Supplement

S1 Calibration of the FT-CRDS with NO

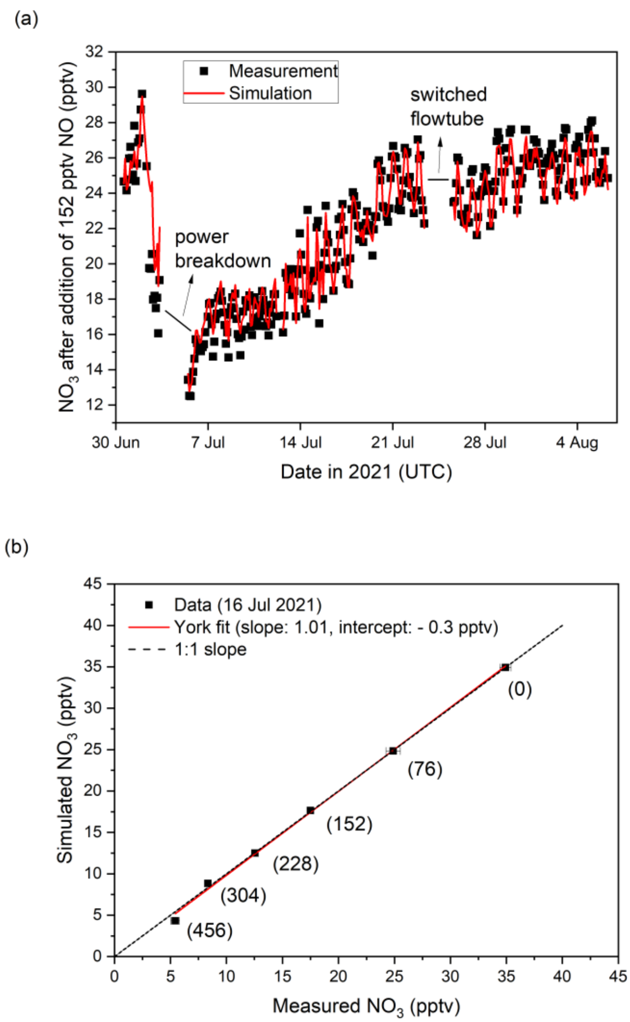

Figure S1: (a) Measured and simulated mixing ratios of (synthetic) NO_3 in the flow-tube obtained after adding 152 pptv of NO ca. every two hours. Ticks represent 00:00 UTC. (b) Comparison between measured and simulated mixing ratios after adding five different, known amounts of NO (values in brackets 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.

S2 Intercomparison of NO_2 measurements

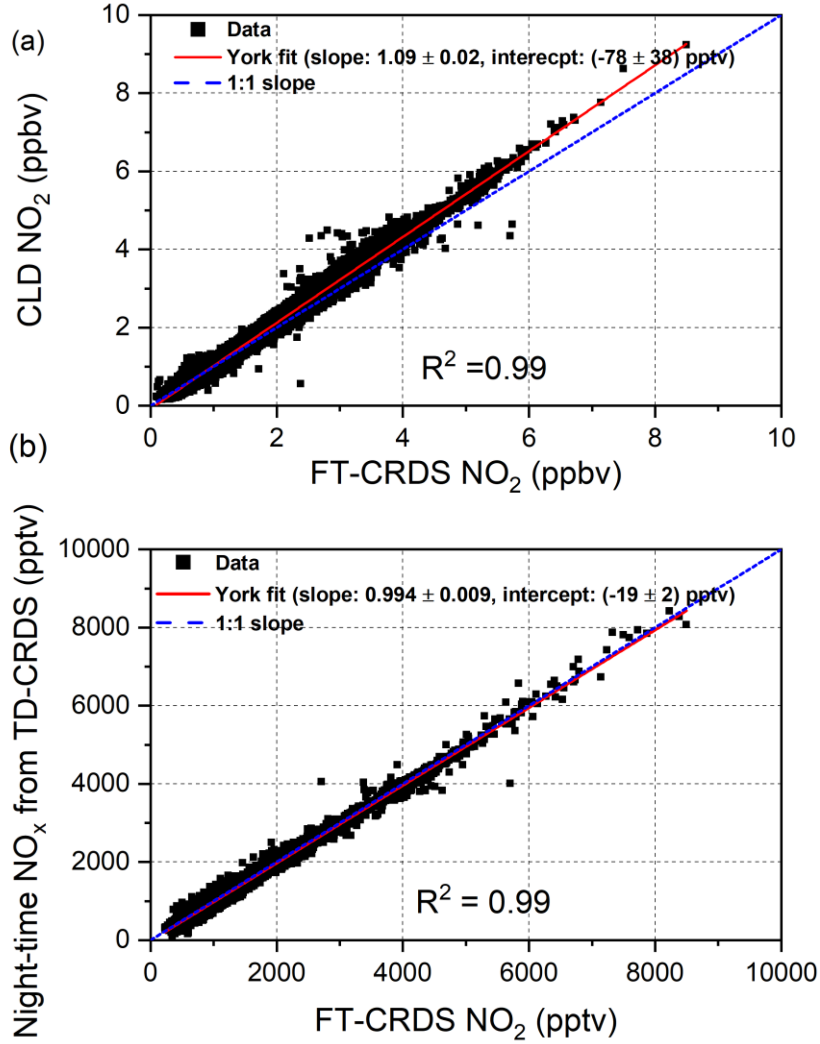

Figure S2: Correlation between NO_2 mixing measured with the FT-CRDS setup and (a) night-time NO_x mixing ratios measured with the TD-CRDS setup (b) NO_2 mixing ratios measured with the CLD instrument. The red solid line indicates a York fit, while the dashed blue line represents an ideal 1:1 agreement.

S3 Wind direction and NO_3 reactivity

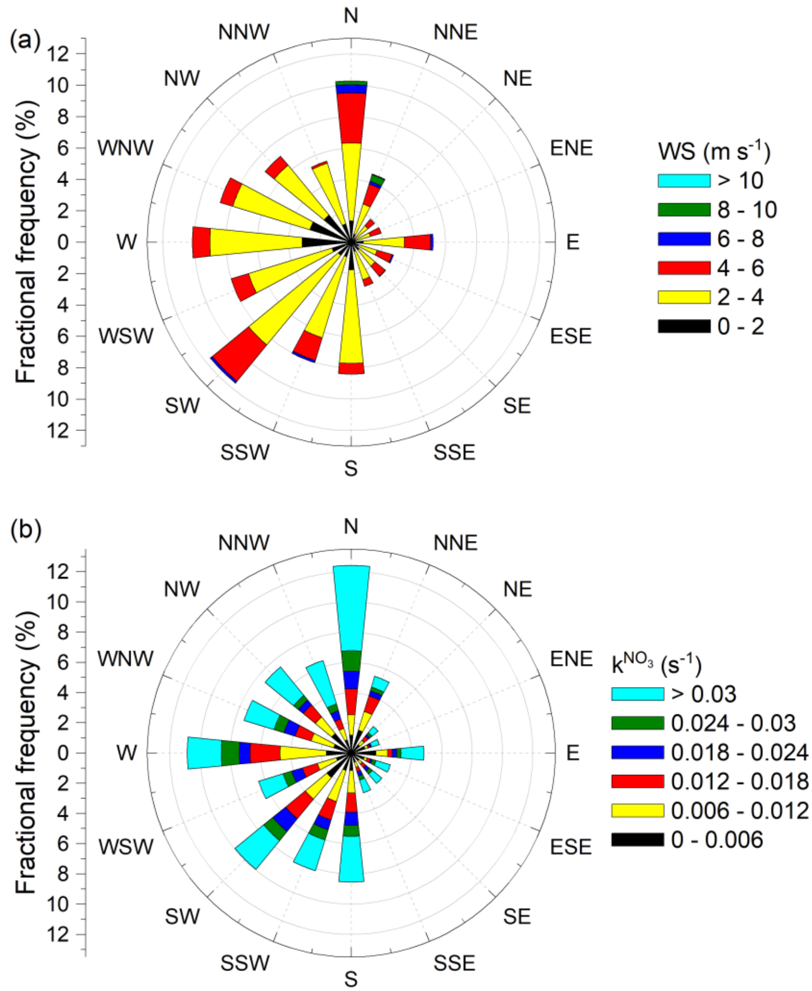

Figure S3: Wind rose of (a) wind speed and (b) NO_3 reactivity measured during the TO2021 campaign.

S4 VOC measurements

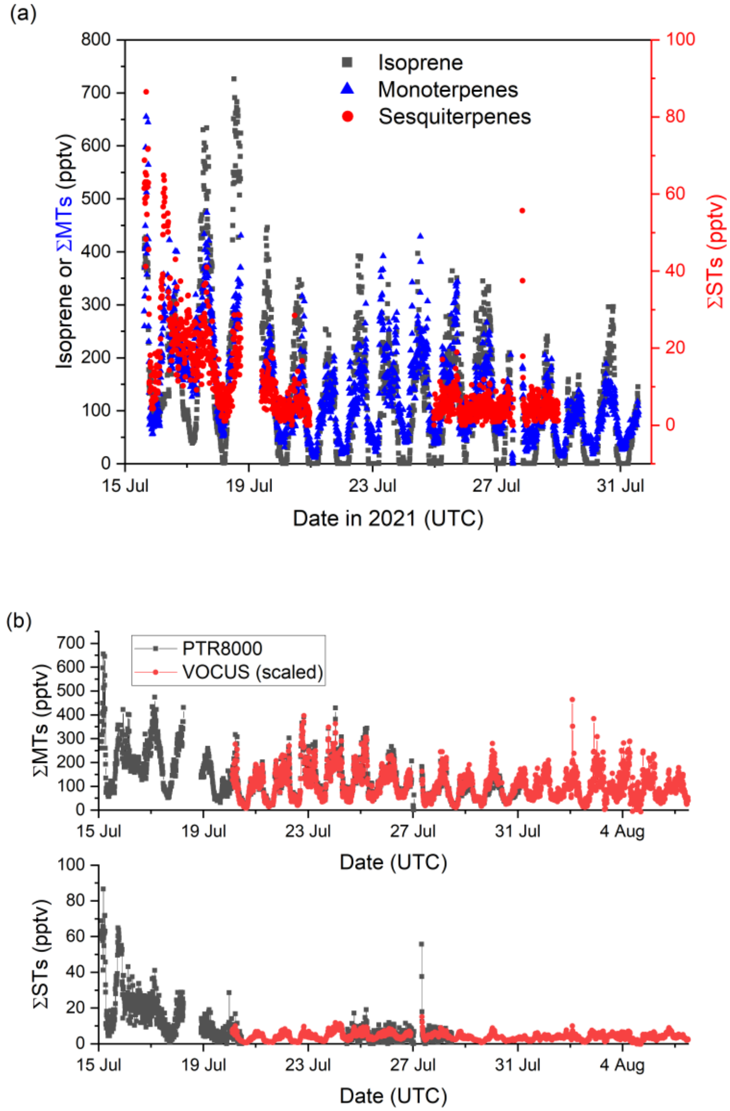

Figure S4: (a) Time-trace of PTR-MS measurements (PTR8000) of isoprene (black squares, left axis), the sum of monoterpenes (ΣMTs, blue triangles, left axis) and the sum of sesquiterpenes (ΣSTs, red circles, right axis) during the second half of the TO2021 campaign. Major ticks mark 00:00 UTC. (b) Time-series 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)))*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
```

```
k2 = ((3.6e-30*(T/300)@-4.1)*M*(1.9e-12*(T/300)@0.2))
/((3.6e-30*(T/300)@-4.1)*M+(1.9e-12*(T/300)@0.2))*
10@(log10(0.35)/(1+(log10((3.6e-30*(T/300)@-4.1)*
M/(1.9e-12*(T/300)@0.2))/(0.75-1.27*log10(0.35)))@2))      ; NO2 + NO3 IUPAC
k3 = 1.8E-11*exp(110/T)                                     ;IUPAC
k4 = 1.4e-13 * exp (-2470/T)                                ;IUPAC
k5 = 2.07e-12 * exp (-1400/T)                               ;IUPAC
**                                                         ;
COMPILE INSTANT                                            ;
open 7   "no3.sim" new                                     ;
open 20 "forFAC.dat" old                                   ;
**                                                         ;
COMPILE BLOCK 3                                            ;
PSTREAM 3                                                  ;
**                                                         ;
COMPILE 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                                                 ;
KVOC = 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                                                       ;
```

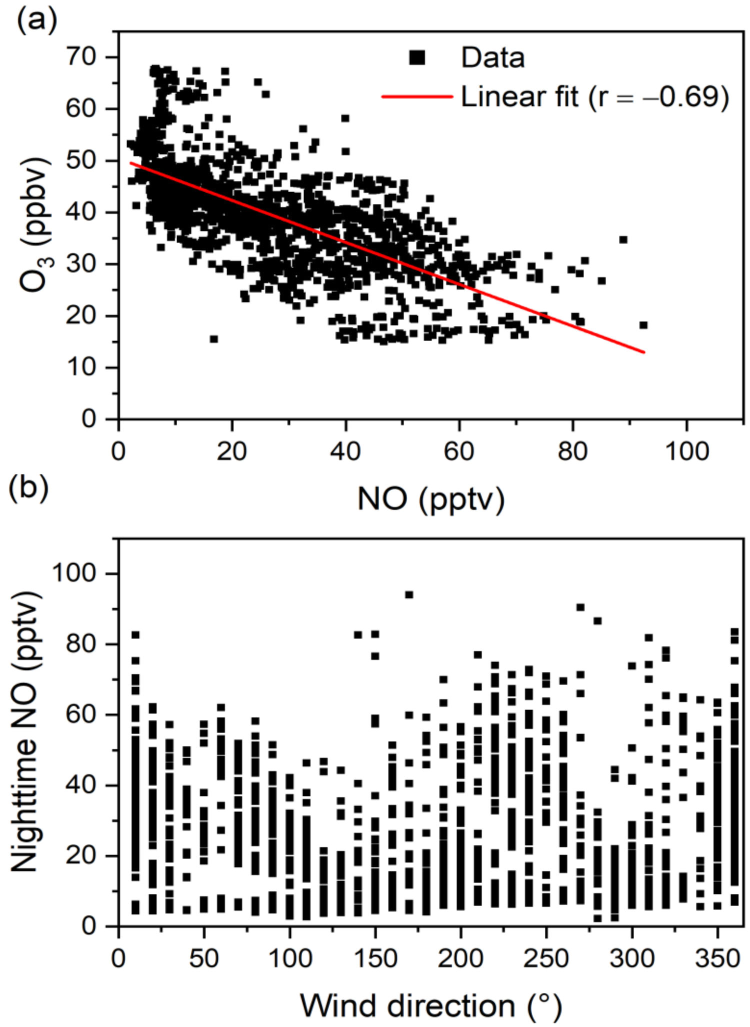

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Figure S5: (a) Nighttime NO mixing ratios plotted against O_3. The red line represents a linear, least-squares fit (correlation coefficient r is −0.69). (b) Dependence of nighttime NO mixing ratios on the wind direction.

S6 Previous measurements on the Kleiner Feldberg

Table S1: Overview of the key parameters of the set-ups deployed to measure NO_2, O_3 and NO_3 mixing ratios during the TO2008, PARADE, INUIT and NOTOMO campaign on the Kleiner Feldberg.

Campaign (Reference)	**NO_2**	**O_3 LOD (Uncertainty) Method; Reference**	**NO_3**
TO2008	80 pptv (10%)	2 ppbv (5%)	1-2 pptv (15%)
(Crowley et al., 2010)	CLD; Crowley et al., 2010	UV, Crowley et al., 2010	CRDS; Schuster et al. 2009
PARADE	30 pptv (6%)	1 ppbv (5%)	2 pptv (15%)
(Sobanski et al., 2016b)	CRDS; Thieser et al., 2016	UV; Drewnick et al., 2012	CRDS; Schuster et al., 2009
INUIT	30 pptv (6%)	1 ppbv (5%)	2 pptv (15%)
	CRDS; Thieser at al., 2016	UV; Drewnick et al., 2012	CRDS; Schuster et al., 2009
NOTOMO	60 pptv (6.5%)	2 ppbv (2%)	1.5 pptv (25%)
(Sobanski et al., 2017)	CRDS; Sobanski et al., 2016a	UV; Sobanski et al., 2016b	CRDS; Sobanski et al., 2016a

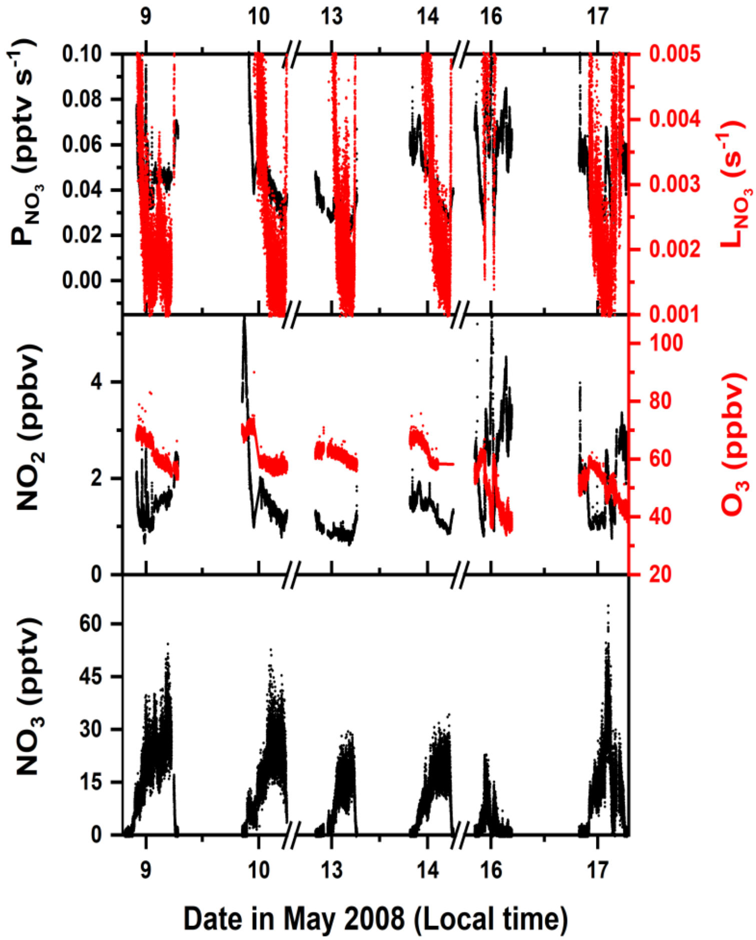
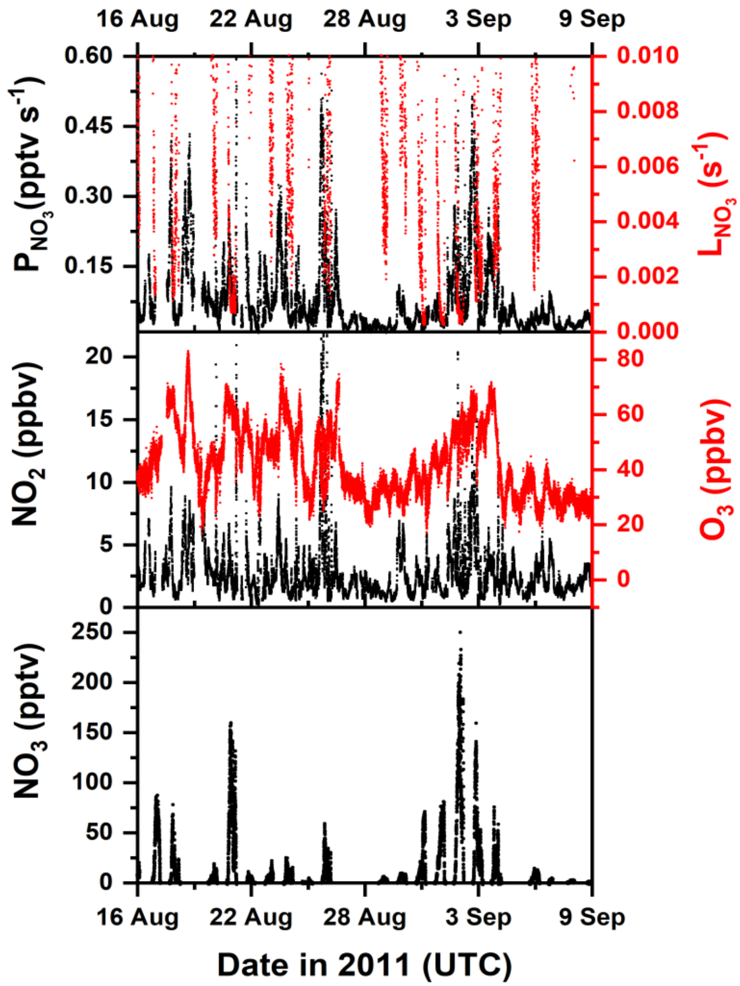


Figure S6: Time-series of NO_3, NO_2 and O_3 mixing ratios as well as NO_3 production and loss rates during the TO2008 campaign. Major ticks represent 00:00 local time. Data was published in Crowley et al. (2010).



145 **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).

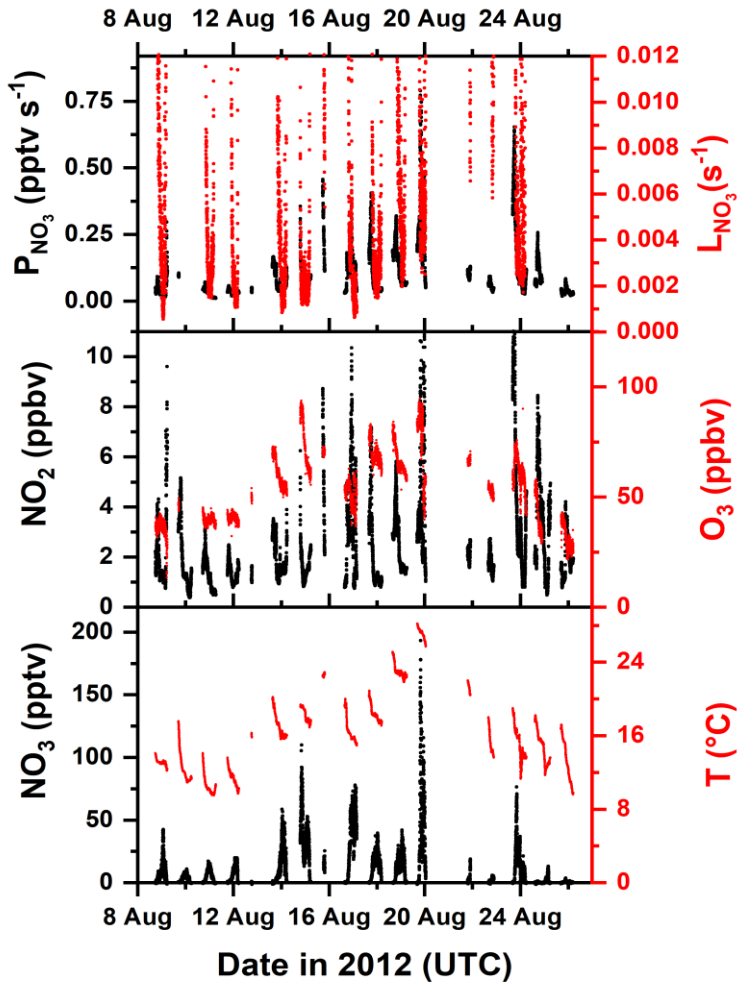


Figure S8: Time-series of temperature, NO_3, NO_2 and O_3 mixing ratios as well as NO_3 production and loss rates during the INUIT campaign. Major ticks represent 00:00 UTC.

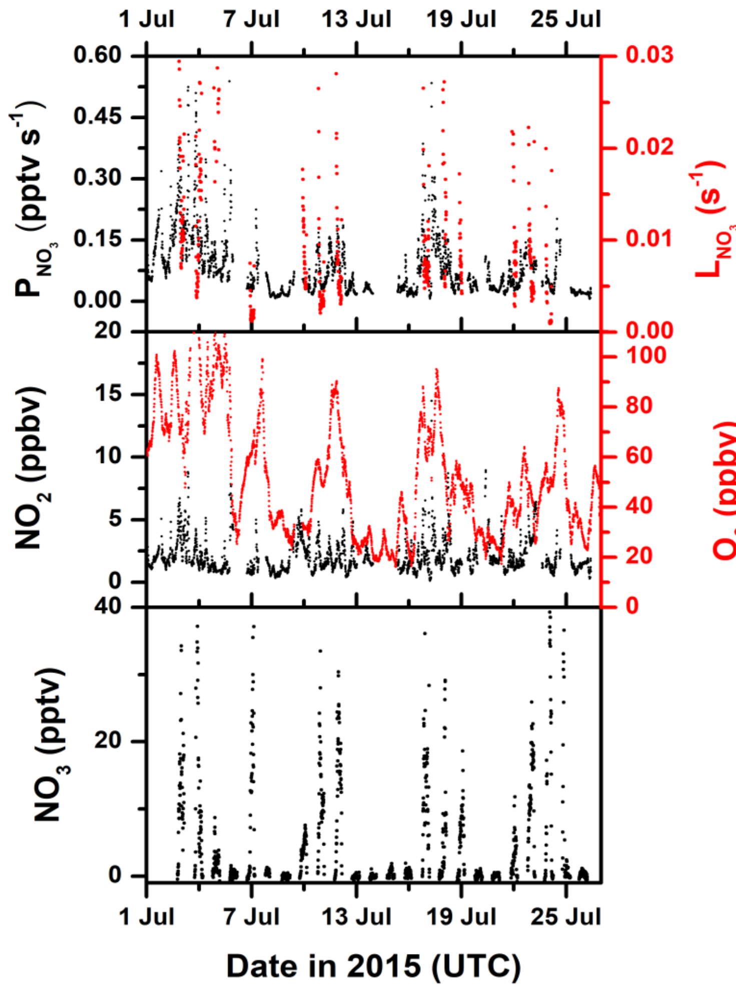


Figure S9: Time-series of NO_3, NO_2 and O_3 mixing ratios as well as NO_3 production and loss rates during the NOTOMO campaign. Major ticks represent 00:00 UTC. Data was published in Sobanski et al. (2017).

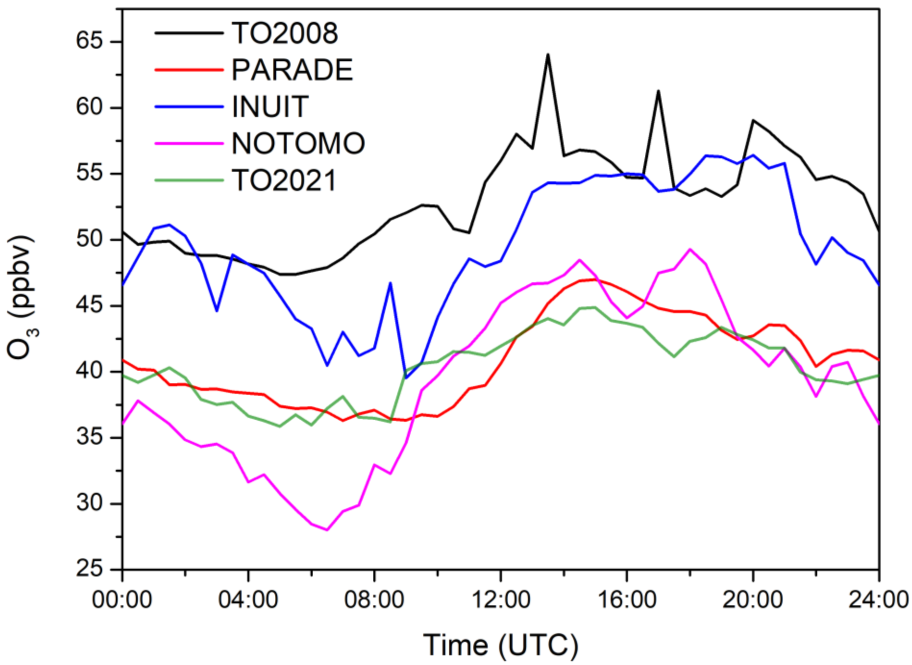


Figure S10: Median diel cycles of O_3 mixing ratios measured during TO2008, PARADE, INUIT, NOTOMO and TO2021.

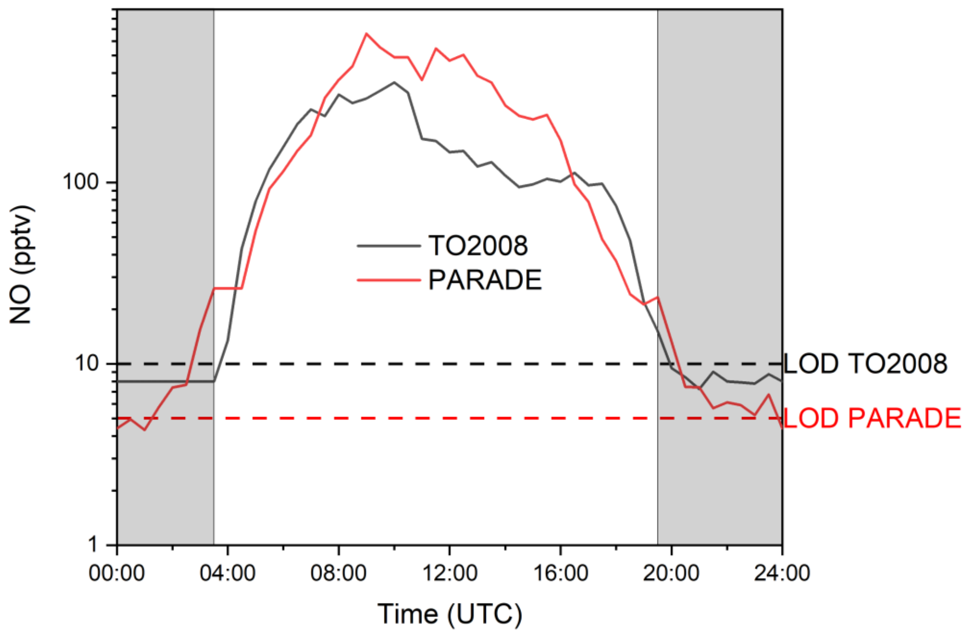


Figure S11: Median diel cycles of NO mixing ratios during TO2008 (black) and PARADE (red). Both measurements were performed with a previous modification of the same CLD setup (Li et al., 2015) described in the main text. Dashed line mark the LODs during the corresponding campaigns. Grey shaded areas denote the nighttime period.

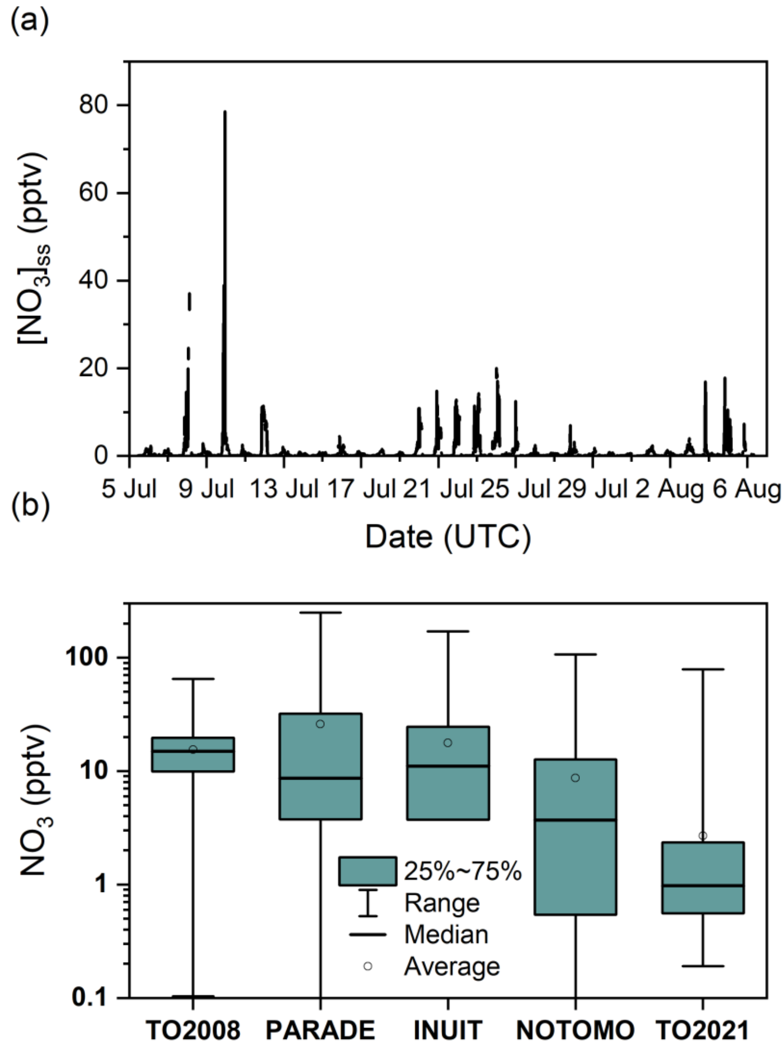


Figure S12: (a) Calculated NO_3 mixing ratios according to Eq. (4) for TO2021 with values for $\boldsymbol{k^{NO_3}}$ < LOD set to 0.002 s^{-1}. (b) Same as Fig. 13c in the main text but using nighttime NO_3 mixing ratios as in Fig. S12a.

References

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