1D multiphase modeling of NO_x and halogen photochemistry at Summit, Greenland

Jennie L. Thomas[1,2]

Jochen Stutz (UCLA), Roland von Glasow (UEA), Jack Dibb (UNH), Barry Lefer (UH), Greg Huey (GaTech), Steve Brooks (NOAA) and the GSHOx team

[1]LATMOS, CNRS, UVSQ, UPMC (Paris, France)

and

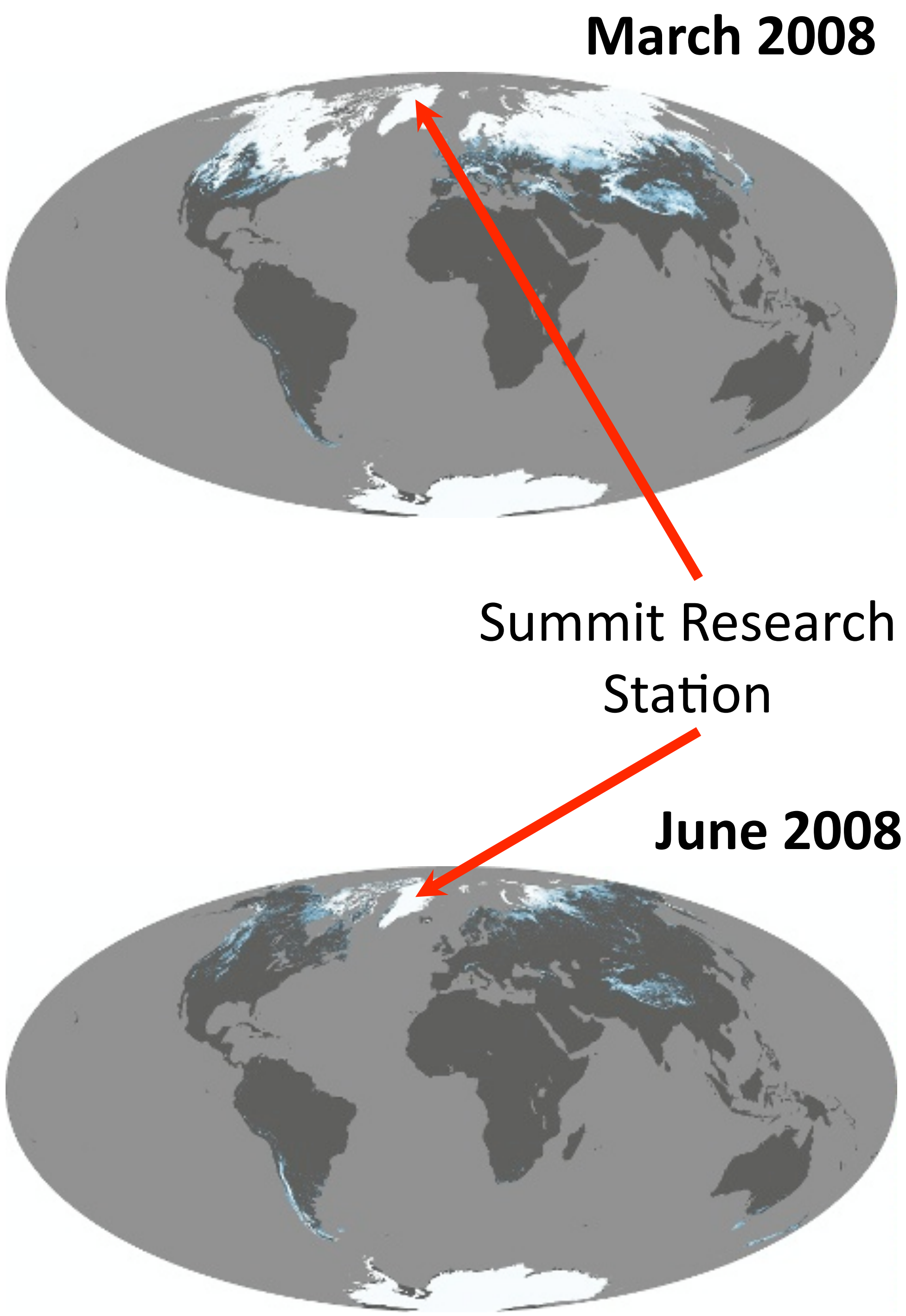
[2]UCLA Department of Atmospheric & Oceanic Sciences

Air-Ice Chemical Interactions Workshop

June 6, 2011

Why study air and snow photochemistry in remote regions?

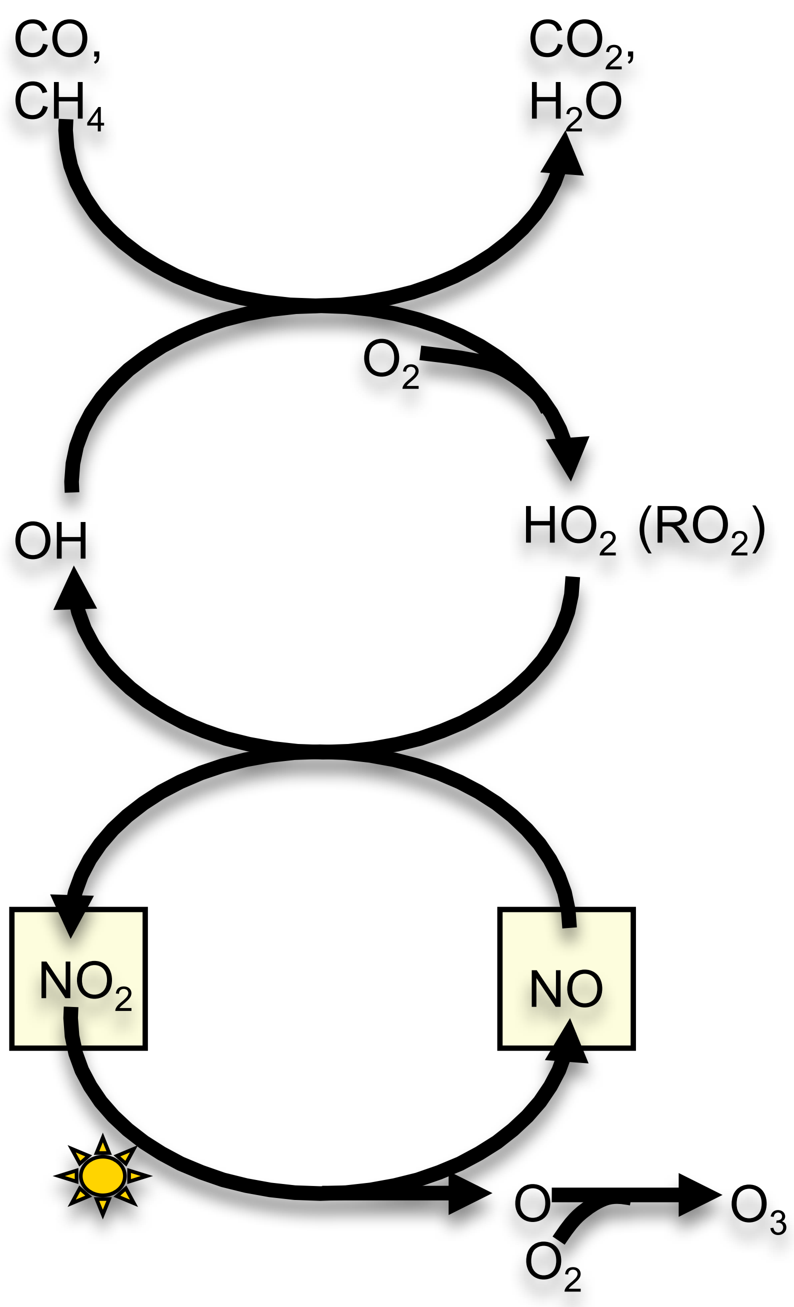
- Recent work shows that photochemistry in and above snow can play an important role in Arctic and Antarctic atmospheric chemistry
    - **Ozone** destruction in the Arctic MBL and in interstitial air
    - **NO_x** emission from snow
    - **Hg** deposition
    - Variation in **oxidative capacity, i.e.** OH/HO_2 levels
- **Questions:**
    - Does snowpack chemistry impact oxidative capacity, ozone, Hg, methane and HC lifetimes, etc.?
    - What role do snow surfaces play? Are all snow surfaces photochemically active?
    - Does snow photochemistry impact atmospheric composition on larger scales?



Snow cover from NASA Earth Observations (NEO) using data from the MODIS sensor on NASA's Terra satellite

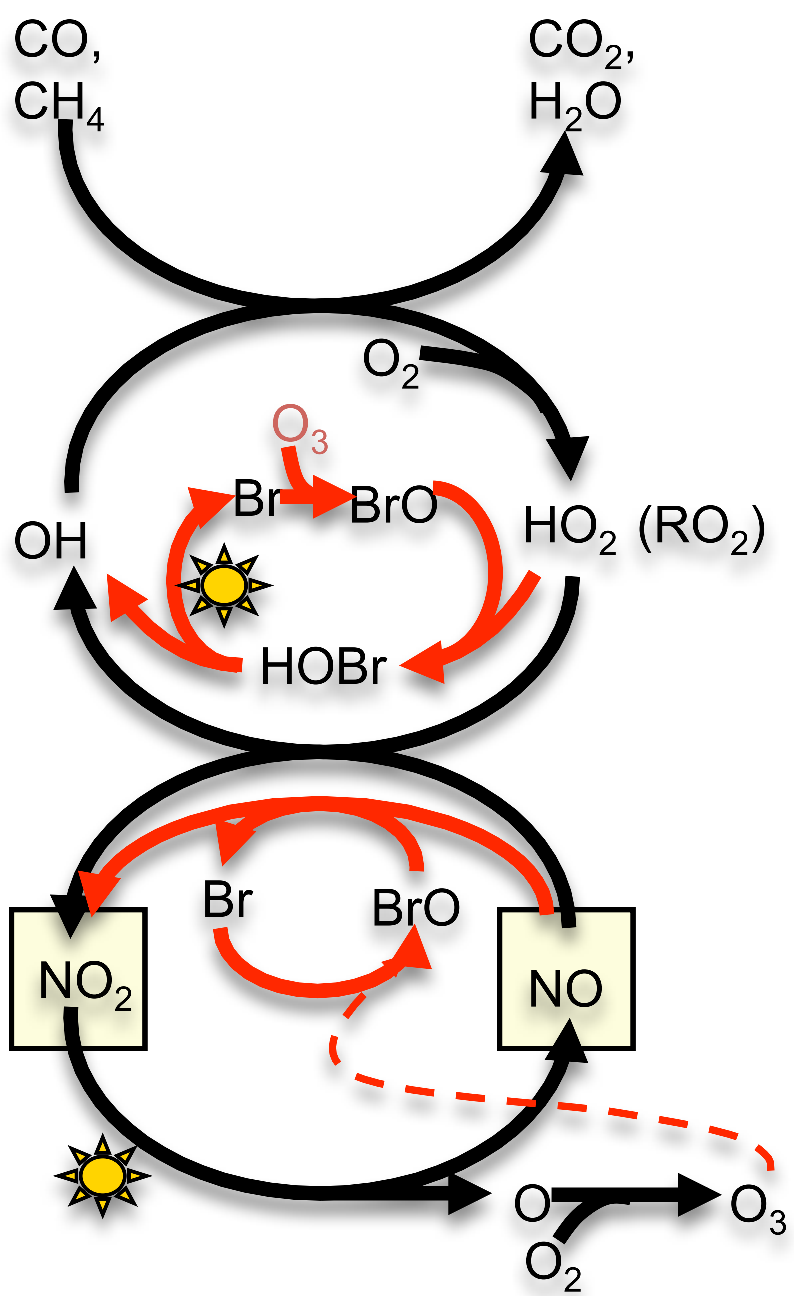
NO_x photochemistry over snow covered regions

- **Nitrate photolysis in snow is a source of atmospheric NO_x**
- NO_x plays a central role in atmospheric radical chemistry
- NO_x levels determine OH and O_3 concentrations, and thus the oxidative capacity of the atmosphere
- NO_x release from the snow pack could impact our understanding of the ice core record
- NO_x is closely coupled to other chemical cycles, i.e. halogen



Potential impact of a bromine source on the oxidation capacity of the atmosphere

- Reactive bromine impacts the most elemental atmospheric radical cycles
- Annually averaged 0.3 – 3 ppt BrO in the Arctic free troposphere (von Glasow et al., 2004) leads to:
  - ~10% reduction of free tropospheric O_3
  - 10-40% increase of the OH/HO_2 ratio and thus a change in methane lifetime
  - possible change in the Hg and DMS lifetime
- There is currently an incomplete understanding of atmospheric bromine sources



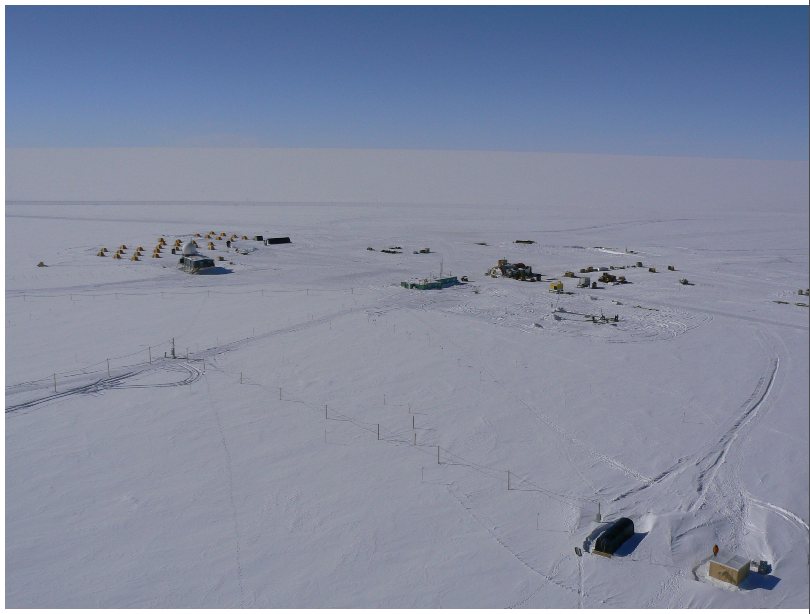
NOx and bromine chemistry above snow have been investigated using field data from June 2008 and a 1D coupled snow atmosphere model

Greenland Summit Halogen and Hydrogen Radical Experiment (GSHOX)

- **Is there evidence for active bromine chemistry on the Greenland ice sheet?**
- **Does it influence atmospheric oxidative chemistry?**
- **Where does the bromine come from and where does it go?**
- **Can a 1D model more completely describe snow-atmosphere photochemistry?**

Field experiment :

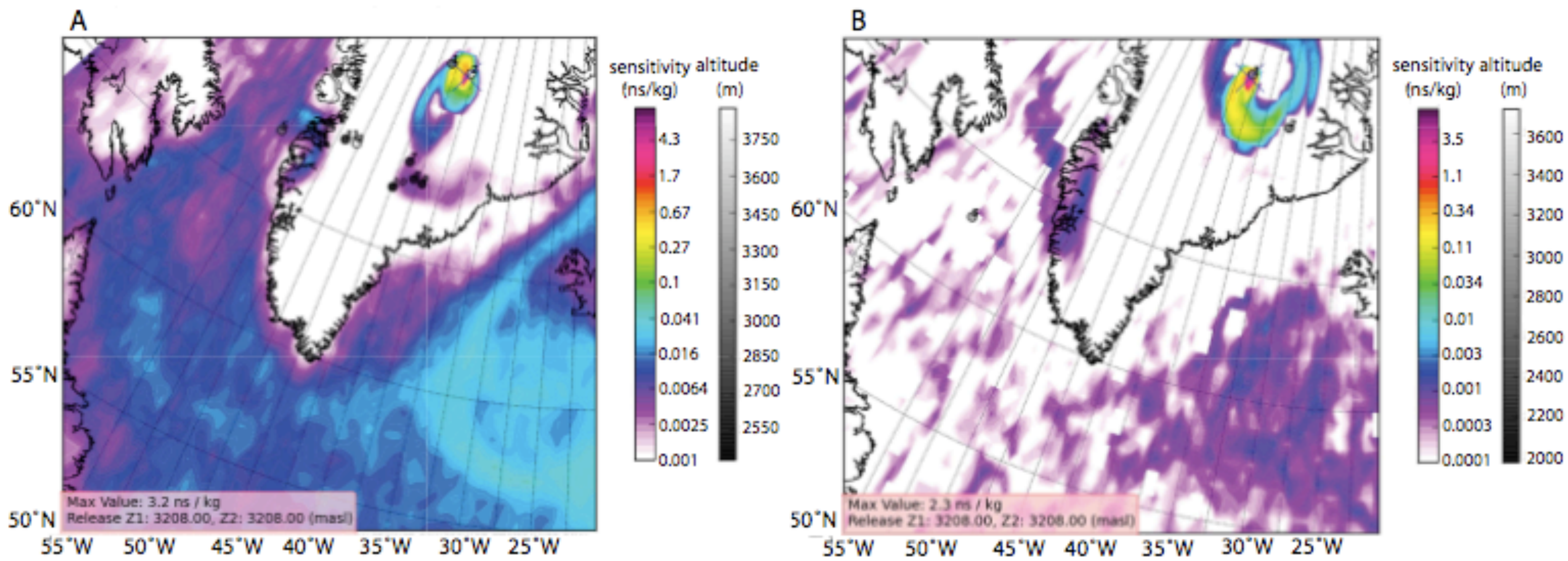
- Spring 2007, Summer 2008 , at GeoSummit
- 6 research groups : UNH, UH, GaTech, UCLA, UCI, NOAA
- Comprehensive suite of measurements:
  - Hg (GEM, RGM, FPM)
  - OH, RO_2
  - NO, O_3
  - BrO
  - H_2SO_4, HCl, HO_2NO_2, SO_2, HCHO
  - Soluble Ions in air, firn, and surface snow (Br^-, Cl^-, etc.)
  - Aerosol size distribution
  - J-values air + firn
  - BL profiles (met)
  - HC, CO



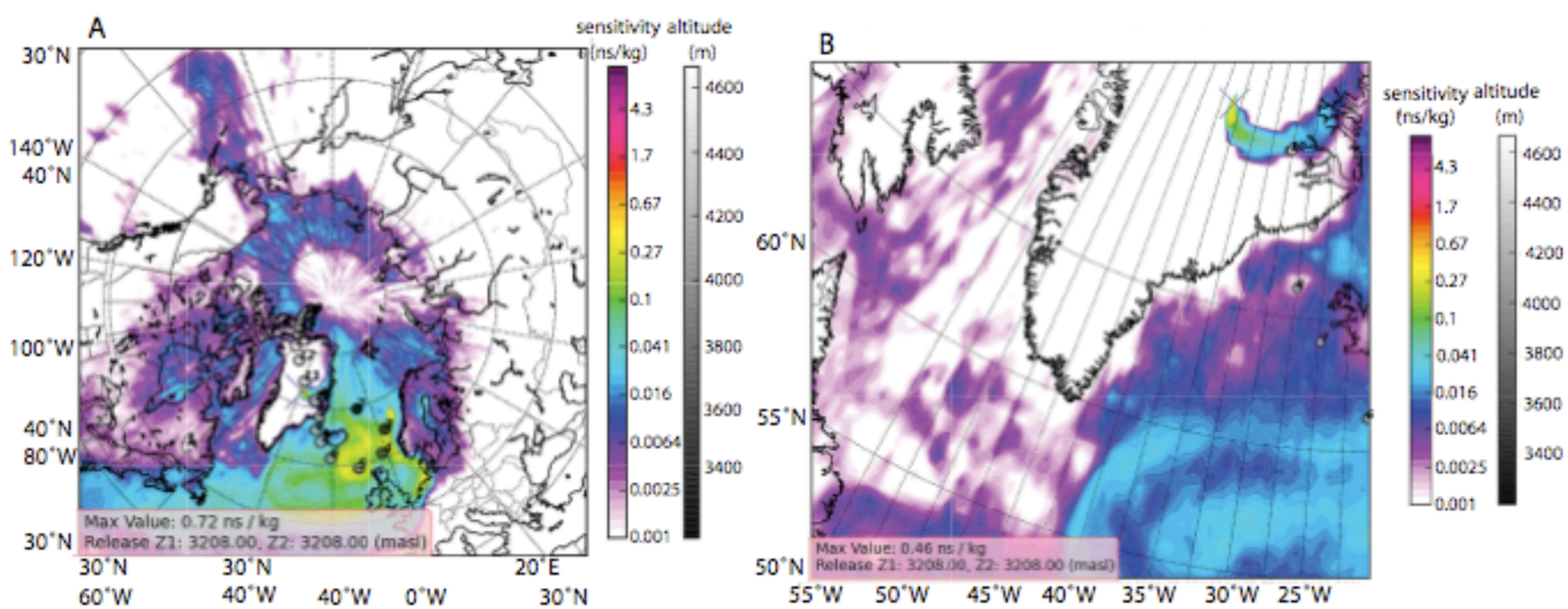
See related poster #34 on measurements during GSHOX!

FLEXPART emission sensitivities indicate there are two types of air masses at Summit, Greenland

Local influenced 10 and 12 June 2008, 00:00–03:00UTC

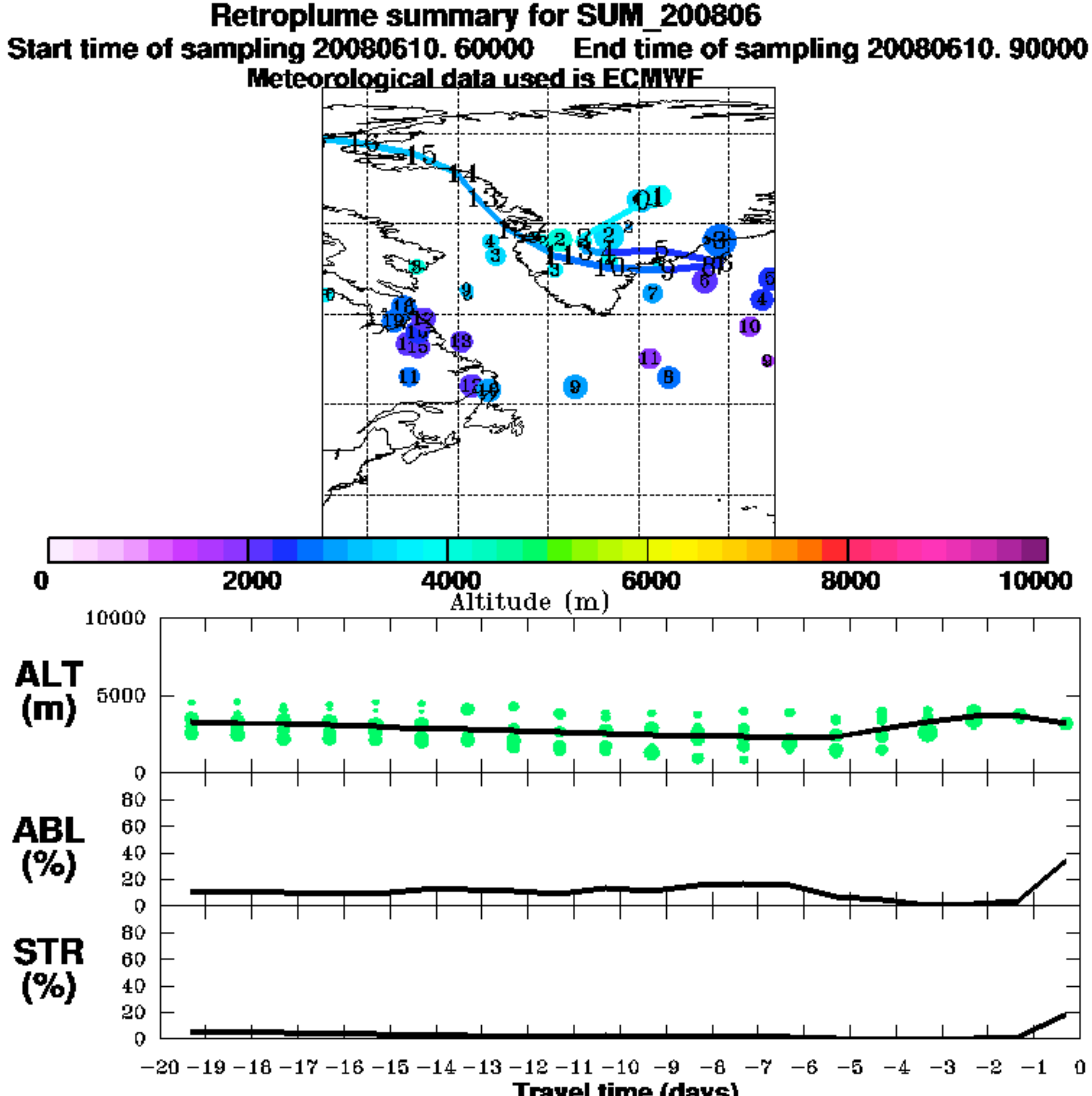


Marine influenced 4 July 2008, 12:00–15:00UTC



Stutz et al., ACPD, 2011.

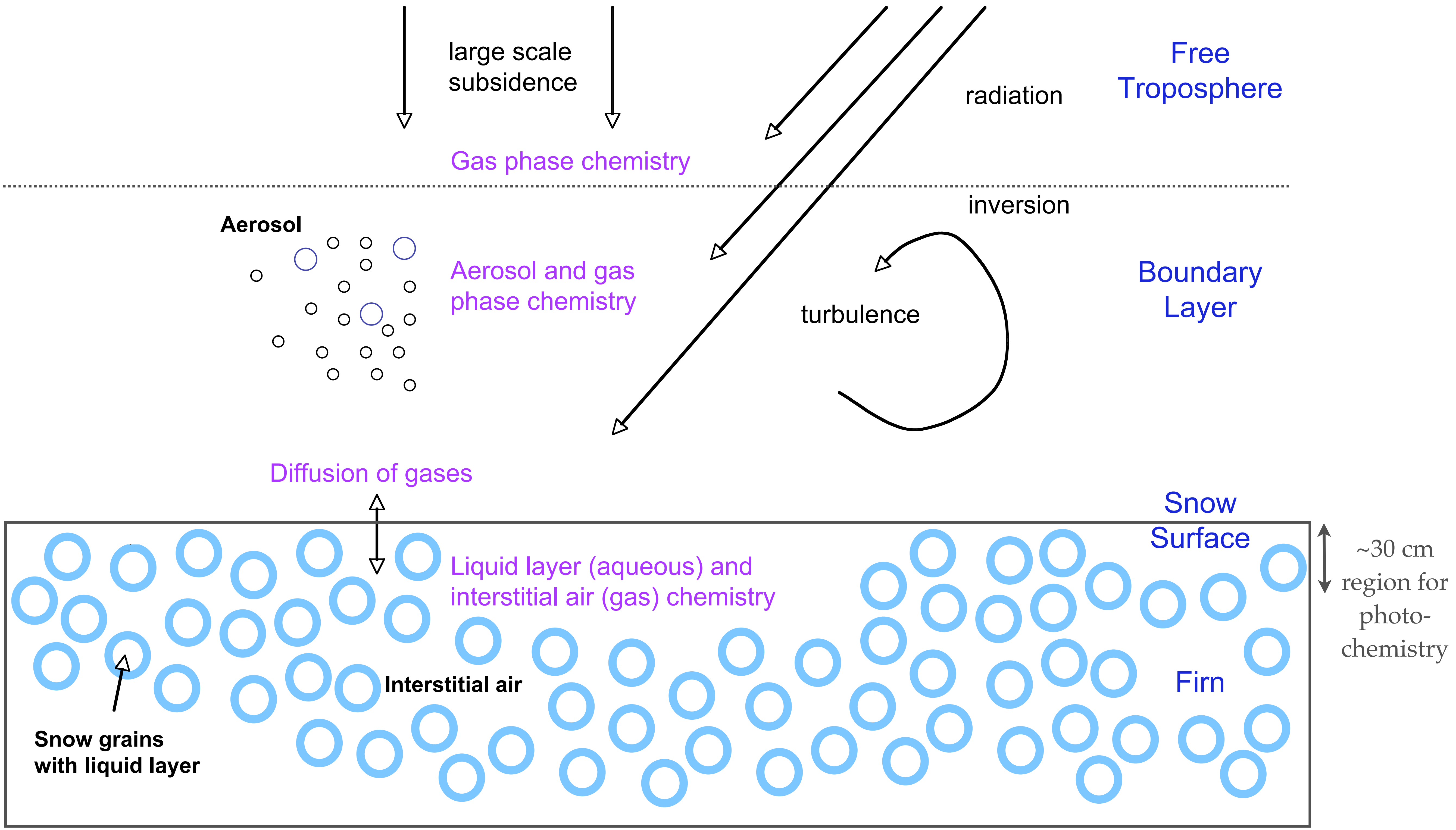
A unique focus period for modeling campaign data: 10-13 June 2008



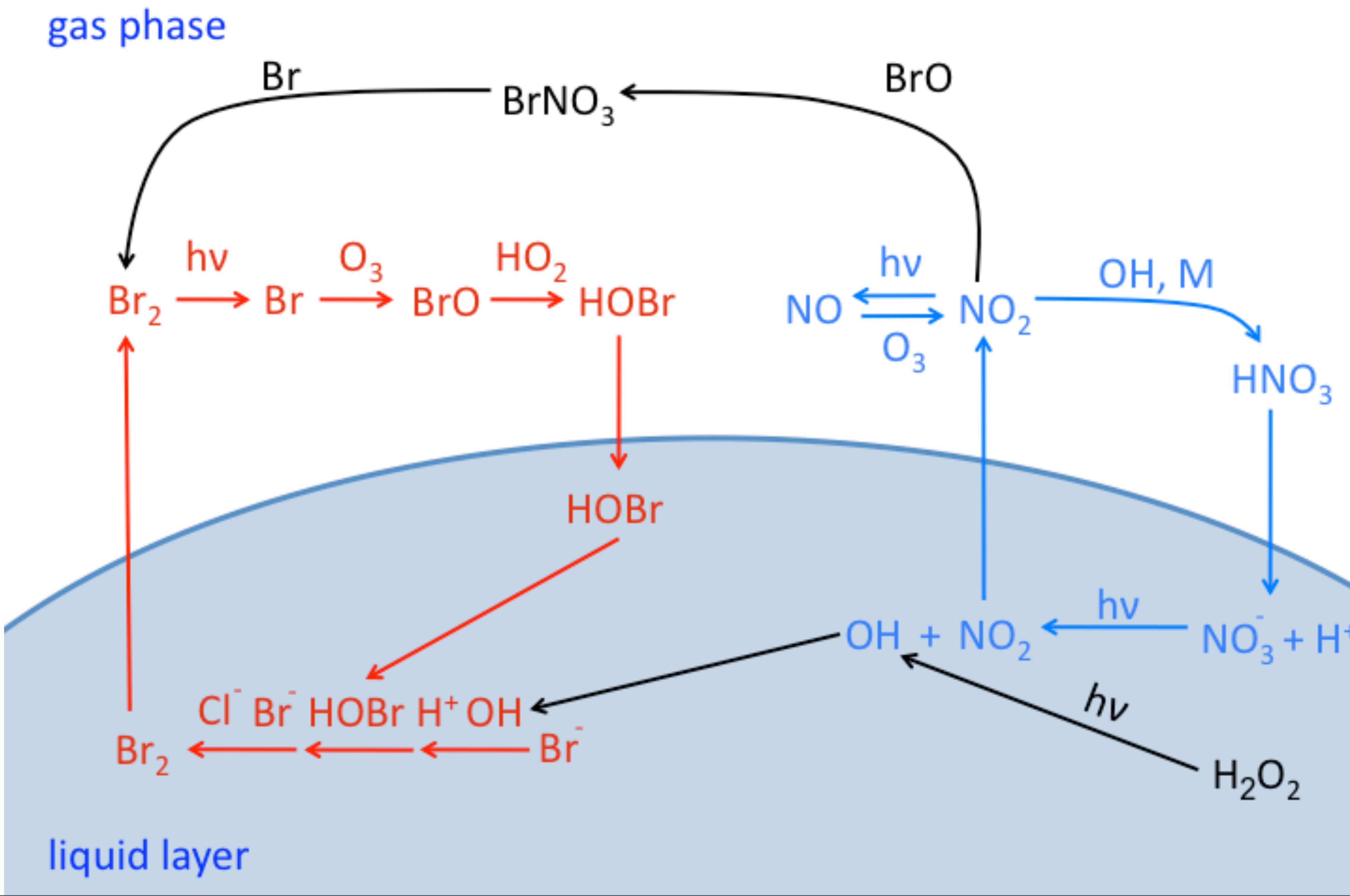
FLEXPART: Retroplume summary shows the air resided over Greenland before reaching Summit

Plot courtesy of John Burkhart

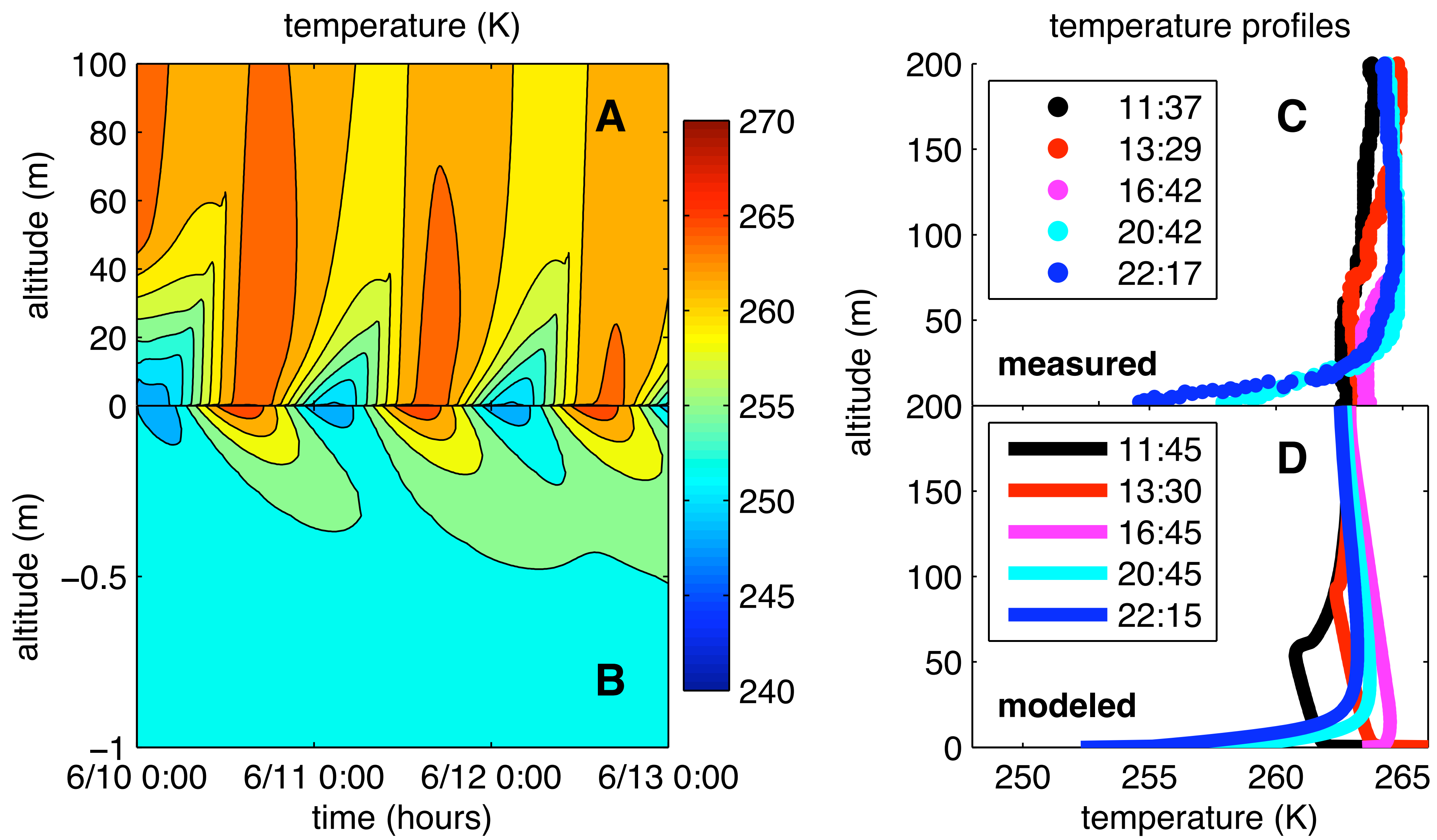
A simplified view of the coupled snow-atmosphere system



Summary of NO_x and bromine chemistry occurring at Summit

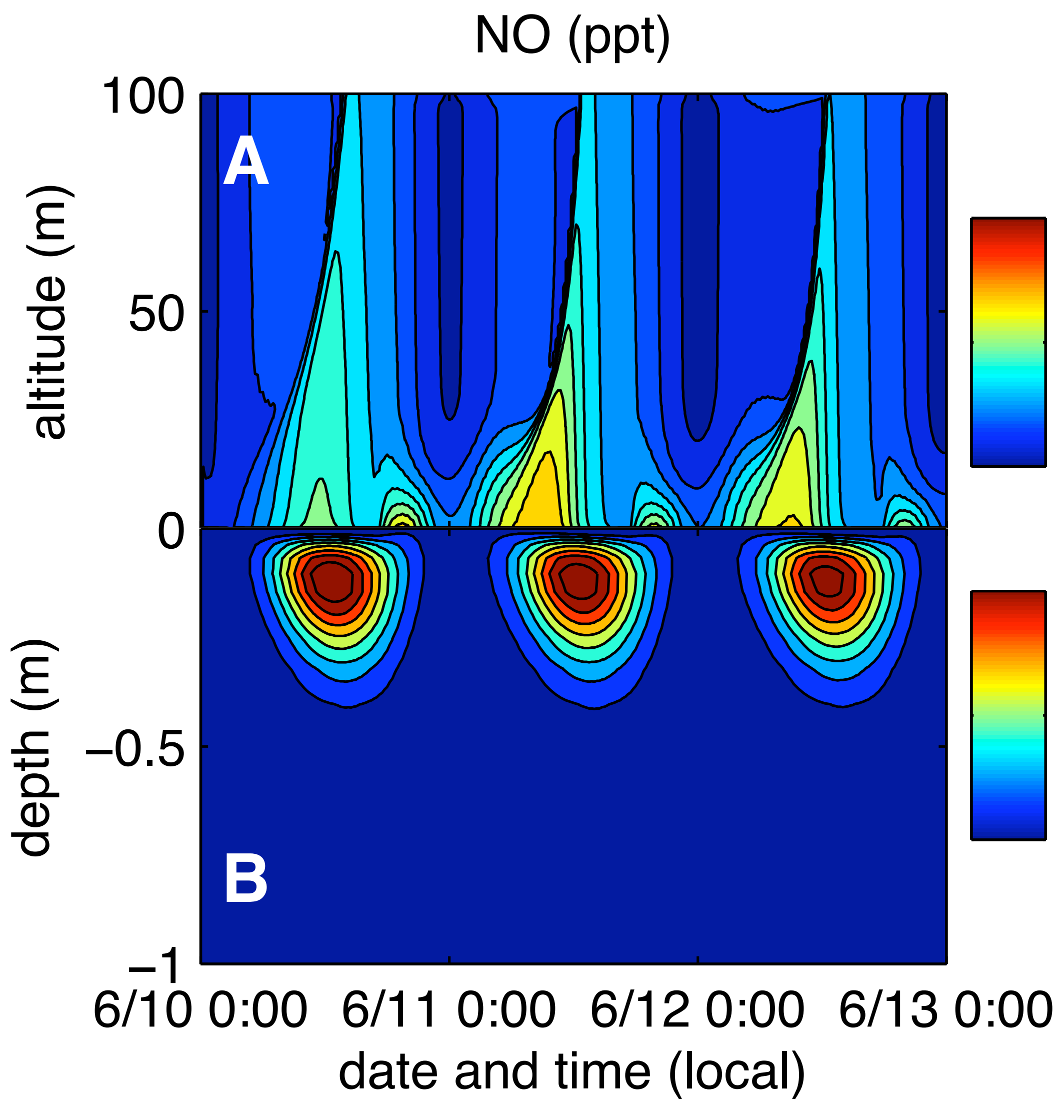


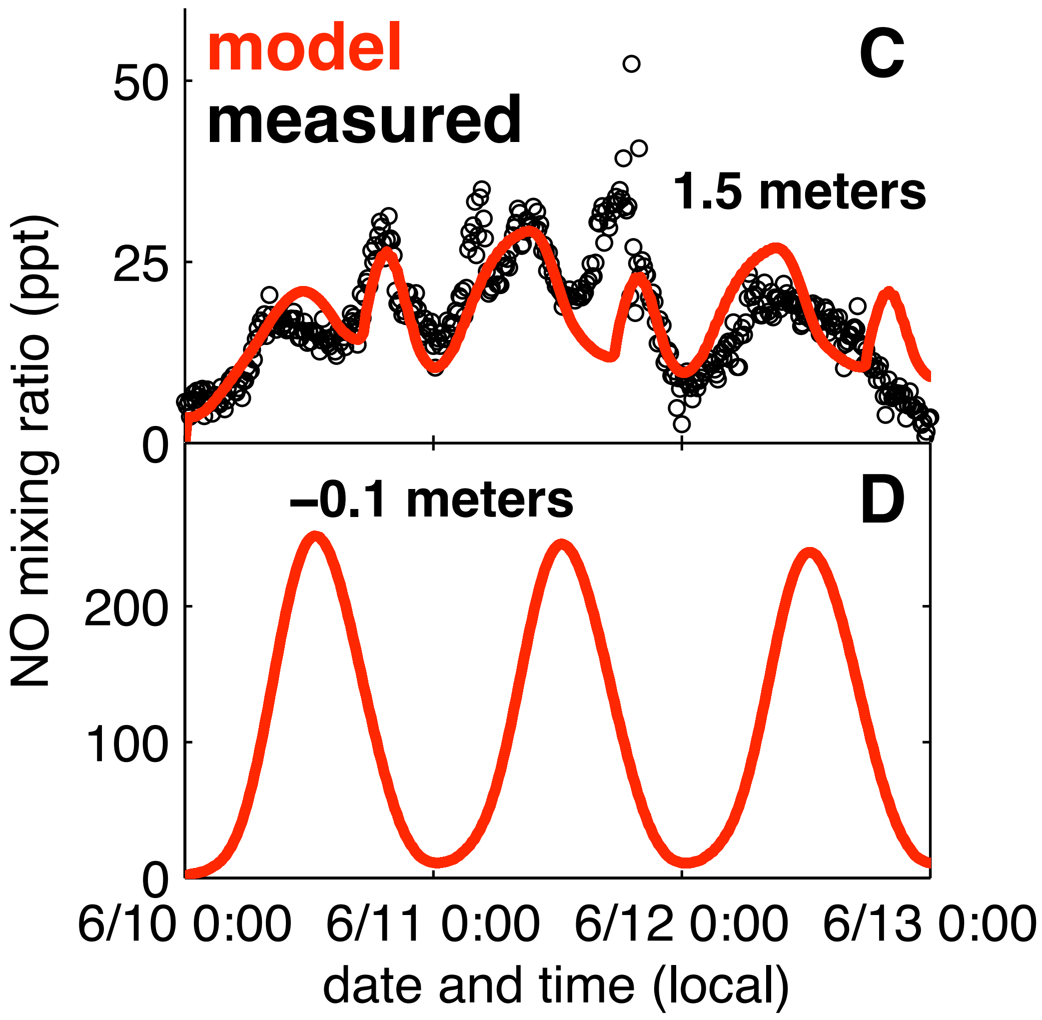
Boundary layer evolution during the focus period in 2008



Thomas et al, ACP, 2011.

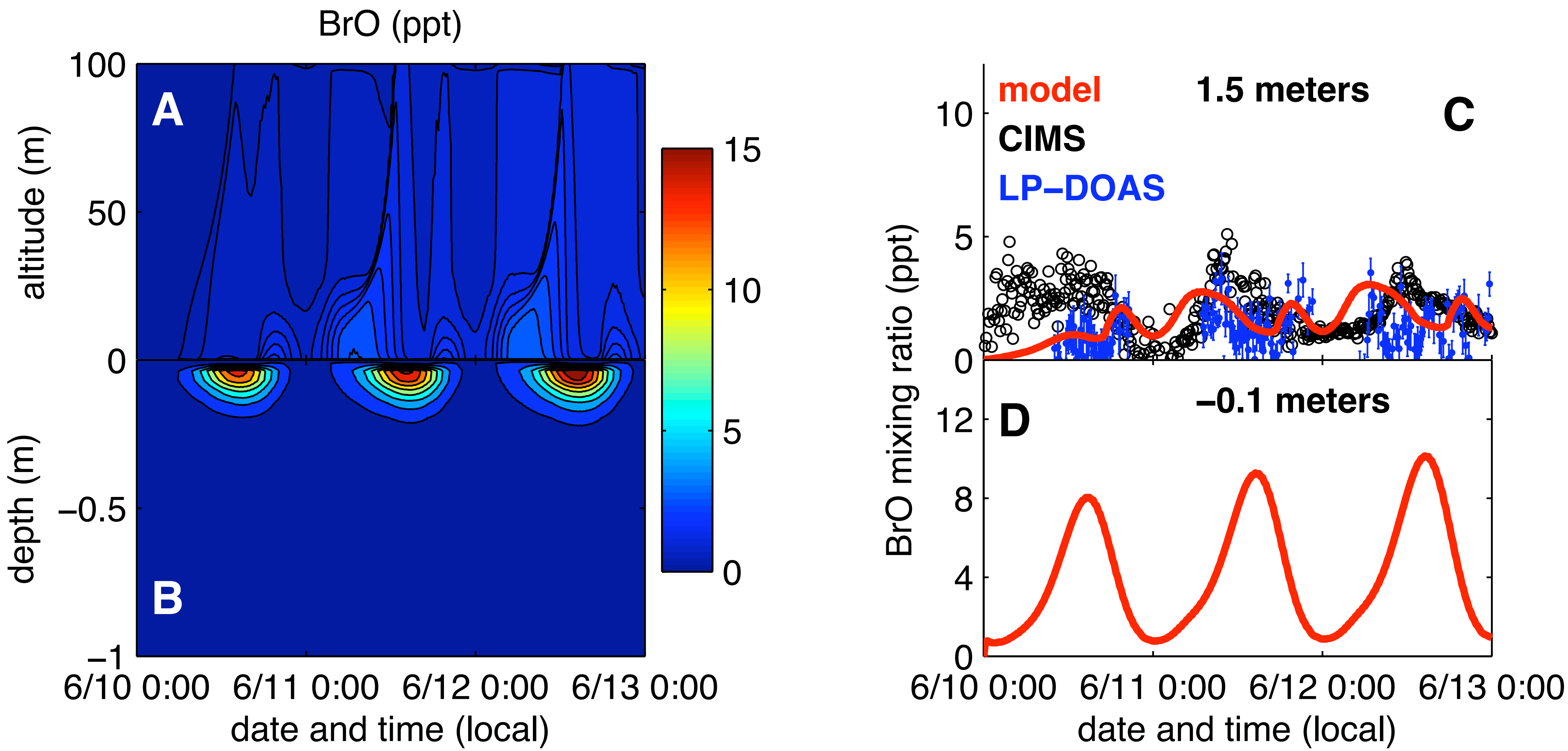
Model predicted NO 10-13 June 2008





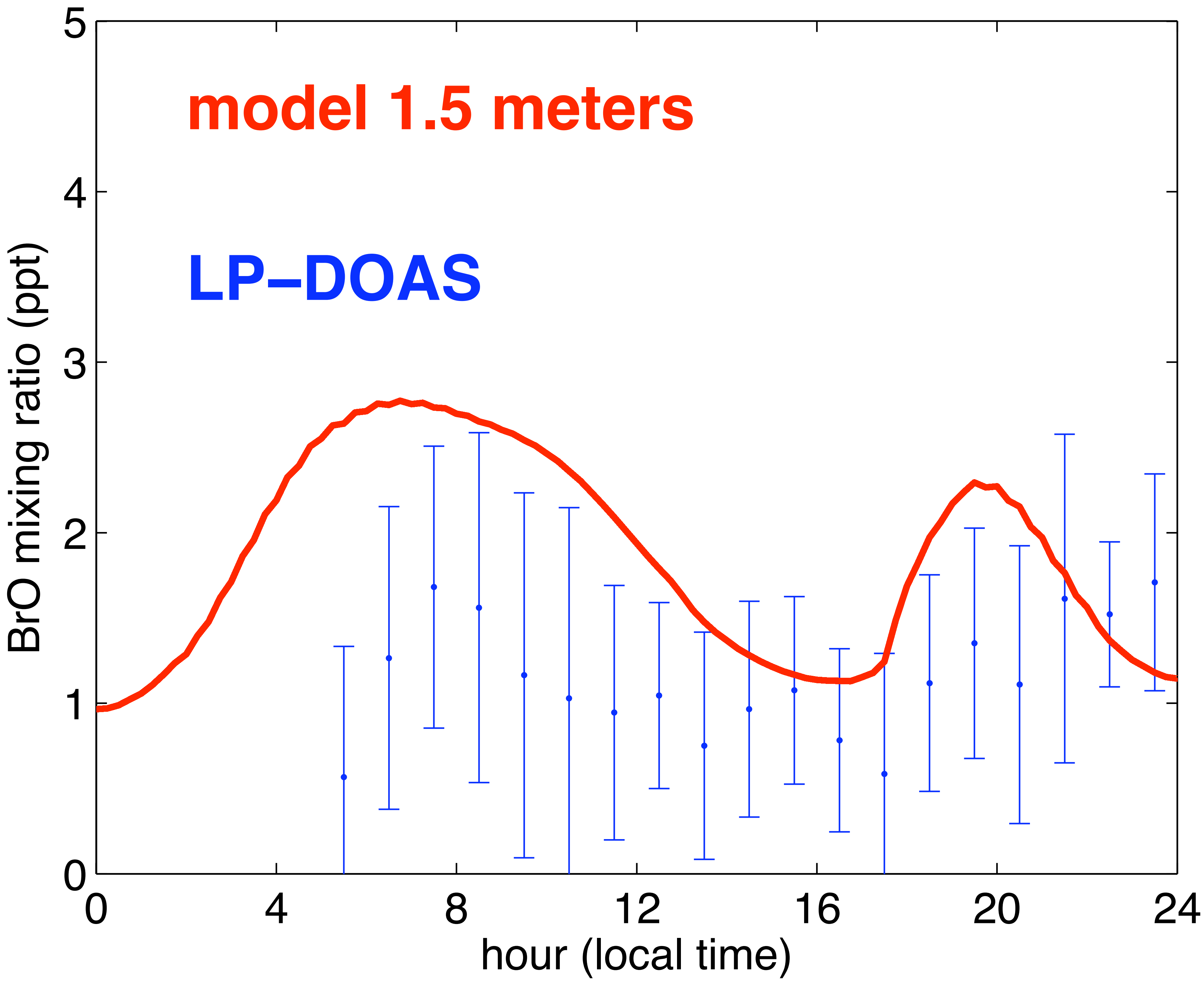
Thomas et al,
ACP, 2011.

Model predicted BrO
10-13 June 2008



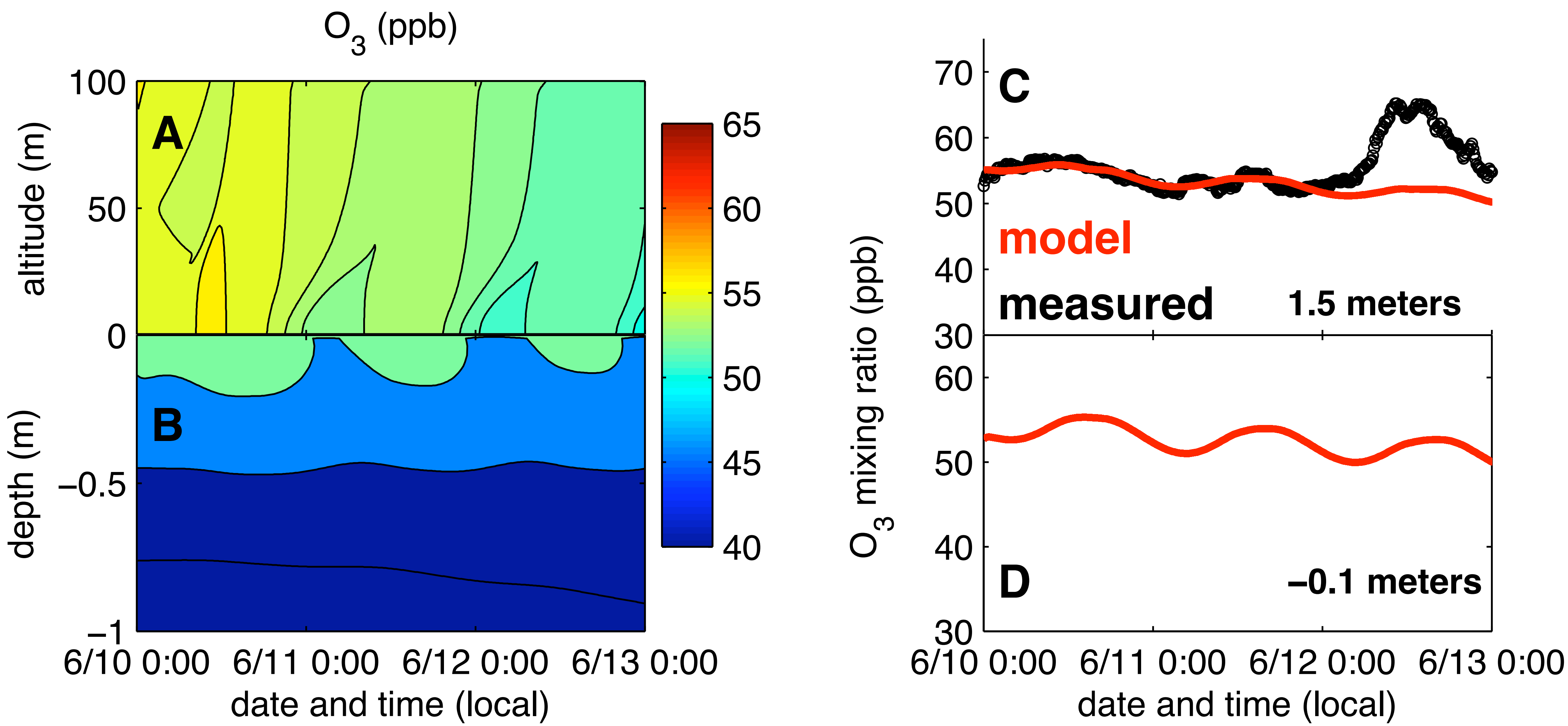
Thomas et al, ACP, 2011.

Hourly averaged BrO model vs LP-DOAS measurement



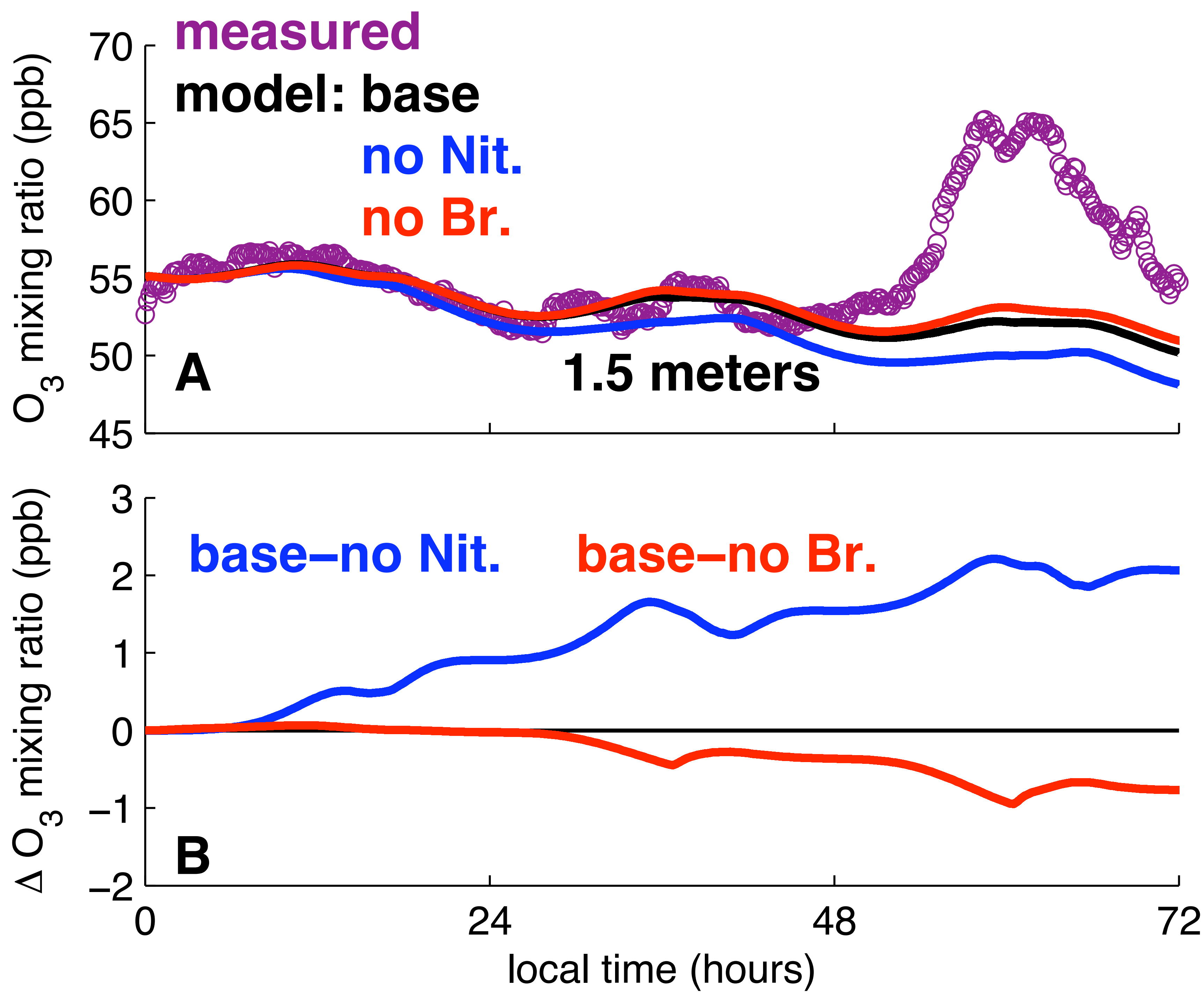
Thomas et al, ACP, 2011.

Model predicted O_3 10-13 June 2008



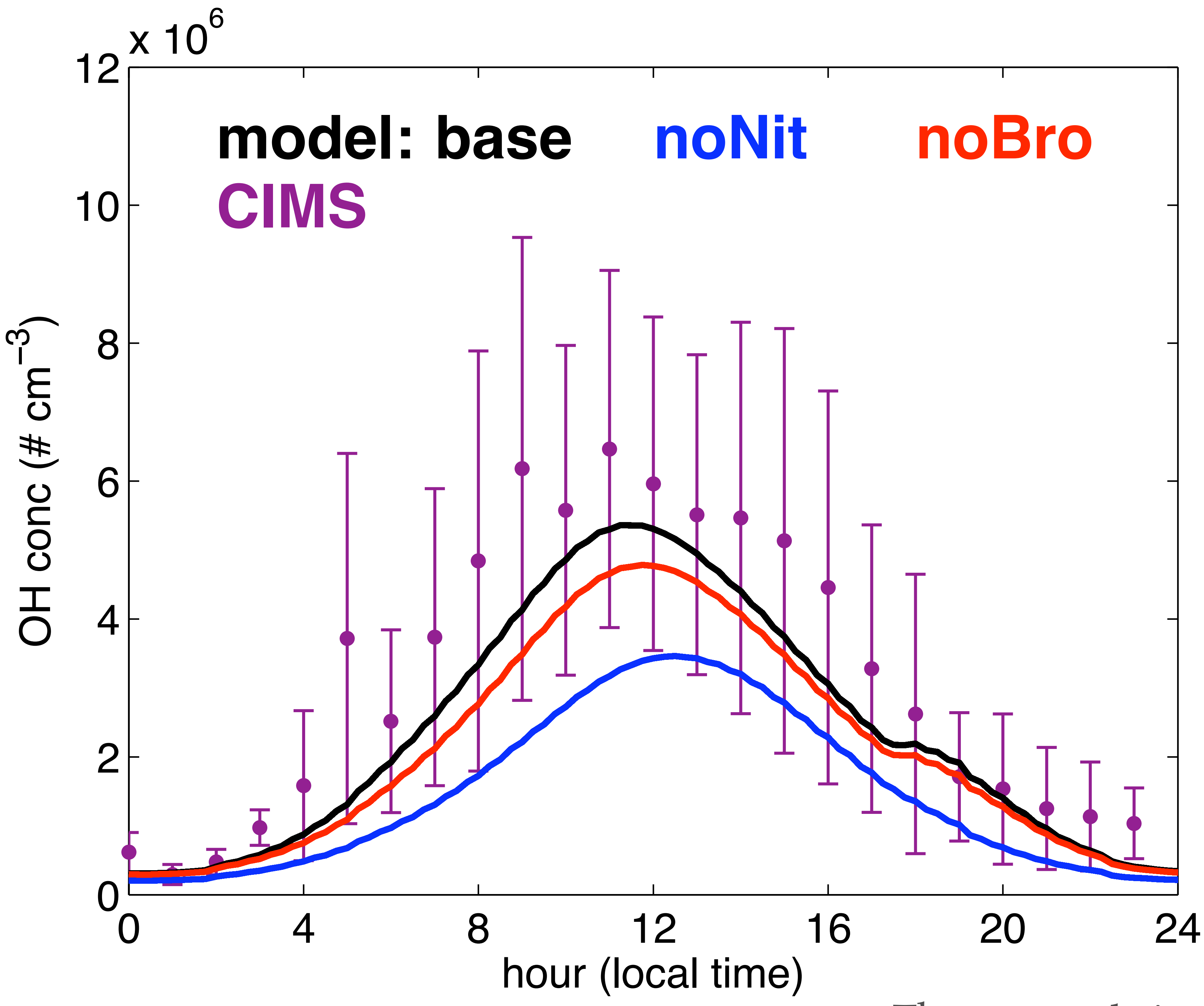
Thomas et al, ACP, 2011.

Impact of snow derived NO_x and bromine chemistry on ozone



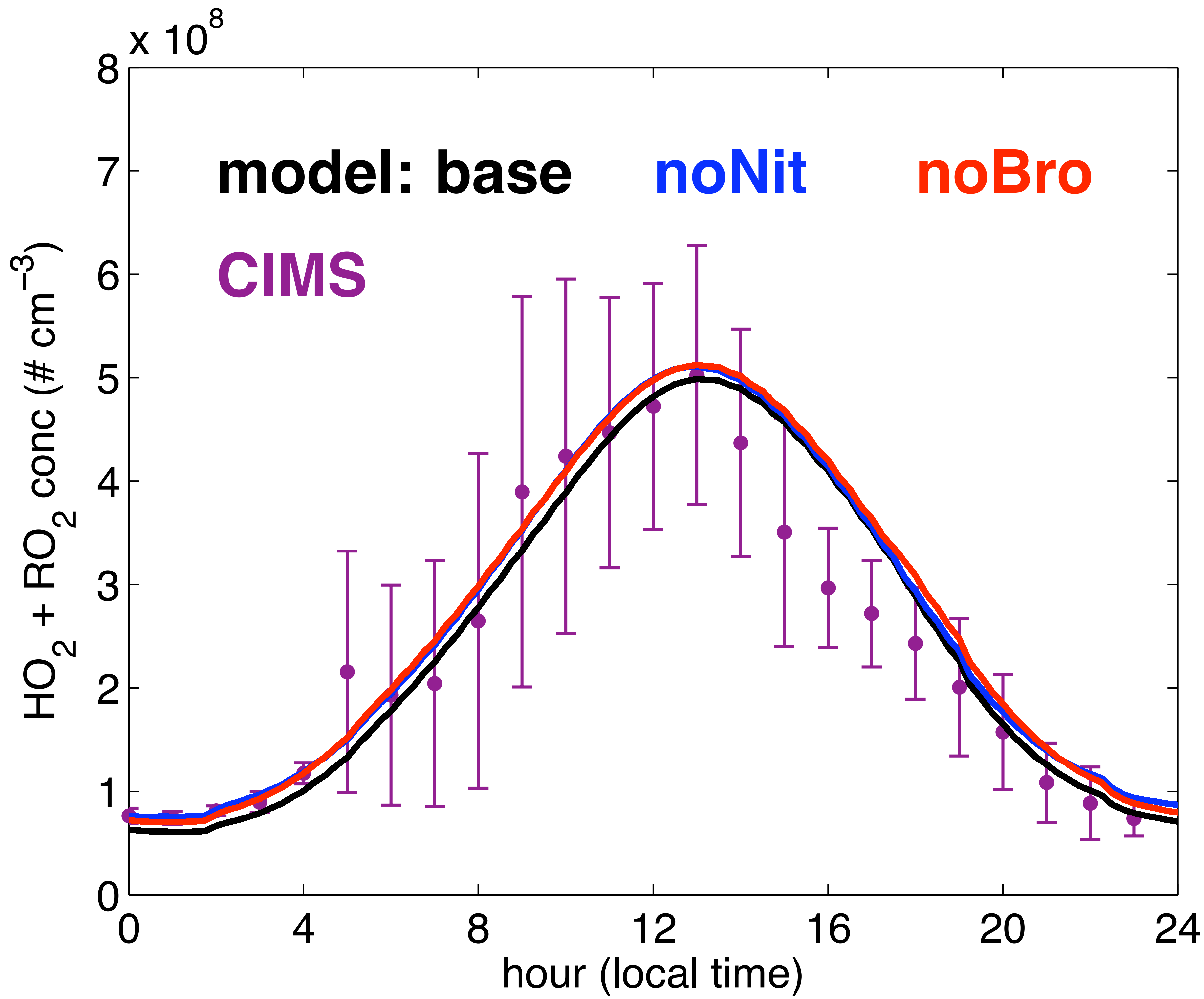
Thomas et al., in preparation, 2011.

Hourly averaged OH model vs CIMS measurement



Thomas et al., in preparation, 2011.

Hourly averaged RO_2 model vs CIMS measurement



Thomas et al., in preparation, 2011.

Conclusions and Questions for ongoing work

- **Conclusions**
  - NO_x and BrO mixing ratios in the BL at Summit can be described by a 1D model including snow chemistry.
  - Snow derived bromine and NO_x impact both ozone and OH present in the boundary layer.

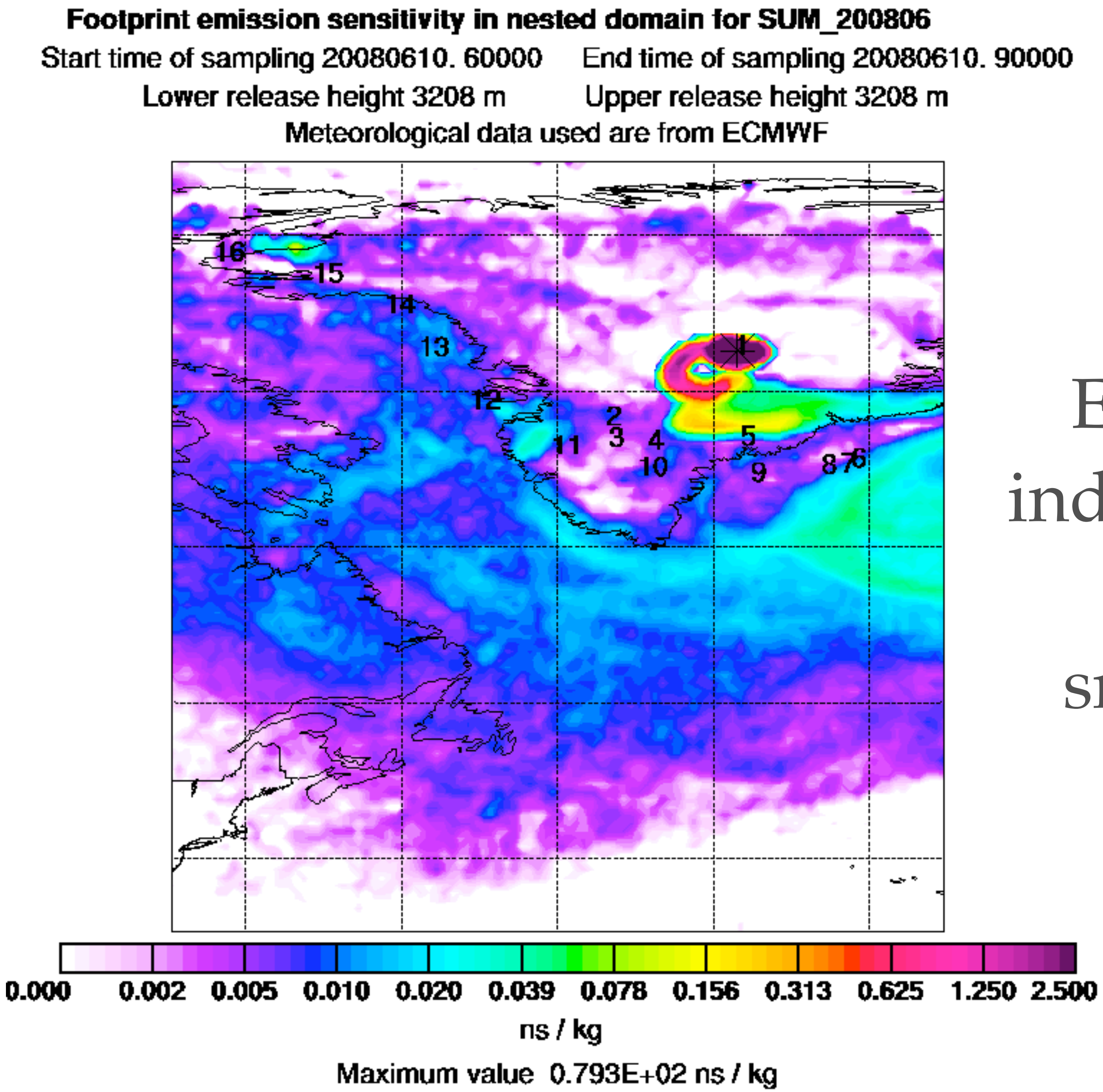
- **Questions**
  - How does this focus period connect to long term trends at Summit?
  - How are boundary layer processes impacting chemistry in the free troposphere?
  - **Bromine**
    - Is gas phase bromine present in low concentrations at a wide range of non-coastal Arctic sites?
    - Does O_3 destruction by such small amounts of Br contribute the vertical profiles of O_3 at Summit (small depletion near the surface)?
  - **Nitrogen**
    - Does nitrogen cycling in the BL impact nitrate measured in ice cores?
    - Does NO_x contribute to O_3 production, impacting the vertical profile of O_3 at Summit?

GSHOX snow photochemistry team

- To all the members of the GSHOX campaign

- To the members of the Stutz Group at UCLA.
- Detlev Helmig and Richard Honrath as well as their groups for collaboration and support.
- Zoe Courville for assistance.
- Kenjiro Toyota for assistance with implementing the wind pumping model.
- John Burkhart for the FLEXPART analysis.
- To the NSF GEO ATM Tropospheric Chemistry program for funding (Grant ATM-0612279:002). Logistic support was provided by NSF OPP Arctic Research Support and Logistics program and CH2MHill Polar Services.
- To the NY ANG for the heavy airlift, and permission to conduct research at Summit granted by the Danish Polar Center and Greenland Home Rule.

A unique focus period for modeling 2008 campaign data: 10-13 June



FLEXPART:
Emission sensitivity indicates measurements are sensitive to snowpack emissions

Stutz et al., ACPD, 2011.