Investigation of boundary layer photochemistry at the WAIS-Divide site through measurement of major photochemically active species in snow and air

Sylvain M. Masclin[1], Markus M. Frey[1,2], Wolfgang F. Rogge[1,3], Roger C. Bales[1,3]

[1]Environmental Systems, University of California, Merced, CA, USA, [2]British Antarctic Survey, Natural Environment Research Council, Cambridge, UK
[3]Sierra Nevada Research Institute, University of California, Merced, CA, USA

Contact: smasclin@ucmerced.edu

UNIVERSITY OF CALIFORNIA UCMERCED — NSF — British Antarctic Survey, NATURAL ENVIRONMENT RESEARCH COUNCIL

The polar snowpack has a significant impact on atmospheric boundary layer photochemistry. Its potential to act as an H_2O_2 reservoir and potential to emit NO_x ($NO+NO_2$) from nitrate photolysis in the near-surface snowpack were recently suggested as important factors in altering the oxidative composition of the overlying troposphere.

We investigated the boundary layer photochemistry at the WAIS-Divide site (79°S, 112°W) measuring key photochemically active species - nitric oxide (NO), ozone (O_3), nitrate (NO_3^-) - during the 08-09 WAIS-Divide campaign (Fig. 1). Overall values are in the range of those measured above the West Antarctic Ice Sheet during the ITASE traverses and of those measured at other Antarctic sites, except South Pole Station (Fig. 2).

Using values of nitrate concentration measured in snow surface and in micro snowpits (30 cm depth), we calculated and compared the NO produced from the nitrate photolysis to measured concentration. Assuming a boundary layer (BL) height of 100 m *[1]*, local atmospheric NO emissions from NO_3^- photolysis in the snowpack is estimated to account for ~ 40% of NO observed above the snow (Fig. 3).

The snowpack source can be significant for NO_x levels in the BL above WAIS-Divide. However this impact depends on BL depth, which is in general larger than on the plateau, resulting in lower NO_x. The site is likely to be affected by transport. Elevated O_3 levels point to outflow off the East Antarctic Plateau (EAP), where net O_3 production has been observed to occur. Analysis of backward trajectories for the WAIS-Divide site and South Pole station suggest that fast outfow from the EAP may result in high O_3 concentrations above the WAIS-Divide site (Fig. 4bA, 4bB). Altitude of the coming air and its residence time above the EAP may also impact the observed level of atmospheric oxidants (Fig 4bB, 4bC). Slower atmospheric transport or transport through Antarctic coastal regions may result in low concentrations of O_3 and other photochemical active species at the WAIS-Divide site (Fig. 4bD, 4bE, 4bF).

Figure 1: Atmospheric and snow observations

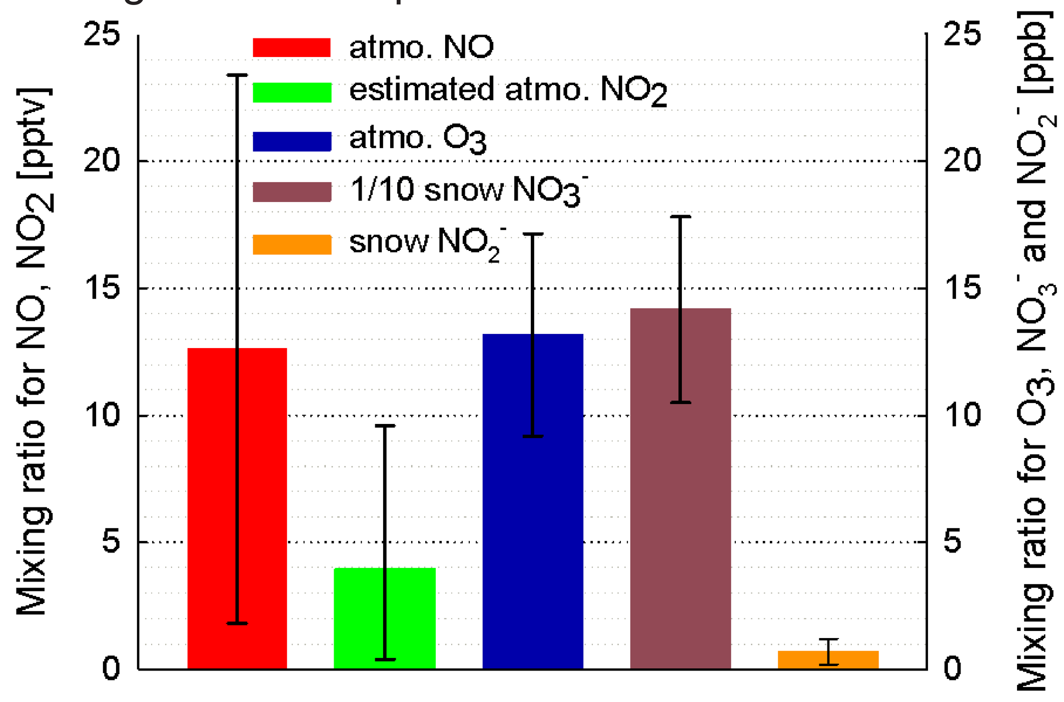


Figure 2a: Atmospheric nitric oxide

1m above snow surface

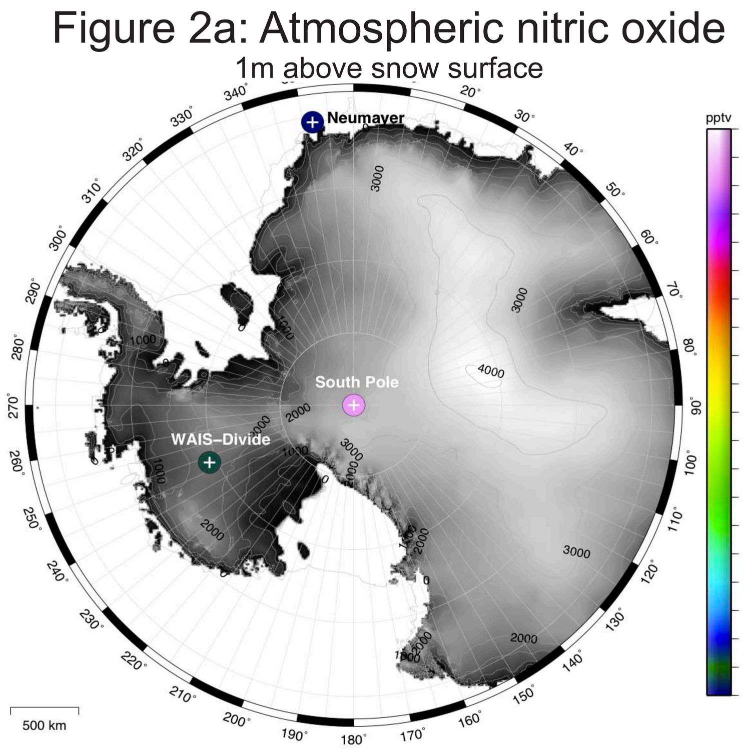


Figure 2b: Surface ozone

1m above snow surface

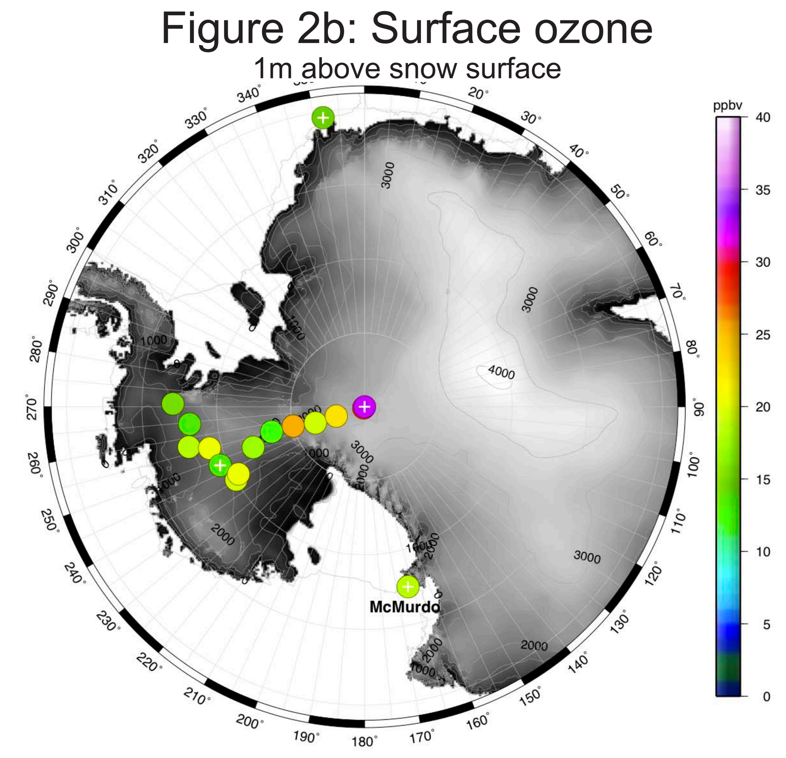
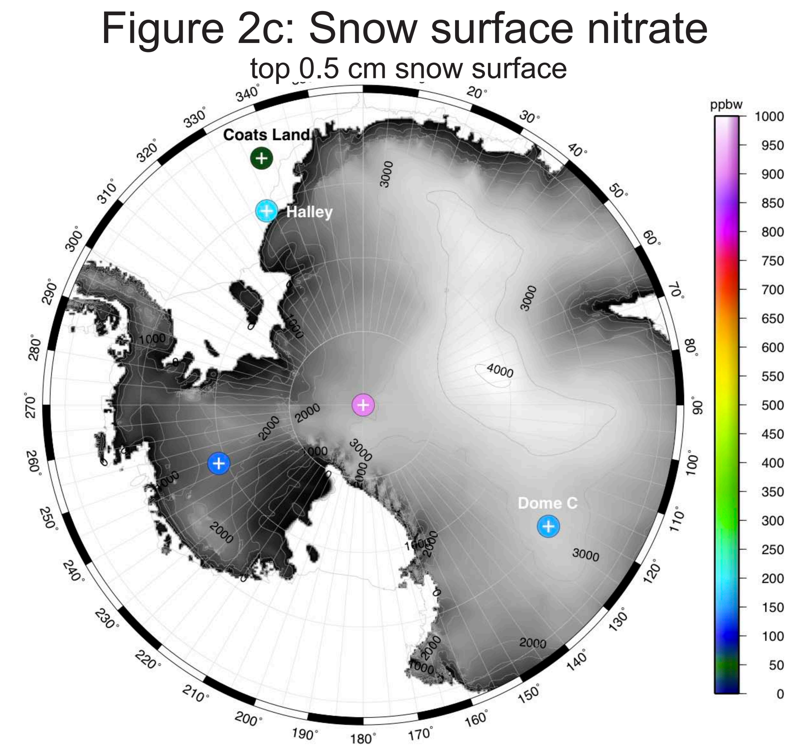


Figure 2c: Snow surface nitrate

top 0.5 cm snow surface



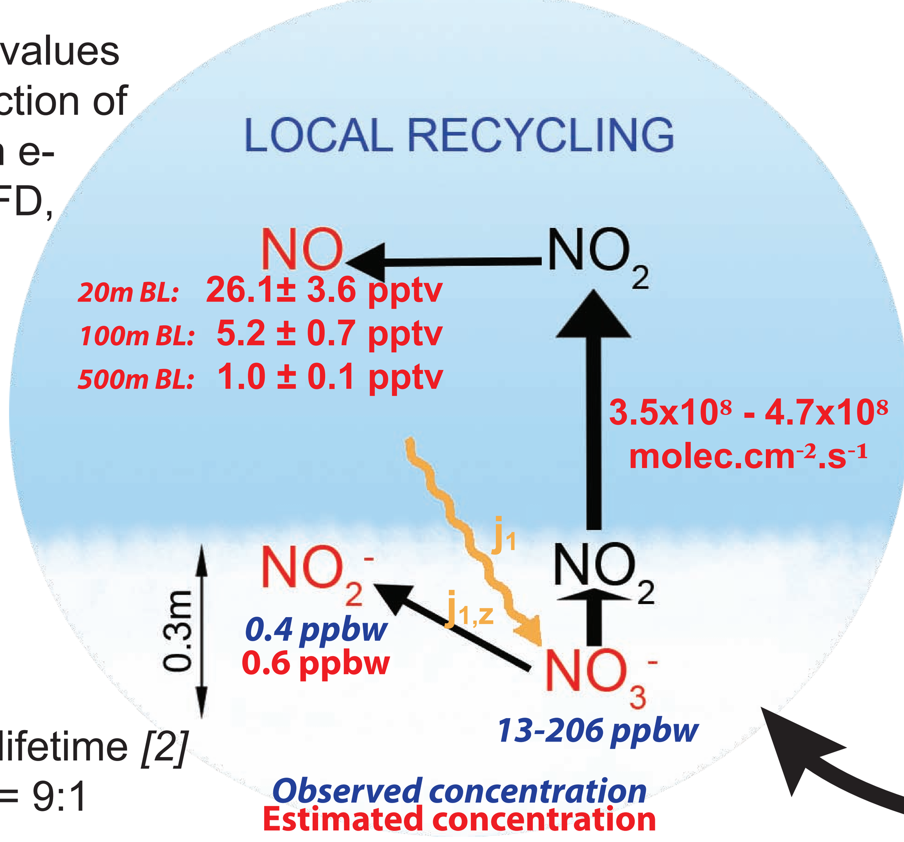
We calculated the rate constant for photolysis of nitrate on snow surface j_1 for the days of snowpit sampling *[4]*:

$$j_1 = \int \sigma_{NO_3^-}(\lambda) \times \phi_{NO_3^-}(\lambda) \times I(\lambda) \times d\lambda \qquad \text{Eq.1}$$

with $\sigma_{NO_3^-}(\lambda)$: Chu and Anastasio (2003)
$\phi_{NO_3^-}(\lambda) = 2.79 \times 10^{-3}$ *[5]*
$I(\lambda)$: radiation transfer model TUV *[6]*.

Snow-surface j_1 values were fit as a function of depth (z) with an e-folding depth, EFD, of 10 cm *[3]*:

$$j_{1,z} = j_1 \times e^{\frac{-z}{EFD}} \qquad \text{Eq.2}$$



Hypothesis:
- 7-hour NO_x lifetime *[2]*
- ratio R1:R2 = 9:1

Figure 3: Simplified photochemistry of the NO_x over the West Antarctic Ice Sheet and the East Antarctic Plateau *[2,3]*

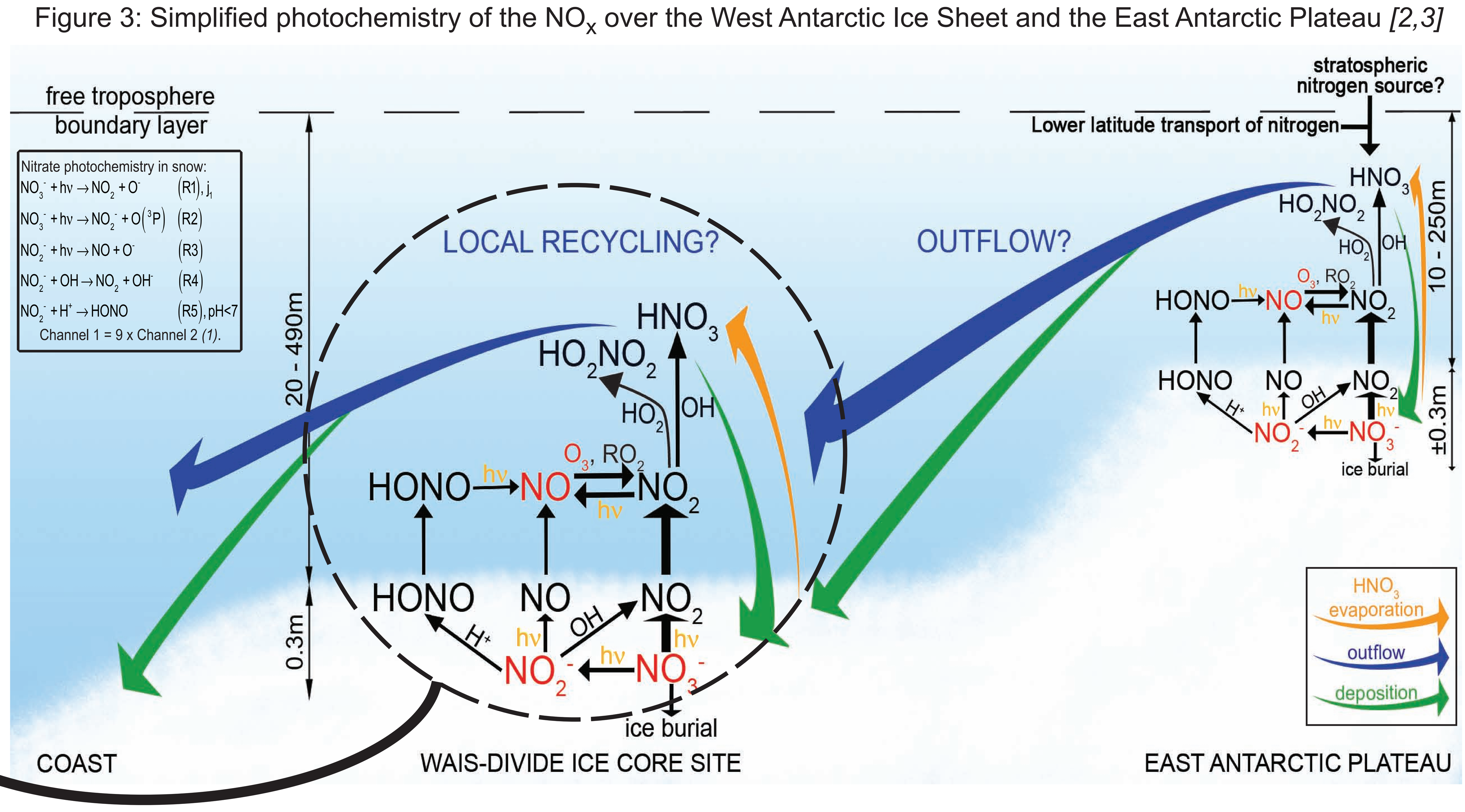


Figure 4a: Surface O_3, atmospheric pressure and NO observed at the WAIS-Divide site and surface O_3 at South Pole station

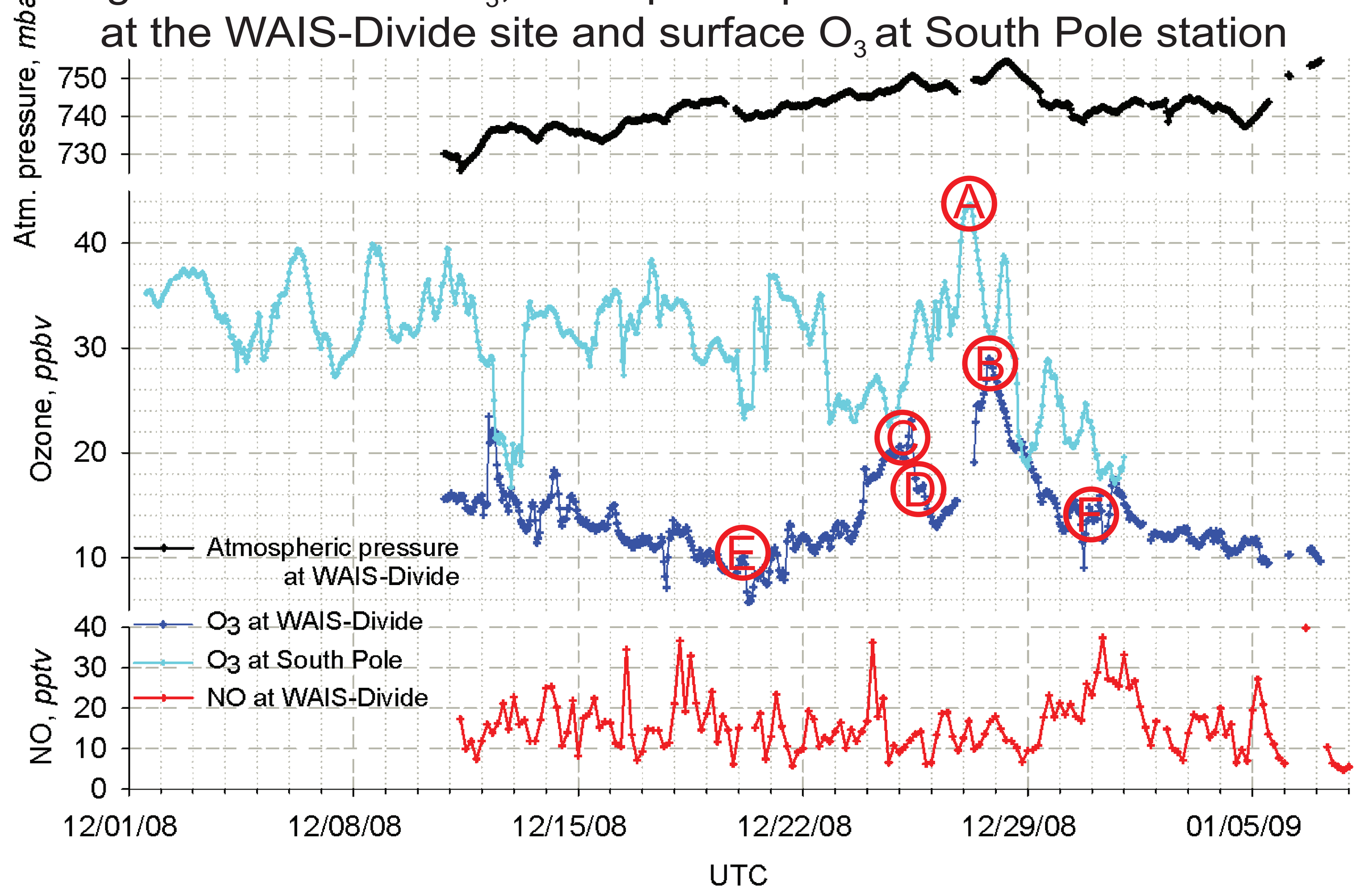
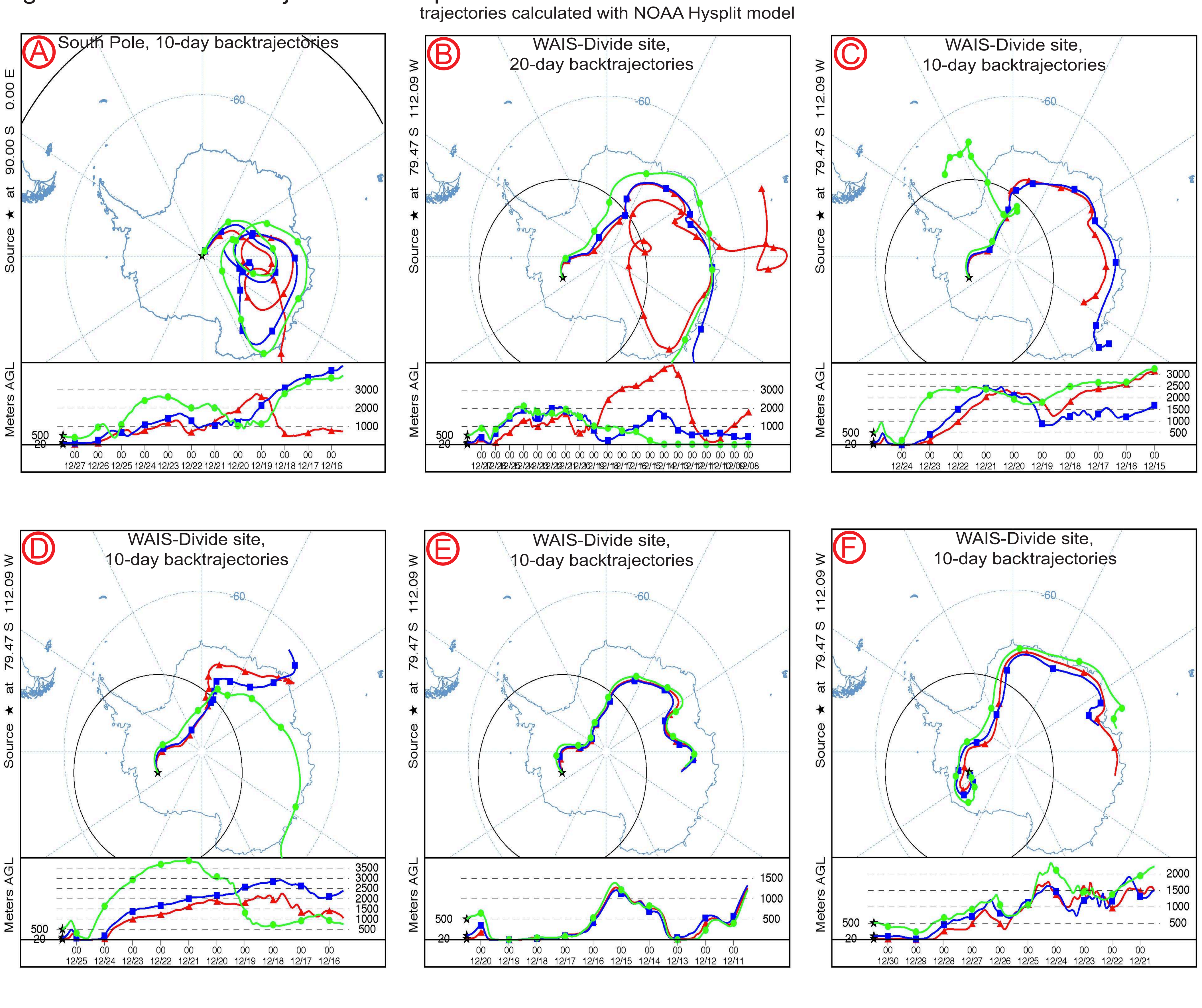


Figure 4b: Backward trajectories of specific events observed at the WAIS-Divide site and at South Pole

trajectories calculated with NOAA Hysplit model



ACKNOWLEDGEMENTS

We thank G. Huey, at Georgia Institute of Technology, for the use of the nitric oxide detector. This research is supported by National Science Foundation, NSF award number: OPP-0636929.

REFERENCES

[1] Frey, M. M., Stewart, R. W., McConnell, J. R., and Bales, R. C.: Atmospheric hydroperoxides in West Antarctica: links to stratospheric ozone and atmospheric oxidation capacity, J. Geophys. Res., 110(D23), 1-17, 2005.

[2] Davis, D., Chen, G., Buhr, M., Crawford, J., Lenschow, D., Lefer, B., Shetter, R., Eisele, F., Mauldin, L., and Hogan, A.: South Pole NOx chemistry: an assessment of factors controlling variability and absolute levels, Atmos. Environ., 38, 5375–5388, 2004.

[3] Grannas, A. M., Jones, A. E., Dibb, J., Ammann, M., Anastasio, C., Beine, H. J., Bergin, M., Bottenheim, J., Boxe, C. S., Carver, G., Chen, G., Crawford, J. H., Domine , F., Frey, M. M., Guzma n, M. I., Heard, D. E., Helmig, D., Hoffmann, M. R., Honrath, R. E., Huey, L. G., Hutterli, M., Jacobi, H. W., Kla n, P., Lefer, B., McConnell, J., Plane, J., Sander, R., Savarino, J., Shepson, P. B., Simpson, W. R., Sodeau, J. R., von Glasow, R., Weller, R., Wolff, E. W., and Zhu, T.: An overview of snow photochemistry: evidence, mechanisms and impacts, Atmos. Chem. Phys., 7, 4329–4373, 2007.

[4] Frey, M. M., Savarino, J., Morin, S., Erbland, J., and Martins, J. M. F.: Photolysis imprint in the nitrate stable isotope signal in snow and atmosphere of East Antarctica and implications for reactive nitrogen cycling, Atmos. Chem. Phys., 9(22), 8681-8696, 2009.

[5] Chu, L. and Anastasio, C.: Quantum yields of hydroxyl radical and nitrogen dioxide from the photolysis of nitrate on ice, J. Phys. Chem. A, 107, 9594–9602, 2003.

[6] Madronich, S. and Flocke, S.: The role of solar radiation in atmospheric chemistry, in: Handbook of Environmental Chemistry, edited by: Boule, P., Springer Verlag, Heidelberg, 1–26, 1998.

World Data Centre for Greenhouse Gases: http://gaw.kishou.go.jp/wdcgg/