S1 Calibration of the FT-CRDS with NO

Figure S1: (a) Measured and simulated mixing ratios of (synthetic) NO$_3$ in the flow-tube obtained after adding 152 pptv of NO ca. every two hours. Ticks represent 00:00 UTC. (b) Comparison between measured and simulated mixing ratios after adding five different, known amounts of NO (values in brackets denote added NO concentrations in pptv). The red line represents a York fit (slope = 1.01 and an intercept of -0.3 pptv). Dashed line indicates 1:1 agreement.
Figure S2: Correlation between NO\textsubscript{2} mixing measured with the FT-CRDS setup and (a) night-time NO\textsubscript{x} mixing ratios measured with the TD-CRDS setup (b) NO\textsubscript{2} mixing ratios measured with the CLD instrument. The red solid line indicates a York fit, while the dashed blue line represents an ideal 1:1 agreement.
Figure S3: Wind rose of (a) wind speed and (b) NO₃ reactivity measured during the TO2021 campaign.
Figure S4: (a) Time-trace of PTR-MS measurements (PTR8000) of isoprene (black squares, left axis), the sum of monoterpenes (ΣMTs, blue triangles, left axis) and the sum of sesquiterpenes (ΣSTs, red circles, right axis) during the second half of the TO2021 campaign. Major ticks mark 00:00 UTC. (b) Time-series of monoterpenes signals (upper panel) and sesquiterpene signals (lower panel) from the VOCUS data (red) scaled to the calibrated data from the PTR8000 setup (black).
S5 Nighttime NO: Model calculation and correlation plots

* NIGHTTIME NO EMISSION SIMULATION

variable N2O5 NO3 NO2 O2

* INITIAL CONCENTRATIONS

parameter T 284.6
parameter O3i 6137372069288.082
parameter NOi 1E-99
parameter P 688
parameter M
parameter k1
parameter k2
parameter k3
parameter k4
parameter k5
parameter kVOC
parameter kVOCi 0.03561
parameter NO
parameter <5> INPARAM
parameter varia press temp ozone EM
parameter kdep 1.5E-5

COMPILE GENERAL
M = P * 3.24E16 * (298/T)

COMPILE INITIAL
NO = NOi
O3 = O3i
kVOC = kVOCi

COMPILE EQUATIONS

% k1 : N2O5 = NO3 + NO2
% k2 : NO2 + NO3 = N2O5
% k3 : NO + NO3 = NO2 + NO2
% k4 : NO2 + O3 = NO3 + O2
% k5 : NO + O3 = NO2 + O2
% kVOC : NO3 = 
% kdep : NO2 = 

*Rate equations
k1 = ((1.3e-3*(T/300)-3.5*exp(-11000/T))*M*
(9.7e14*(T/300)*0.1*exp(-11080/T)))/(1.3e-3*
(T/300)-3.5*exp(-11000/T))*M+(9.7e14*(T/300)*0.1*exp(-11080/T))
exp(-11080/T)))*10@(log10(0.35)/(1+(log10((1.3e-3*(T/300)-3.5
*exp(-11000/T))*M+(9.7e14*(T/300)*0.1*exp(-11080/T))
/(0.75-1.27*log10(0.35))@2))

; N2O5 decomp IUPAC
\[ k_2 = \frac{(3.6 \times 10^{-30} (T/300)^{0.1} \times M \times (1.9 \times 10^{-12} (T/300)^{0.2}))}{(3.6 \times 10^{-30} (T/300)^{0.1} \times M + (1.9 \times 10^{-12} (T/300)^{0.2}))} \times 10^{\frac{\log(0.35)}{1 + \frac{\log((3.6 \times 10^{-30} (T/300)^{0.1} \times 80 M)}{0.75 - 1.27 \log(0.35)}})^2}} \]

\[ k_3 = 1.8 \times 10^{-11} \exp\left(\frac{110}{T}\right) \quad \text{IUPAC} \]

\[ k_4 = 1.4 \times 10^{-13} \exp\left(\frac{-2470}{T}\right) \quad \text{IUPAC} \]

\[ k_5 = 2.07 \times 10^{-12} \exp\left(\frac{-1400}{T}\right) \quad \text{IUPAC} \]

**

COMPILE INSTANT

open 7 "no3.sim" new

open 20 "forFAC.dat" old

**

COMPILE BLOCK 3

PSTREAM 3

**

COMPIL BLOCK 4

READ 20 INPARAM <5>

varia = INPARAM<0>
press = INPARAM<1>
temp = INPARAM<2>
ozone = INPARAM<3>
EM = INPARAM<4>

P = press
T = temp
NO = EM
O3 = ozone

K VOC = varia

PSTREAM 3 7
time NO NO3 NO2 O3 N2O5 M T kVOC

**

when
1) time = 0 + 600*1798 call block 3
2) time = time + 600 call block 4 restart

**

*hmax 0.1

BEGIN
STOP
Figure S5: (a) Nighttime NO mixing ratios plotted against O₃. The red line represents a linear, least-squares fit (correlation coefficient r is −0.69). (b) Dependence of nighttime NO mixing ratios on the wind direction.
Table S1: Overview of the key parameters of the set-ups deployed to measure NO₂, O₃ and NO₃ mixing ratios during the TO2008, PARADE, INUIT and NOTOMO campaign on the Kleiner Feldberg.

<table>
<thead>
<tr>
<th>Campaign</th>
<th>NO₂</th>
<th>O₃</th>
<th>NO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Reference)</td>
<td>LOD (Uncertainty) Method; Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO2008 (Crowley et al., 2010)</td>
<td>80 pptv (10%)</td>
<td>2 ppbv (5%)</td>
<td>1-2 pptv (15%)</td>
</tr>
<tr>
<td>PARADE (Sobanski et al., 2016b)</td>
<td>30 pptv (6%)</td>
<td>1 ppbv (5%)</td>
<td>2 pptv (15%)</td>
</tr>
<tr>
<td>INUIT</td>
<td>CRDS; Thieser et al., 2016</td>
<td>UV; Drewnick et al., 2012</td>
<td>CRDS; Schuster et al., 2009</td>
</tr>
<tr>
<td>NOTOMO (Sobanski et al., 2017)</td>
<td>60 pptv (6.5%)</td>
<td>2 ppbv (2%)</td>
<td>1.5 pptv (25%)</td>
</tr>
<tr>
<td></td>
<td>CRDS; Sobanski et al., 2016a</td>
<td>UV; Sobanski et al., 2016b</td>
<td>CRDS; Sobanski et al., 2016a</td>
</tr>
</tbody>
</table>
Figure S6: Time-series of NO$_3$, NO$_2$ and O$_3$ mixing ratios as well as NO$_3$ production and loss rates during the TO2008 campaign. Major ticks represent 00:00 local time. Data was published in Crowley et al. (2010).
Figure S7: Time-series of NO$_3$, NO$_2$ and O$_3$ mixing ratios as well as NO$_3$ production and loss rates during the PARADE campaign. Major ticks represent 00:00 UTC. Data was published in Sobanski et al. (2016b).
Figure S8: Time-series of temperature, NO₃, NO₂ and O₃ mixing ratios as well as NO₃ production and loss rates during the INUIT campaign. Major ticks represent 00:00 UTC.
Figure S9: Time-series of NO$_3$, NO$_2$ and O$_3$ mixing ratios as well as NO$_3$ production and loss rates during the NOTOMO campaign. Major ticks represent 00:00 UTC. Data was published in Sobanski et al. (2017).
Figure S10: Median diel cycles of O₃ mixing ratios measured during TO2008, PARADE, INUIT, NOTOMO and TO2021.
Figure S11: Median diel cycles of NO mixing ratios during TO2008 (black) and PARADE (red). Both measurements were performed with a previous modification of the same CLD setup (Li et al., 2015) described in the main text. Dashed line mark the LODs during the corresponding campaigns. Grey shaded areas denote the nighttime period.
Figure S12: (a) Calculated NO$_3$ mixing ratios according to Eq. (4) for TO2021 with values for $k^{NO_3} \leq$ LOD set to 0.002 s$^{-1}$. (b) Same as Fig. 13c in the main text but using nighttime NO$_3$ mixing ratios as in Fig. S12a.
References


