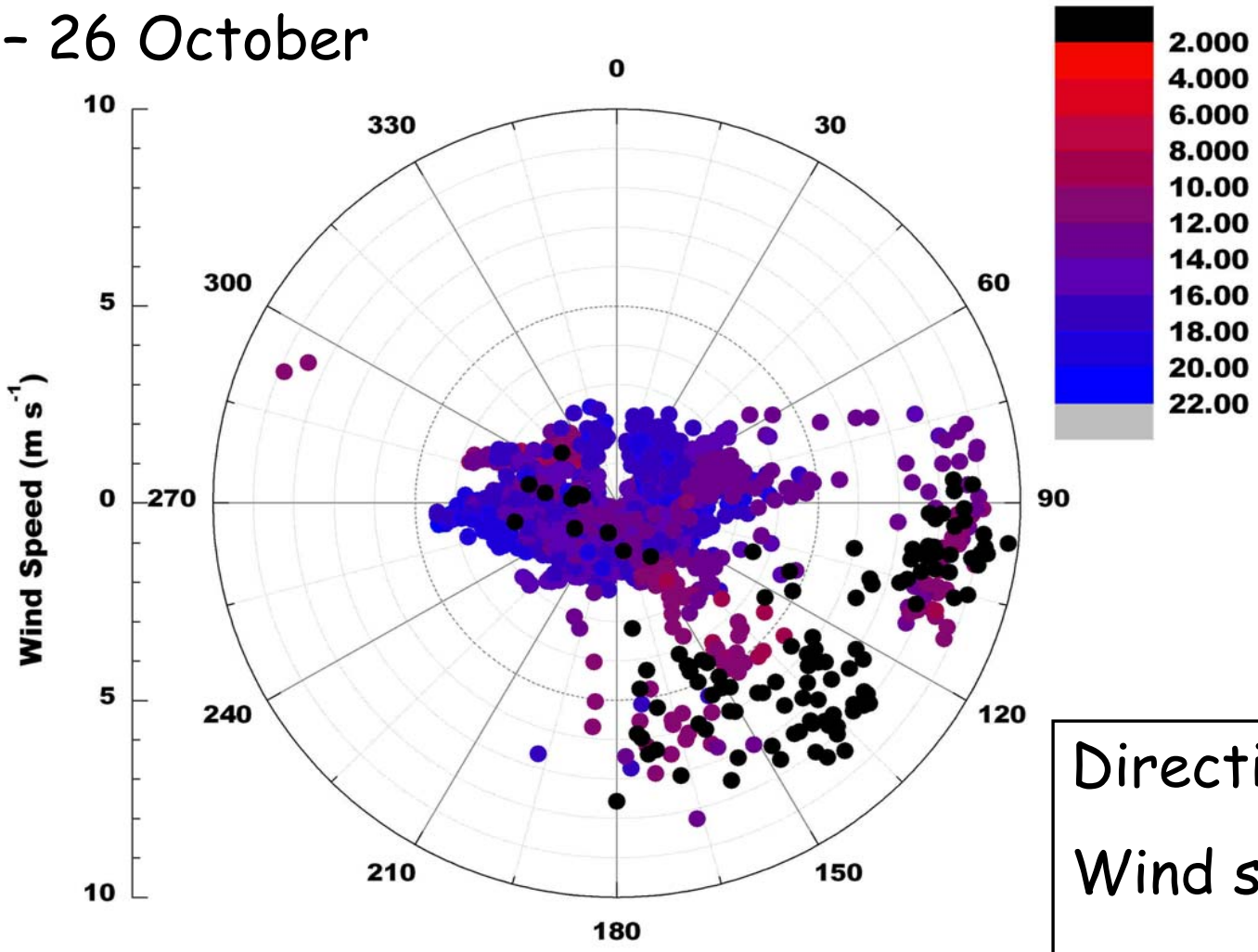


Ozone in town – for contrast



Ozone Behavior

23 – 26 October



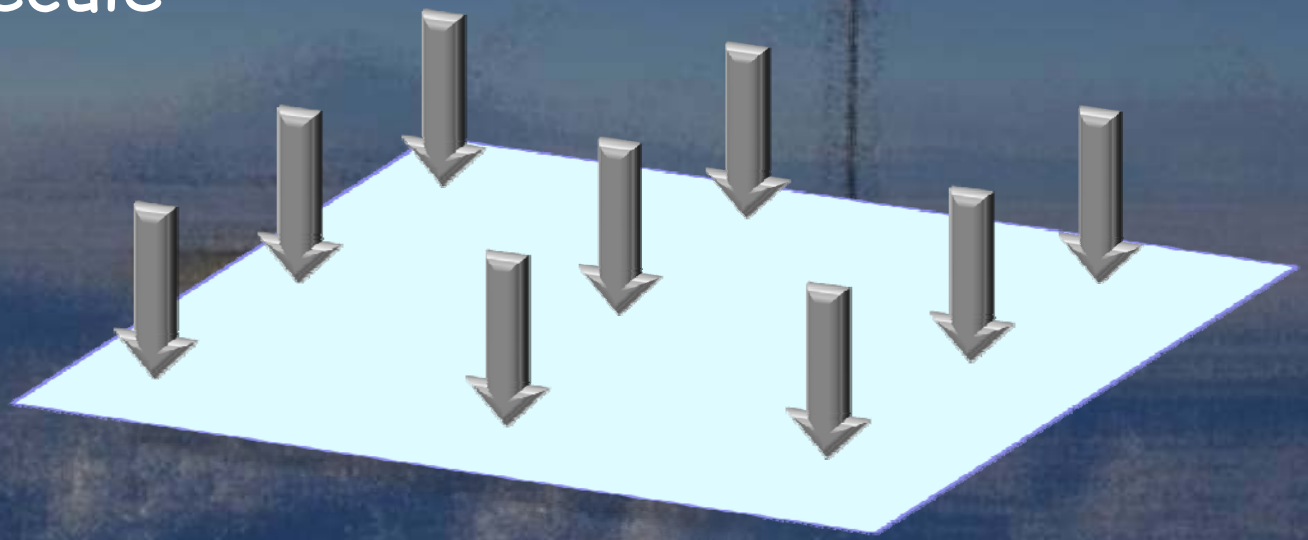
Direction?

Wind speed?

Blowing snow?

Ozone Surface Flux

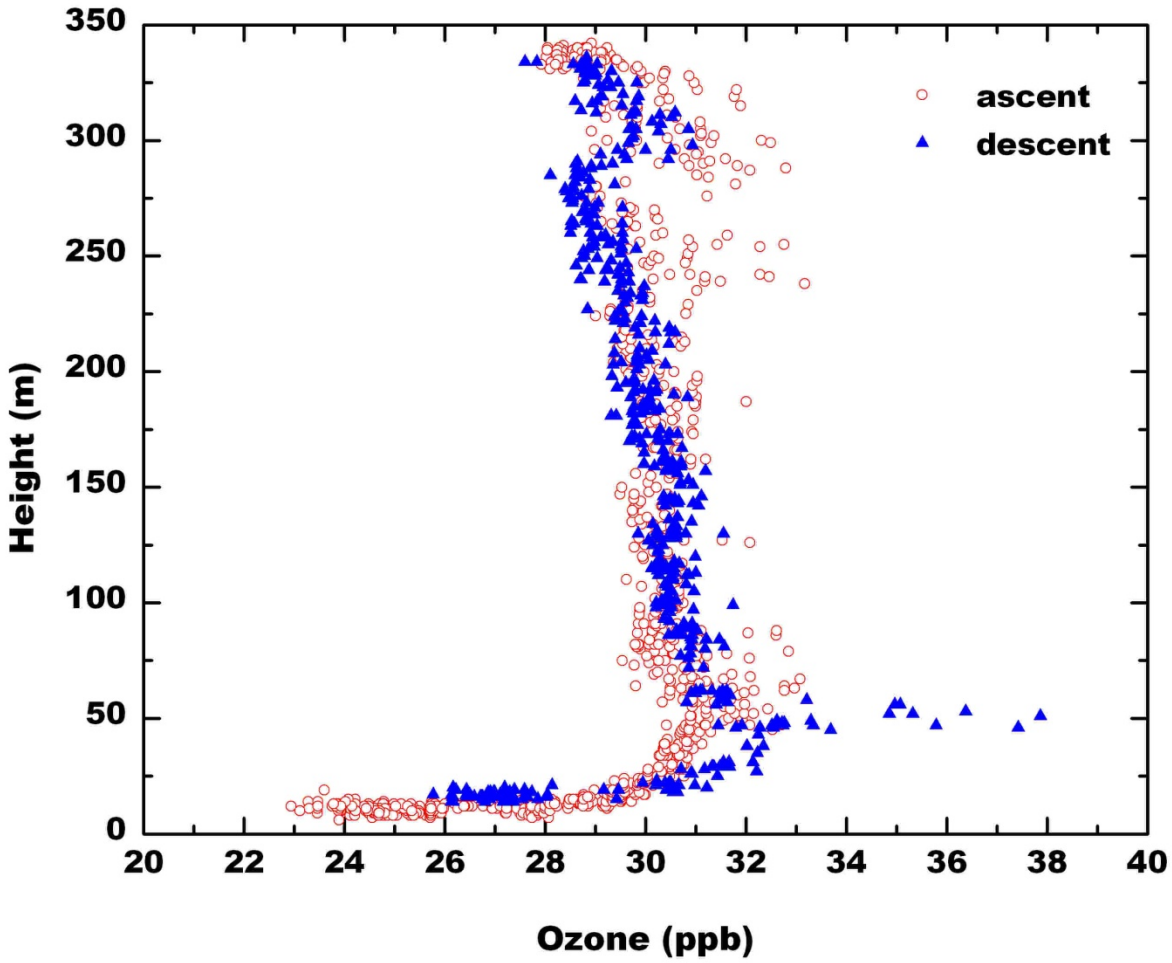
- Definition: Number of molecules per second crossing a surface parallel to the ground.
- Expressed as a deposition velocity – average vertical velocity of an ozone molecule



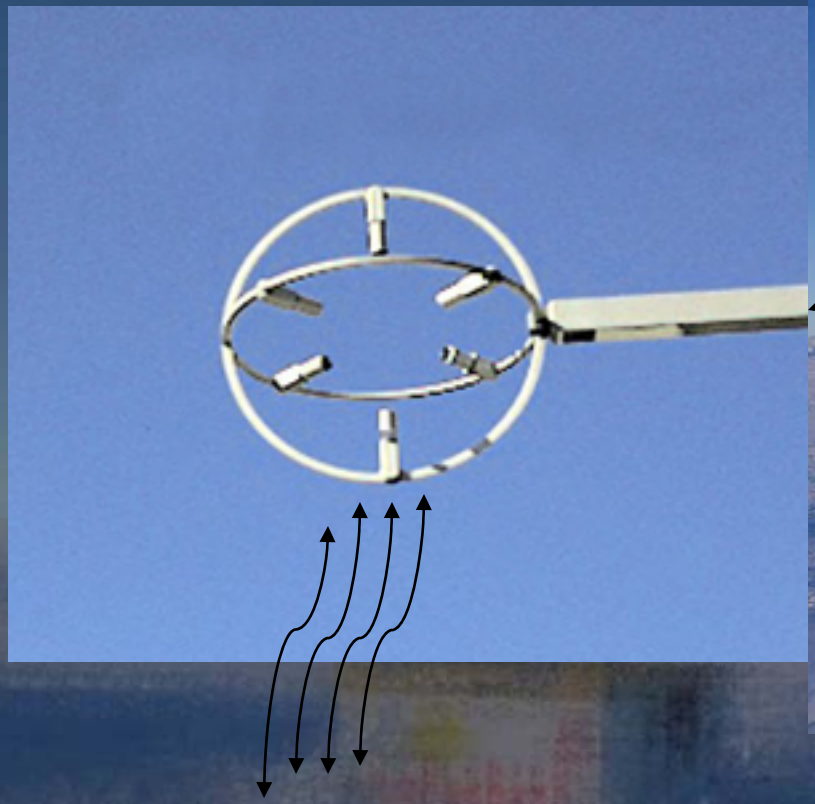
Vertical Profiles of Ozone

- Can we learn about the chemistry of ozone from its vertical profile?
- Ran a tethered balloon using a Univ. Wyoming ozonesonde

Vertical Profile of Ozone

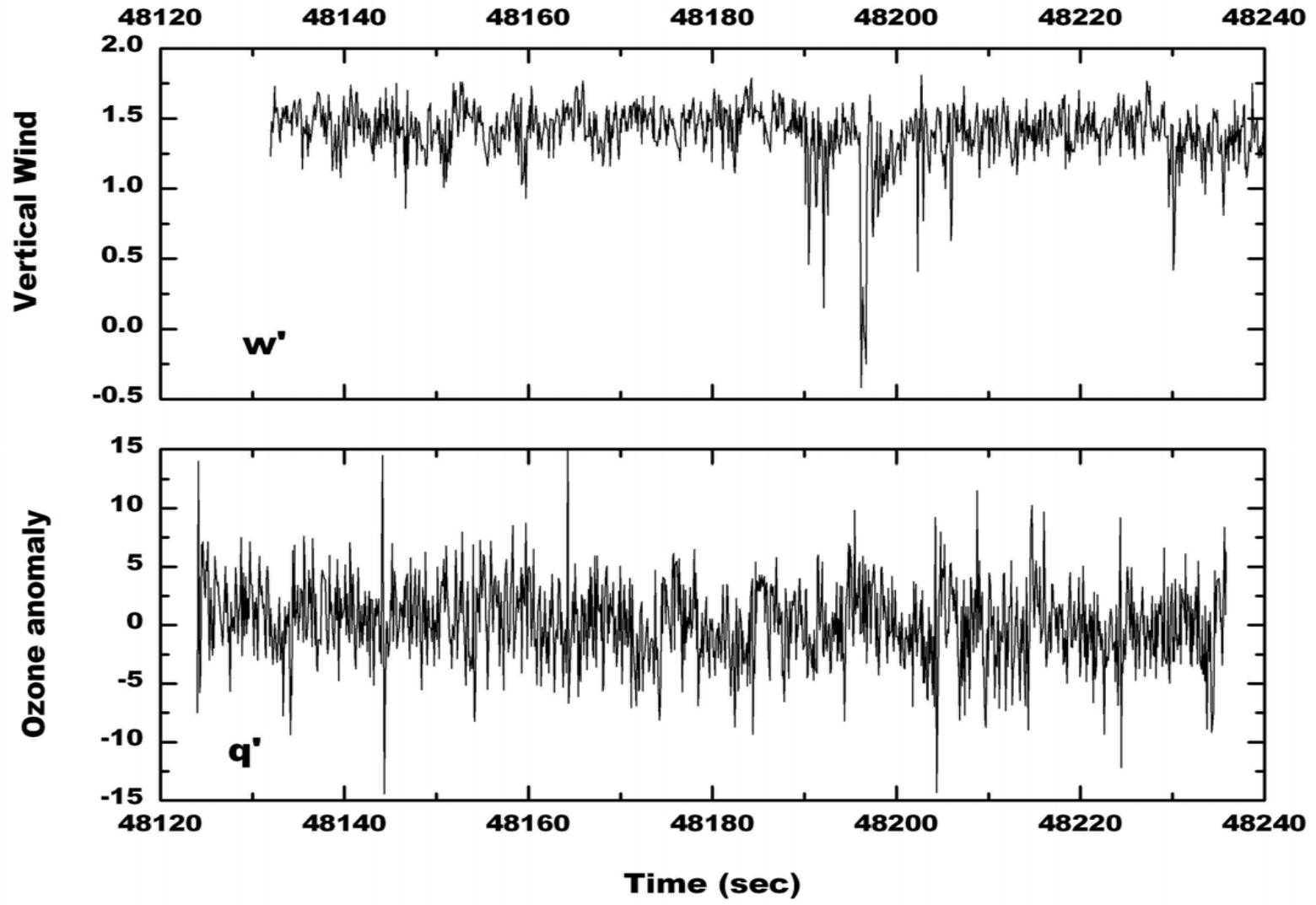


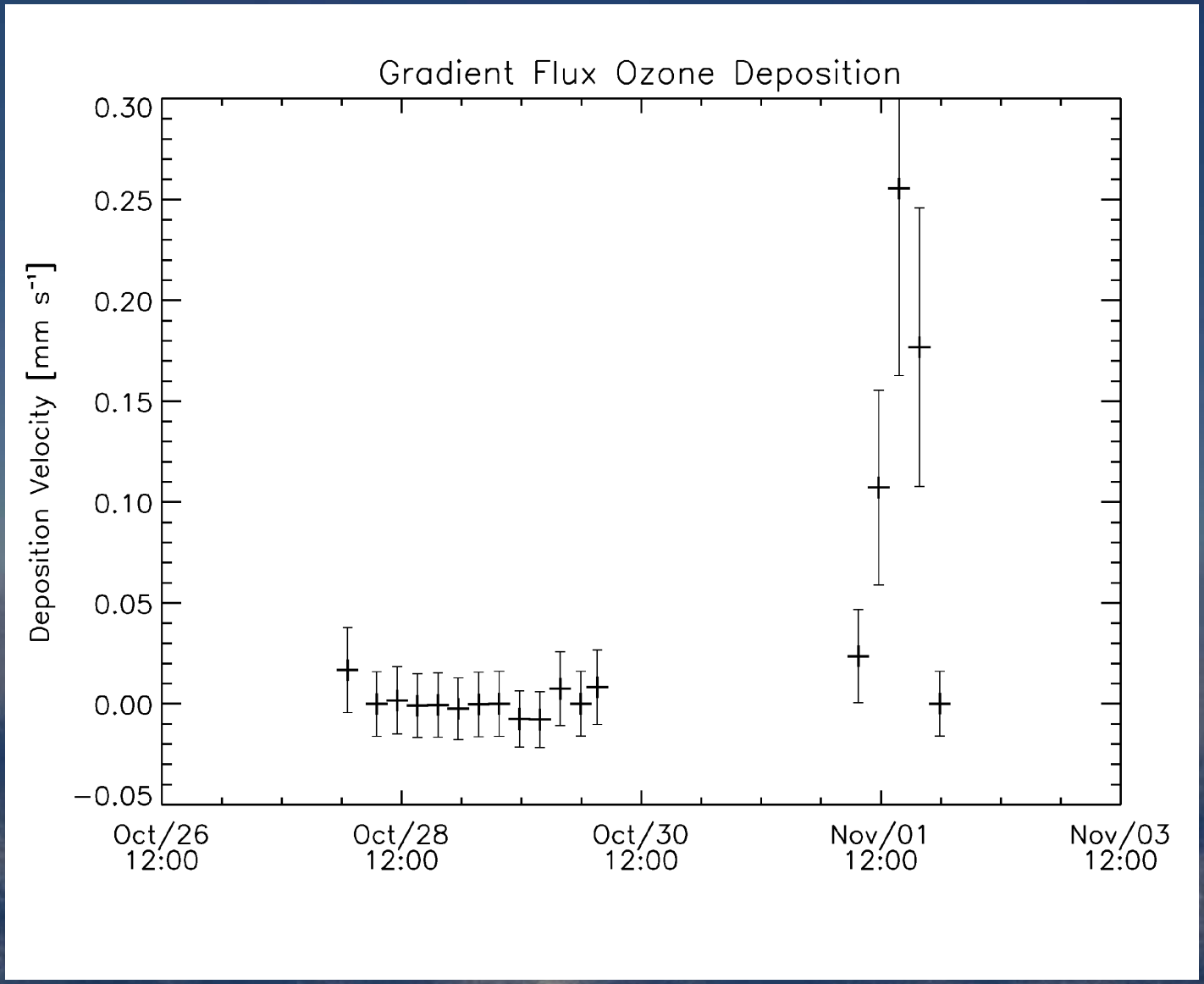
Flux Measurements

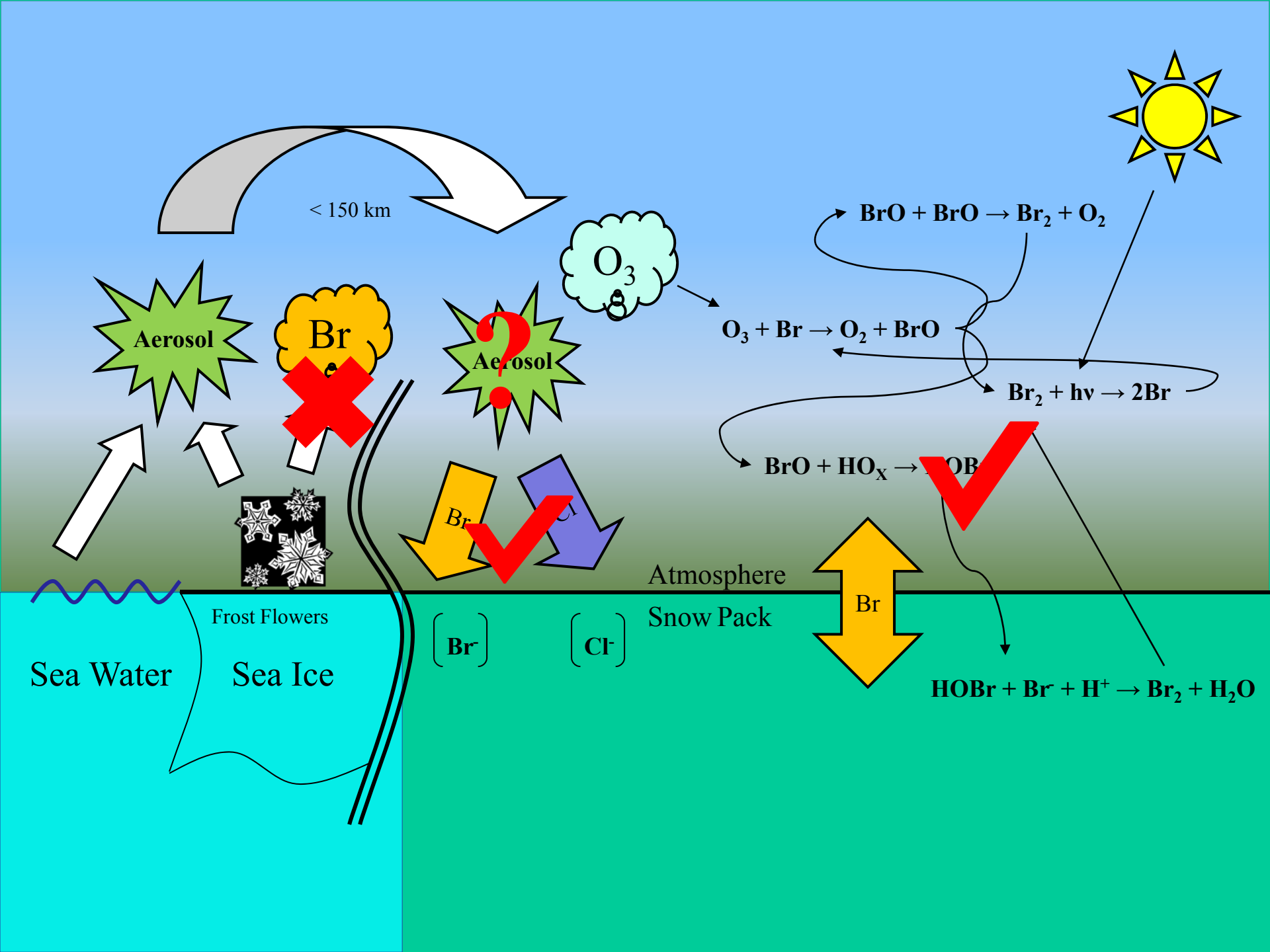


10 Hz (0.1 sec) measurements of ozone and CO_2

Flux Measurements




Gradient Flux Ozone Deposition
Deposition Velocity [mm s-1]
0.30
0.25
0.20
0.15
0.10
0.05
0.00
−0.05
Oct/26 12:00
Oct/28 12:00
Oct/30 12:00
Nov/01 12:00
Nov/03 12:00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Br
Cl
Atmosphere
Snow Pack
Br
Frost Flowers
Br^-
Cl^-
Sea Water
Sea Ice
$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$

Outstanding Issues

- What is the real source of bromine to the atmosphere? Is direct BrO release from the snowpack important?
- What is the role of aerosols in ODEs?
- Are inter-halogen reactions important (Iodine?)
- Do these ODEs occur by the same mechanism in the Arctic and Antarctic?