Supplement of

Laser-induced fluorescence-based detection of atmospheric nitrogen dioxide and comparison of different techniques during the PARADE 2011 field campaign

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Supplements:

S1.1 Instrumental

S1.1.1 Diode Laser

Fig. S1: Wavelength plot for the diode laser, operated with repetition rate of 5MHz. The wavelength of the diode laser is measured with a spectrometer\(^1\).

![Wavelength plot](image)

Fig. S2: Multiple passes of the laser beam are visible in the detection cell (left) and in between the Herriott cell’s mirrors on an optical bench (right).

\(^1\) HR4000 High-Resolution Spectrometer, Ocean Optics, USA
S1.1.2 ON-OFF Laser cycle simulation

Fig. S3: Simulated ON/OFF cycles for operating the diode-laser

Fig. S4: A schematic of the data acquisition system

NOTE: $t_{\text{prop}}$ = Propagation delay due to cable and electronics. $t_{\text{delay}}$ = Propagation delay due to cable and electronics. $t_{\text{delay}}$ = Delay because of latency in the FPGA logic. All delays do not change unless electronics / hardware / cables modified.
S1.1.3 Reactions for calibration simulations

Note; all reactions and rate coefficients from k1 to k64 are taken from (Atkinson et al., 2004) except k54 (temperature dependent) from (Sander et al., 2011). The impact of the difference between the JPL and IUPAC rate constant is less than 1 % on our results.

\[ \begin{align*}
    k1 & : \quad O + O_2 & = & \quad O_3; \\
    k25 & : \quad OH + O_3 & = & \quad HO_2 + O_2; \\
    k28 & : \quad HO_2 + O_3 & = & \quad OH + O_2 + O_2; \\
    k31 & : \quad O + NO & = & \quad NO_2; \\
    k32 & : \quad O + NO_2 & = & \quad O_2 + NO; \\
    k33 & : \quad O + NO_2 & = & \quad NO_3; \\
    k34 & : \quad O + NO_3 & = & \quad O_2 + NO_2; \\
    k39 & : \quad OH + HONO & = & \quad H_2O + NO_2; \\
    k40 & : \quad OH + HNO_3 & = & \quad H_2O + NO_3; \\
    k41 & : \quad OH + HNO_4 & = & \quad \text{products}; \\
    k42 & : \quad OH + NO & = & \quad HONO; \\
    k43 & : \quad OH + NO_2 & = & \quad HNO_3; \\
    k44 & : \quad OH + NO_3 & = & \quad HO_2 + NO_2; \\
    k45 & : \quad HO_2 + NO & = & \quad OH + NO_2; \\
    k46 & : \quad HO_2 + NO_2 & = & \quad HNO_4; \\
    k47 & : \quad HNO_4 & = & \quad HO_2 + NO_3; \\
    k48 & : \quad HO_2 + NO_3 & = & \quad \text{products}; \\
    k53 & : \quad NO + NO + O_2 & = & \quad NO_2 + NO_2; \\
    k54 & : \quad NO + O_3 & = & \quad NO_2 + O_2; \\
    k55 & : \quad NO + NO_2 & = & \quad N_2O_3; \\
    k56 & : \quad N_2O_3 & = & \quad NO + NO_2; \\
    k57 & : \quad NO + NO_3 & = & \quad NO_2 + NO_2; \\
    k58 & : \quad NO_2 + O_3 & = & \quad NO_3 + O_2; \\
    k59 & : \quad NO_2 + NO_2 & = & \quad N_2O_4; \\
    k60 & : \quad N_2O_4 & = & \quad NO_2 + NO_2; \\
    k61 & : \quad NO_2 + NO_3 & = & \quad N_2O_5; \\
    k62 & : \quad N_2O_5 & = & \quad NO_2 + NO_3; \\
    k63 & : \quad N_2O_5 + H_2O & = & \quad HNO_3 + HNO_3; \\
    k64 & : \quad N_2O_5 + H_2O + H_2O & = & \quad HNO_3 + H_2O;
\end{align*} \]
S1.1.4 Box Model simulated temperature and pressure effect on calibrator

Fig. S5: In the left panel, NO\textsubscript{2} concentrations inside the calibrator as a function of time based on different temperatures. While the right panel shows NO\textsubscript{2} concentrations inside the calibrator as a function of time for different pressures (mbar or hPa).

S1.1.5 Gas phase titration NO\textsubscript{GPT}

Fig. S6: NO\textsubscript{GPT} based on a CLD measurements as a function of the reaction chamber O\textsubscript{3} mixing ratios.
S1.1.6 Limit of Detection

Fig. S7: An example for the limit of detection of GANDALF based on different calibrations, taken from an automated calibrated period of PARADE-2011 according to the Eq. 4 (Section 2.3) in the main draft.

S1.2 PARADE-2011

S1.2.1 Air Mass Origin

Fig. S8: Origin of air mass for PARADE-2011 [Figure is taken from Crowley, J., 2012 (left)]. Frequency distributions of wind directions with wind speed (colour-coded: wind speed in ms$^{-1}$). [Google Map view (www.google.com/maps)]. While shaded area in R.H.S is showing possible anthropogenic influence from nearby cities.
S1.2.2 Frequency plot of NO₂ measurements

![Frequency plot of NO₂ measurements](image)

Fig. S9: Histogram of the distribution of the data for different NO₂ measurements during PARADE 2011.

S1.2.3 Time series of NO₂ measurements

![Time series of NO₂ measurements](image)

Fig. S10: PARADE 2011 time series (10 min. averages) of NO₂ observations (y-axis in ppb) based on different instruments.
S1.2.4 Individual correlation with GANDALF (x-axis)

Fig. S11: The individual correlation of different NO$_2$ instruments (y-axis) versus GANDALF (x-axis) is shown for available 10 minutes data averages. The two different fitting procedures i.e. based on least square fit (Bevington and Robinson, 1992) and York method (York et al., 2004) are applied.
S1.2.5 NO₂ Ratios Correlations

This section is related to NO₂ comparison for PARADE. A series of upcoming figures shows ratio (between all NO₂ measurements and GANDALF) as a function of different observed quantities to see any systematic correlation. Each figure is a set of four subplots according to different instruments. Y-axis of figures below is shown as follow (with data colour to show sequence of upcoming figures for quick go through).

<table>
<thead>
<tr>
<th>LP-DOAS / GANDALF</th>
<th>CRDS / GANDALF</th>
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</thead>
<tbody>
<tr>
<td>CE-DOAS / GANDALF</td>
<td>CRD / GANDALF</td>
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Fig. S12: Ratios of different NO₂ measurements with respect to GANDALF as a function of different measured species and parameters based on 10 minute averages.

Fig. S12: continue
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S1.3 References


Crowley, J., PArticles and RAdicals: Diel observations of the impact of urban and biogenic Emissions, PARADE data meeting at Max Planck Institute for Chemistry, Mainz, 10th May, 2012.
