Reply to comments of Referee No.1

We thank Referee No.1 for insightful comments which helped to further improve the manuscript. Referee comments (in italics) are addressed below. Revised text, where necessary, is shown in blue, and is included in the final manuscript we will submit to ACP.

General: I enjoyed the paper and appreciate the challenges in linking NO_x chemistry, the diurnal cycle, and boundary layer effects. The discussion of limitations in the evaluation of the effects of interferences was quite complete. It is clear that much has been accomplished but more remains to be done. A peeve of mine that the various papers in this collection do not appear to have been coordinated in the time Periods highlighted (particularly in the figures): For example, Gallee et al provides details on model versus observed boundary layer depth for 26-28 December but the really interesting chemistry is earlier in Periods II and III in Frey. Similarly earlier published work (Argentini et al.) looked carefully at 10 January boundary layer behaviour but Frey et al. did detailed profile measurements a day earlier. It would useful in collections such as these to identify specific Periods of common interest prior to extensive analysis.

Reply: Thank you. The comparison of modelled boundary layer depth with observations based on sodar measurements presented in Gallée et al. (2014) was possible on a few days only during the OPALE campaign (see also reply to a similar reviewer comment to Gallée et al. (2014)). NO_x concentrations were measured from 23 November 2011 to 12 January 2012 (this work), HONO from 4 December 2011 to 11 January 2012 (Legrand et al., 2014), HO_x radicals from 19 December 2011 to 9 January 2012 (Kukui et al., 2014), and CH_2O from 14 December 2011 to 11 January 2012 (Preunkert et al., 2014). However, sodar measurements were only available on 12, 13, 18, 21 26, 27, 28 December 2011 and on 3, 4 and 10 January 2012. The best period to compare the MAR model with sodar measurements was 26 to 28 December 2011, because it was the longest Period and also included all chemical trace gases targeted during OPALE.

Regarding NO_x observations, additional modelled and observed BL heights were available only during Period III. (9-22 December 2011), which we'll note in the manuscript. Unfortunately, the NO_x vertical profiles measured on 9 January 2012 can only be compared to modelled BL heights due to the lack of sodar data.

Revised text 31298, Lines 8-13: The strong increase of NO_x around 11 December 2011 falls into a Period when F_{NO_x} almost tripled, while wind speeds slightly decreased and shallow boundary layer heights prevailed with daily h_z maxima below 100-200 m (Fig.1, Table 2). On 12 December and 13 December the modelled diurnal ranges of h_z were 3.4-224 m and 3.6-251 m, respectively, while sodar observations yielded 10-150 m and 5-125 m, respectively (Gallée et al., 2014). After 13 December 2011 F_{NO_x} remained at high values, thus, the decrease of NO_x mixing ratios appears to be primarily caused by stronger upward mixing into a larger volume, i.e. wind speeds increased and daily h_z maxima grew, exceeding 600 m on 18 December (Fig. 1).

Specific:

Abstract: Should be more specific about the difference between the South Pole and Concordia: It is not just the diurnal cycle but the sudden collapse of the boundary layer in the evening that is unique to Concordia (when the surface flux of NO_x is suddenly confined to a shallow layer).

Revised text 31283, Lines 5-7: Profiles of NO_x mixing ratios of the lower 100 m of the atmosphere confirm that, in contrast to South Pole, air chemistry at Dome C is strongly influenced by large diurnal cycles in solar irradiance and a sudden collapse of the atmospheric boundary layer in the early evening.

31284, Lines 15-19: You list four factors leading to high NO_x at the South Pole (Davis et al. 2008) in the introduction. Your conclusion should come back and summarize which of these are relevant to Concordia. In particular, the statement low temperatures leading to low primary production rates of HOx Radicals should be addressed insofar as Davis et al argue that this is what contributes to the non-linear increase in the lifetime of NO_x and high accumulation levels at the South Pole is there any relevance to the chemistry at Concordia.

Reply: The flux values observed at Dome C are typically large enough to explain the average increase in mixing ratios in the early evening (1700-1800 LT). For example net production rates of NO_x at night estimated for 2009-10 are on the order of 100 pptv/h and are consistent with the average increase in NO_x from 110 to 300 pptv over about 2 h from 1700 to 1900 LT (Frey et al., 2013). It is therefore in general not necessary to invoke non-linear HO_x-NO_x chemistry and associated increase in NO_x lifetime as suggested in the case of South Pole (Davis et al., 2008, and references therein). We will adjust the text accordingly.

31284, Line 28: A more current reference using sodar data is: B. Van Dam, D. Helmig, W. Neff, and L. Kramer, 2013: Evaluation of Boundary Layer Depth Estimates at Summit Station, Greenland. J. Appl. Meteor. Climatol., 52, 23562362. doi:10.1175/JAMC-D-13-055.1
Reply: Agreed, we replaced the Cohen et al. (2007) reference with the one above.

31290, Lines 11-12: Can you argue that the NO_x flux is constant with time through the collapse of the boundary layer. Eliminating 22% of the data when the boundary layer depth is <10m may be problematic if this 22% occurs during the evening transition when NOX levels get large.
Reply: The point raised is unclear. We do not argue that flux is constant with time. To the contrary, we argue that the application of MOST requires that at a given time flux is constant between the two measurement heights (condition (a)). Constant flux can be assumed if the chemical lifetime (τ_{chem}) of NO_x is much longer than the turbulent transport time scale (τ_{trans}). This condition is met during OPALE, as detailed in the revised text below.
However, modelled mixing heights indicate that the upper inlet is frequently above the surface layer (condition (c)) during and after the collapse of the convective BL, as pointed out by the reviewer. Thus the removal of flux estimates (22% of the total available) affects mostly the evening and night, when the BL is shallow. Hence, fluxes during night time are less well constrained, but nevertheless support a significant diurnal cycle (see Figure 6b,g and Figure 9 in Frey et al. (2013)). We clarify this point in the revised text.
Revised text 31290, Lines 8-17: Condition (a) is met in the surface layer if the chemical lifetime τ_{chem} of NO_x is much longer than the turbulent transport time scale τ_{trans}. Based on observed OH and HO_2 τ_{chem} for NO_x is estimated to be 3 h at 1200 LT and 7 h at 0000 LT during OPALE (Legrand et al., 2014). Estimating τ_{trans} following the approach described previously (Eq. 6 and 7 in Frey et al., 2013) yields 0.6, 1.7 and 2.5 min during the day (0900-1700 LT), the typical time of BL collapse (1700-1900 LT) and during the night (1900-0900 LT), respectively. Thus, τ_{chem} exceeds τ_{trans} by at least a factor 100, confirming that vertical mixing always dominates over the gas phase photochemical sink and flux can be assumed constant between the two inlets. Condition (b) is met as discussed in Frey et al. (2013). For (c) the upper inlet height of 1 m is compared to estimates of mixing height h_z from the MAR model (Gallée et al., 2014). Calculated flux values of NO_x were removed when $h_z < 10$m resulting in the removal of 22 % (773 values) of all available 10 min flux averages. Flux estimates are removed specifically during the evening and night, when the BL is shallow. Hence, fluxes during night time are less well constrained, but nevertheless support a significant diurnal cycle (see Figure 6b,g and Figure 9 in Frey et al. (2013))

31293, Lines 10-19: This description of changes in NOX levels could use a bit more work. The intraseasonal trend should be characterized as intraseasonal variability.
Reply: As suggested we now characterise in the text the 'trend' as intra-seasonal variability.

31293, Lines 10-19 (continued): Also, there is a gap in wind data Dec 3-7. I looked at the AWS data (ftp://amrc.ssec.wisc.edu/pub/aws /10min/rdr/2011/089891211.r) for this Period and it looks like the wind speed was greater in Period II compared to Period III. The AWS anemometer data shows frequent stalling in Period III. However, a simple average yields Period II: 2.4 m/s whereas Period III: 1.3 m/s. This suggests a closer look at the depth of mixing between the two Periods.
Reply: Indeed, the statistics for Periods I-IV listed already in Table 2 indicate that wind speeds at 3.3 m were greater during Period II (median 3.6 m/s) than during Period III (median 2.5 m/s). We

closed the gap in wind data Dec 3-7 using measurements at 2.0m height from the AWS managed by Univ. of Wisconsin, which reduces the median wind speeds during Period II to 3.0 m/s. Recalculating the average wind speeds from the Wisconsin AWS yields 2.98 and 2.34 m/s for Periods II and III, respectively, higher values but with a smaller difference than suggested by the reviewer. Thus, wind speeds in the two Periods are different, but not by much. The primary change driving the increase of NO_x mixing ratios is the increase in flux combined with lower wind speeds and a relatively shallow BL (see above for revised text 31298, Lines 8-13).
Revised Table 2 and Fig. 1: Median wind speed for Period II updated to 3.0 m/s and Fig. 1 includes now wind speed observations during 3-7 December.

31293, Lines 10-19 (continued): With respect to the correlation between wind speed and $\mathrm{NO_x}$ levels, another factor to look at is the response of $\mathrm{NO_x}$ concentrations to the sudden collapse of the boundary layer in the evening. Ideally, one should compare average winds during just the Period of collapse and higher $\mathrm{NO_x}$: the correlation might come out differently.
Reply: Regarding wind speeds, we looked at the correlation with NO_x mixing ratios during the time of collapse of the daytime convective BL, i.e. 1700-1900 LT, and find a slightly stronger negative correlation ($R=-0.45$, $p<0.001$) than when including all data ($R=-0.37$, $p<0.001$).
Revised text 31293, Lines 6-9: As seen previously at Dome C and other locations, NO_x mixing ratios were weakly but significantly anti-correlated with wind speed ($R=-0.37$, $p<0.001$), especially when only the time Period of the daily collapse of the convective boundary layer, i.e. 1700-1900 LT, was considered ($R=-0.45$, $p<0.001$).

31293, Lines 10-19 (continued): There were also significant changes in the behaviour of the wind direction: Early Period III shows a 180 degree rotation of the wind whereas Period II shows a most consistent wind direction centered from the SE. In Period III, when the wind was rotating from SW to SE to N, could there have been contamination from the station? (Frey et al 2013, Figure 1; also see Gallee this issue, their Figure 3).
Reply: Wind directions changed during Period III and rotated through northerly directions, potentially carrying contamination from the generator at Concordia station. However, our data filtering efficiently removes any pollution spikes, which typically exceed 10 ppbv of NO_x (see also Frey et al., 2013). The regular appearing diurnal NO_x maxima are clearly linked to the drastic BL decreases in the early evening, including Period III (Fig. 1). To illustrate this point better we updated Fig.1 and include also a time series of wind direction (Fig. 1). In the method section we provide more detail on how we removed NO_x data affected by local air pollution using a filtering method described previously (Frey et al., 2013).
Revised text in section 2.1: The mean wind direction during the measurement period was from S (176°) with an average speed of 4.0 m s^{-1} (Fig. 1b). During 2.5% of the time winds came from the direction of Concordia station, i.e. the 355-15° sector (see Fig.1 in Frey et al., 2013), carrying potentially polluted air from the station power generator to the measurement site. For example, during Period III winds rotated 4 times through northerly directions (Fig. 1b). Pollution spikes in the raw 1-s data typically exceeded 10 ppbv of NO_x and were effectively removed before computing the 1-min averages by applying a moving 1-min standard deviation filter. Observations were rejected when 1-σ of NO and NO_2 mixing ratios within a 1-min window exceeded 24 and 90 ppt, respectively.

Figure 2: The discussion of this figure might want to include a reference to Argentini et al. 2013 (Annals of Geophysics 56, 5, 2013; 10.4401/ag-6347) which shows the negative heat flux at sunset as well as the decrease in downward longwave radiation for 9 January 2012 (rapid cooling of the surface resulting in a strong shallow surface inversion. That paper also shows fairly graphically, using sodar data, the evolution of the boundary layer on 10 January 2012 it would be nice to have a similar figure for the 9th together with Gallees simulation (note that the Gallee paper in this special issue compares modeled versus sodar observed BLD for 26-28 December 2011) It would be nice if these comparisons could be coordinated and cross referenced between the papers (e.g. the high $\mathrm{NO_x}$ Period 12-16 December). Also, Gallees Figure 6 shows a later falloff in BLD in his model than does

the sodar does the same result hold for the 9th.
Reply: In the discussion of Fig.2 we now include a reference to the observations reported in Argentini et al. (2014). As mentioned above in the reply to the first comment, a comparison with modelled and observed BL heights is possible only during a few days of the OPALE campaign. In particular, no sodar data are available for 9 January 2012 and therefore we compare measured NO$_x$ vertical profiles only to modelled BL heights.
Added text in section 3.2; 31294, after Line 12 : At Dome C rapid cooling of the surface in the evening results in a strong shallow surface inversion (e.g. Frey et al., 2013), and is illustrated by a decrease in downward long-wave radiation and a negative heat flux, as observed in the evening of 9 January 2012 (Fig.4 in Argentini et al., 2014).

Section 3.5.2, : This section should probably reference/compare other NOX flux measurements. See Davis et al 2008 and references therein (Onckley et al, Wolff eta al., Wang et al. and Neff et al) that discuss the magnitudes, estimates, and boundary depth effects relevant to the NOX flux (esp. Wang et al).
Reply: As suggested we expand the discussion referring to previous estimates of NO$_x$ emission flux (F$_{NO_x}$) from polar snow based on observations and models.
Added text in section 3.2; 31294, after Line 12 : The NO$_x$ flux observed above polar snow is on the order of 10^{12} to 10^{13} molecule m^{-2} s^{-1} and contributes significantly to the NO$_x$ budget in the polar boundary layer. At the lower end of the range are F$_{NO_x}$ observations at Summit, Greenland (Honrath et al., 2002) and at Neumayer in coastal Antarctica (Jones et al., 2001) with 2.5 x 10^{12} molecule m^{-2} s^{-1}, whereas on the Antarctic Plateau F$_{NO_x}$ values are up to ten times larger (Oncley et al., 2004; Frey et al., 2013, and this study). The average F$_{NO_x}$ at South Pole during 26-30 November 2000 was 3.9 x 10^{12} molecule m^{-2} s^{-1} (Oncley et al., 2004), whereas at Dome C observed fluxes are 2-6 times larger, with seasonal averages of 8-25 x 10^{12} molecule m^{-2} s^{-1} (Frey et al., 2013, this work). Due to the uncertainties in the processes leading to NO$_x$ production it had been difficult to explain inter-site differences, e.g. by simply scaling F$_{NO_x}$ with UV irradiance and nitrate in the surface snow pack (Davis et al., 2004). Some of the variability in flux values may be due to differences in experimental set up or in the employed flux estimation method (e.g. Davis et al., 2004; Frey et al., 2013). For example, the F$_{NO_x}$ estimates for South Pole are based on measured NO gradients only, inferring NO$_x$ from photochemical equilibrium and using the Bowen ratio method (Oncley et al., 2004), whereas the F$_{NO_x}$ estimates for Dome C are based on observations of both atmospheric nitrogen oxides (NO and NO$_2$) and the flux-gradient method (Frey et al., 2013).
Model predictions of F$_{NO_x}$ show in general a low bias on the Antarctic Plateau when compared to observations. A first 3-D model study for Antarctica included NO$_x$ snow emissions parameterised as a function of temperature and wind speed to match the observed F$_{NO_x}$ at South Pole (Wang et al., 2007). However, the model under-predicts NO mixing ratios observed above the wider Antarctic Plateau highlighting that the model lacks detail regarding the processes driving the emission flux (Wang et al., 2007). The first model study to calculate F$_{NO_x}$ based on NO$_3^-$ photolysis in snow, as described in this work, reports 1-1.5 x 10^{12} molecule m^{-2} s^{-1} for South Pole in summer (Wolff et al., 2002), about a factor 4 smaller than the observations by Oncley et al. (2004) and up to 16 times smaller than what is needed to explain rapid increases in NO$_x$ mixing ratios over a few hours (Davis et al., 2008, and references therein). Recent model improvements reduced the mismatch with the South Pole flux observations and included the use of updated absorption cross sections and quantum yield of the nitrate ion, as well as e-folding depths measured in surface snow on the Antarctic Plateau, and resulted in a factor 3 increase of flux calculated for South Pole (France et al., 2011). In light of major remaining uncertainties, which include the spatial variability of nitrate in snow and the quantum yield of nitrate photolysis (Frey et al., 2013), we discuss below the variability of F$_{NO_x}$ observed at Dome C.

References

Argentini, S., Petenko, I., Viola, A., Mastrantonio, G., Pietroni, I., Casasanta, G., Aristidi, E., and Genthon, C.: The surface layer observed by a high-resolution sodar at DOME C, Antarctica, Annals of Geophysics, 56, 1–10, doi:10.4401/ag-6347, 2014.

Bauguitte, S. J.-B., Bloss, W. J., Evans, M. J., Salmon, R. A., Anderson, P. S., Jones, A. E., Lee, J. D., Saiz-Lopez, A., Roscoe, H. K., Wolff, E. W., and Plane, J. M. C.: Summertime NO_x measurements during the CHABLIS campaign: can source and sink estimates unravel observed diurnal cycles?, Atmos. Chem. Phys., 12(2), 989–1002, doi:10.5194/acp-12-989-2012, 2012.

Davis, D. D., Seelig, J., Huey, G., Crawford, J., Chen, G., Wang, Y. H., Buhr, M., Helmig, D., Neff, W., Blake, D., Arimoto, R., and Eisele, F.: A reassessment of Antarctic plateau reactive nitrogen based on ANTCI 2003 airborne and ground based measurements, Atmos. Environ., 42, 2831–2848, doi:10.1016/j.atmosenv.2007.07.039, 2008.

Davis, D. D., Chen, G., Buhr, M., Crawford, J., Lenschow, D., Lefer, B., Shetter, R., Eisele, F., Mauldin, L., and Hogan, A.: South Pole NO_x chemistry : an assessment of factors controlling variability and absolute levels, Atmos. Environ., 38(32), 5275–5388, doi:10.1016/j.atmosenv.2004.04.039, 2004.

France, J. L., King, M. D., Frey, M. M., Erbland, J., Picard, G., Preunkert, S., MacArthur, A., and Savarino, J.: Snow optical properties at Dome C (Concordia), Antarctica; implications for snow emissions and snow chemistry of reactive nitrogen, Atmos. Chem. Phys., 11(18), 9787–9801, doi:10.5194/acp-11-9787-2011, 2011.

Frey, M. M., Brough, N., France, J. L., Anderson, P. S., Traulle, O., King, M. D., Jones, A. E., Wolff, E. W., and Savarino, J.: The diurnal variability of atmospheric nitrogen oxides (NO and NO_2) above the Antarctic Plateau driven by atmospheric stability and snow emissions, Atmos. Chem. Phys., 13, 3045–3062, doi:10.5194/acp-13-3045-2013, 2013.

Gallée, H., Preunkert, S., Argentini, S., Frey, M. M., Genthon, C., Jourdain, B., Pietroni, I., Casasanta, G., Barral, H., Vignon, E., and Legrand, M.: Characterization of the boundary layer at Dome C (East Antarctica) during the OPALE summer campaign, Atmos. Chem. Phys. Disc., 14, 33 089–33 116, doi:10.5194/acpd-14-33089-2014, 2014.

Honrath, R., Lu, Y., Peterson, M., Dibb, J., Arsenault, M., Cullen, N., and Steffen, K.: Vertical fluxes of NOx, HONO, and HNO3 above the snowpack at Summit, Greenland, Atmos. Environ., 36, 2629–2640, doi:10.1016/S1352-2310(02)00132-2, 2002.

Jones, A. E., Weller, R., Anderson, P. S., Jacobi, H. W., Wolff, E. W., Schrems, O., and Miller, H.: Measurements of NO_x emissions from the Antarctic snow pack, Geophys. Res. Lett., 28(8), 1499–1502, 2001.

Kukui, A., Legrand, M., Preunkert, S., Frey, M. M., Loisil, R., Gil Roca, J., Jourdain, B., King, M. D., France, J. L., and Ancellet, G.: Measurements of OH and RO_2 radicals at Dome C, East Antarctica, Atmos. Chem. Phys., 14, 12 373–12 392, doi:10.5194/acp-14-12373-2014, 2014.

Legrand, M., Preunkert, S., Frey, M., Bartels-Rausch, Th., Kukui, A., King, M. D., Savarino, J., Kerbrat, M., and Jourdain, B.: Large mixing ratios of atmospheric nitrous acid (HONO) at Concordia (East Antarctic Plateau) in summer: a strong source from surface snow?, Atmos. Chem. Phys., 14, 9963–9976, doi:10.5194/acp-14-9963-2014, 2014.

Oncley, S. P., Buhr, M., Lenschow, D. H., Davis, D., and Semmer, S. R.: Observations of summertime NO fluxes and boundary-layer height at the South Pole during ISCAT 2000 using scalar similarity, Atmos. Environ., 38(32), 5389–5398, doi:10.1016/j.atmosenv.2004.05.053, 2004.

Preunkert, S., Legrand, M., Frey, M., Kukui, A., Savarino, J., Gallée, H., King, M., Jourdain, B., Vicars, W., and Helmig, D.: Formaldehyde (HCHO) in air, snow and interstitial air at Concordia (East Antarctic plateau) in summer, Atmos. Chem. Phys. Disc., 14, 32 027–32 070, doi:10.5194/acpd-14-32027-2014, 2014.

Wang, Y. H., Choi, J., Zeng, T., Davis, D., Buhr, M., Huey, G., and Neff, W.: Assessing the photochemical impact of snow NO_x emissions over Antarctica during ANTCI 2003, Atmos. Environ., 41, 3944–3958, 2007.

Wolff, E. W., Jones, A. E., Martin, T. J., and Grenfell, T. C.: Modelling photochemical NO_x production and nitrate loss in the upper snowpack of Antarctica, Geophys. Res. Lett., 29(20), doi:10.1029/2002GL015823, 2002.

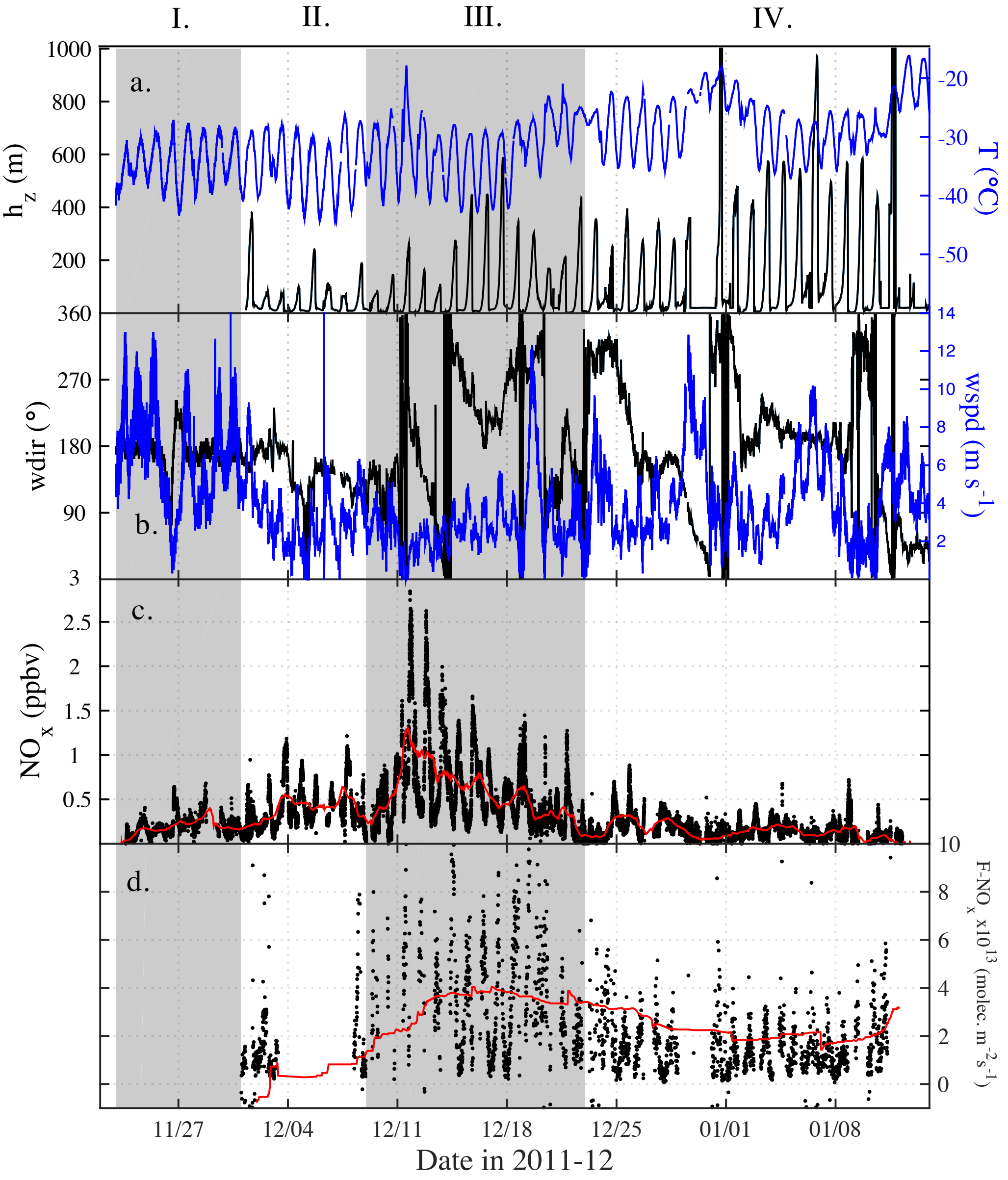

Figure 1: Meterorology and NO_x observations at Dome C in summer 2011–2012 (highlighted Periods I.–IV. as referred to in text and Table 2): **(a)** air temperature (T) at 1.6m and modeled mixing height (h_z) (Gallée et al., 2014), **(b)** wind speed (wspd) and direction (wdir) at 3.3 m **(c)**, 1 min averages of NO_x mixing ratios at 1 m (red line is 1 day running mean) and **(d)** 10 min averages of observational estimates of NO_x flux (F_{NO_x}) between 0.01 and 1 m (red line is 14 day running mean).