



Supplement of

Vertical distribution of pollution trapped by wintertime surface inversions in Fairbanks, Alaska, during the ALPACA experiment

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S1 DOAS Analysis

The analysis of the LP-DOAS spectra measured during ALPACA followed the principles outlined in Platt and Stutz (2008) and Stutz and Platt (1996). Trace gas concentrations from overlaying absorptions are retrieved using the combination of a linear and non-linear least squares fit of the sum of a scaled set of reference spectra (Stutz and Platt, 1996). Reference spectra were simulated using literature absorption cross sections convoluted with a slit function derived from a mercury emission line measured during ALPACA (Platt and Stutz, 2008). For NO₂, HCHO and O₃ we chose absorption cross section at 246 K, 253 K, and 253 K, respectively (Table S1). Since high spectral resolution, low-temperature cross-section are not available for HONO or SO₂, we used room temperature cross sections (Table S1). Temperature variation in the SO₂ absorption cross section at lower spectral resolution are less than 10% (Bogumil et al., 2003). The temperature dependence of HONO absorptions is currently unknown, but it is likely in a similar range ($< \sim 10\%$) than NO₂. Temperature dependence of ozone and NO₂ were considered in the HONO, HCHO and SO₂ retrievals by including a reference spectrum describing the temperature dependence of NO₂ and O₃ (calculated as the orthogonal of reference spectra at two different temperatures) to reduce the error of these retrievals. Note that we did not consider temperature dependence of the O₃ and NO₂ cross sections when calculating the mixing ratios of these gases. We also included reference spectra for oxygen and oxygen collisional complexes. O₂ and O₂N₂ reference spectra were calculated for the light path length and O₂ and N₂ concentrations averaged over the campaign. The sources of these absorption cross sections are also listed in Table S1.

Concentrations of each trace gas were retrieved in specific wavelength windows to reduce systematic and random errors. These wavelength windows and the trace gases included in the fit are listed in Table S2. To take advantage of the larger differential absorption structures towards shorter wavelengths we performed an additional ozone measurement and retrieval for the lowest LP-DOAS path in a different wavelength window (282 nm – 307 nm). Because this wavelength range was measured about 5 minutes after our main UV range, we interpolated its O₃ data onto the time grid of the main range. Aside from the trace gas absorptions listed in Table S2 the first three orthogonal components of a singular value decomposition of all lamp spectra throughout the campaign was included in the fitting procedure, with the goal of capturing variations in the lamp spectra. In addition, a polynomial of degree 5 or 7 was included. All gas absorption spectra were shifted and squeezed with one set of common parameters to compensate for grating rotation errors and thermal shifts.

The results of our analysis for the entire experiment are shown in Figure S1. Data is displayed as mixing ratio at ambient temperature together with the measurement errors that

Table S1. Absorption cross-section used in the DOAS analysis

Trace gas	Temperature [K]	Reference
O ₃	253	Birk and Wagner (2018)
SO ₂	298	Vandaele et al. (1994)
HCHO	253	Meller and Moortgat (2000)
NO ₂	246	Voigt et al. (2002)
HONO	293	Stutz et al. (2000)
O ₂	293	Rothman et al. (2010)
O ₄	293	Hermans et al. (1999)
O ₂ N ₂	293	Fally et al. (2000)

were determined by each fitting procedure (Platt and Stutz, 2008; Stutz and Platt, 1997). Campaign average errors and errors at optimal instrument performance (best) are listed in Table S3 for the lowest path, 1, and the upper three paths, 2-4. The difference between the errors is due to the different path lengths. Detection limits are twice these errors.

S2 In-situ Observations

SO₂ was measured in-situ at 3 m agl with a Thermo Scientific 43C instrument located in a stationary trailer parked next to the CTC building. Multi-point calibration of the SO₂ monitor was performed by overflowing the inlet with an EPA-certified mixed standard (containing zero air, 5.190 ppm SO₂, and 508.4 ppm CO) diluted with zero air using an Environics 9100 calibration system and zero air.

Ozone and NO_x were measured at the same location and height using a Thermo Scientific 49C and 42C instruments, respectively. A zero and multipoint calibration of the O₃ monitor was performed using the O₃ generator and calibration dilution system of the Environics 9100 system. A second ozone monitor (Teledyne 400E) was deployed at Birch Hill at an altitude of 158 m above the valley floor. This monitor was calibrated through a ten-day intercomparison with the CTC monitor at the end of the field experiment. The NO_x monitor was calibrated using a similar method as SO₂ using a EPA certified NO standard of 50.12 ppm NO. NO₂ was produced using an excess of O₃ in the gas stream. All monitors were calibrated roughly every week.

NO₂ was measured by converting it to NO via a heated molybdenum converter. Molybdenum converters are known to partially convert NO_z = NO_y – NO_x to NO, thus potentially introducing artifacts in measured NO₂ mixing ratios. However, in Fairbanks winter, freshly emitted NO and NO₂, as well as NO₂ from the rapid reaction of NO with ozone, are the dominant part of NO_y. Potential interfering species, such as HONO and nitric acid, contribute at most a few percent to NO_y. This understanding of NO_x/NO_y chemistry in Fairbanks has been confirmed by a direct comparison of NO_x and NO_y by Roberts et al. (2025) (Figure S1 in Roberts et al. (2025)), which shows a close correlation of $R^2 = 0.99$

Table S2. Details on DOAS analysis

Trace gas	WL (nm)	Fitted Trace gases
O ₃	292.1 – 320.5	O ₃ , SO ₂ , HCHO, NO ₂
O ₃ (lowest path)	282 – 307	O ₃ , SO ₂ , HCHO, NO ₂ , O ₂ , O ₂ N ₂
SO ₂	292.1-312.4	SO ₂ , O ₃ , HCHO, NO ₂
NO ₂	344.8 – 371.0	NO ₂ , HONO, HCHO, O ₃ , O ₄
HCHO	311.1 – 332.0	HCHO, O ₃ , SO ₂ , NO ₂
HONO	340.12 – 380.0	HONO, NO ₂ , HCHO, O ₃ , O ₄ (HCHO and NO ₂ fixed to shorter WL fit results)

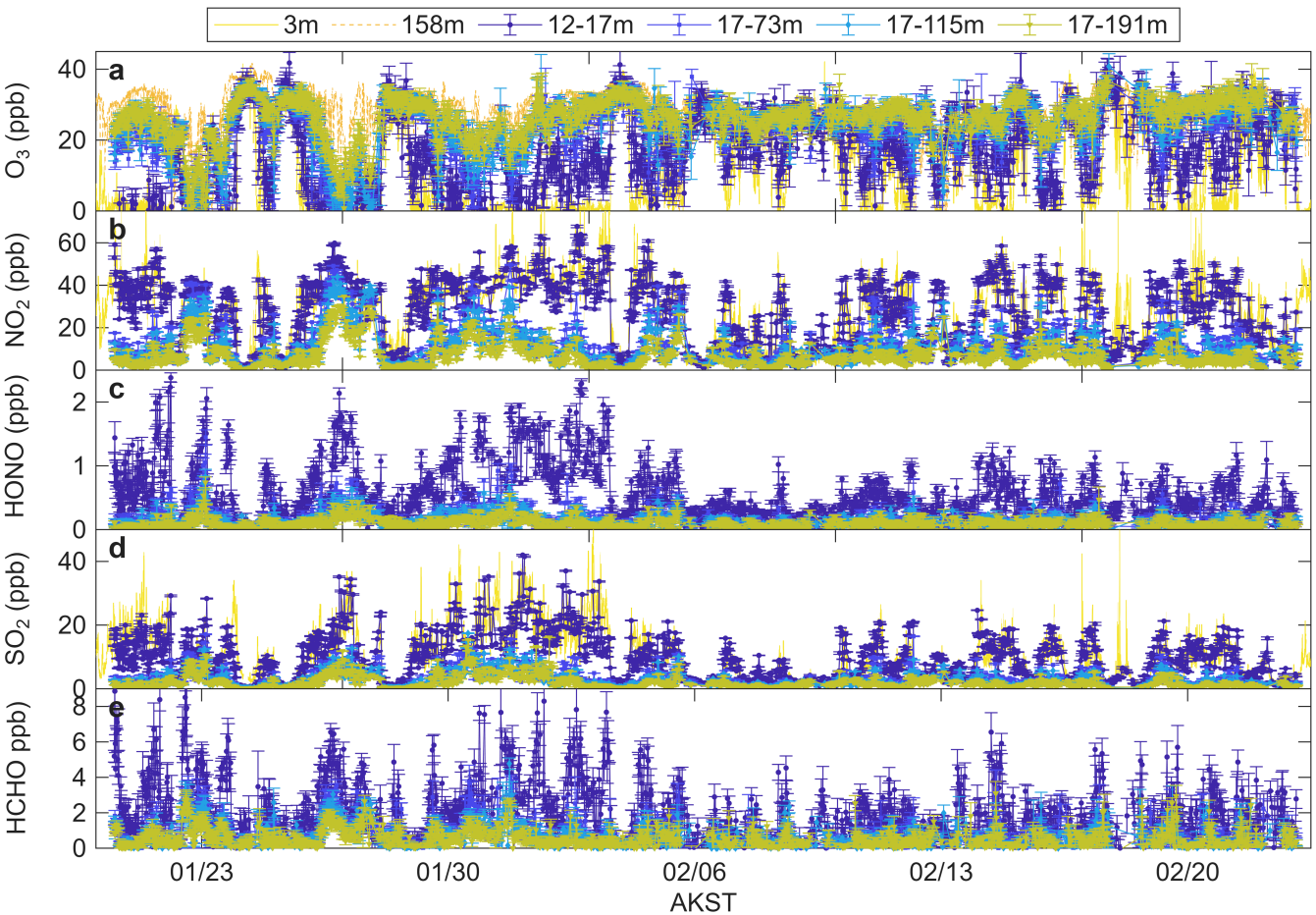


Figure S1. Campaign overview of the path-averaged LP-DOAS data along the four different lightpath using the same color coding as in Figure 2. Surface in-situ data is shown as a magenta line.

and a slope near unity. Landis and Edgerton (2024) also compared a heated molybdenum converter instrument under high NO_x conditions in northeastern Alberta, Canada, with a spectroscopic and chemiluminescence with photolytic converter NO₂ instruments. They found agreement of NO₂ of better than 7% over NO and NO₂ mixing ratio ranges similar to the one we report here. Both studies thus confirm that under conditions of fresh emissions, as found at the surface in wintertime Fairbanks, NO₂ observations using a heated molybdenum converter are not noticeably impacted by po-

tential NO_z interferences. It should be noted that these considerations do not contradict prior findings of interferences introduced by heated molybdenum converters; rather, they show that conditions in Fairbanks make these interferences too small to affect the conclusions of our study.

S3 Scaling of NO and NO₂ emissions

As mentioned in the main text, Brett et al. (2025) reported that the current ADEC emission inventory substantially un-

Table S3. Campaign average and best measurement errors for path 1 and path 2-4

	Path 1		Path 2-4	
	best	average	best	average
	ppb	ppb	ppb	ppb
O ₃	1.10	1.58	1.48	3.27
NO ₂	0.08	0.15	0.13	0.33
SO ₂	0.03	0.05	0.05	0.12
HCHO	0.13	0.28	0.24	0.58
HONO	0.02	0.04	0.03	0.08

derestimated NO_x, most likely due to uncertainties in the emission factors of combustion sources at the cold temperatures in Fairbanks. We confirmed this result by comparing a run of our model with the original ADEC emission data (yellow line, Figure S2) with a run where NO emissions were increased by a factor of 2.3 and NO₂ emissions were increased by a factor of 3 (red line, Figure S2). With the original ADEC emission data, modeled NO mixing ratios are considerably lower than the observations. Modeled NO₂ mixing ratios are slightly smaller than the observations, while modeled ozone mixing ratios are slightly larger. The smaller model-observation difference of NO₂ and ozone can be explained by the efficient conversion of NO to NO₂ by the $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$ reaction. The run with the increased NO and NO₂ emissions leads to much better agreement with the observations for all three trace gases (red line, Figure S2). This independently confirms the findings by Brett et al. (2025) that ADEC NO_x emissions for Fairbanks are too low.

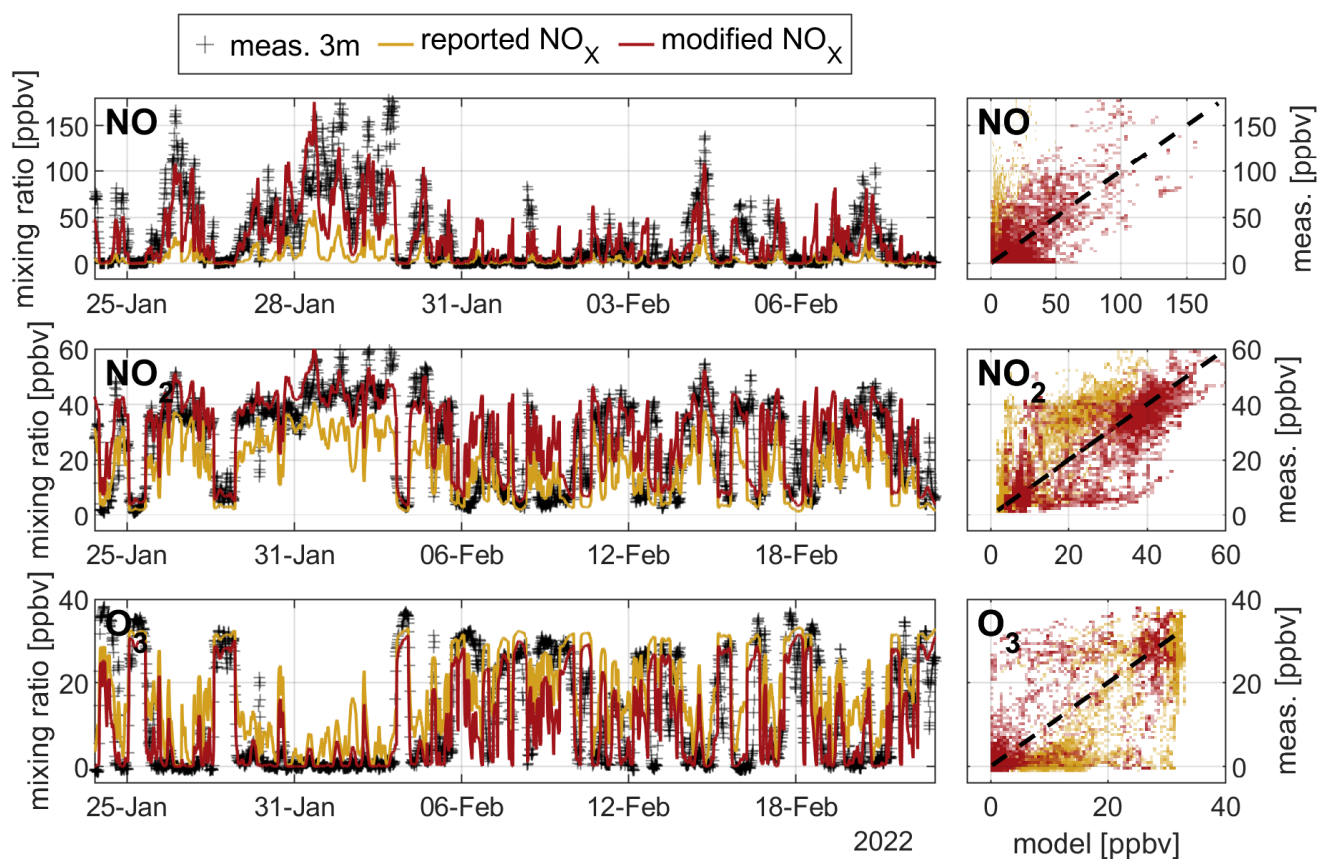


Figure S2. Comparison of model runs using the original and scaled ADEC NO and NO₂ emissions with 3 m in situ observations.

S4 Additional Figures

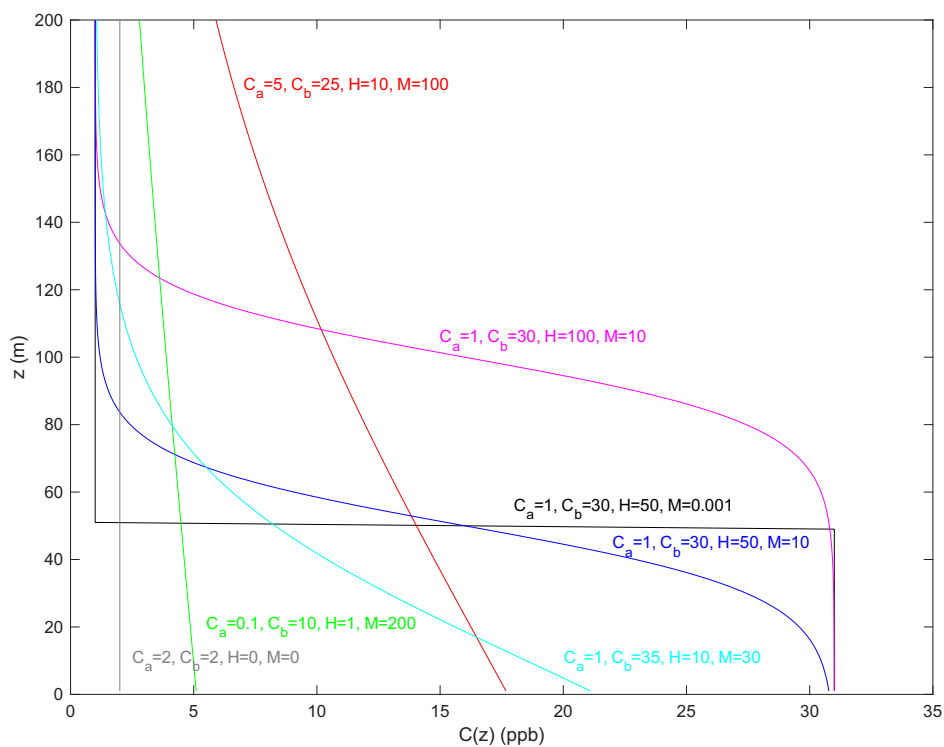


Figure S3. Shape of the sigmoid function (Eq. 1) used for the retrieval of vertical trace gas profiles from the LP-DOAS data. The curves show how various parameter combinations in Eq. 1 (Section 2.3) lead to different vertical profile shapes.

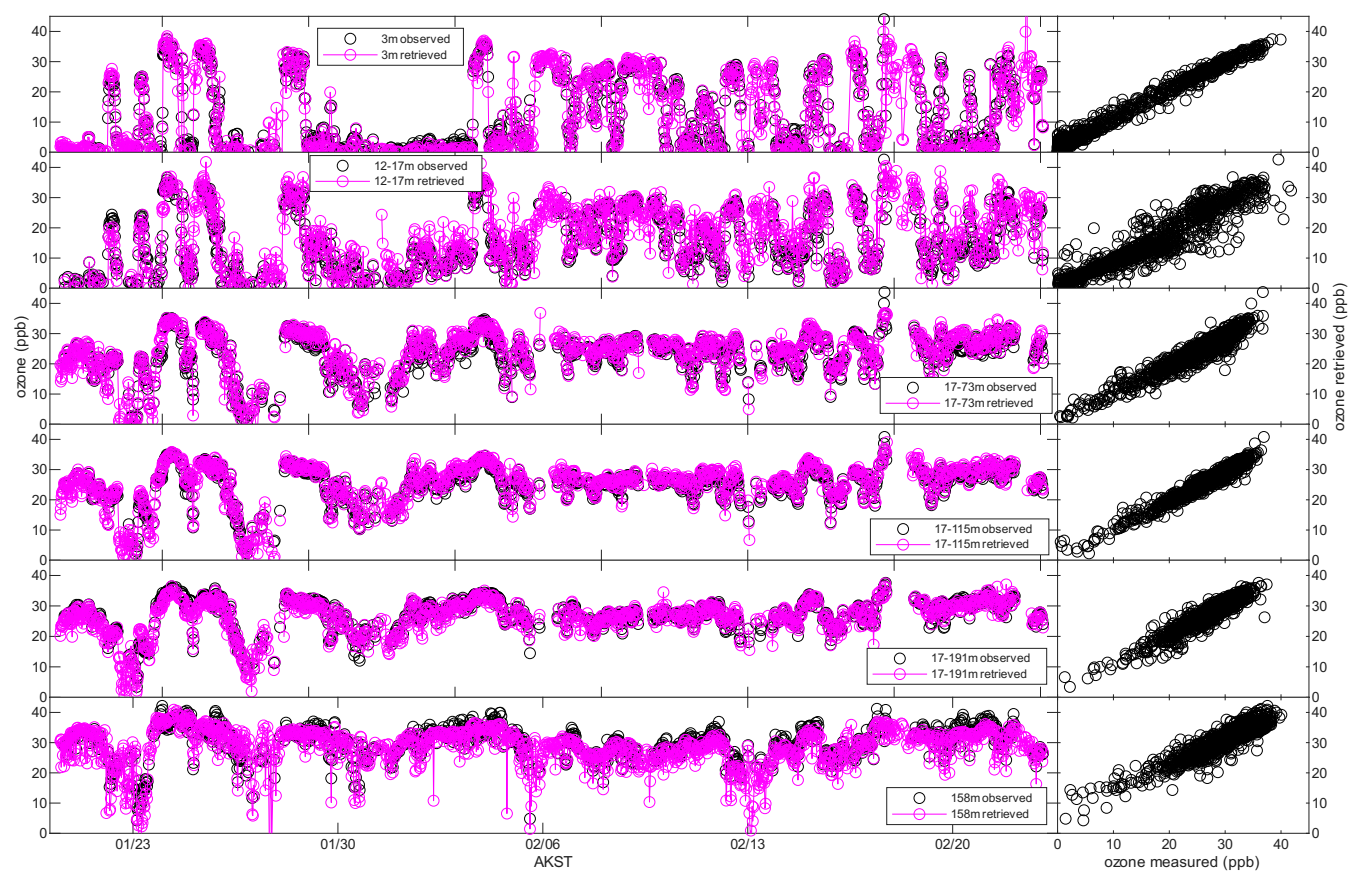


Figure S4. Comparison of retrieved (magenta) and observed (black) in-situ and path-averaged ozone mixing ratios. The panels on the right show the close correlation between retrieved and observed values.

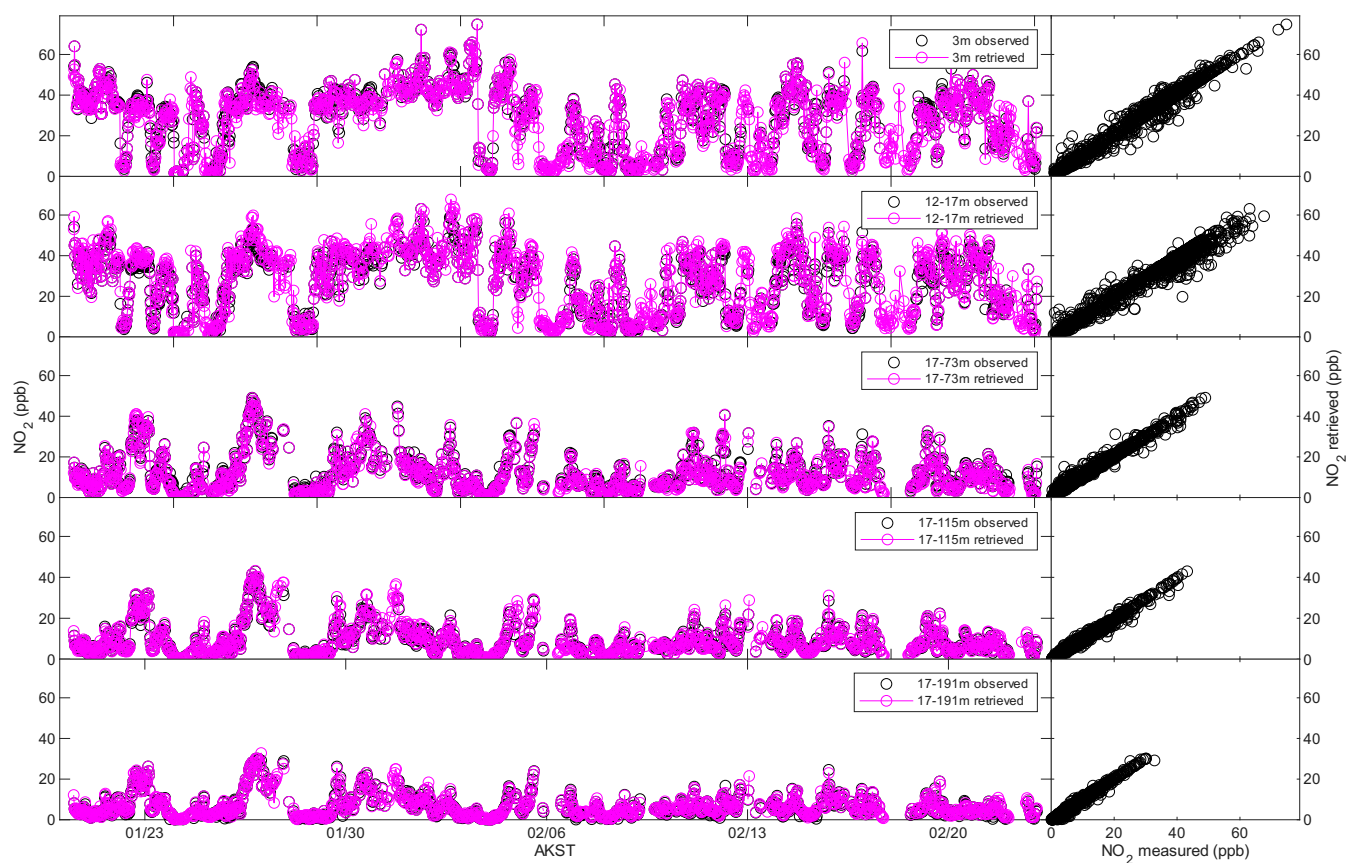


Figure S5. Comparison of retrieved (magenta) and observed (black) in-situ and path-averaged NO_2 mixing ratios. The panels on the right show the close correlation between retrieved and observed values.

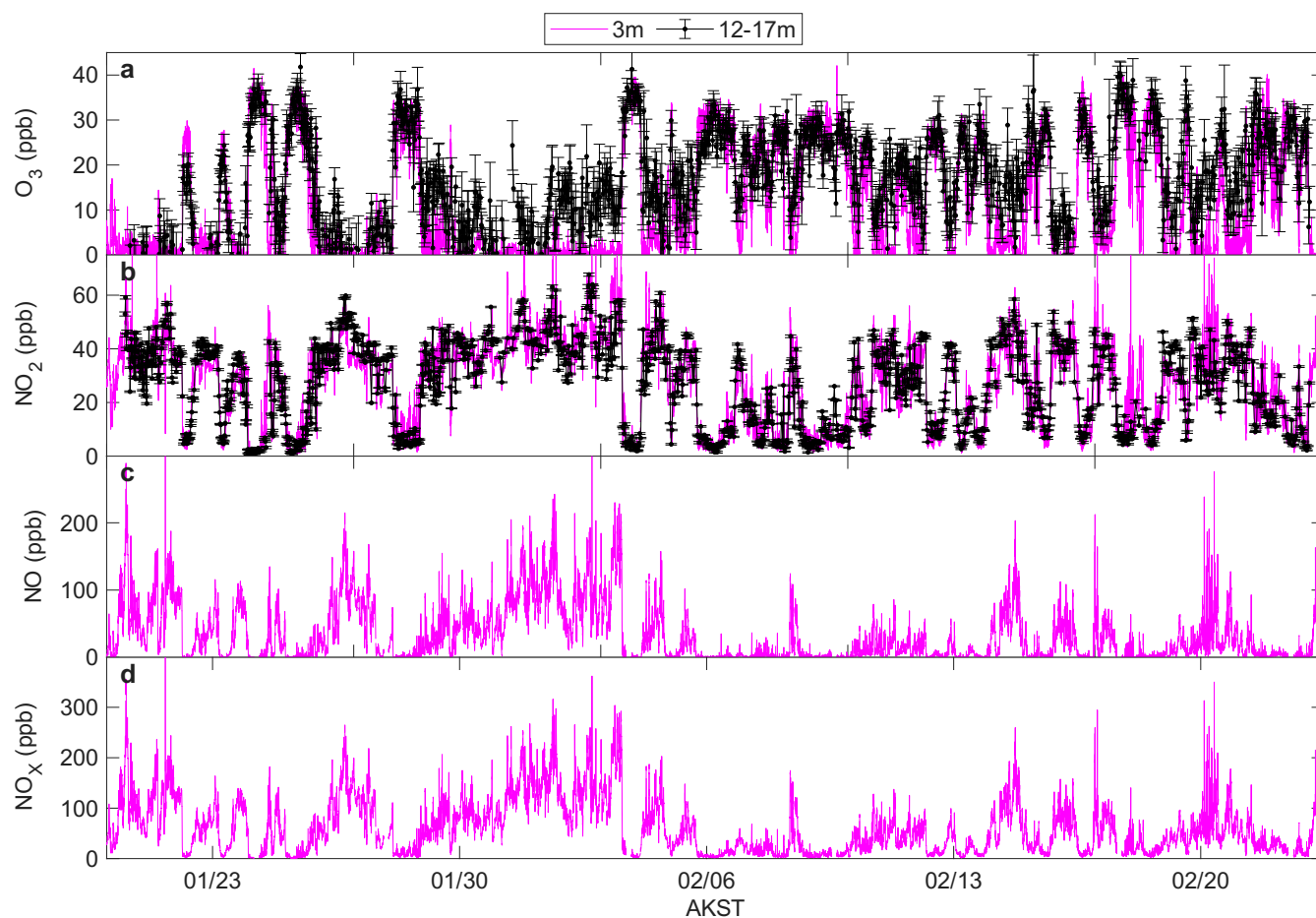


Figure S6. Campaign overview of PSL observations of (a) O₃, (b) NO₂, (c) NO, and (d) NO_x = NO + NO₂. Panels (a) and (b) compare LP-DOAS (12 - 17 m, black) and in-situ (3m, magenta) data. Only in-situ (3 m) data are shown in panels (c) and (d). Further explanation of this figure can be found in Section 3.1 in the main text.

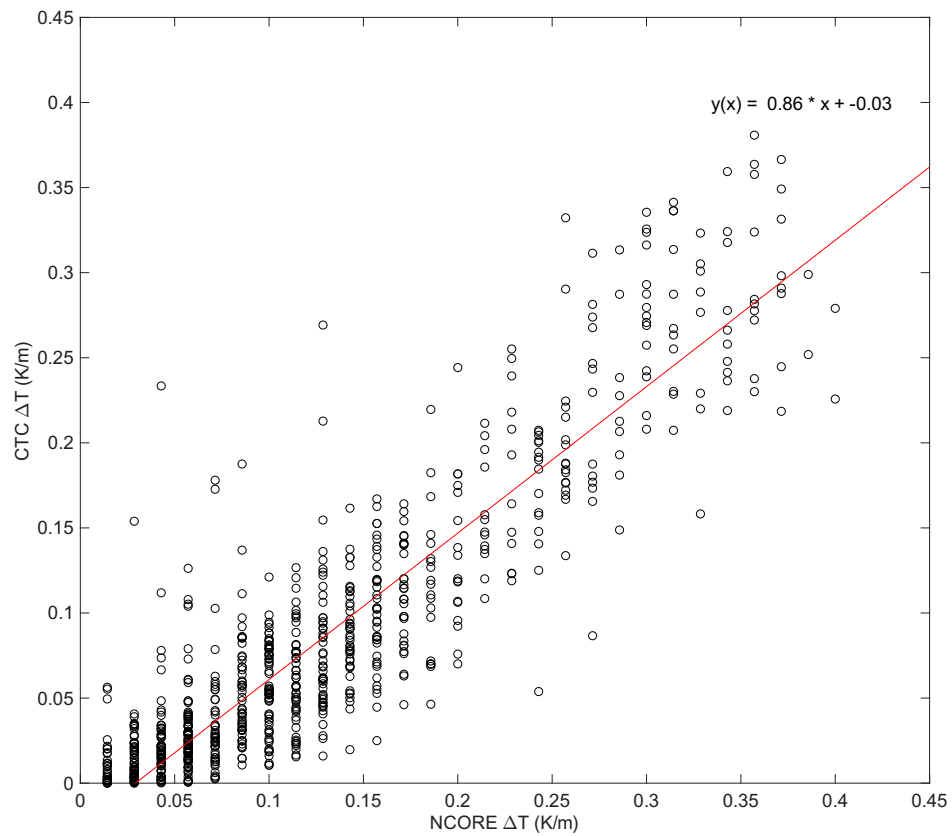


Figure S7. Comparison of CTC (11 - 3 m) and NCORE (10 - 3 m) temperature gradients (gradients below zero and above 0.4 °C/m) were omitted from the fitting procedure to remove outliers). On average, the CTC temperature gradients are about 14% smaller than the ones at NCORE.

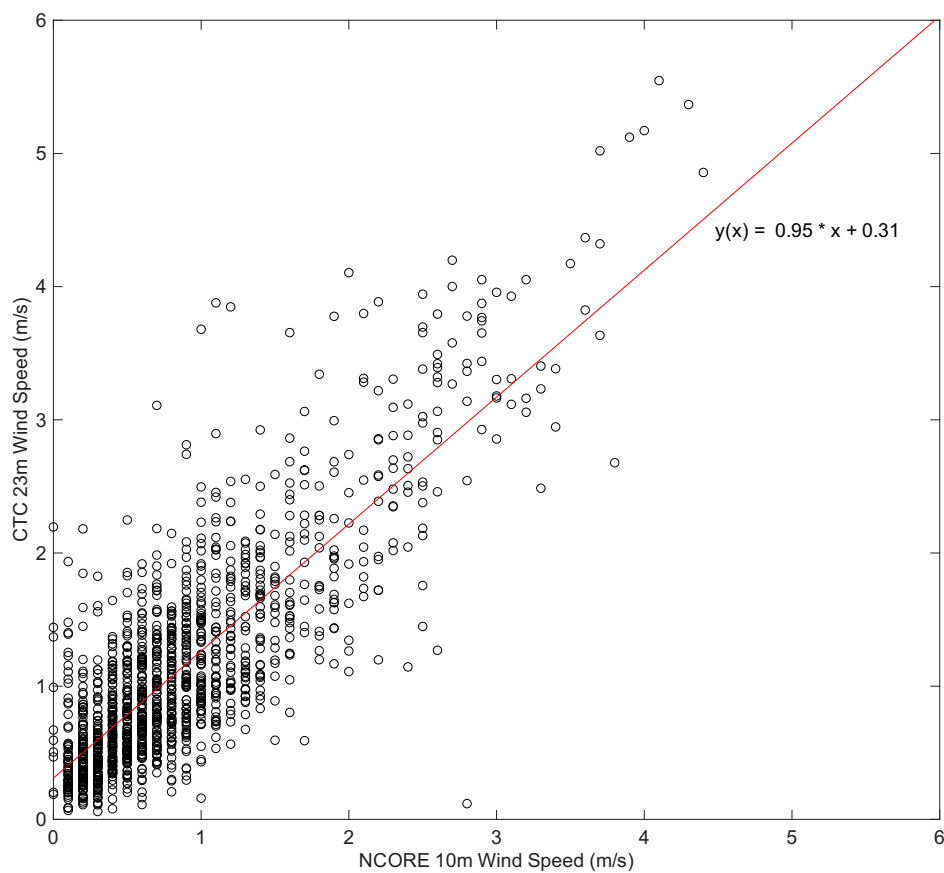


Figure S8. Comparison of CTC 23 m wind speed with NCORE 10 m wind speed. The two wind speeds agree surprisingly well with a slope of 0.95.

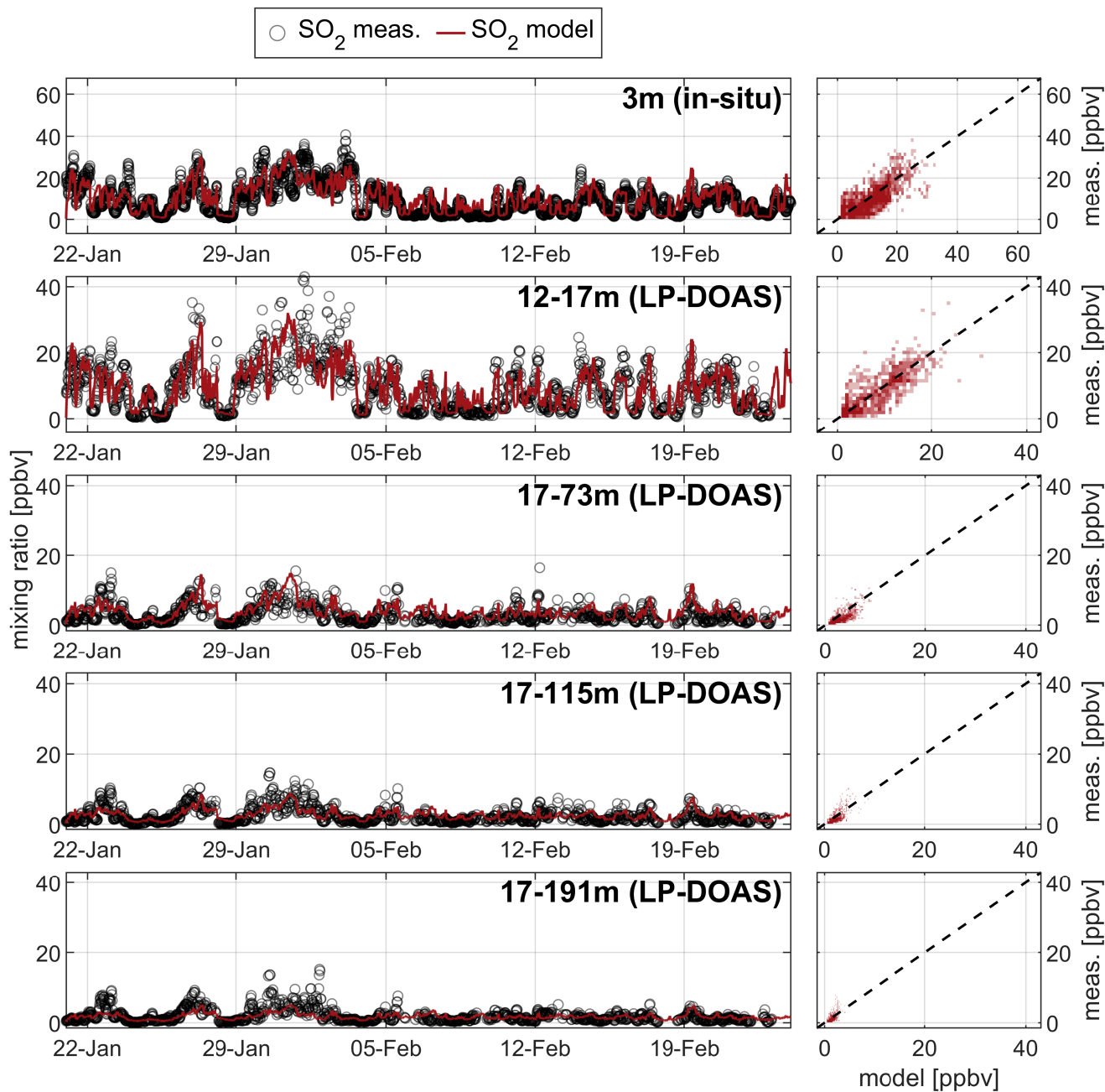


Figure S9. Comparison of in-situ and LP-DOAS observations of SO_2 with model output. The model data for the LP-DOAS comparison was averaged over the same height intervals as the respective light paths.

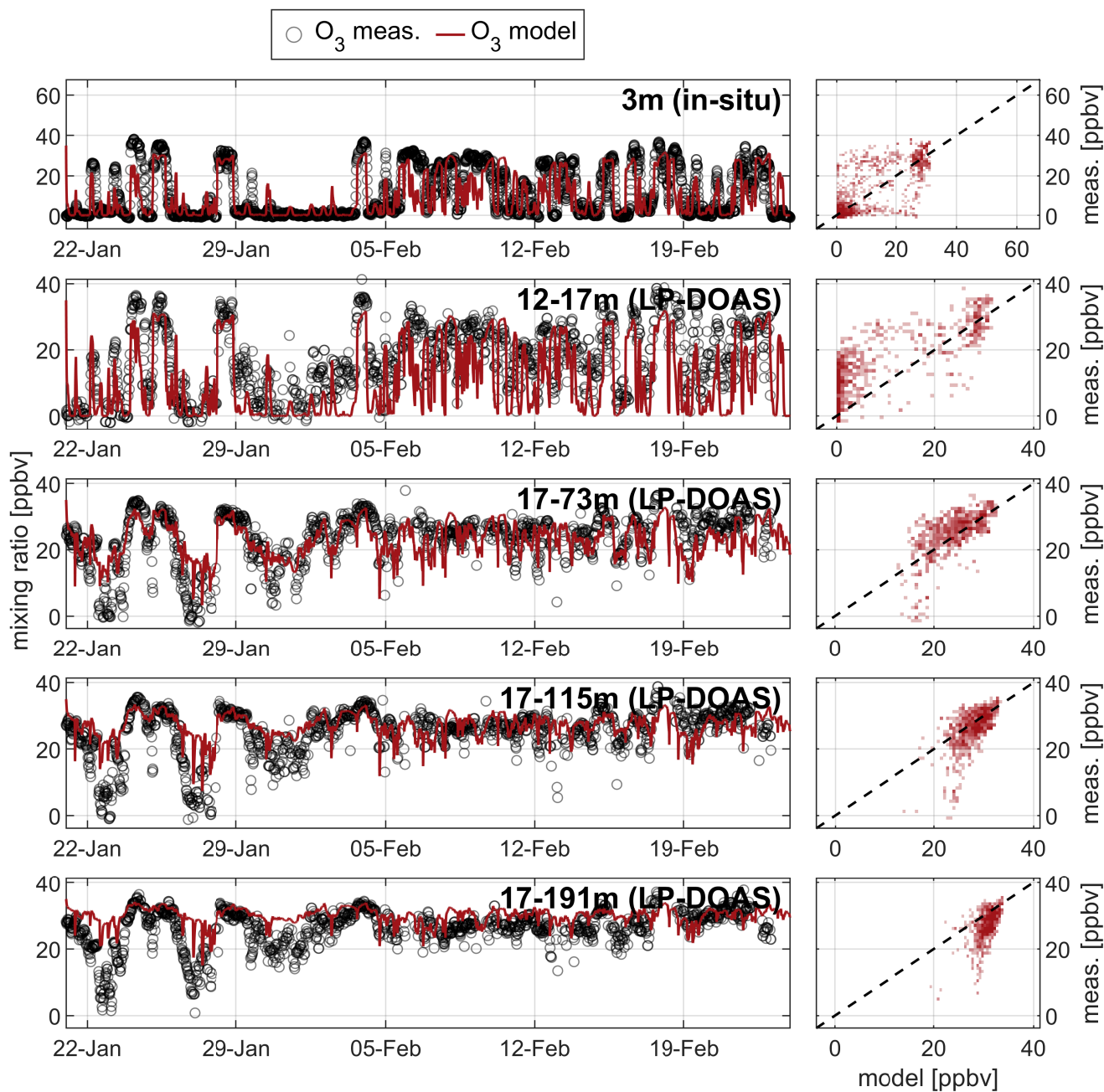


Figure S10. Comparison of in-situ and LP-DOAS observations of O₃ with model output. The model data for the LP-DOAS comparison was averaged over the same height intervals as the respective light paths.

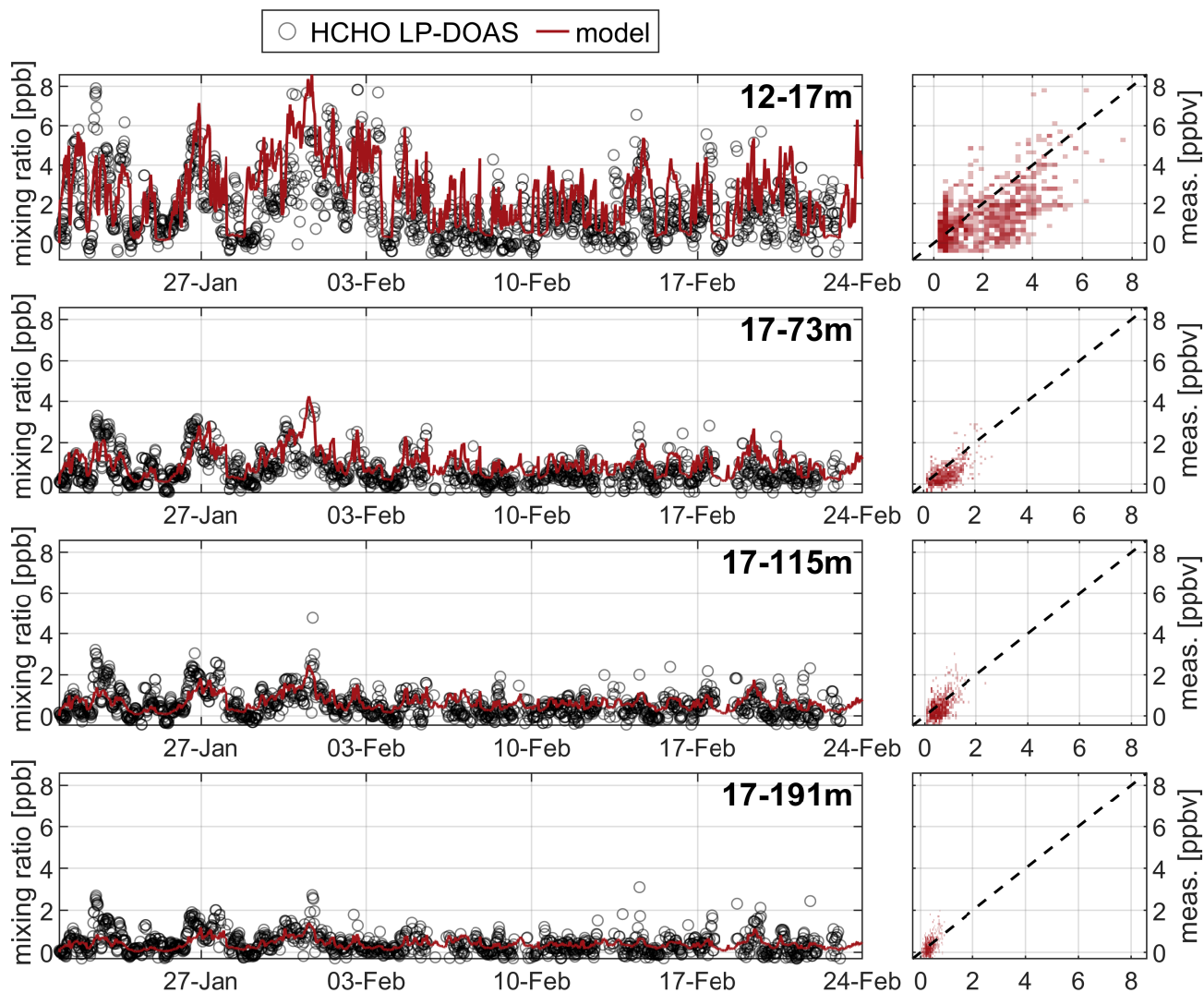


Figure S11. Comparison of LP-DOAS observations of HCHO with model output. The model data for the LP-DOAS comparison was averaged over the same height intervals as the respective light paths.

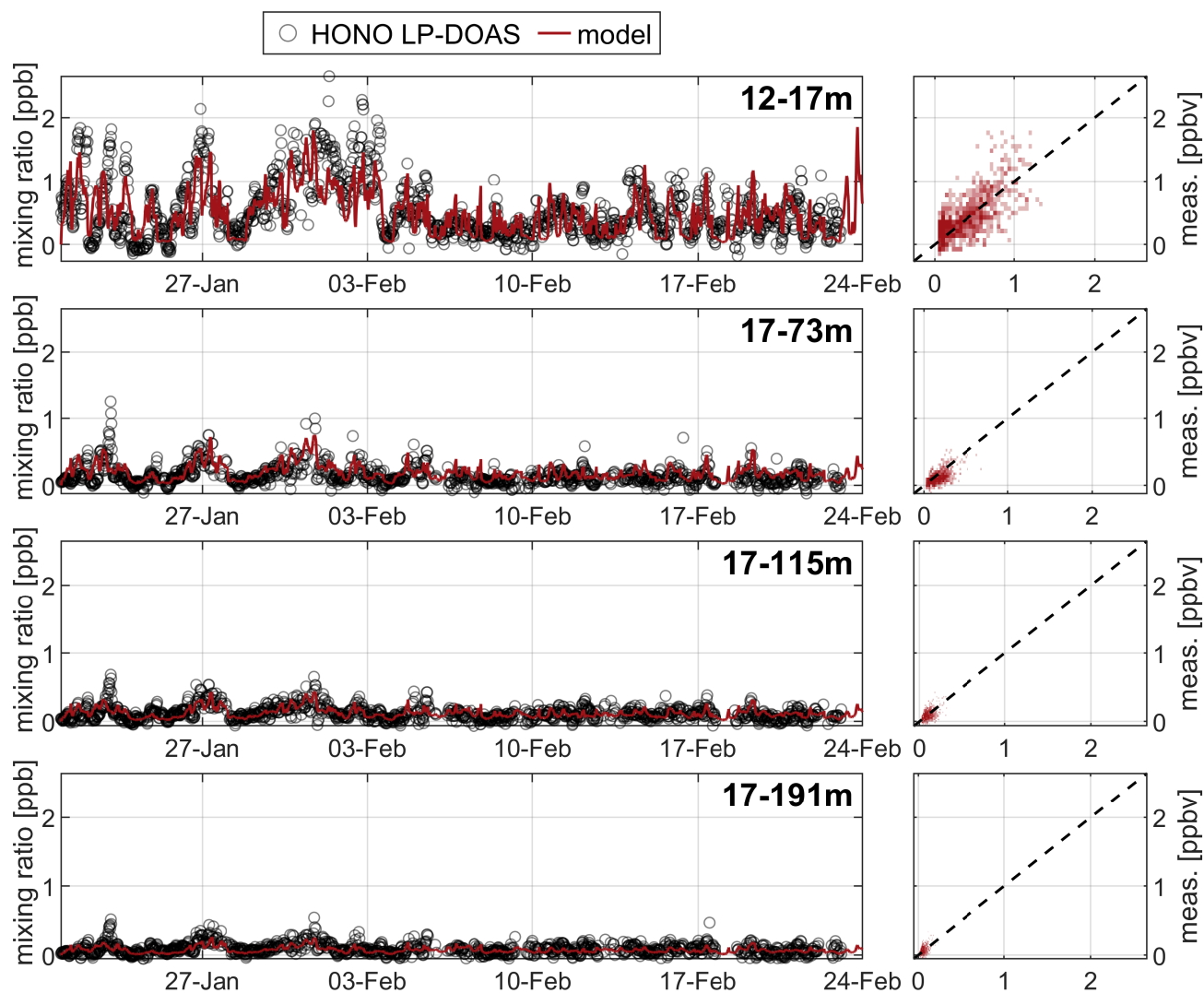


Figure S12. Comparison of LP-DOAS observations of HONO with model output. The model data for the LP-DOAS comparison was averaged over the same height intervals as the respective light paths.

References

- Birk, M. and Wagner, G.: ESA SEOM-IAS – Measurement and ACS database O₃ UV region, <https://doi.org/10.5281/zenodo.1485588>, 2018.
- Bogumil, K., Orphal, J., Homann, T., Voigt, S., Spietz, P., Fleischmann, O., Vogel, A., Hartmann, M., Kromminga, H., Bovensmann, H., Frerick, J., and Burrows, J.: Measurements of molecular absorption spectra with the SCIAMACHY pre-flight model: instrument characterization and reference data for atmospheric remote-sensing in the 230–2380 nm region, *J. Photochem. Photobiol. A: Chem.*, 157, 167–184, [https://doi.org/10.1016/S1010-6030\(03\)00062-5](https://doi.org/10.1016/S1010-6030(03)00062-5), 2003.
- Brett, N., Law, K. S., Arnold, S. R., Fochesatto, J. G., Raut, J.-C., Onishi, T., Gilliam, R., Fahey, K., Huff, D., Pouliot, G., Barret, B., Dieudonné, E., Pohorsky, R., Schmale, J., Baccarini, A., Bekki, S., Pappaccogli, G., Scoto, F., Decesari, S., Donato, A., Cesler-Maloney, M., Simpson, W., Medina, P., D'Anna, B., Temime-Roussel, B., Savarino, J., Albertin, S., Mao, J., Alexander, B., Moon, A., DeCarlo, P. F., Selimovic, V., Yokelson, R., and Robinson, E. S.: Investigating processes influencing simulation of local Arctic wintertime anthropogenic pollution in Fairbanks, Alaska, during ALPACA-2022, *Atmos. Chem. Phys.*, 25, 1063–1104, <https://doi.org/10.5194/acp-25-1063-2025>, 2025.
- Fally, S., Vandaele, A., Carleer, M., Hermans, C., Jenouvrier, A., Mérienne, M., Coquart, B., and Colin, R.: Fourier transform spectroscopy of the O₂ Herzberg Bands. III. Absorption cross sections of the collision-induced bands and of the Herzberg continuum., *J. Molec. Spect.*, 204, 10–20, <https://doi.org/10.1006/jmsp.2000.8204>, 2000.
- Hermans, C., Vandaele, A. C., Carleer, M., Fally, S., Colin, R., Jenouvrier, A., Coquart, B., and Mérienne, M. F.: Absorption cross-sections of atmospheric constituents: NO₂, O₂, and H₂O., *Environ. Sci. Poll. Res.*, 6, 151, <https://doi.org/10.1007/BF02987620>, 1999.
- Landis, M. S. and Edgerton, E. S.: Field intercomparison of continuous ambient FRM and FEM NO₂ instruments in the Athabasca Oil Sands Region, Alberta, Canada and the potential impact on ambient regulatory compliance, *Journal of the Air & Waste Management Association*, 74, 11–24, <https://doi.org/10.1080/10962247.2023.2279169>, 2024.
- Meller, R. and Moortgat, G. K.: Temperature dependence of the absorption cross sections of formaldehyde between 223 and 323 K in the wavelength range 225–375 nm, *J. Geophys. Res.: Atmos.*, 105, 7089–7101, <https://doi.org/10.1029/1999JD901074>, 2000.
- Platt, U. and Stutz, J.: *Differential Optical Absorption Spectroscopy*, Springer Berlin Heidelberg, Berlin, Heidelberg, <https://doi.org/10.1007/978-3-540-75776-4>, 2008.
- Roberts, T. J., Cesler-Maloney, M., and Simpson, W. R.: Low-cost electrochemical gas sensing of vertical differences in wintertime air composition (CO, NO, NO₂, O₃) in Fairbanks, Alaska, *Faraday Discussions*, 258, 307–327, <https://doi.org/10.1039/D4FD00177J>, 2025.
- Rothman, L. S., Gordon, I. E., Barber, R. J., Dothe, H., Gamache, R. R., Goldman, A., Perevalov, V. I., Tashkun, S. A., and Tennyson, J.: HITRAN, the high-temperature molecular spectroscopic database, *J. Quant. Spect. Rad. Trans.*, 111, 2139–2150, <https://doi.org/10.1016/j.jqsrt.2010.05.001>, 2010.
- Stutz, J. and Platt, U.: Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least-squares methods, *Appl. Opt.*, 35, 6041–6053, <https://doi.org/10.1364/AO.35.006041>, 1996.
- Stutz, J. and Platt, U.: Improving long-path differential optical absorption spectroscopy with a quartz-fiber mode mixer, *Appl. Opt.*, 36, 1105–1115, <https://doi.org/10.1364/AO.36.001105>, 1997.
- Stutz, J., Kim, E. S., Platt, U., Bruno, P., Perrino, C., and Febo, A.: UV-visible absorption cross sections of nitrous acid, *J. Geophys. Res.: Atmos.*, 105, 14 585–14 592, <https://doi.org/10.1029/2000JD900003>, 2000.
- Vandaele, A., Simon, P., Guillemot, J., Carleer, M., and Colin, R.: SO₂ absorption cross section measurement in the UV using a Fourier transform spectrometer, *J. Geophys. Res.*, 99, 25 599–25 605, <https://doi.org/10.1029/94JD02187>, 1994.
- Voigt, S., Orphal, J., and Burrows, J.: The temperature and pressure dependence of the absorption cross-sections of NO₂ in the 250–800 nm region measured by Fourier-transform spectroscopy, *Journal of Photochemistry and Photobiology A: Chemistry*, 149, 1–7, [https://doi.org/10.1016/S1010-6030\(01\)00650-5](https://doi.org/10.1016/S1010-6030(01)00650-5), 2002.