Atmospheric nitrogen oxides (NO and NO_2) at Dome C: first observations & implications for reactive nitrogen cycling above the East Antarctic Ice Sheet

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3rd Workshop on Air-Ice Chemical Interactions (AICI) - Jun 6-8 2011, Columbia University, New York

BAS Contribution to NITEDC 2009/10

"NItrate Evolution in Surface Snow at Dome C" (LGGE, France)

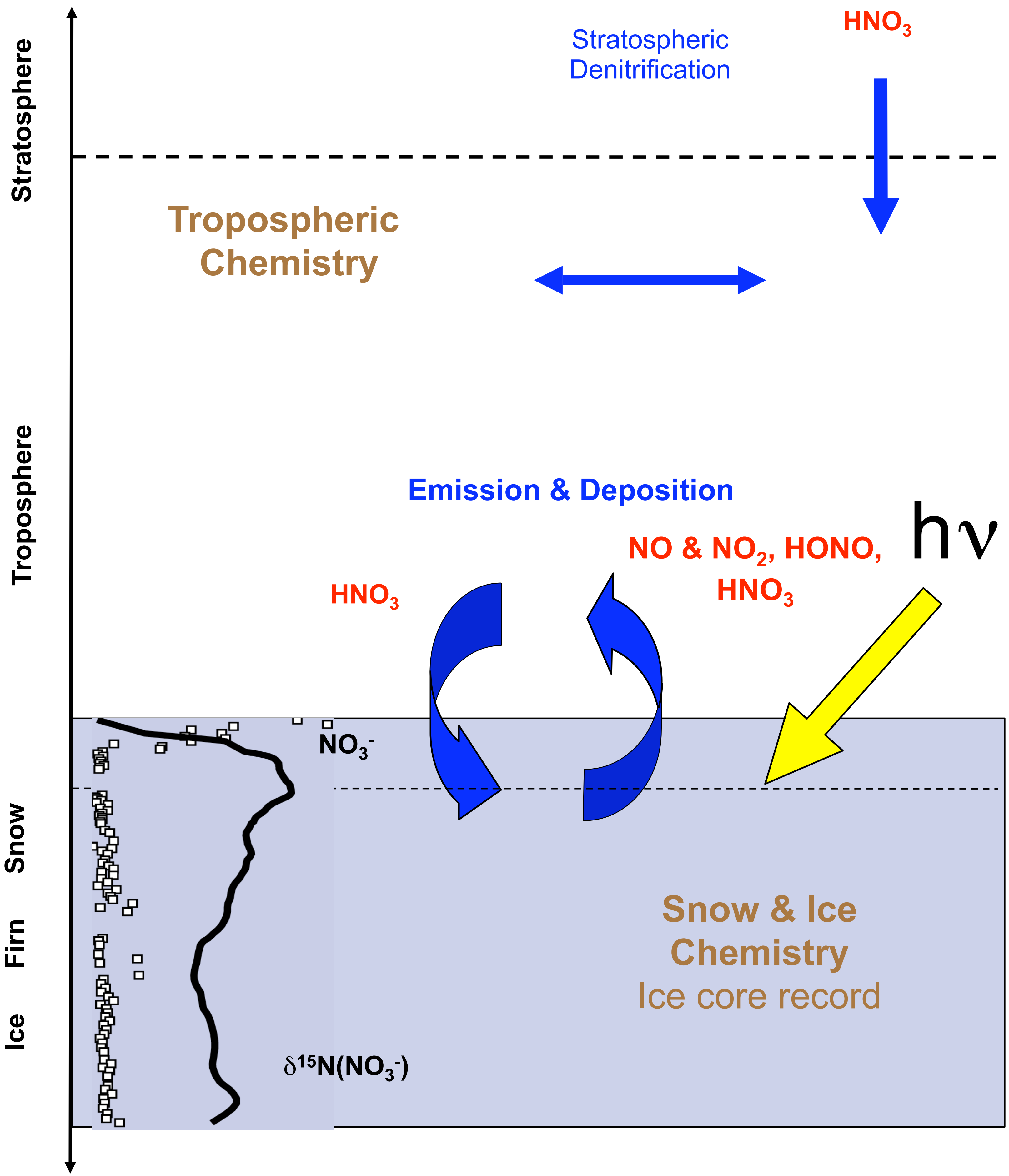
see poster for overview by Savarino et al.

Thanks to ...

A.E. Jones, BAS
N. Brough, BAS
P. Anderson, BAS
E.W. Wolff, BAS

J.L. France, RHUL
M.D. King, RHUL
J. Savarino, LGGE

Reactive nitrogen cycling at the snow pack & ice sheet scale

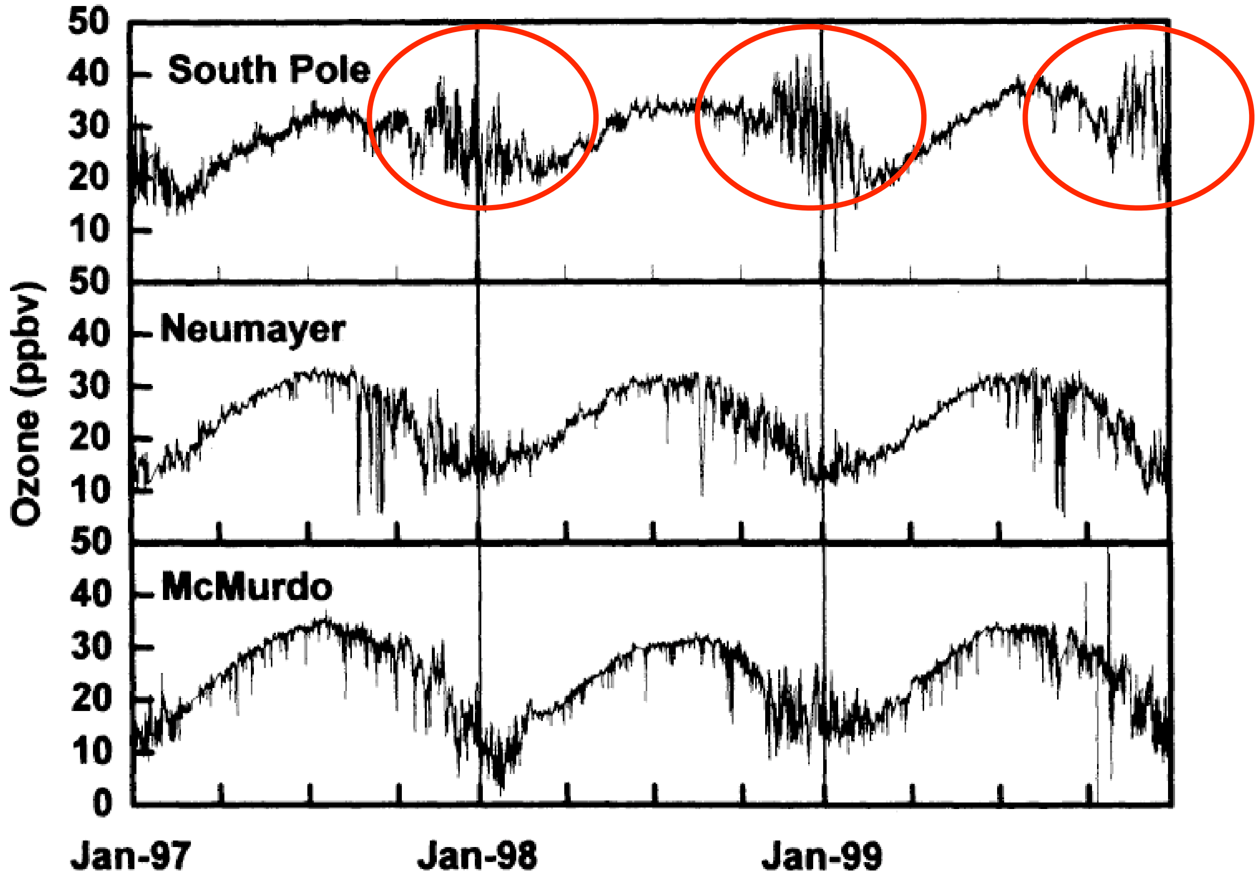


Observed in the **Arctic** & **Antarctic** with impact on

1. oxidazing capacity of air above & within snow: **O_3, HO_x, H_2O_2**

2. **ice core record** of NO_3^- concentration & stable isotopic composition

a. Net O_3 production



Crawford et al., GRL, 2001

b. HO_x partitioning towards OH

$NO + HO_2 \rightarrow NO_2 + OH$

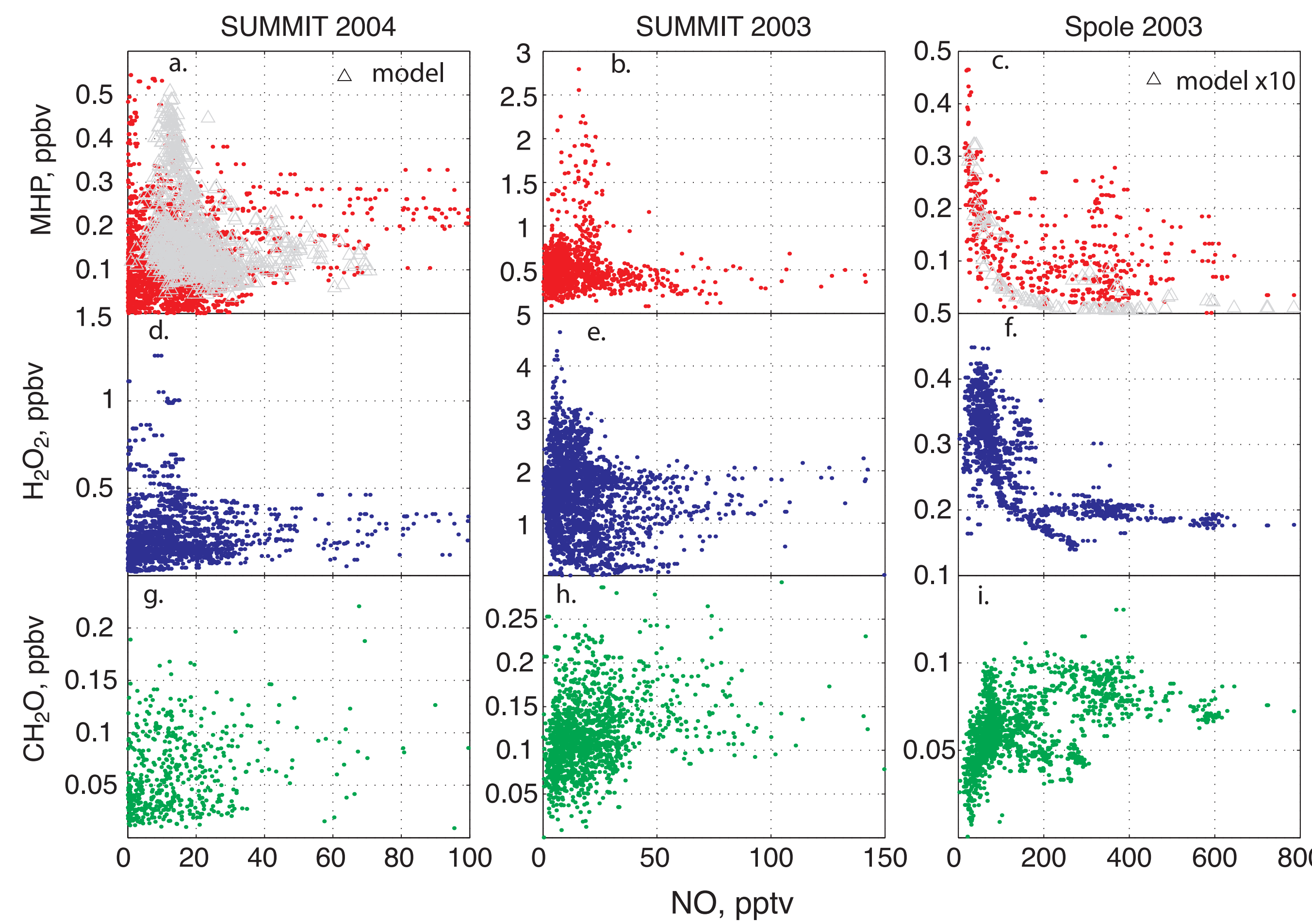
Reactive nitrogen cycling

1. Impact on oxidation capacity

c. Control of H_2O_2/ROOH formation

$HO_2 + HO_2 \rightarrow H_2O_2$

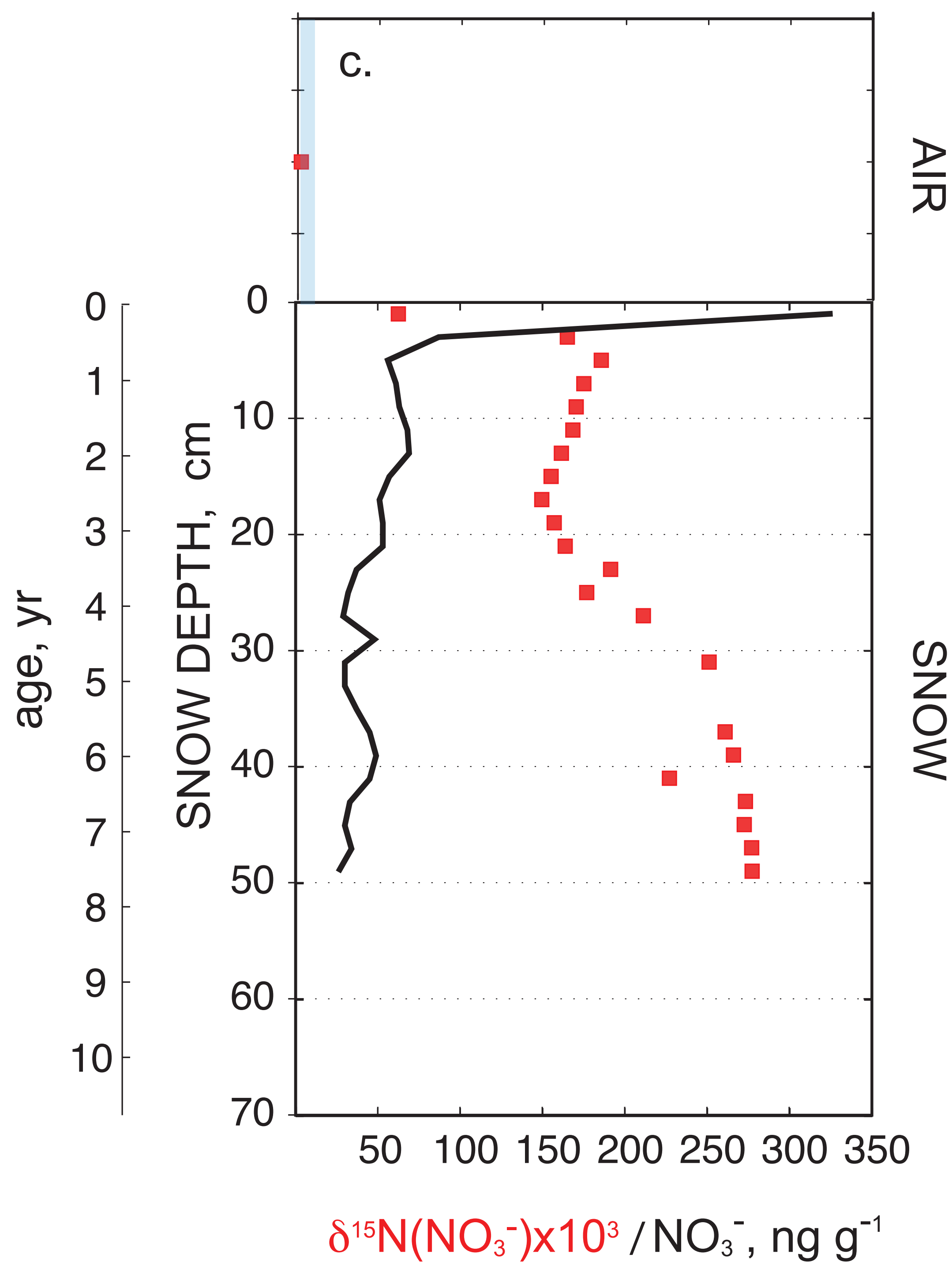
$NO + HO_2 \rightarrow NO_2 + OH$



Frey et al., ACP, 2009

Reactive nitrogen cycling
2. Impact on firn & ice core record

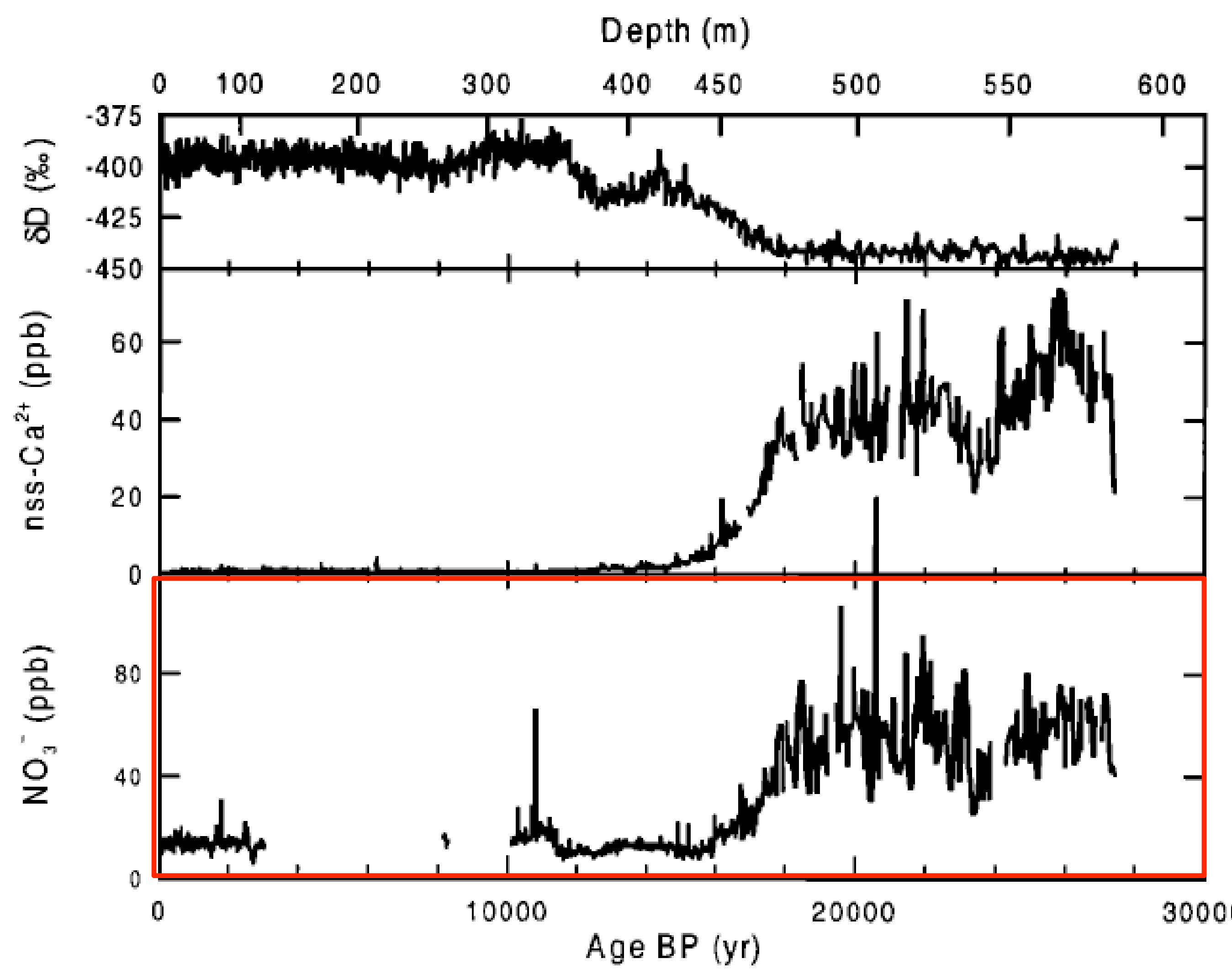
NO_3^- concentration & isotopic composition in surface snow



Frey et al., ACP, 2009

e.g. Dome C (East Antarctica)

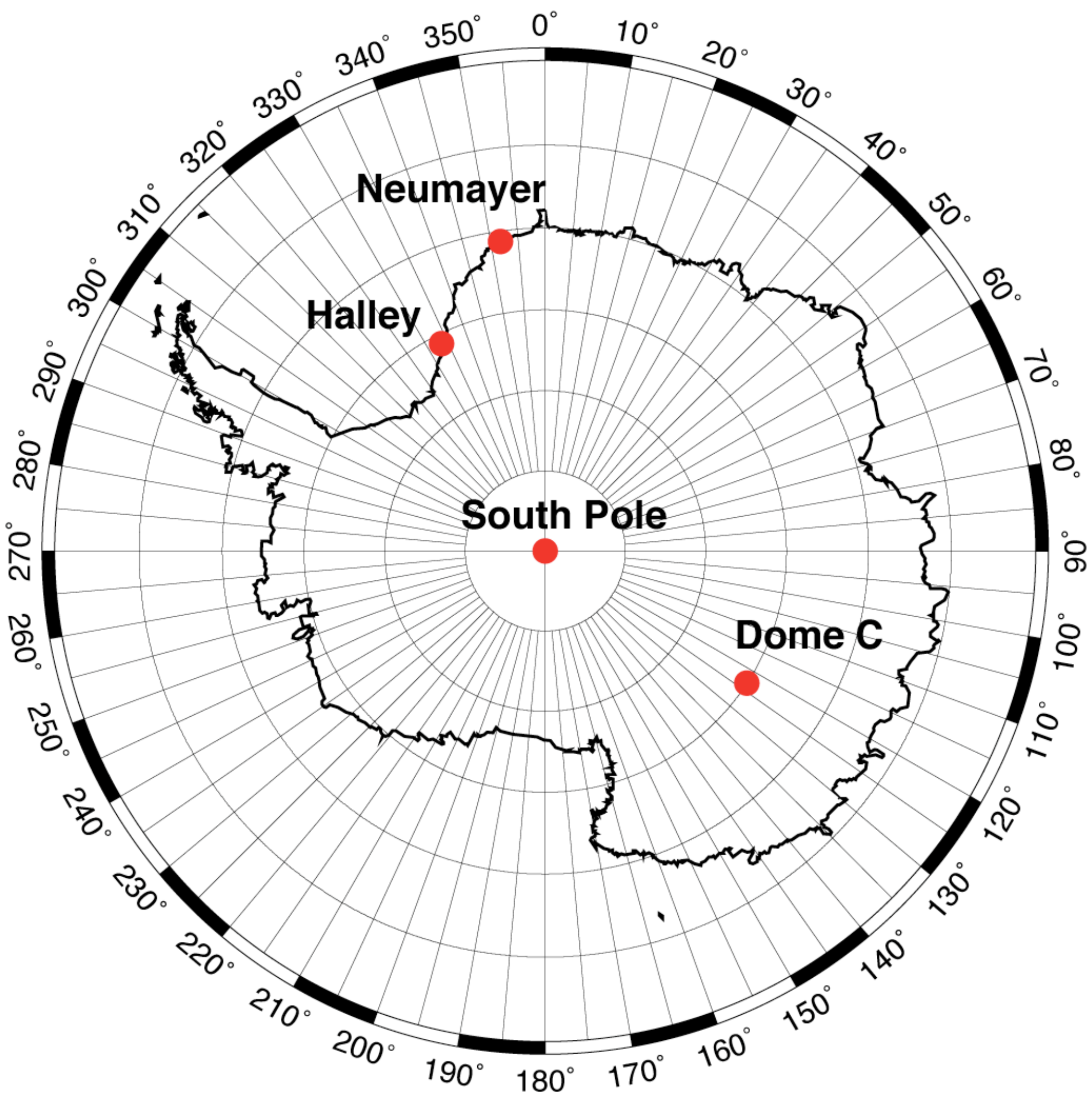
The NO_3^- ice core record



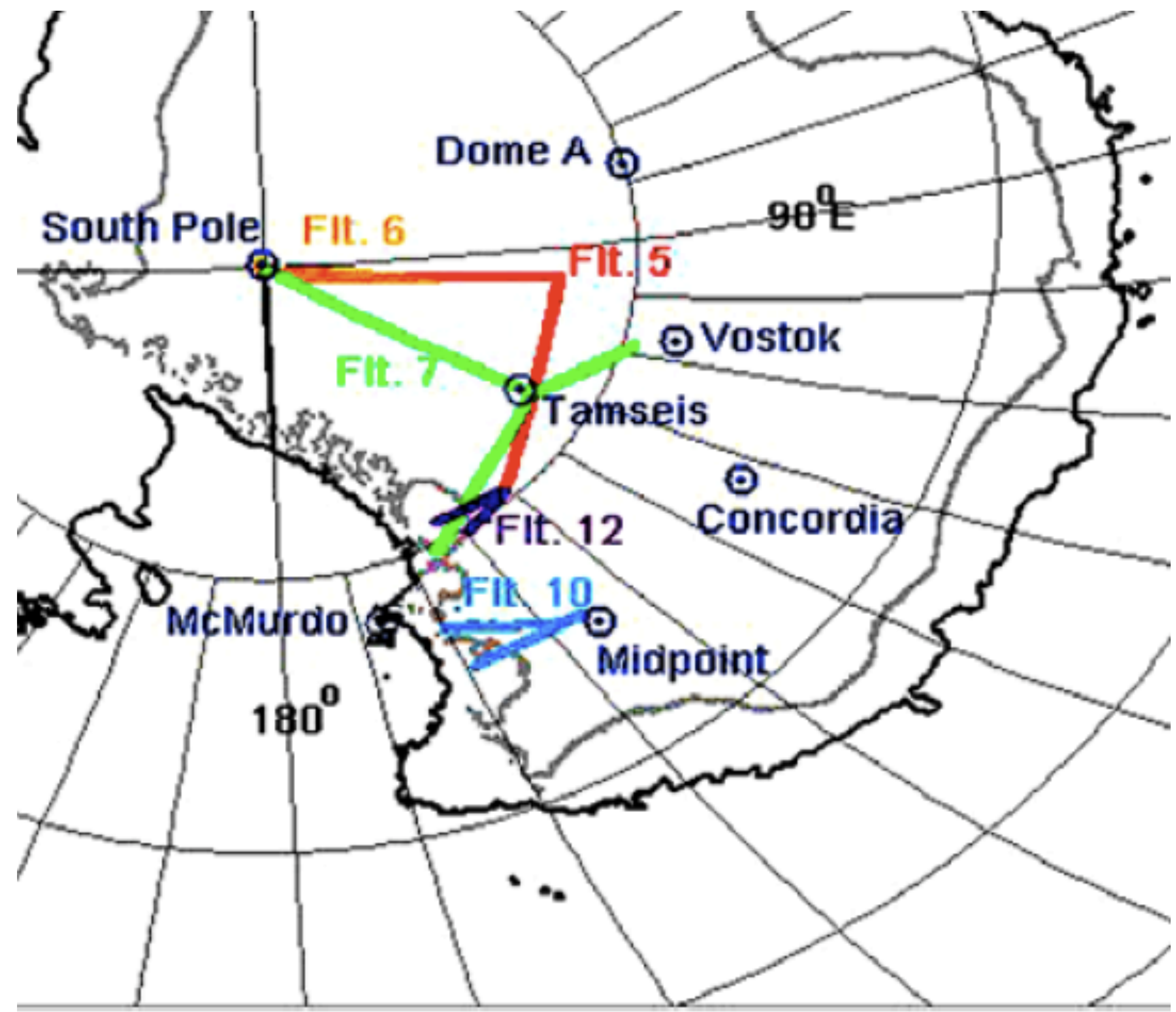
Roethlisberger et al., 2000

Spatial coverage of current NO_x measurements in Antarctica

Recent intensive measurement campaigns

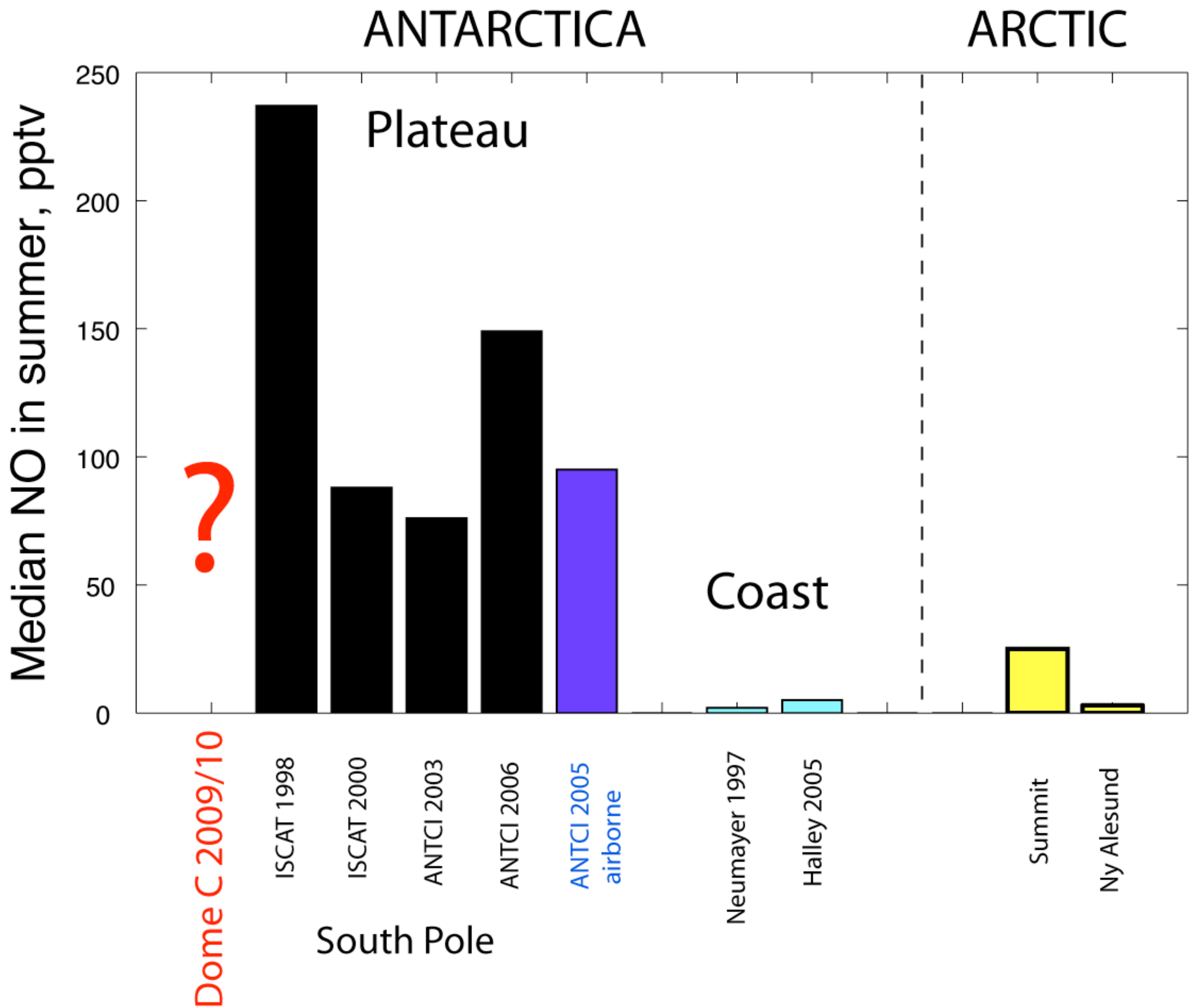


ANTCI 2005 Airborne Campaign



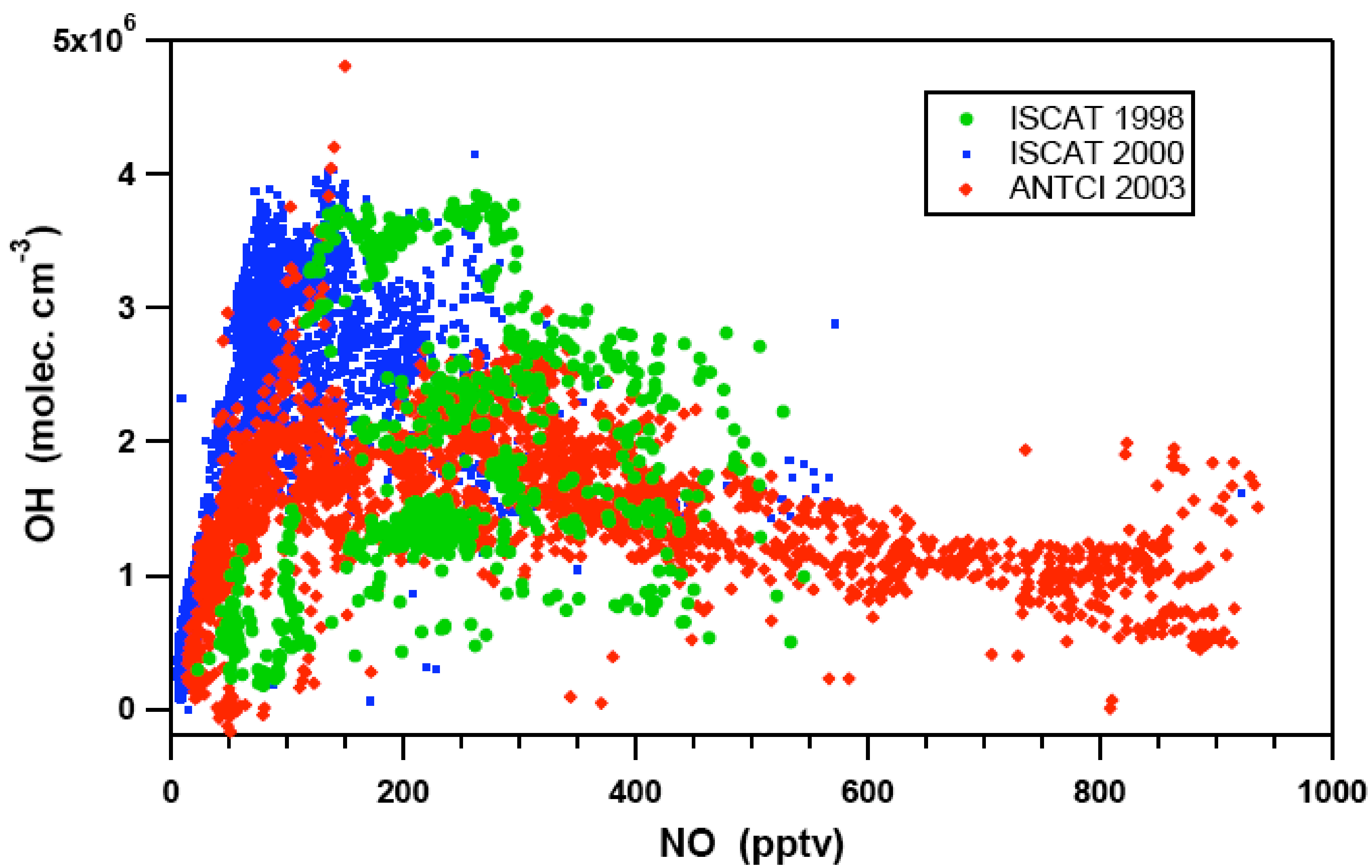
Slusher et al., 2010

High NO_x and OH and South Pole. Typical for the East Antarctic Ice Sheet?


ANTARCTICA
ARCTIC
Plateau
Coast
Median NO in summer, pptv
250
200
150
100
50
0
?
Dome C 2009/10
ISCAT 1998
ISCAT 2000
ANTCI 2003
ANTCI 2006
ANTCI 2005 airborne
Neumayer 1997
Halley 2005
Summit
Ny Alesund
South Pole

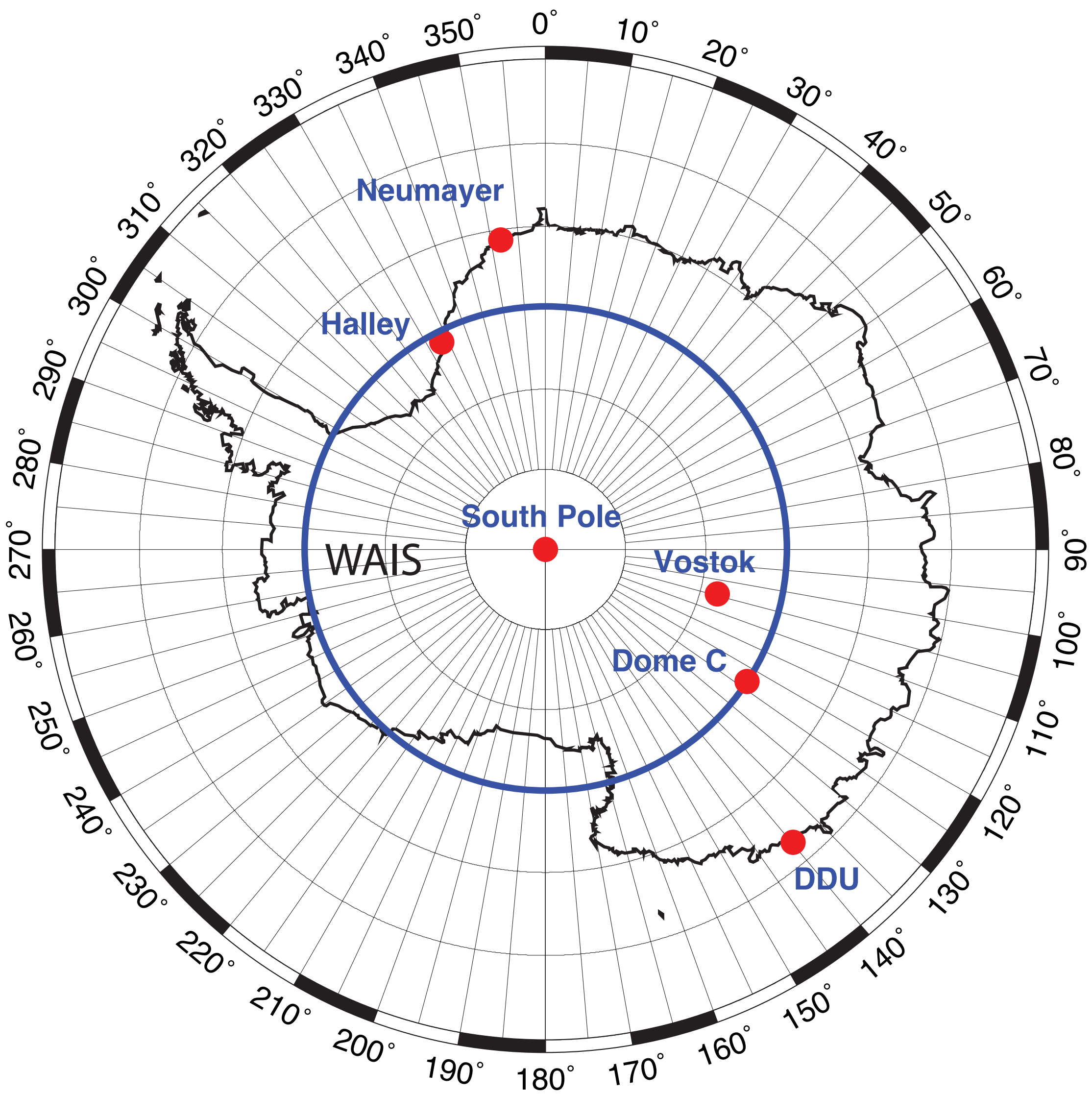
High NO at South Pole in summer because

- 24hr sunlight
- shallow atmospheric boundary layer
- located at base of large airshed
- low T leading to low primary production of HO_x



Grannas et al., 2007

South Pole is a singular case: no diurnal forcing



- Magnitude and variability of NO_x concentrations & flux on diurnal to seasonal time scales elsewhere on EAIS?
- What are the drivers of variability & snow emissions?
- What else needed to parameterize NO_x emissions on the ice sheet scale?

EAIS 67-90º S

Dec-21 ΔSEA range 46º - 0º

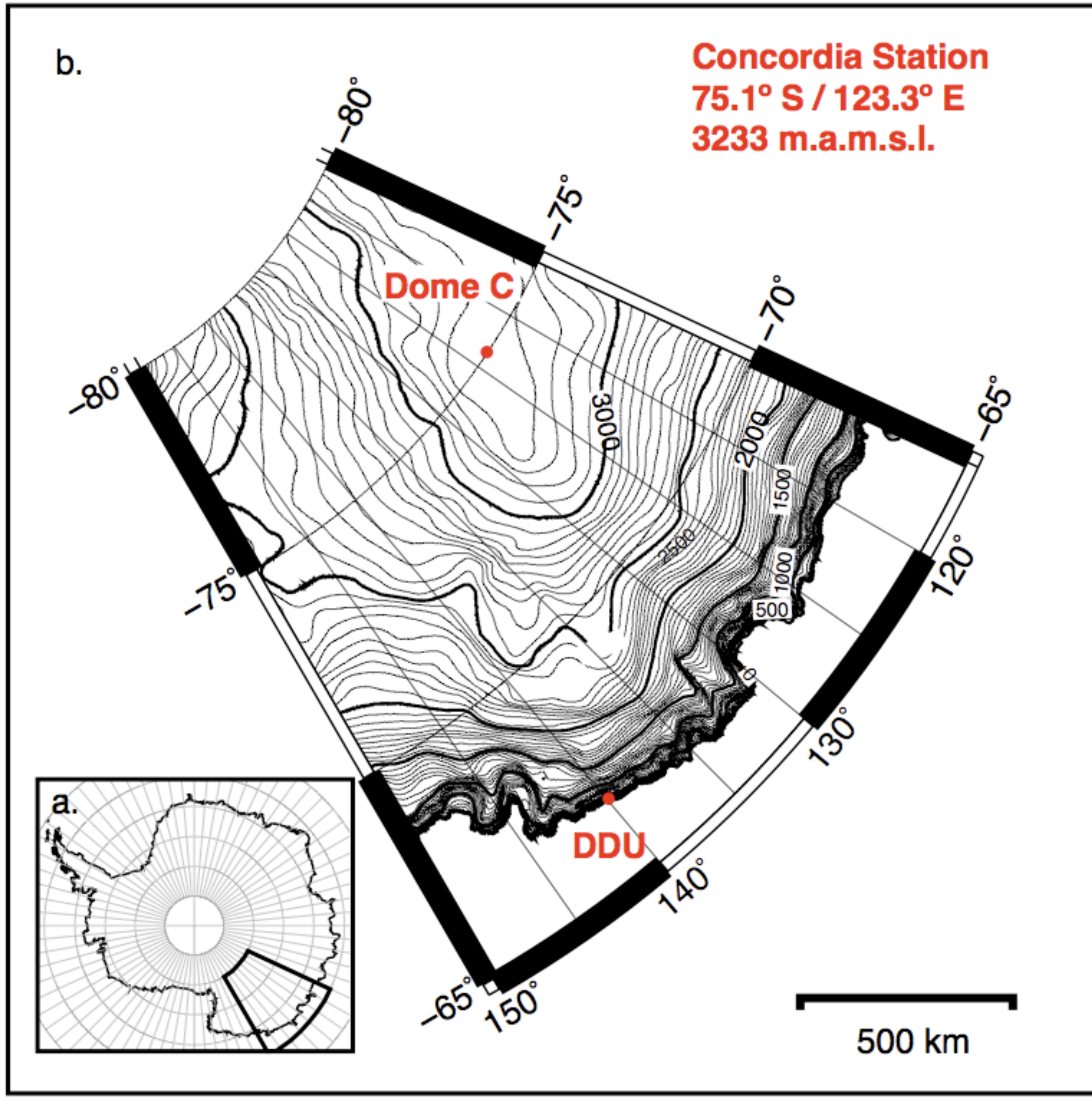
The Summer 2009/10 campaign at Dome C

10 week Field Season
19-Nov ’09 until 3-Feb ’10

French-Italian Concordia Station (IPEV/PNRA)

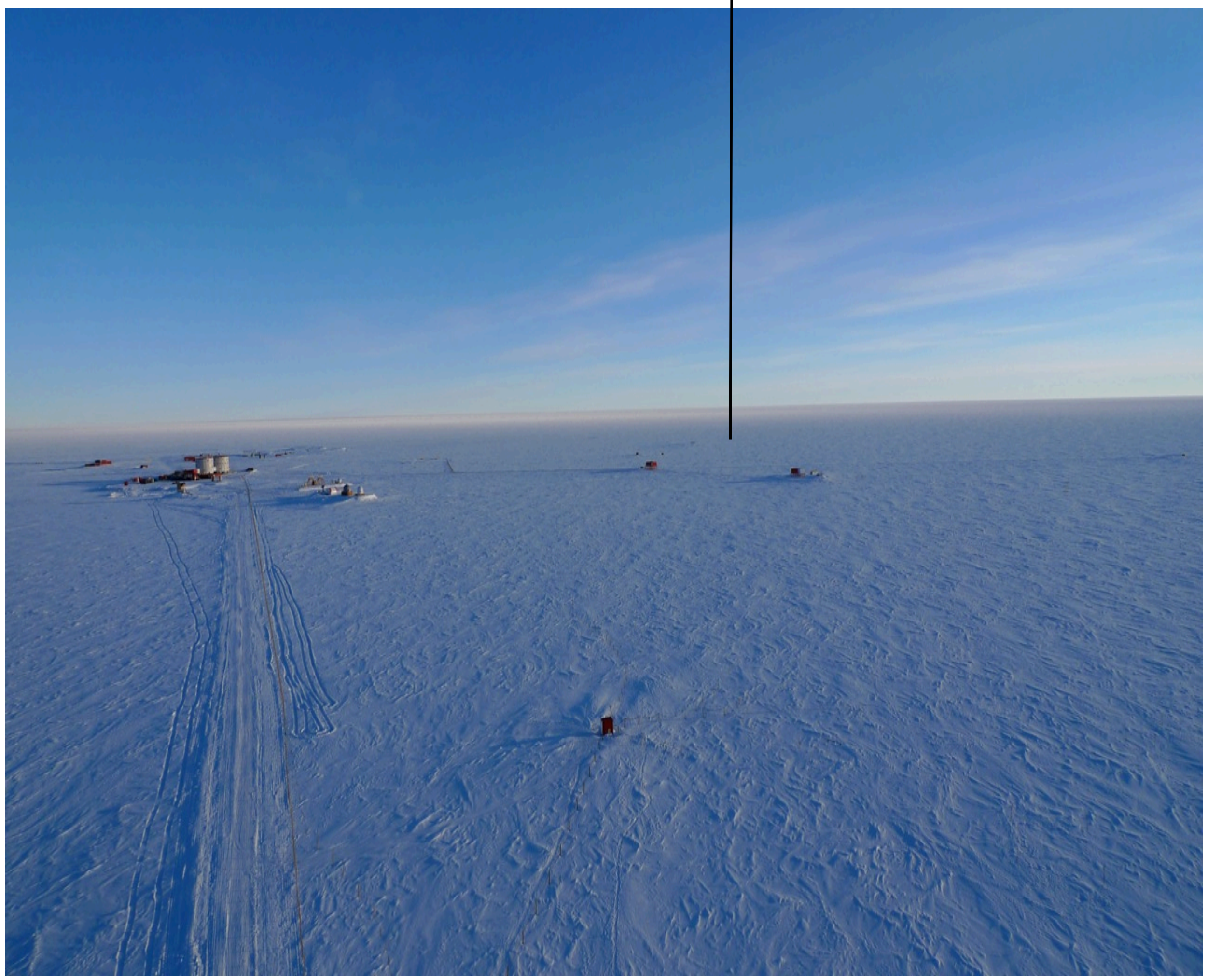
EPICA ice core site

- 1100 km from the coast
- 24 hr sunlight
- 75º S (as Halley)
- -22 to -50 ºC



The Summer 2009/10 campaign at Dome C

'Tenda Astrofisica' - Atmospheric Chemistry Lab at 0.7 km



The Summer 2009/10 campaign at Dome C

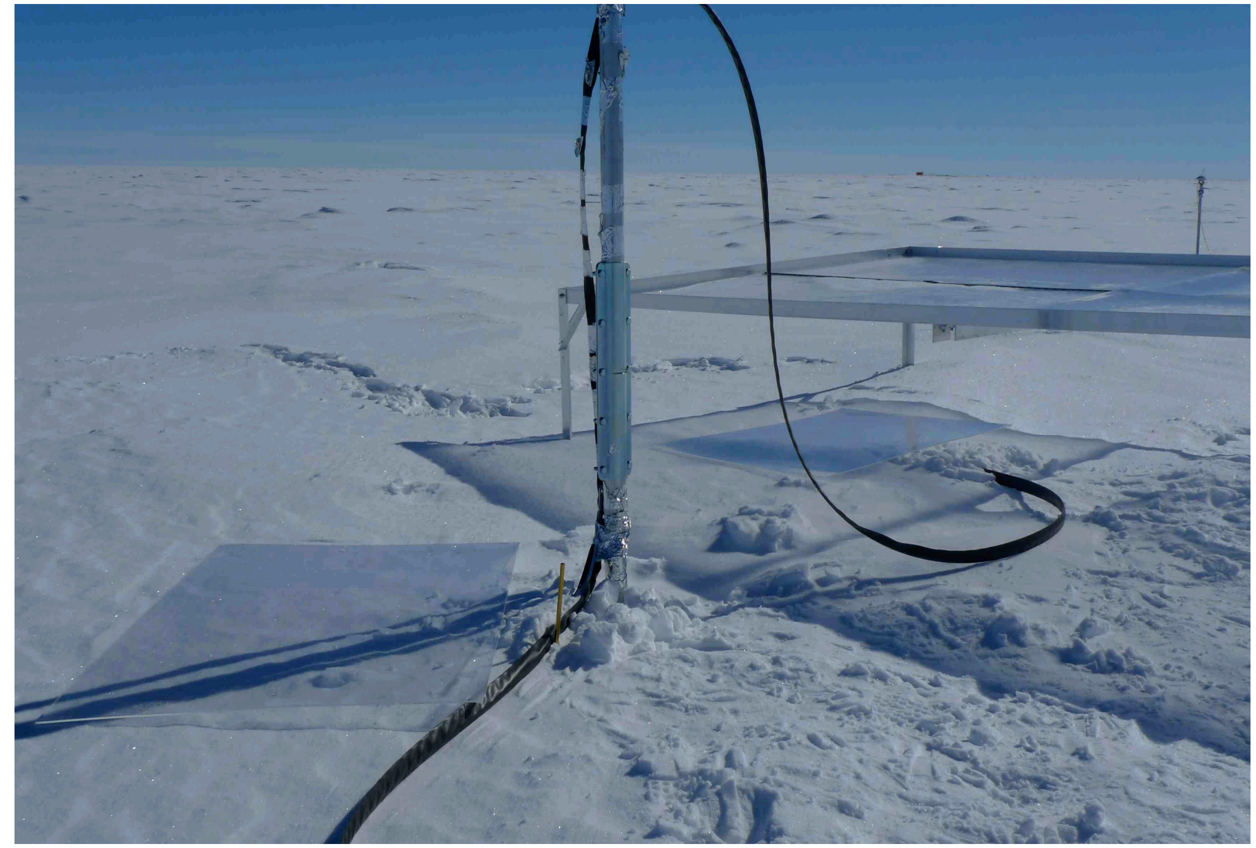
Firn Air Sampling

Experiments

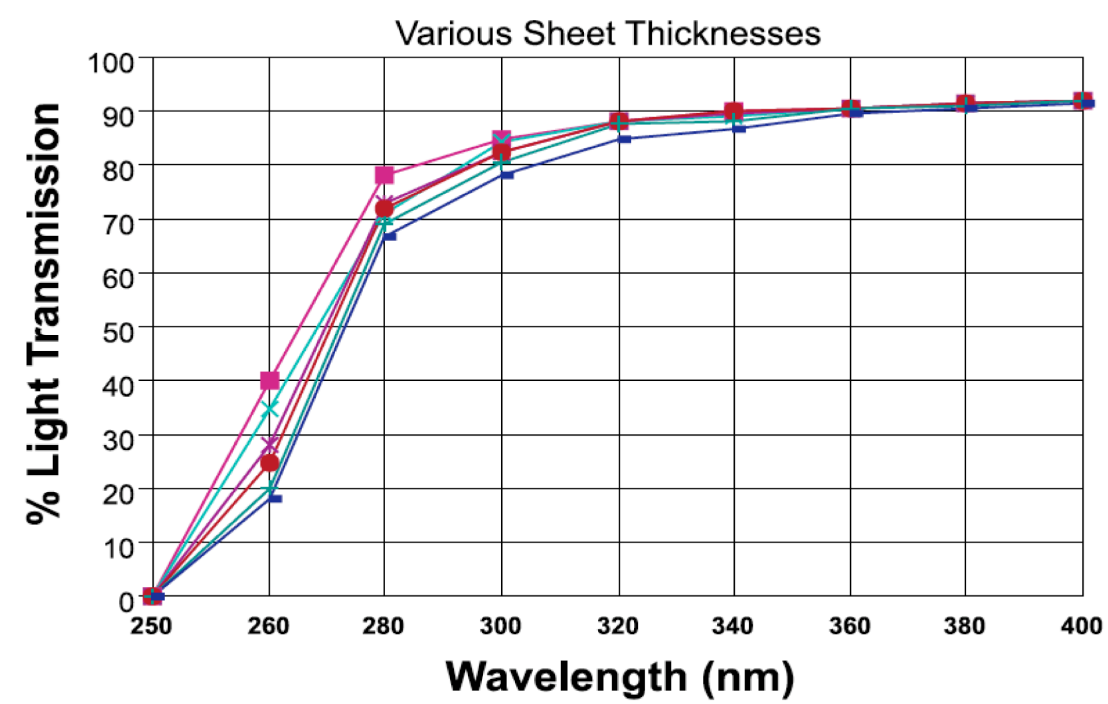
1) Concentration gradients: 0.01, 1.0 & 4.0m

2) Firn air concentration

3) UV filter



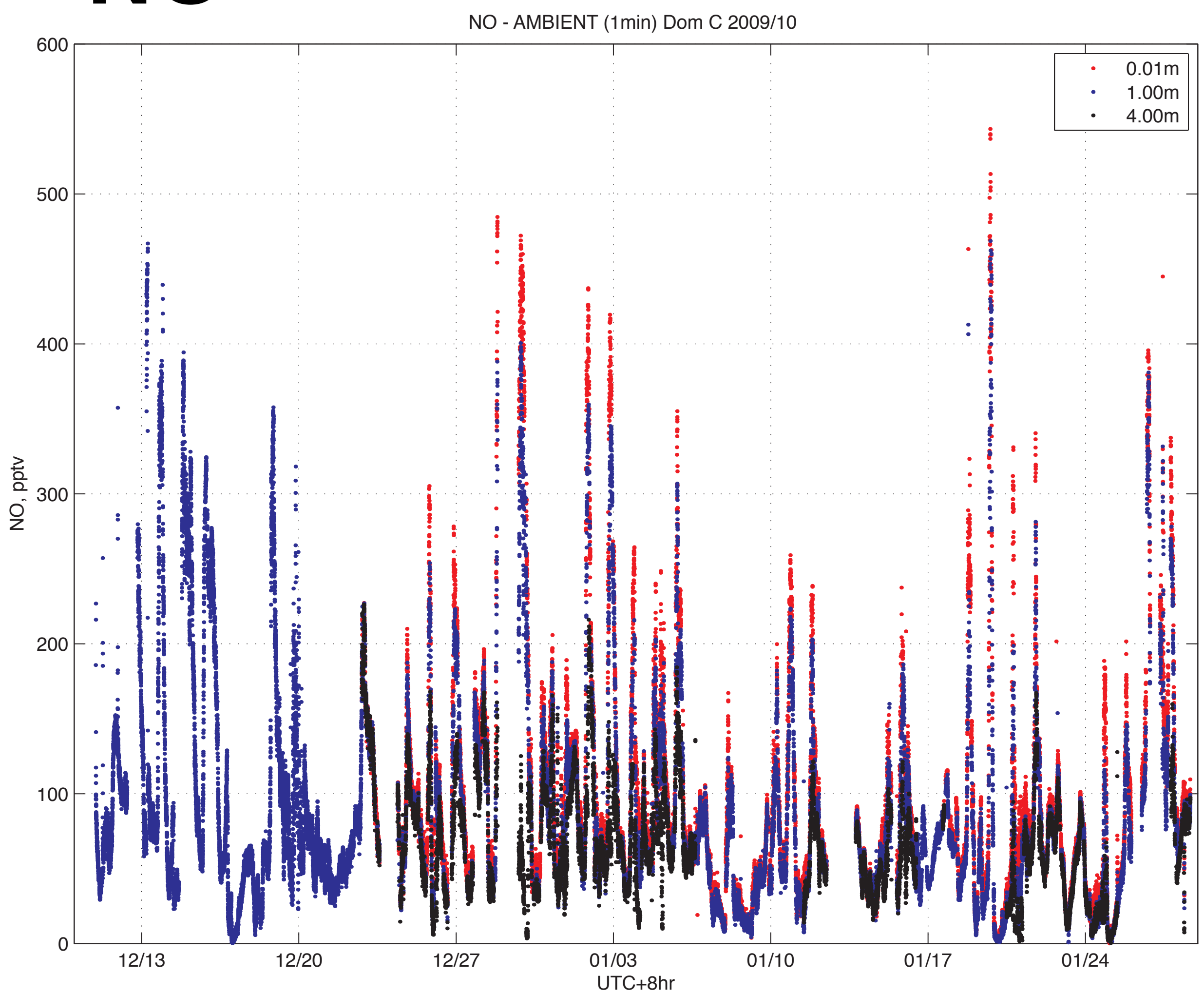
- **NO & NO_2 : 2-channel chemiluminescence analyzer**
- UV-A broadband radiometer
- T_{air} (1.0m) and T_{snow} (skin-T, profiles)
- snow NO_3^- profiles



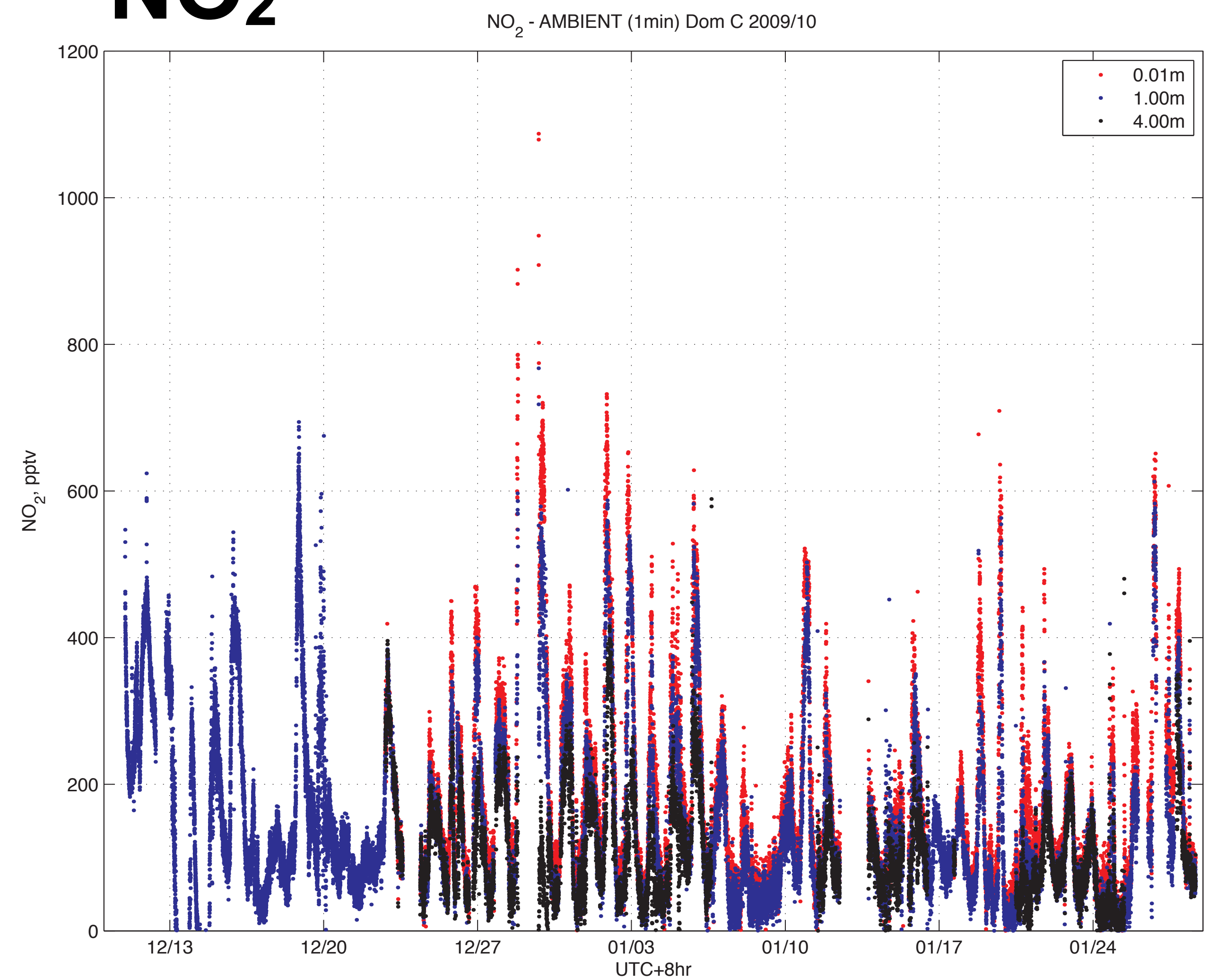
Use of UV-transparent plexi-glass as “flow inhibitor”

Dome C 10-Dec-2009 - 28-Jan 2010

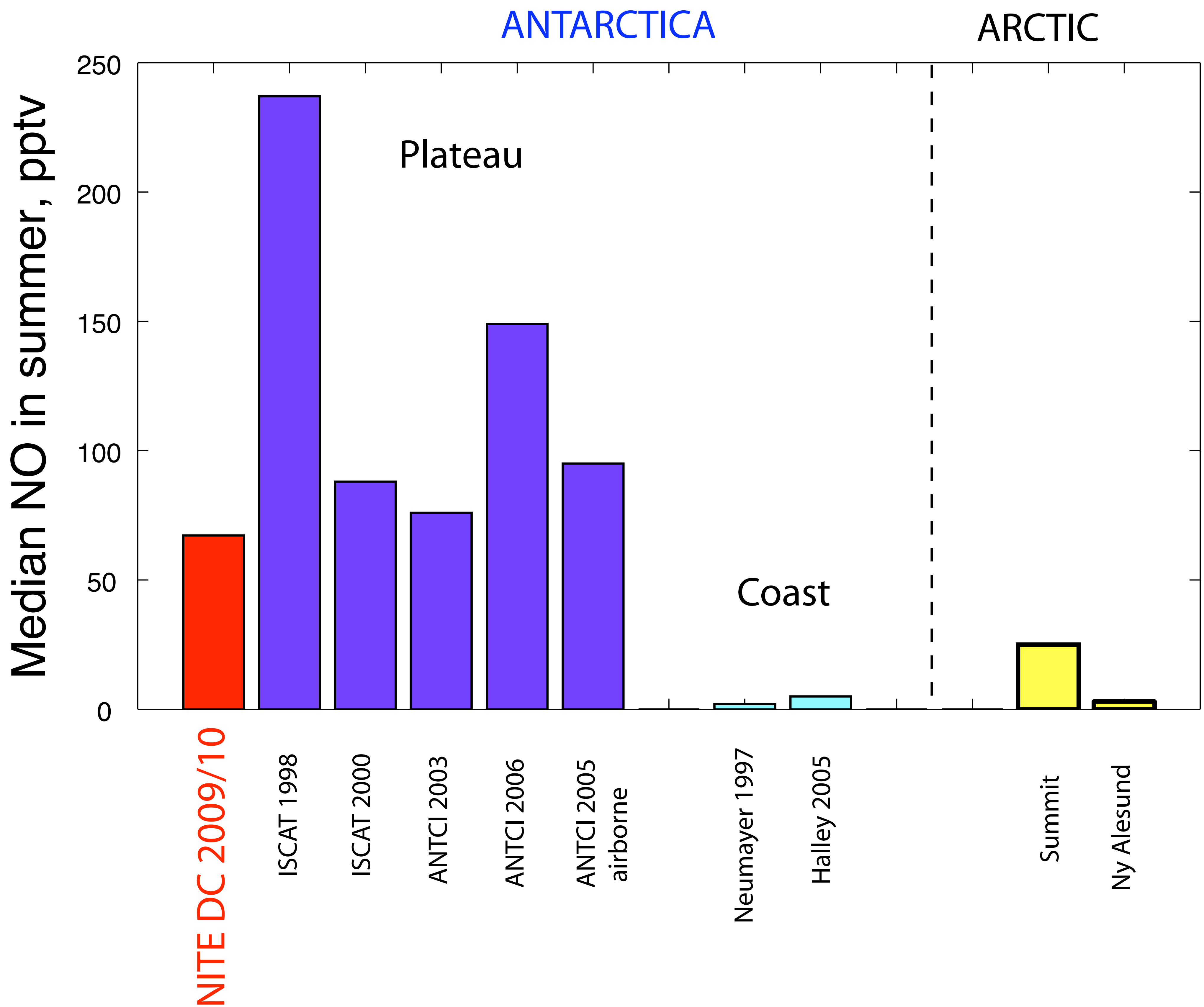
NO



NO_2



NO	NO_2
Mean±σ (median)	Mean±σ (median)
95±77 pptv (72 pptv)	166±124 pptv (124 pptv)
90±73 pptv (68 pptv)	153±115 pptv (115 pptv)
67±37 pptv (61 pptv)	110±69 pptv (93 pptv)


ANTARCTICA
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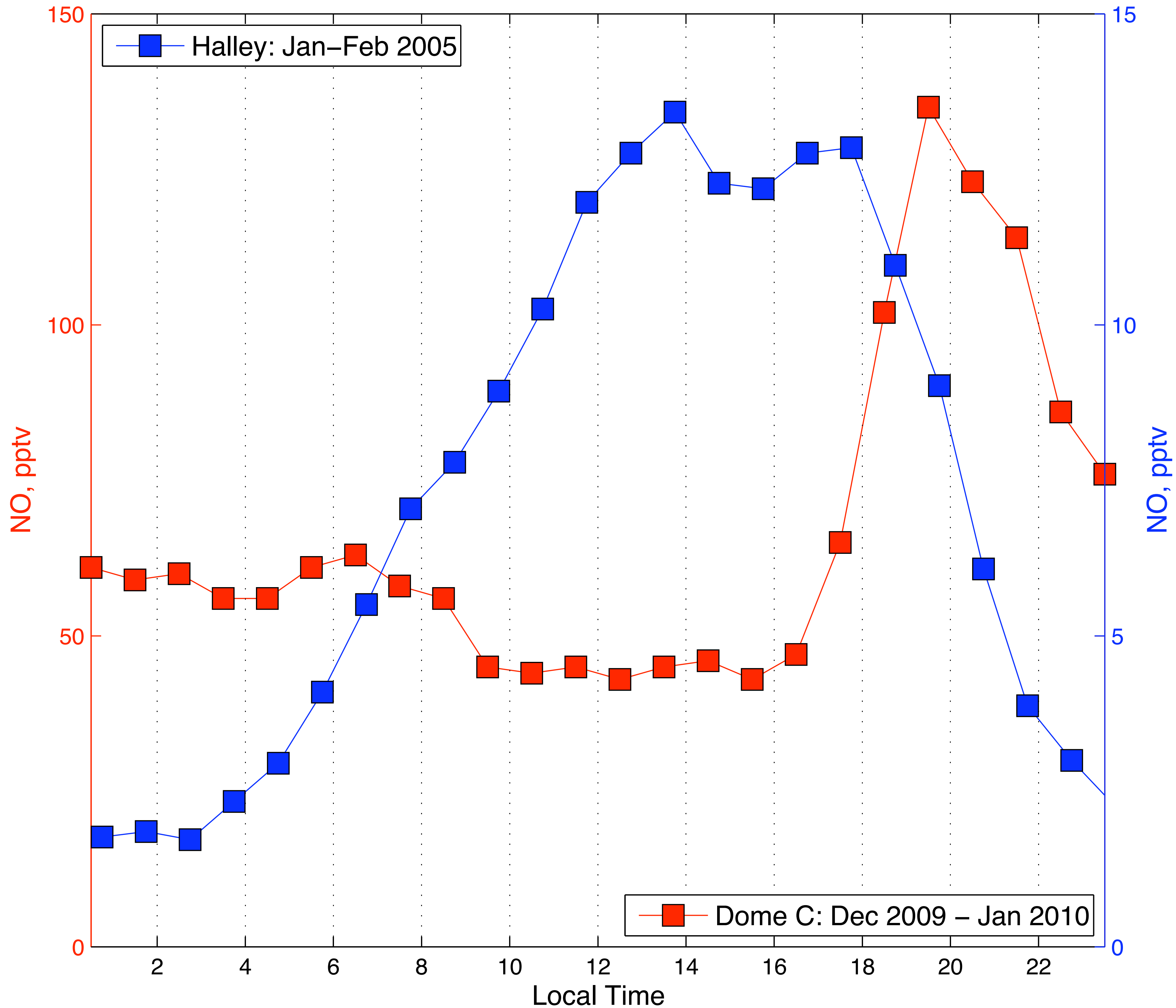
ANTCI 2006
ANTCI 2005 airborne
Neumayer 1997
Halley 2005
Summit
Ny Alesund

Diurnal Variability at Dome C: **Plateau vs. Coast Comparison at 75º S**



Differences

- absolute levels
- amplitude
- phase

COAST

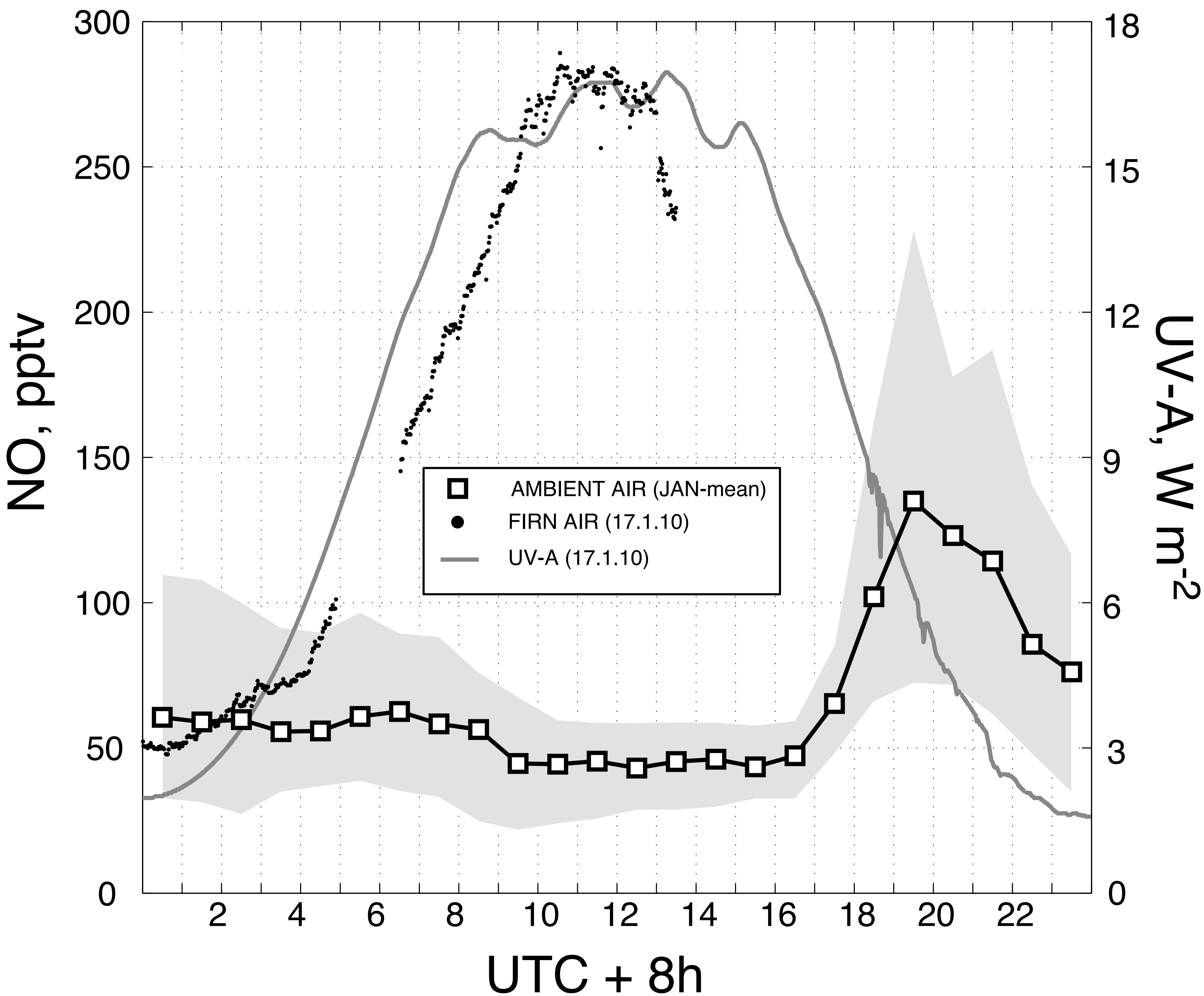
- small diurnal variability in T, wind & BL depth (max 150 m)
- NO_x lifetime controlled by halogen processing (formation & uptake of $BrNO_3$ and INO_3)
- reduced O_3 production potential

Bauguitte et al., ACPD, 2009

PLATEAU

- larger diurnal variability in T, wind & BL depth (max 350 m)

Diurnal Variability at Dome C: **Ambient vs. Firn air levels**



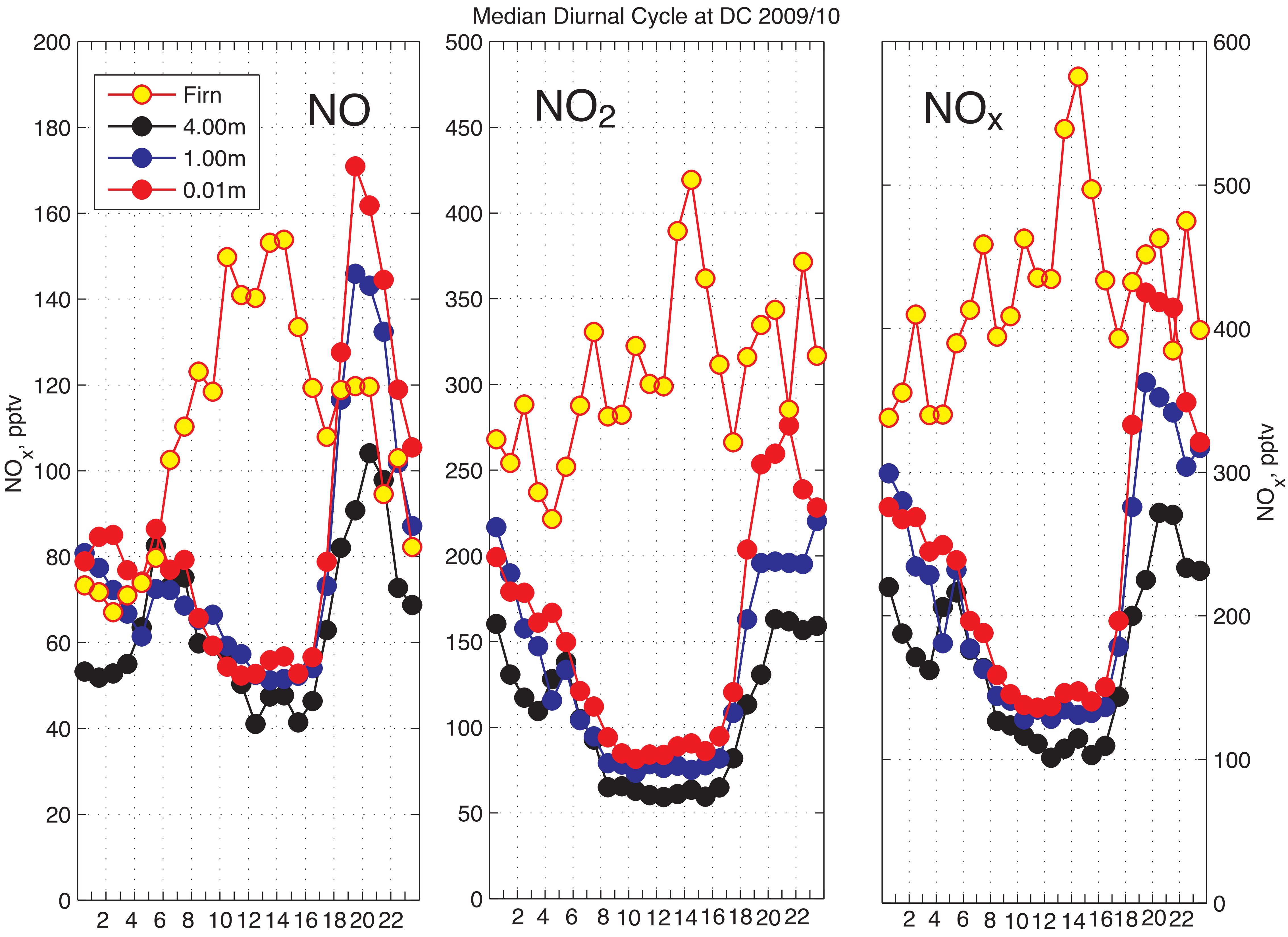
Ambient **NO** disconnected from firn air levels, i.e. the photolytic snow pack source.

Hypothesis

NO_x at surface controlled by the interplay between the **photolytic source strength** in the snow & **BL physics** above it.

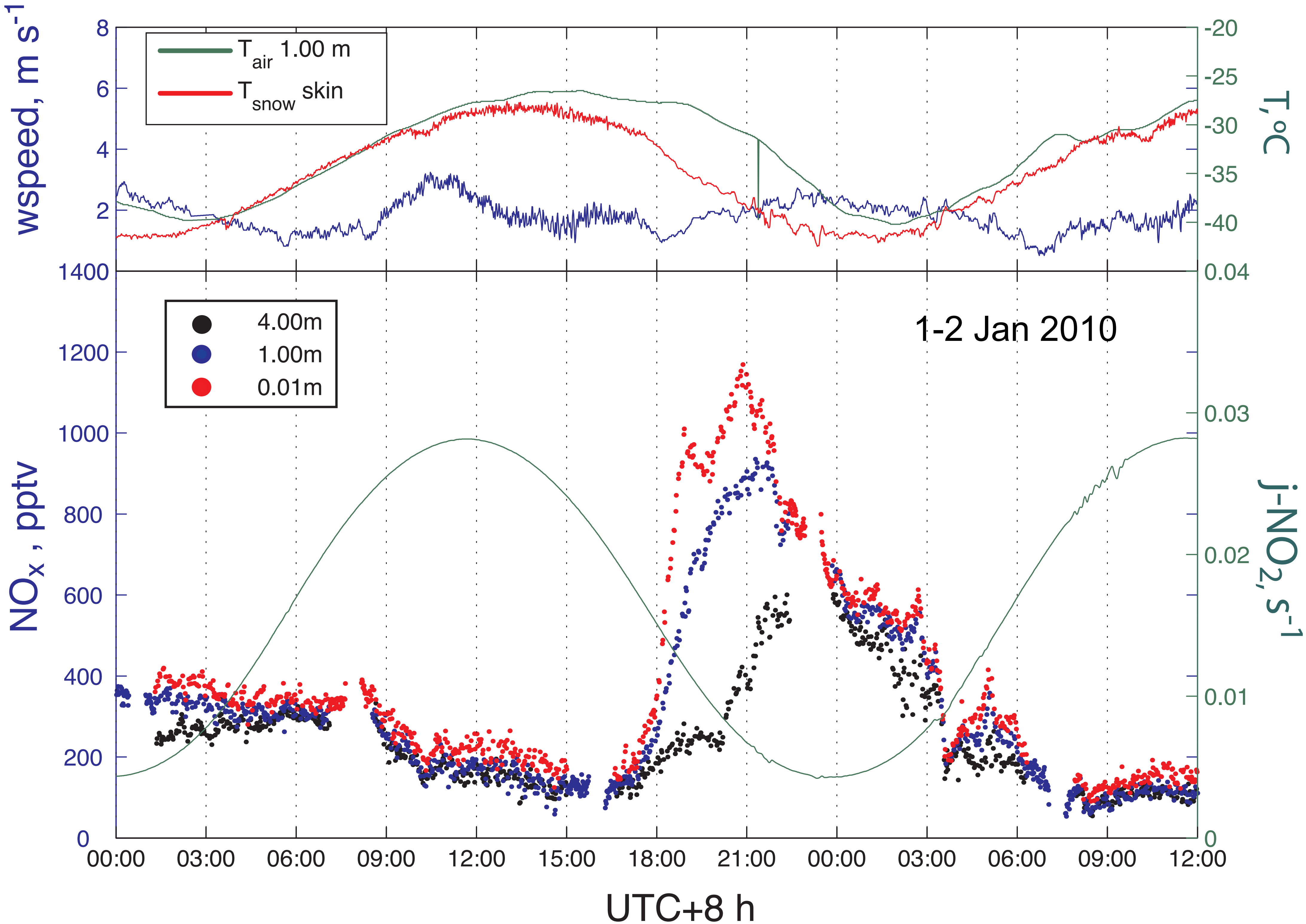
Surface inversion acts as a very shallow 'lid' keeping emissions close to the ground.

Diurnal Variability at Dome C: **Ambient vs. Firn air levels**



Frey et al., in preparation

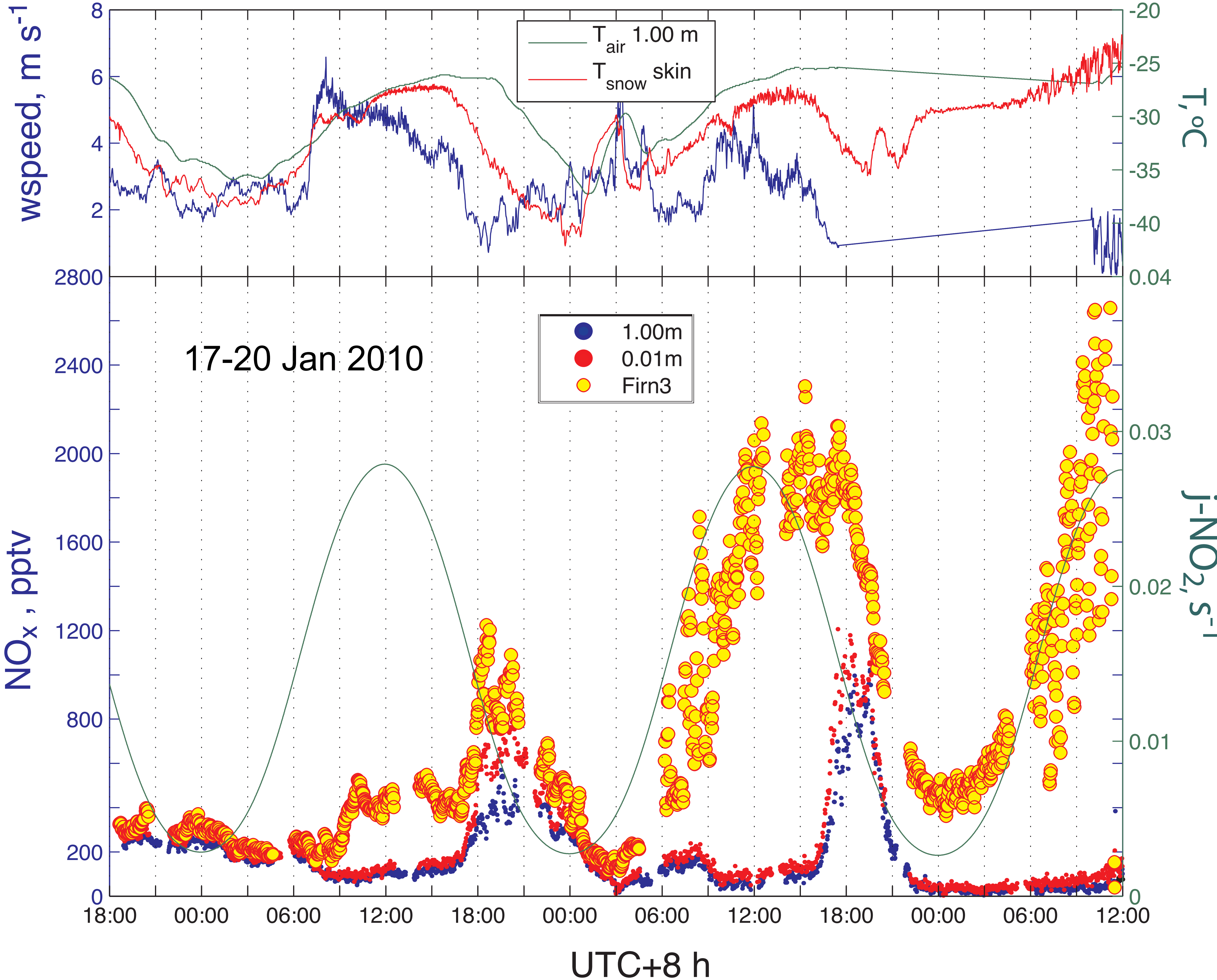
Diurnal Variability at Dome C: **Ambient NO_x at 3 levels**



→ Build up of NO emissions above a strongly cooling snow surface

→ Concentration gradients follow temperature gradients

Diurnal Variability at Dome C: **Ambient & Firn NO_x**



NOx reservoir?

Diurnal Variability of Boundary Layer Depth at Dome C

- daily build-up of a convective BL (~350m)
- decay of CBL between 17-18 LT
- shallow nocturnal layer (<50m), likely stable stratification

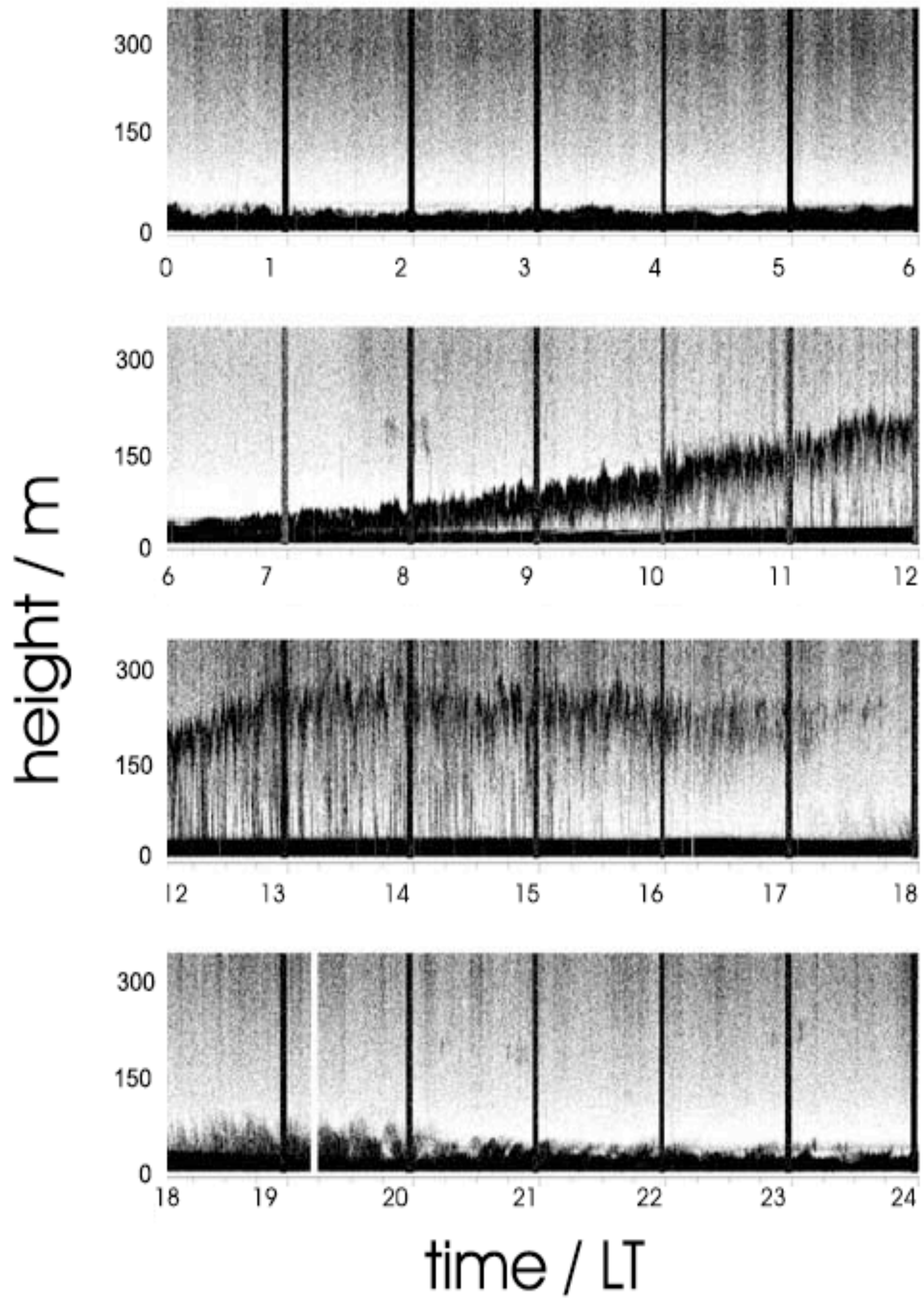


Figure 4a. Sodar record for Dome C, 28 January 1999. Time axis is local time.

King & Argentini (JGR, 2006)

Diagnostic analysis of atmospheric turbulence - **Bulk Richardson Number**

$$R_{ib} = \frac{g[\theta_v(z_r) - \theta_v(z_0)](z_r - z_0)}{\theta_v(z_0)[u(z_r)^2 + v(z_r)^2](z_r - z_0)}$$

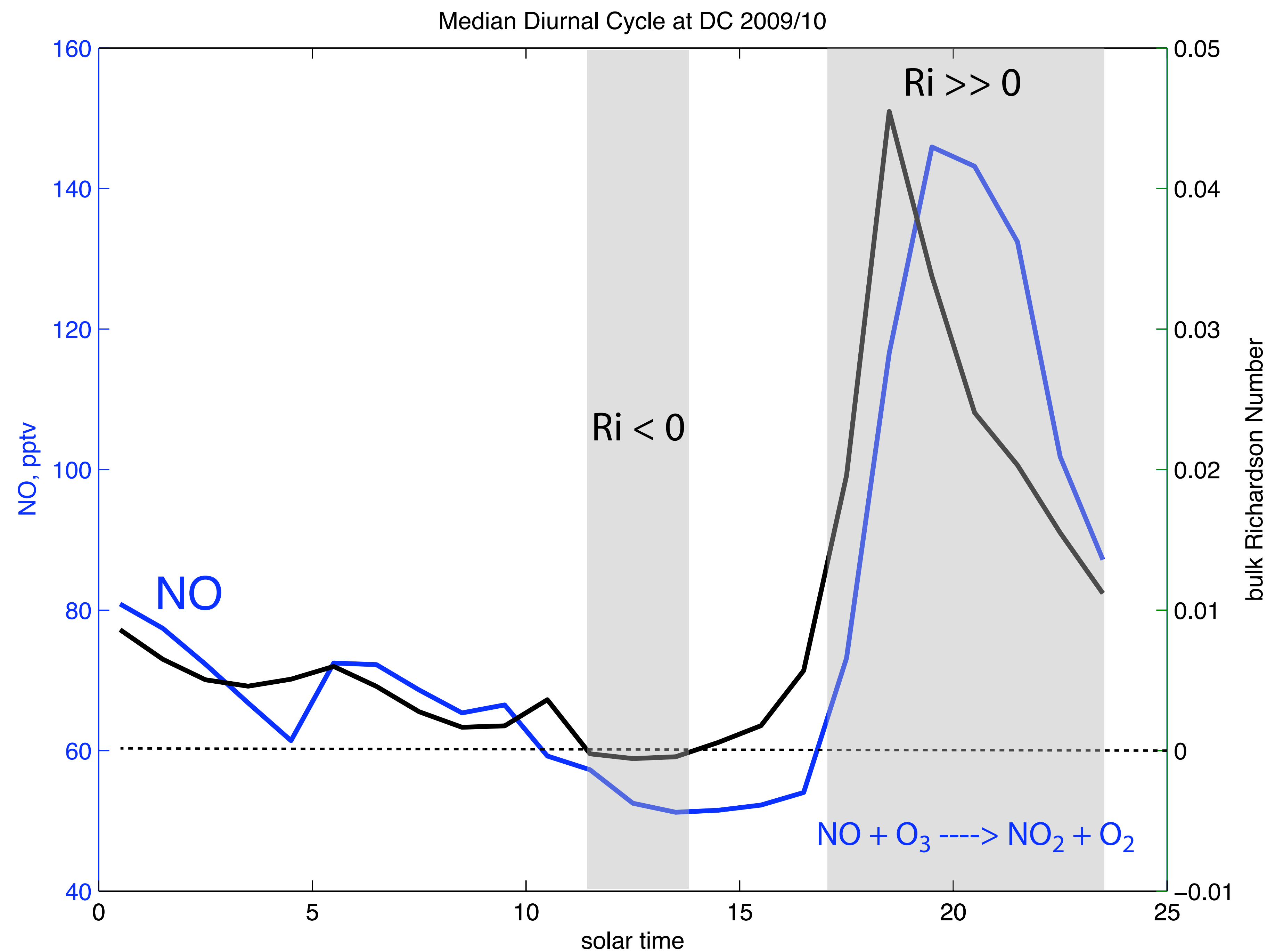
$$R_{ib} = \frac{\textbf{\textit{buoyancy (free convection)}}}{\textbf{wind shear (forced convection)}}$$

Diagnostic analysis of atmospheric turbulence - Bulk Richardson Number

R_i > 0
atmosphere buoyantly stable,
no turbulence due to convection
only due to wind shear

R_i >> 0
no turbulence due to forced or free convection

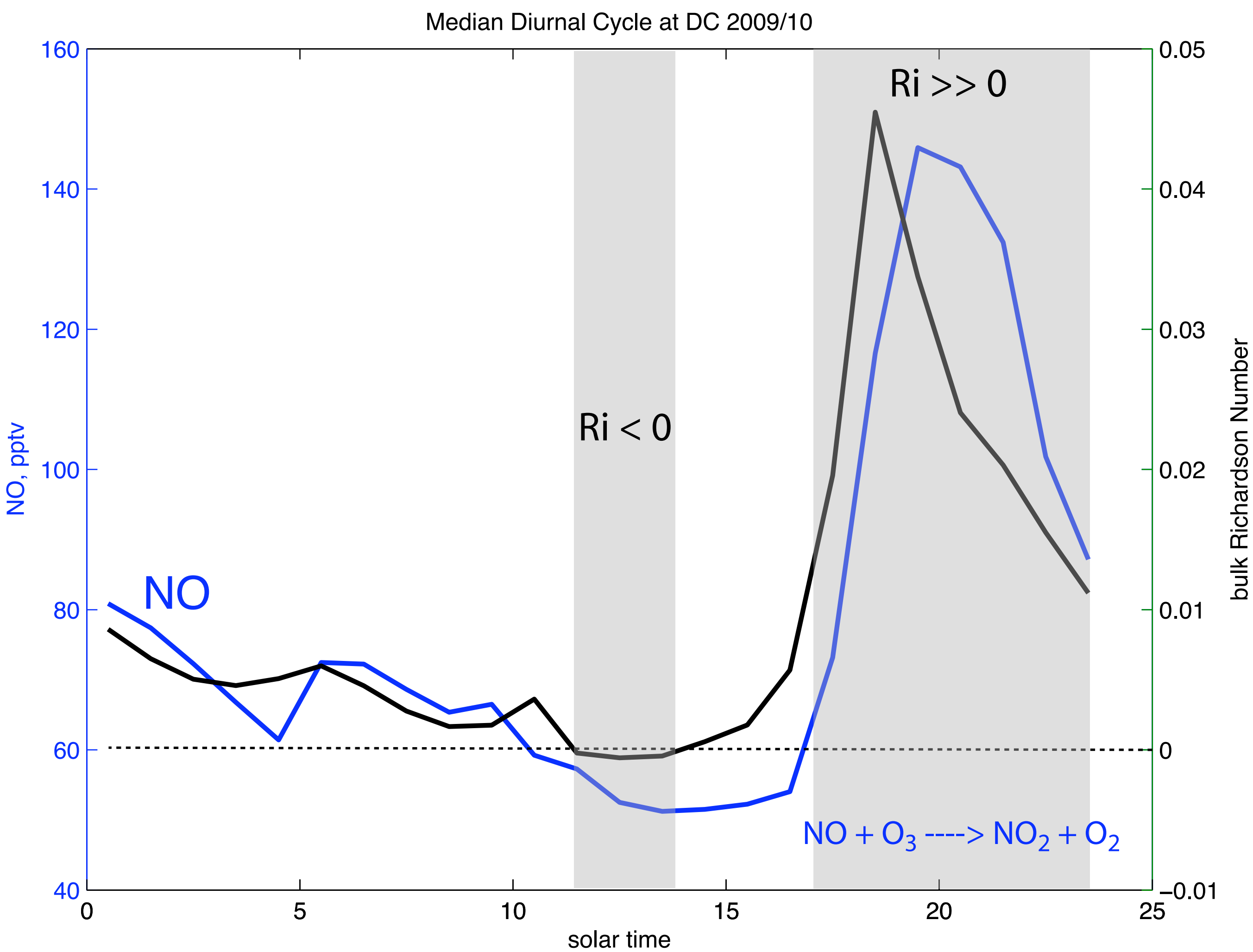
R_i < 0
buoyantly unstable & turbulent



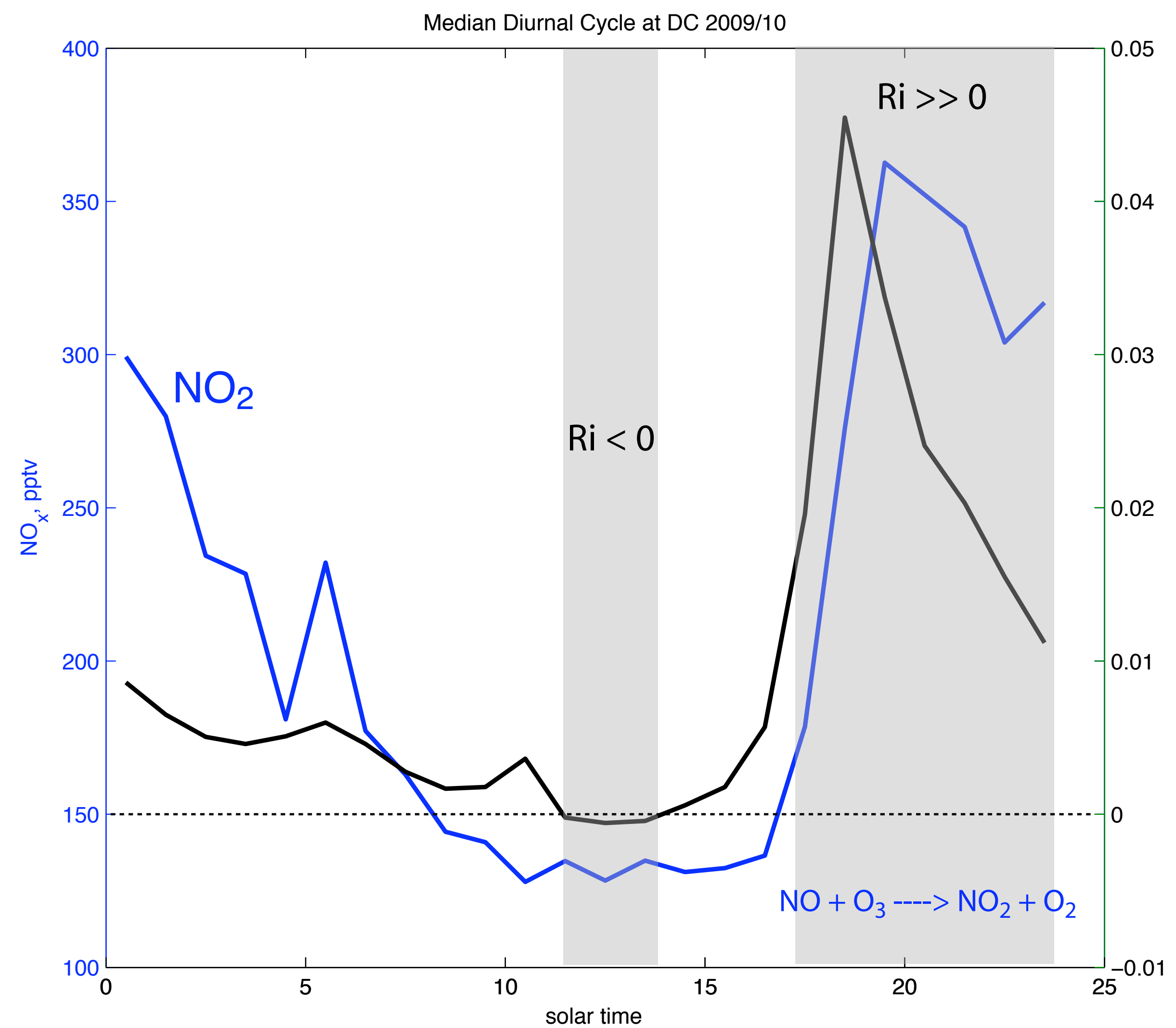
Frey et al., in preparation

Diagnostic analysis of atmospheric turbulence - **Bulk Richardson Number**

NO

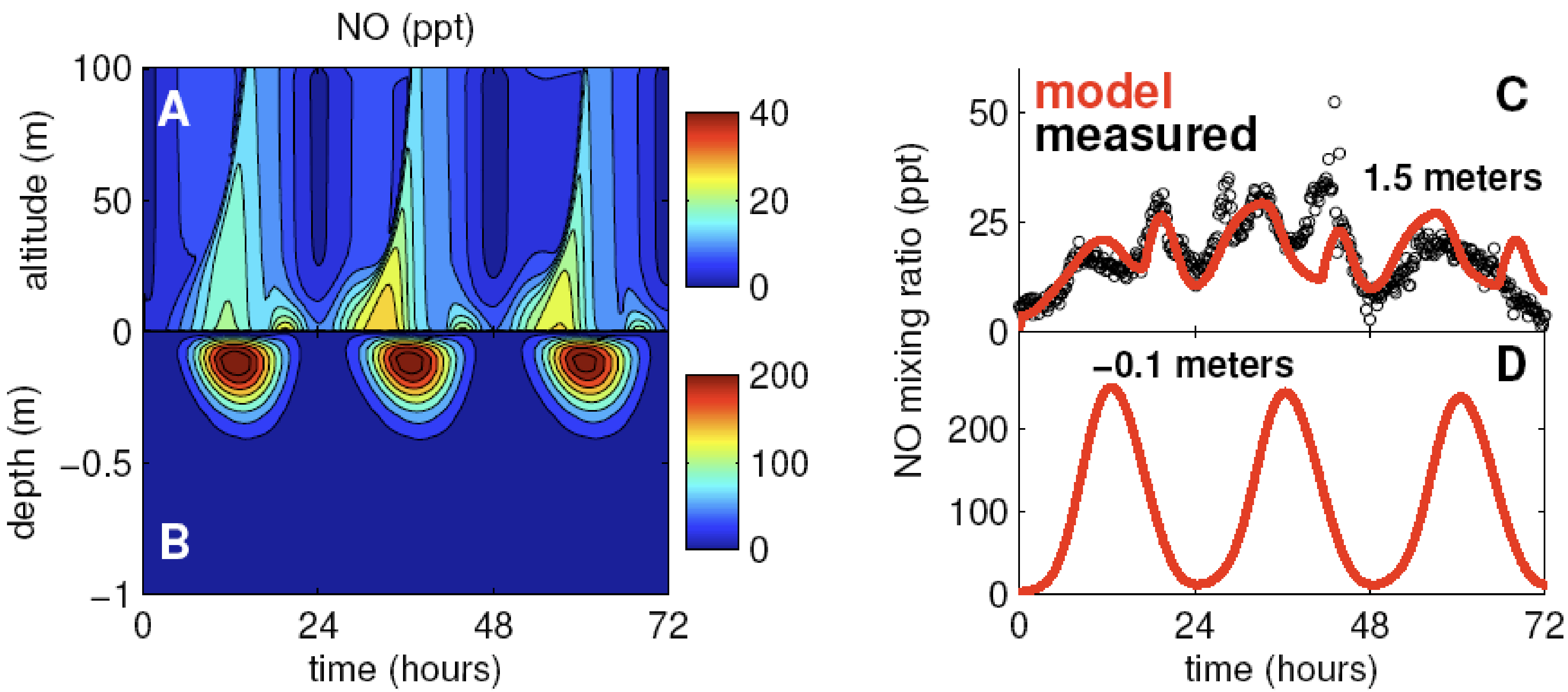


NO_2

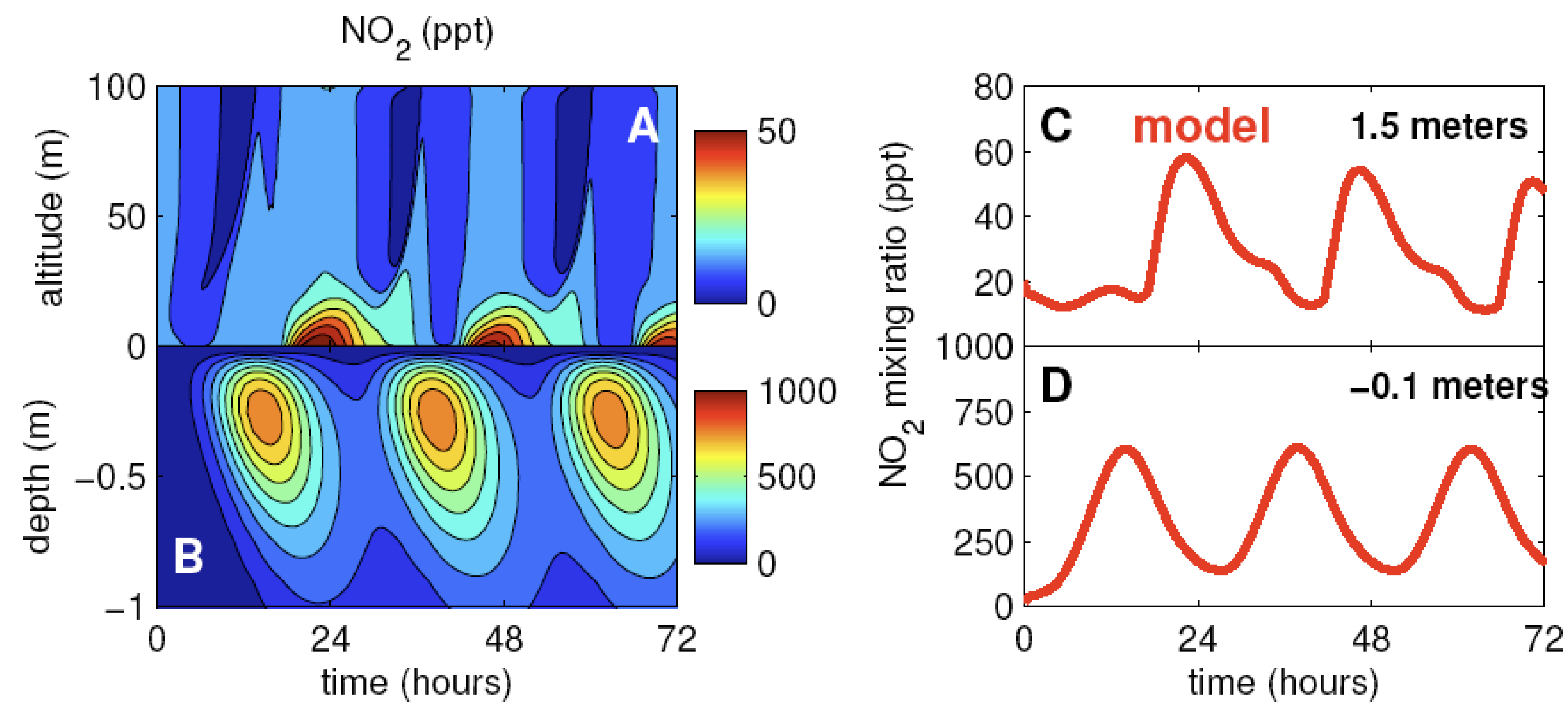


Comparison to Summit, Greenland

Thomas et al., ACP, 2011

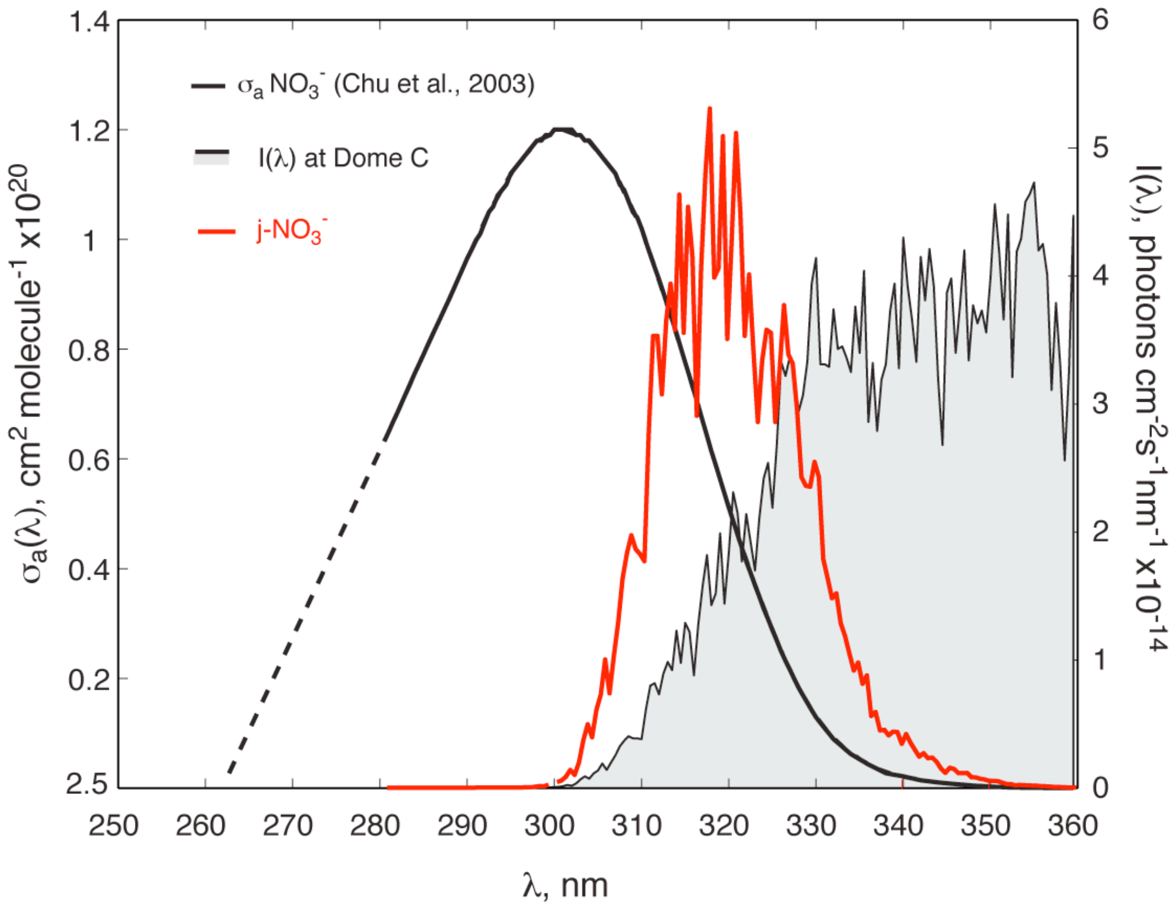


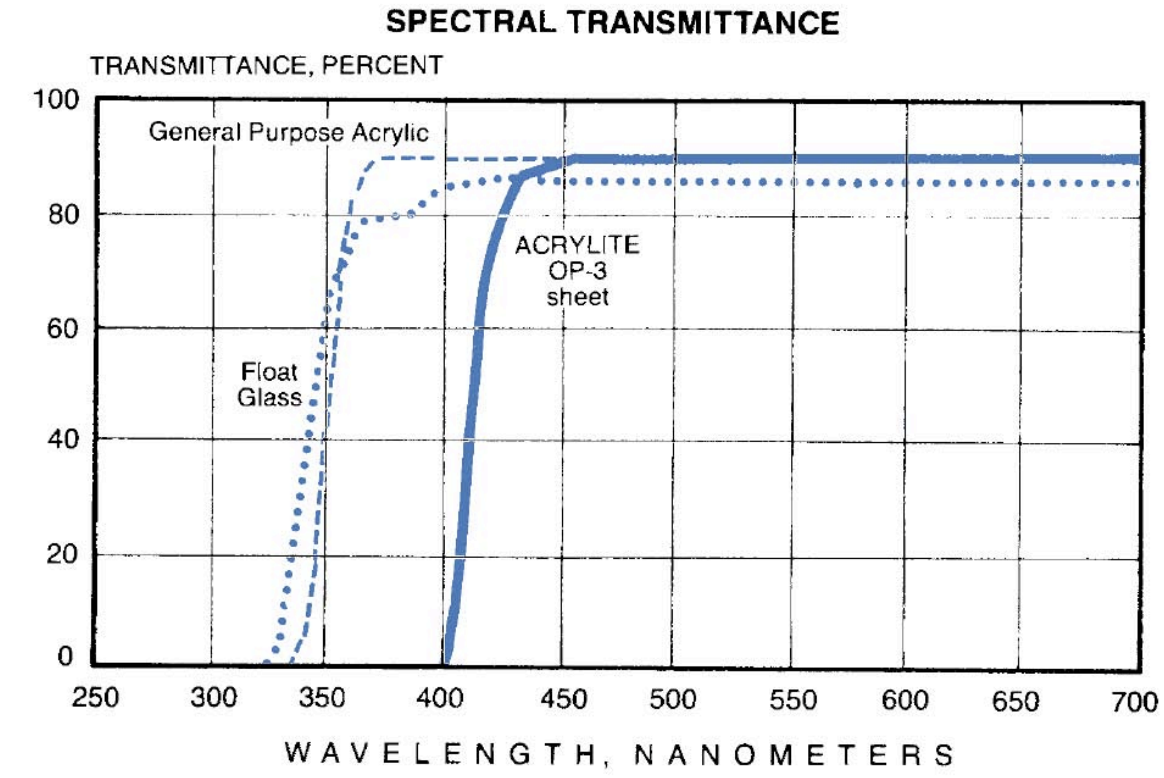
NO



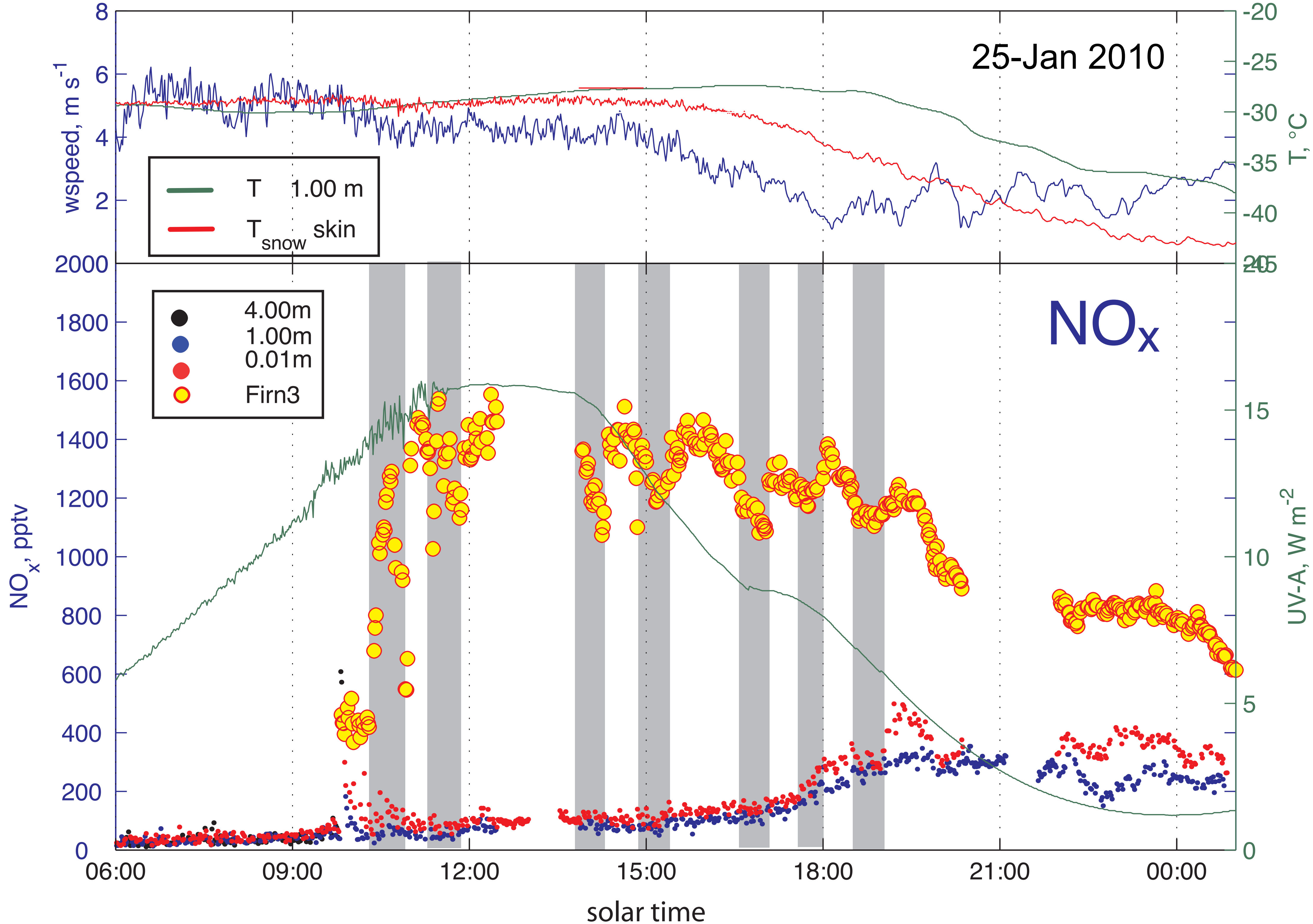
NO_2

UV Filter Experiments



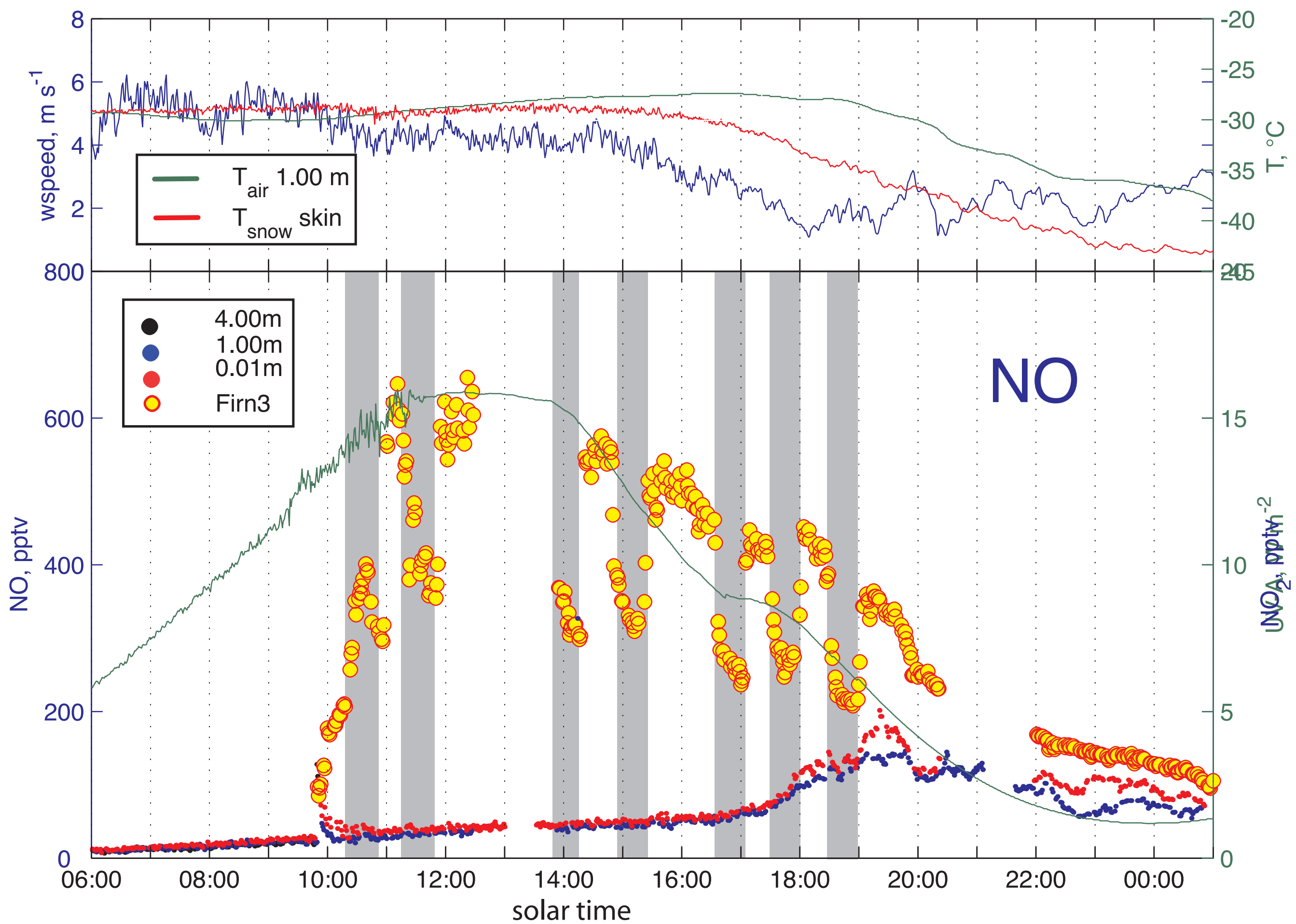


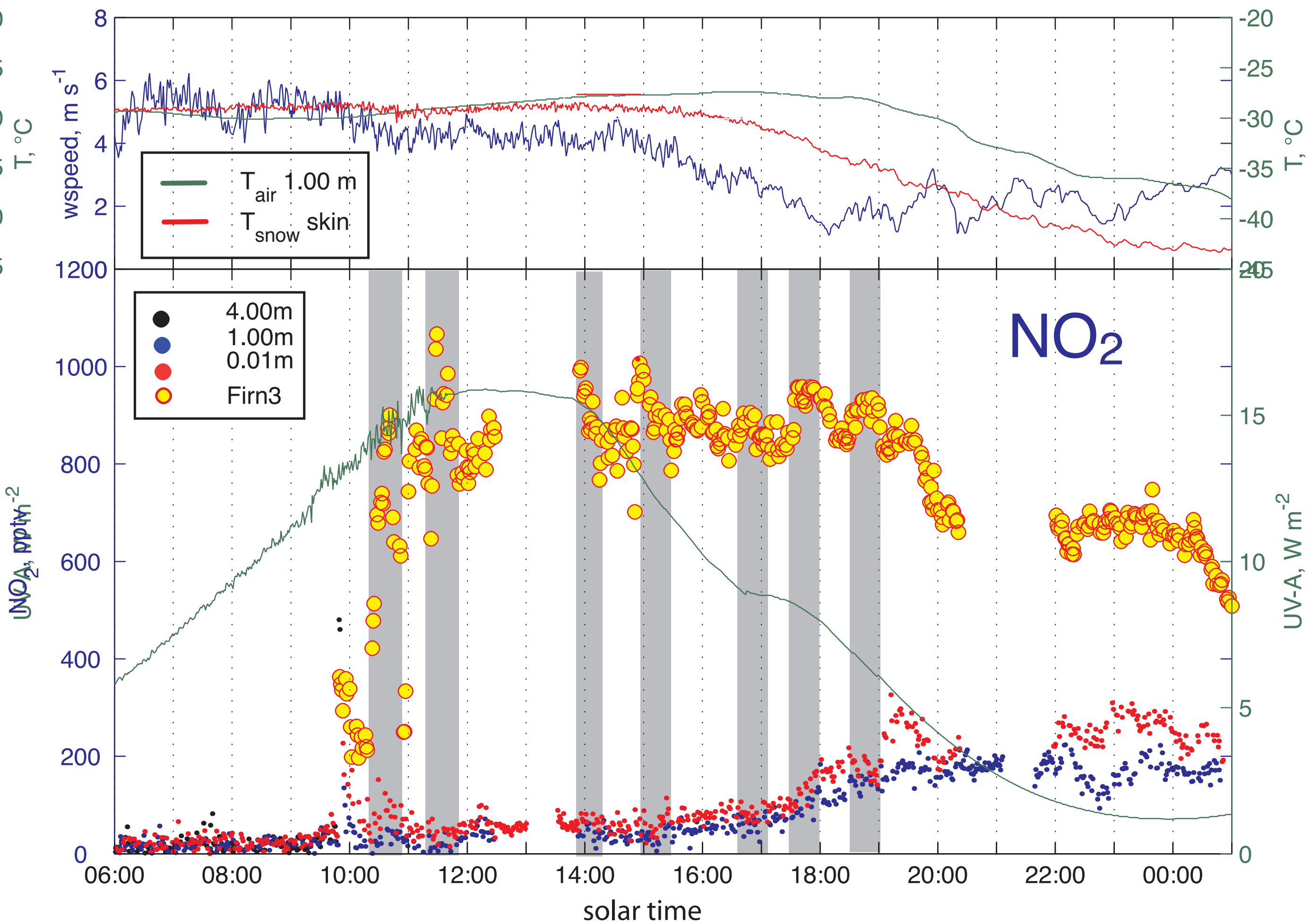
UV Filter Experiments



UV Filter Experiments

NOx reservoir?





UV-Filter 'off'

$NO_2 + h\nu \rightarrow NO + O(^3P)$

$NO + O_3 \rightarrow NO_2 + O_2$

UV-Filter 'on'

~~$NO_2 + h\nu \rightarrow NO + O(^3P)$~~

$NO + O_3 \rightarrow NO_2 + O_2$

Comparison of observed NO_x flux with model estimates

A. Estimate **NO_x flux** from concentration gradient observations; assume neutral BL

$$F = -K \frac{\partial c}{\partial z} \quad (1)$$

Flux **F** between 0.01 & 1.00 m

$$K(z) = \kappa \, z \, u^* \quad (2)$$

Eddy diffusivity **K**

$$\frac{\kappa \, u(z)}{u^*} = \ln\left(\frac{z}{z_0}\right) \quad (3)$$

Friction velocity **u^***

B. Model **NO_2 flux** (France et al., ACPD, 2011)

Input

Observed snow profiles of albedo, irradiance & NO_3^-

→

Radiation Transfer Model (TUV-Snow)

photolysis rate

$$\mathbf{j} = \int \sigma_a(\lambda)\, \phi(\lambda)\, I(\lambda)\, d\lambda$$

→

Output

depth-integrated potential emission flux of NO_2

- **e-fold depth 10-20 cm!!**

- **no cage effect**
- **immediate venting to surface**

Comparison of observed NO_x flux with model estimates

1) Observed F-NO_2 > Model

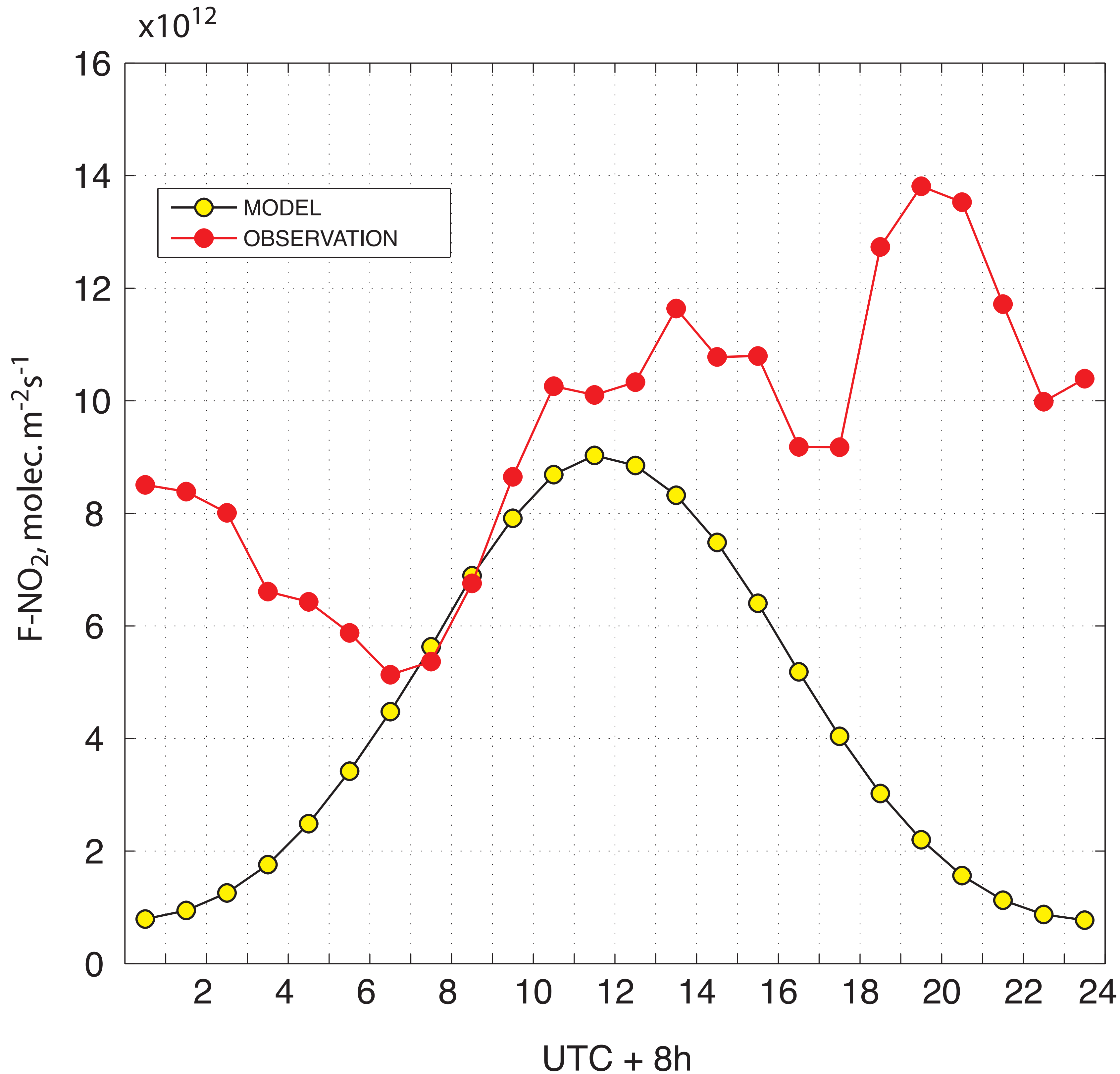
contribution from surface adsorbed HNO_3 photolysis at cold temperatures

- no cage effect
- quantum yield 0.6 (Zhu, 2010)
- supported by isotopic evidence

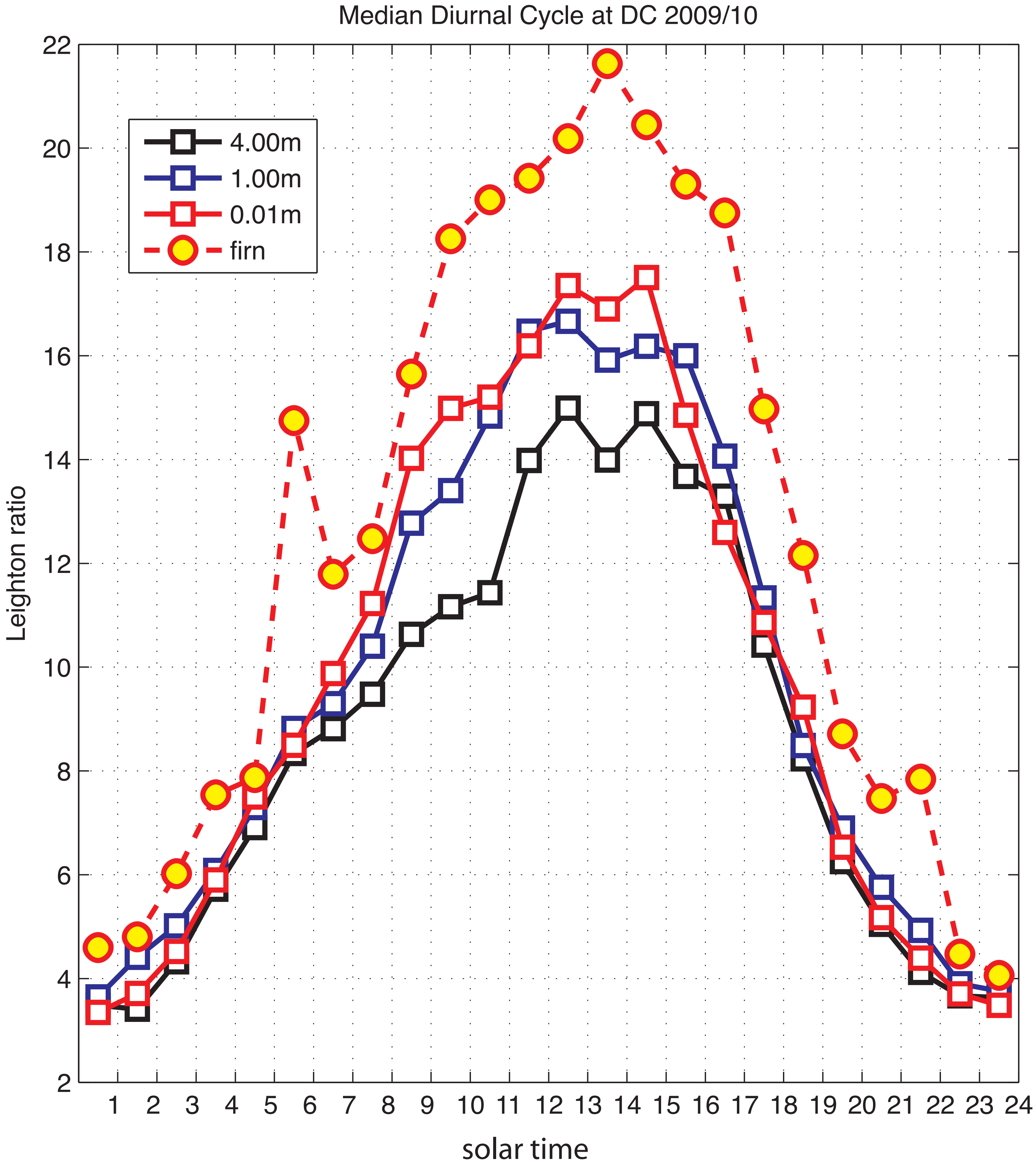
2) Different variability

10-20% uncertainty in observed F-NO_2 in stable BL

venting of the NO_x firn air reservoir in the evening?



Devation from PSS



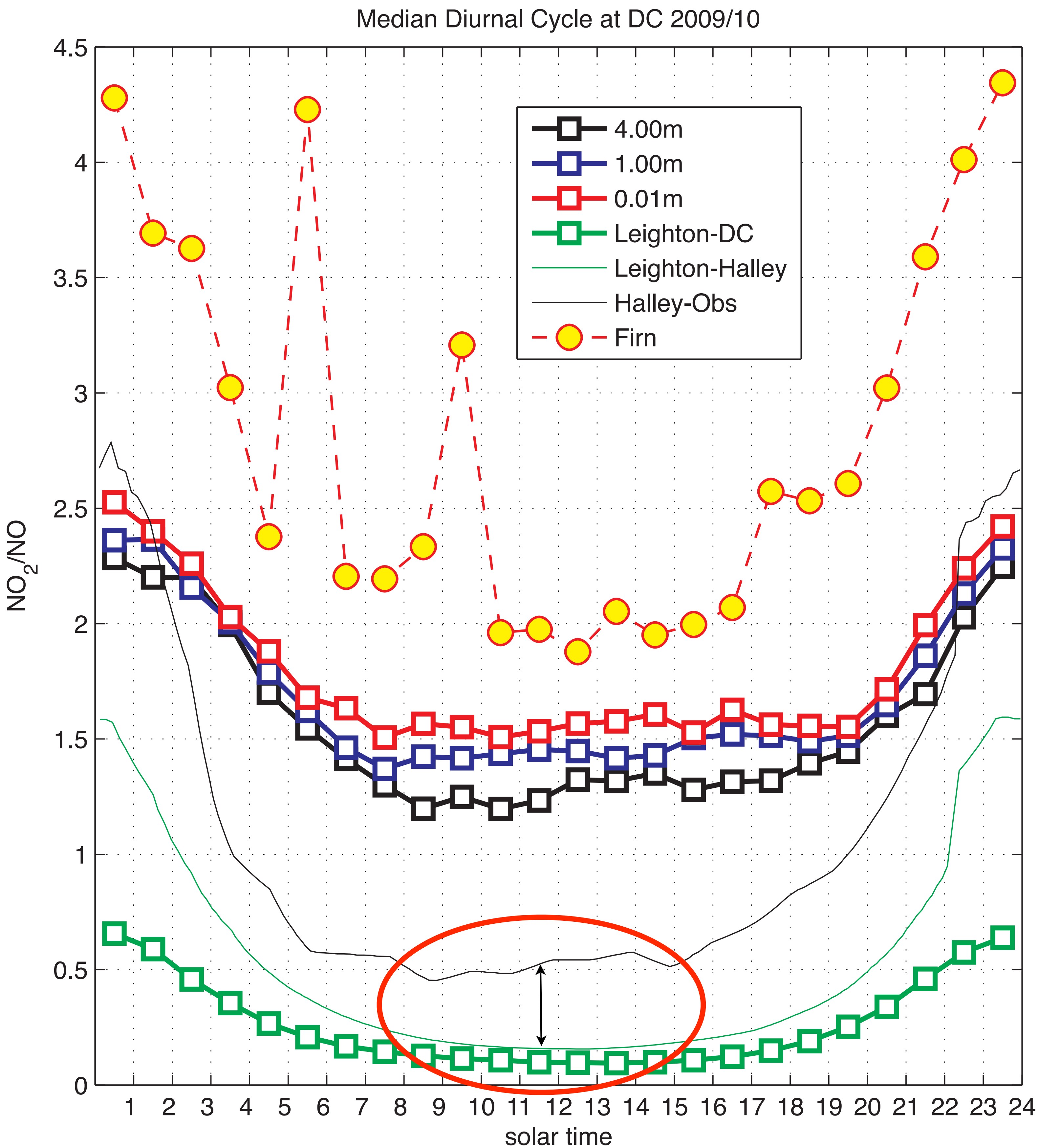
Leigthon Ratio

$$\phi = \frac{j_{NO_2}[NO_2]}{k[O_3][NO]}$$

Φ > 1

- HO_2 + RO_2
- XO
- O_3 loss other than O_3+NO
- other NO_2 sources (PNA, snow emissions ...)

Devation from PSS



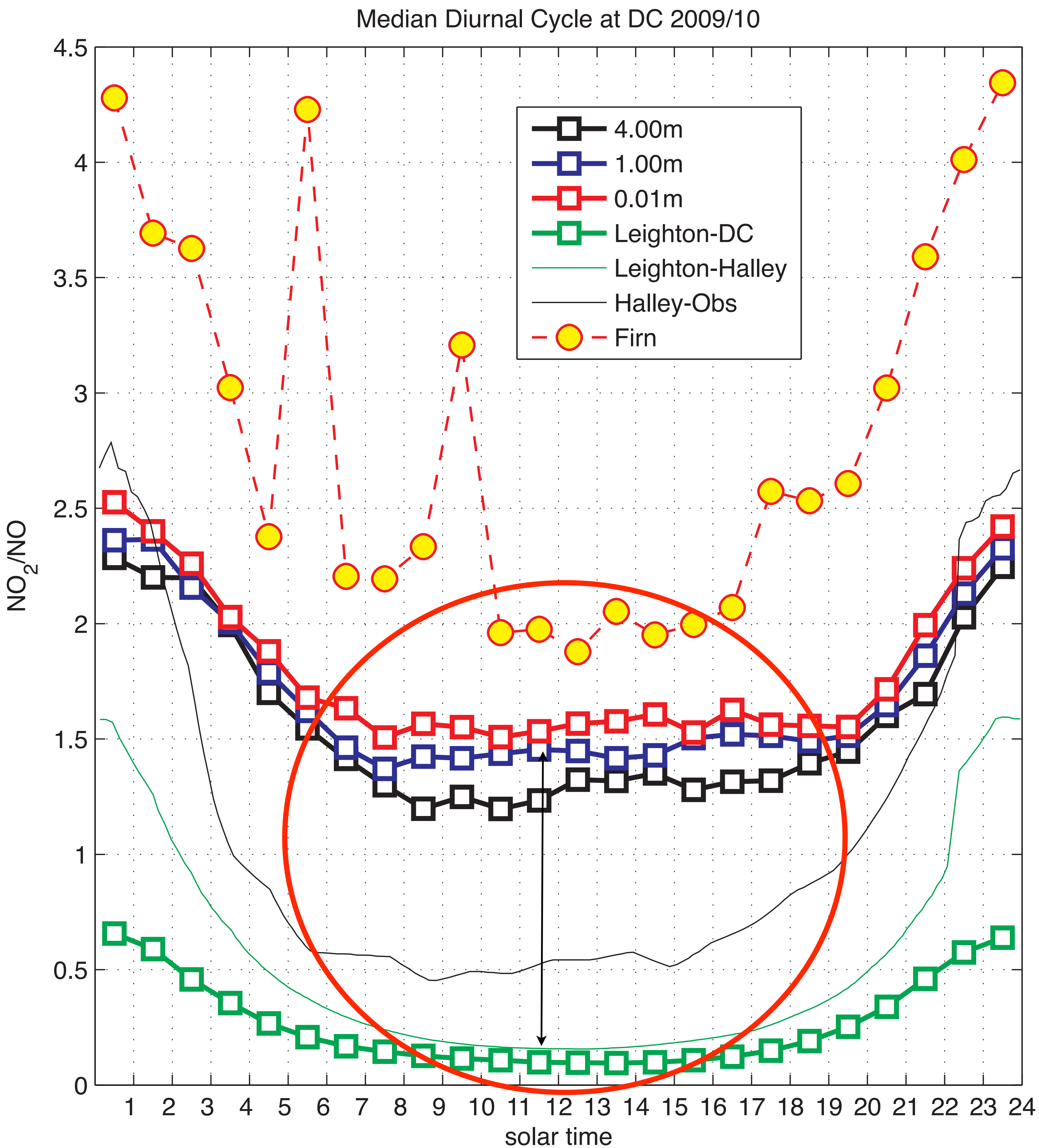
$\Phi > 1$

- $HO_2 + RO_2$
- XO
- O_3 loss other than O_3+NO
- other NO_2 sources (PNA, snow ...)

Halley

IO (0.5-4.3 pptv)

BrO (1.4-3.8 pptv)



Devation from PSS

Φ > 1

- $HO_2 + RO_2$
- XO
- O_3 loss other than O_3+NO
- other NO_2 sources (PNA, snow ...)

Dome C

- high HO_2 (2.8×10^9 molec. cm^{-3})
  Spole 2.3×10^7 molec. cm^{-3}
  Summit 2.8×10^8 molec. cm^{-3}
- snow NO_2 emission
- IO + BrO ??

CONCLUSIONS & PERSPECTIVES

• Confirmation of 'anomalously' high NO & NO_2 above EAIS

• NO_x diurnal variability controlled by BL physics (convection & wind shear)
applicable to other trace chemical species; more collaboration between atmospheric chemists & BL physicists

• Firn air obs suggest existence of a NO_x reservoir
vertical extent? more firn air measurements, comparison to 1-D snow-atmo models, ice core interpretation

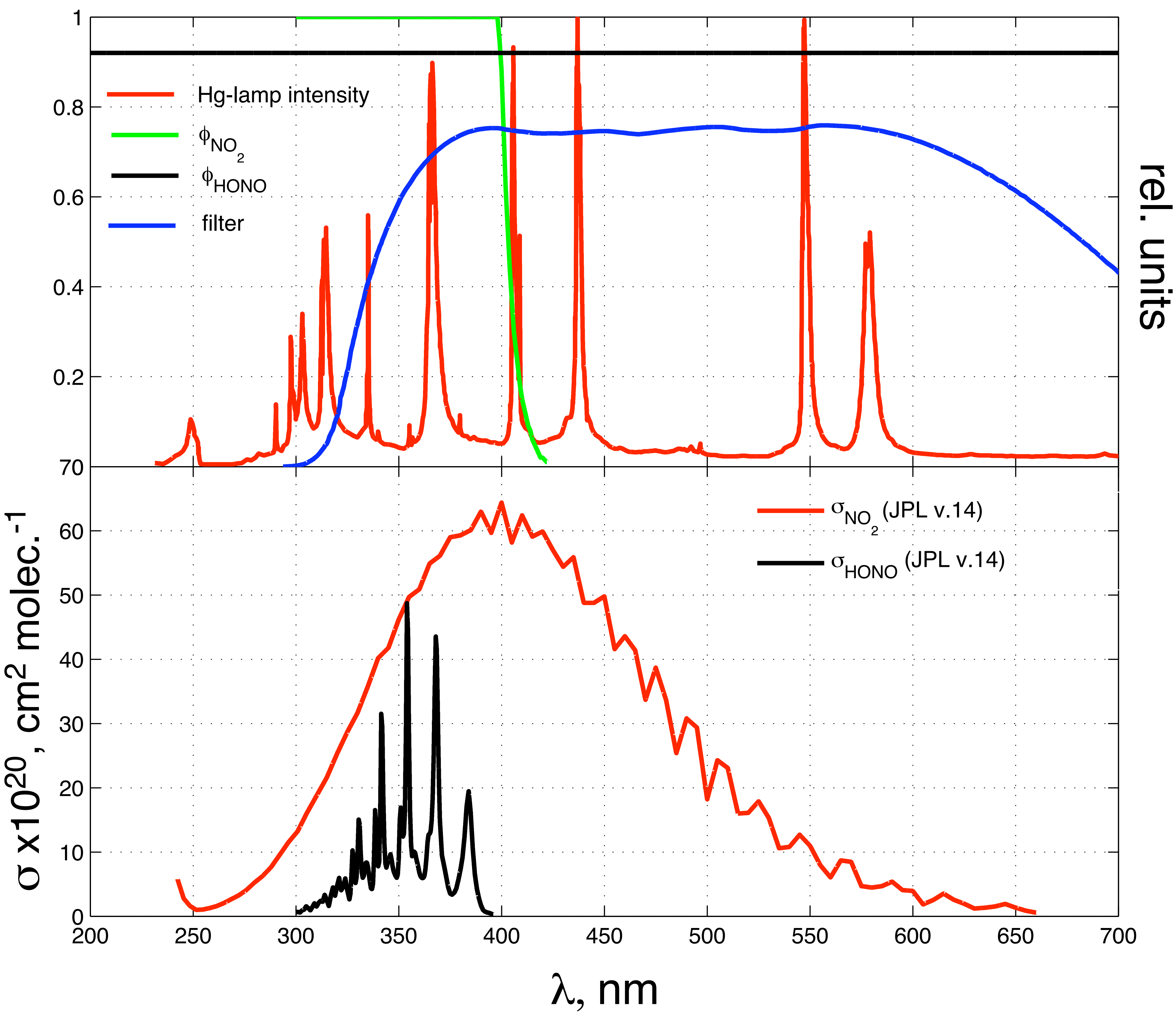
• PSS analysis indicates high oxidant levels & importance of flux for NO_2 : NO

• Observed F-NO_2 > model:
a) photolysis might still explain >90% NO_3^- loss from snow at DC
b) insufficient understanding of processes, i.e. total photolysis rate
lab studies, use of stable isotopes to identify process

Photolytic conversion of NO_2: interference by HONO

BAS detector - optical set up

Absorption Cross Sections



Photolytic conversion of NO_2: interference by HONO

South Pole

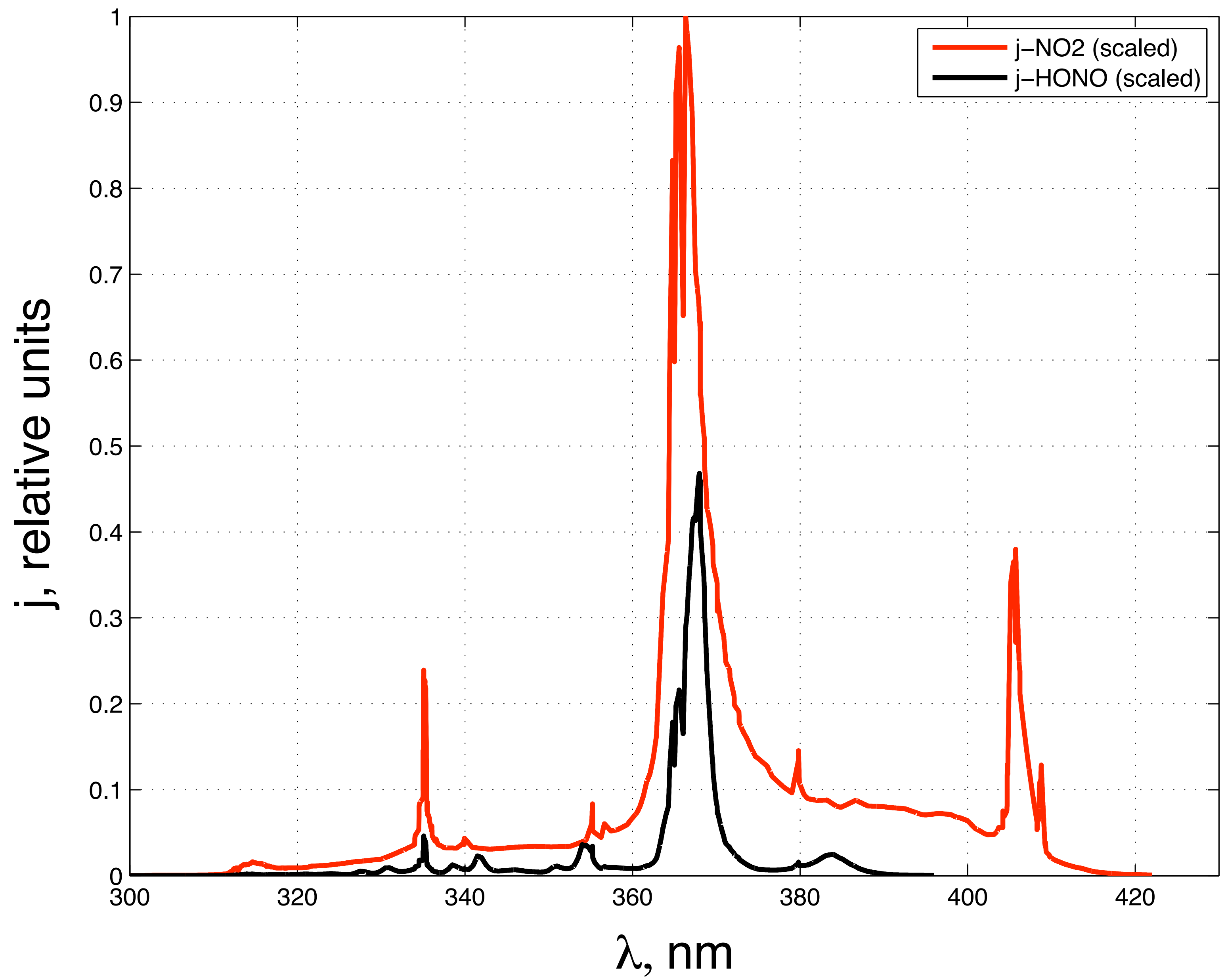
HONO with LIF
6-18 pptv

(Liao et al., GRL, 2006)

Dome C

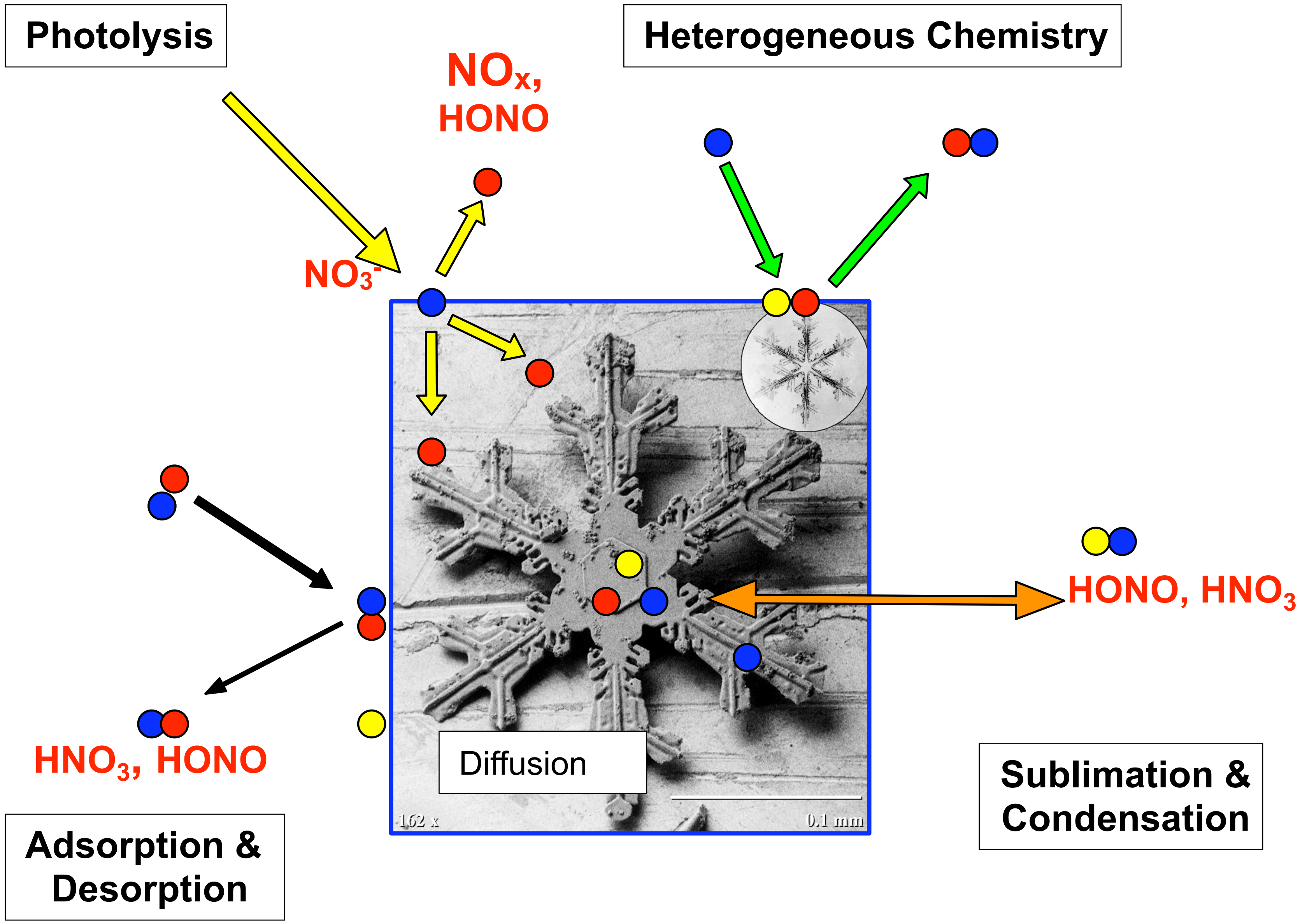
NO_2 overestimate by 1-4 pptv

(e.g. 0.7-2.6%)



j-HONO / j-NO_2 = 0.22

Reactive nitrogen cycling at the snow grain scale



physical & (photo)chemical processes

- physical properties of snowpack & snowgrain
- location of impurities

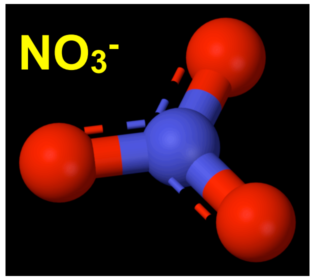
Oxidant Formation

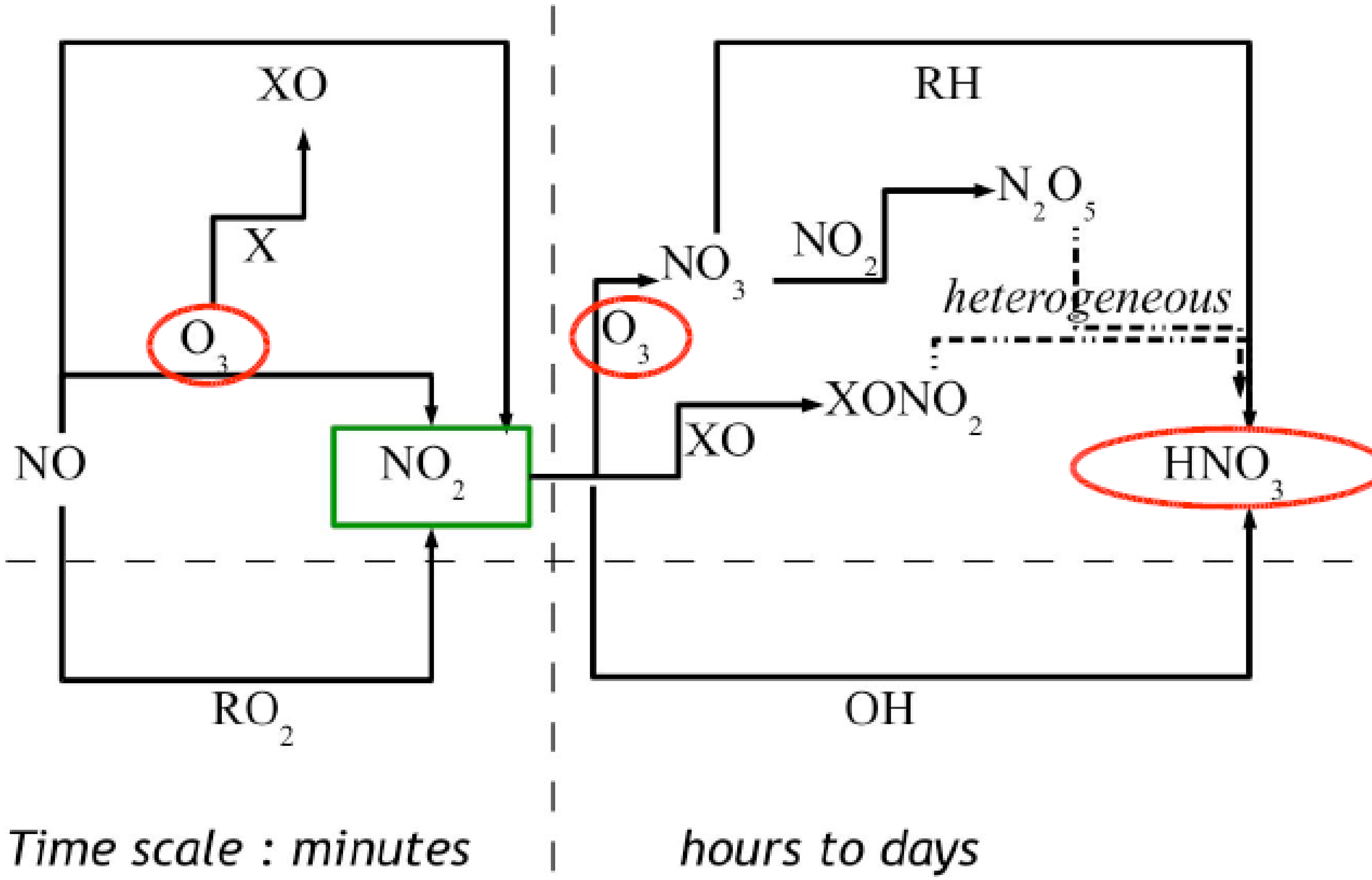
$O^- + H^+ \rightarrow$ **OH**
$O(^3P) + O_2 \rightarrow$ **O_3**
OH, O_3, $O(^3P)$ + DOM → carbonyl compounds

Nitrate Photolysis in Snow

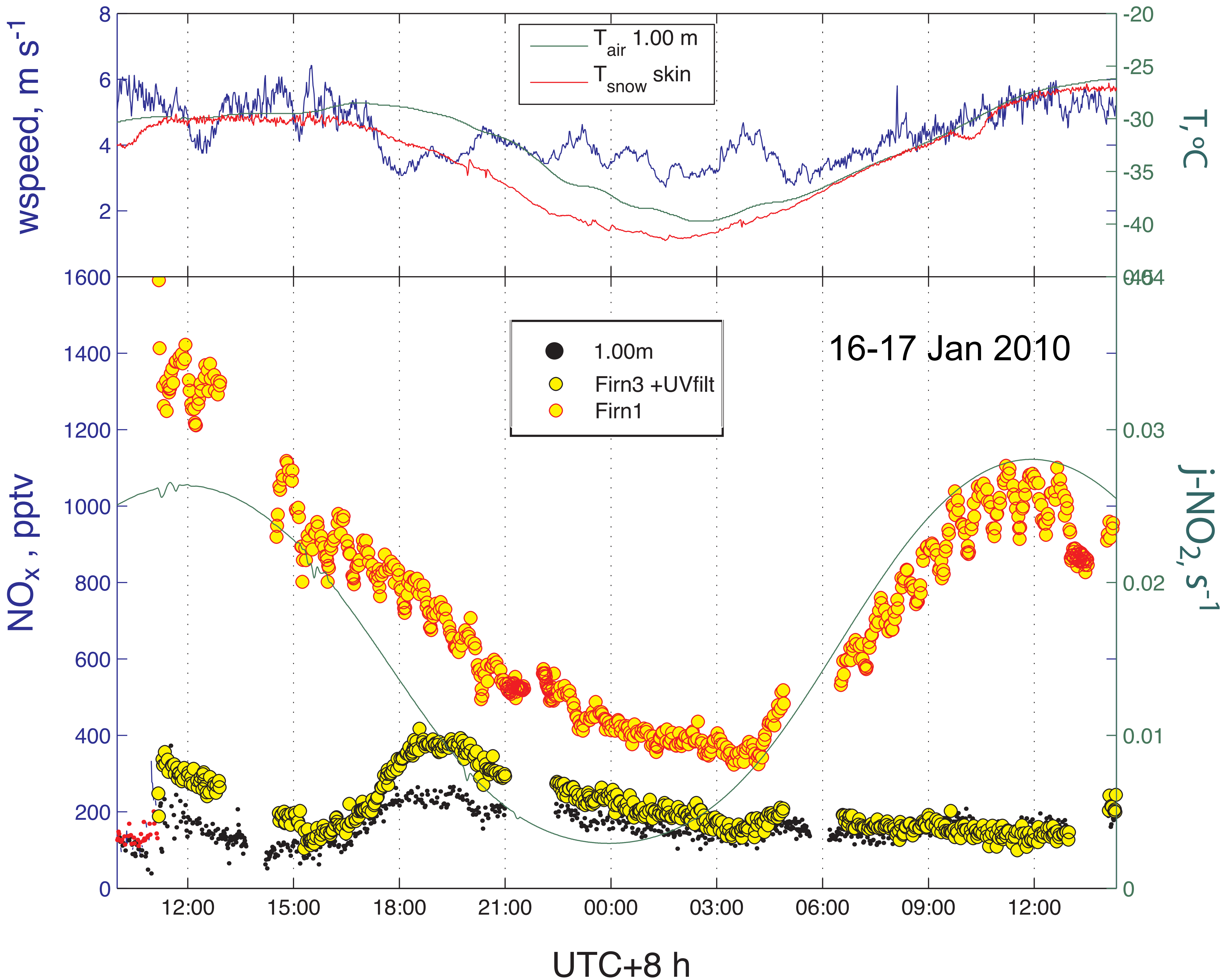
Channel 1:
$NO_3^- + h\nu \rightarrow$ **NO_2** $+ O^-$ λ=302 nm

Channel 2:
$NO_3^- + h\nu \rightarrow NO_2^- + O(^3P)$
$NO_2^- + h\nu \rightarrow$ **NO** $+ O^-$ λ=318/354 nm
$NO_2^- + OH \rightarrow$ **NO_2** $+ OH^-$
$NO_2^- + H^+ \rightarrow$ **HONO**


NO_3^-


XO
X
O_3
NO
NO_2
RO_2
RH
NO_3
NO_2
N_2O_5
heterogeneous
O_3
$XONO_2$
XO
HNO_3
OH
Time scale : minutes
hours to days

Diurnal Variability at Dome C: **Ambient & Firn NO_x**



NOx reservoir?