



Supplement of

Fate of the nitrate radical at the summit of a semi-rural mountain site in Germany assessed with direct reactivity measurements

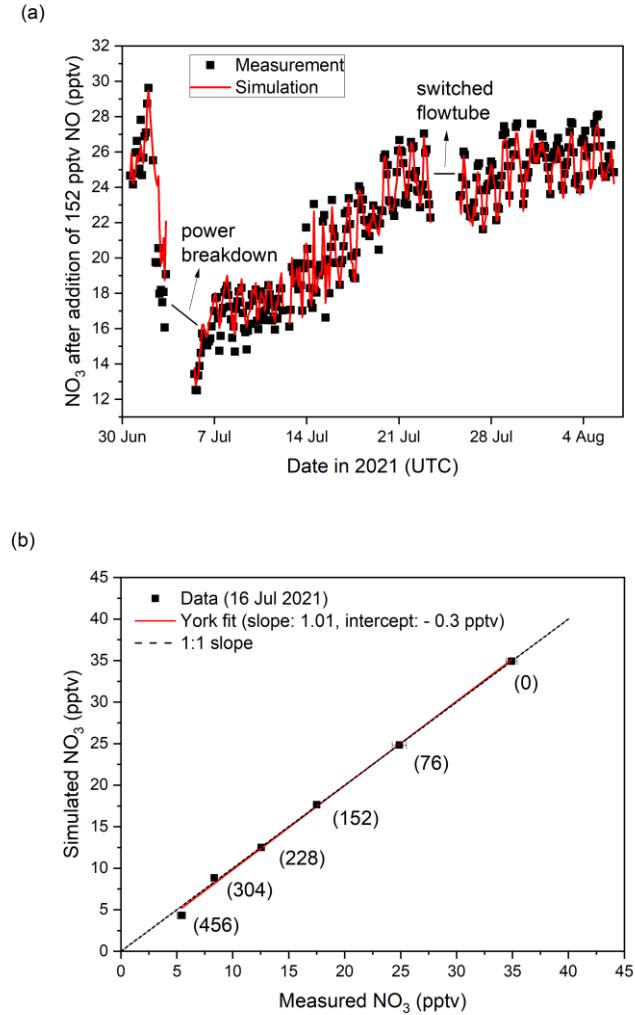
Patrick Dewald et al.

Correspondence to: John N. Crowley (john.crowley@mpic.de)

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Supplement

S1 Calibration of the FT-CRDS with NO



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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.

10 S2 Intercomparison of NO₂ measurements

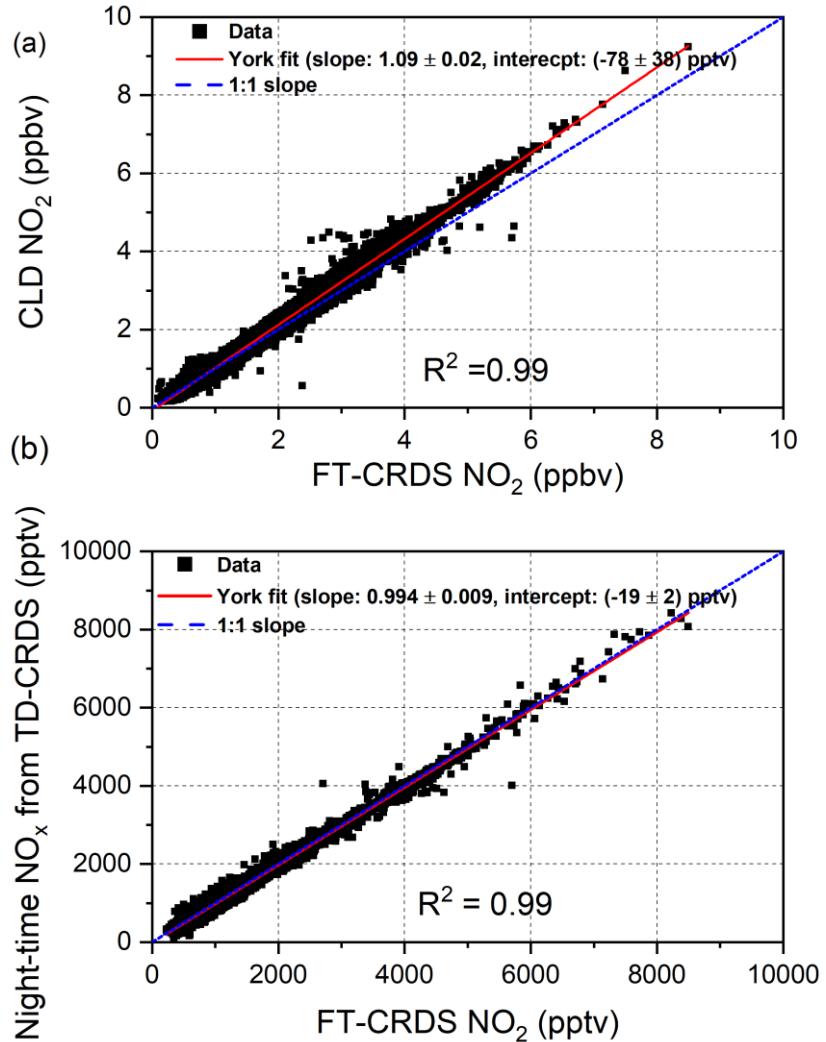


Figure S2: Correlation between NO₂ mixing measured with the FT-CRDS setup and (a) night-time NO_x mixing ratios measured with the TD-CRDS setup (b) NO₂ mixing ratios measured with the CLD instrument. The red solid line indicates a York fit, while the dashed blue line represents an ideal 1:1 agreement.

15 S3 Wind direction and NO_3 reactivity

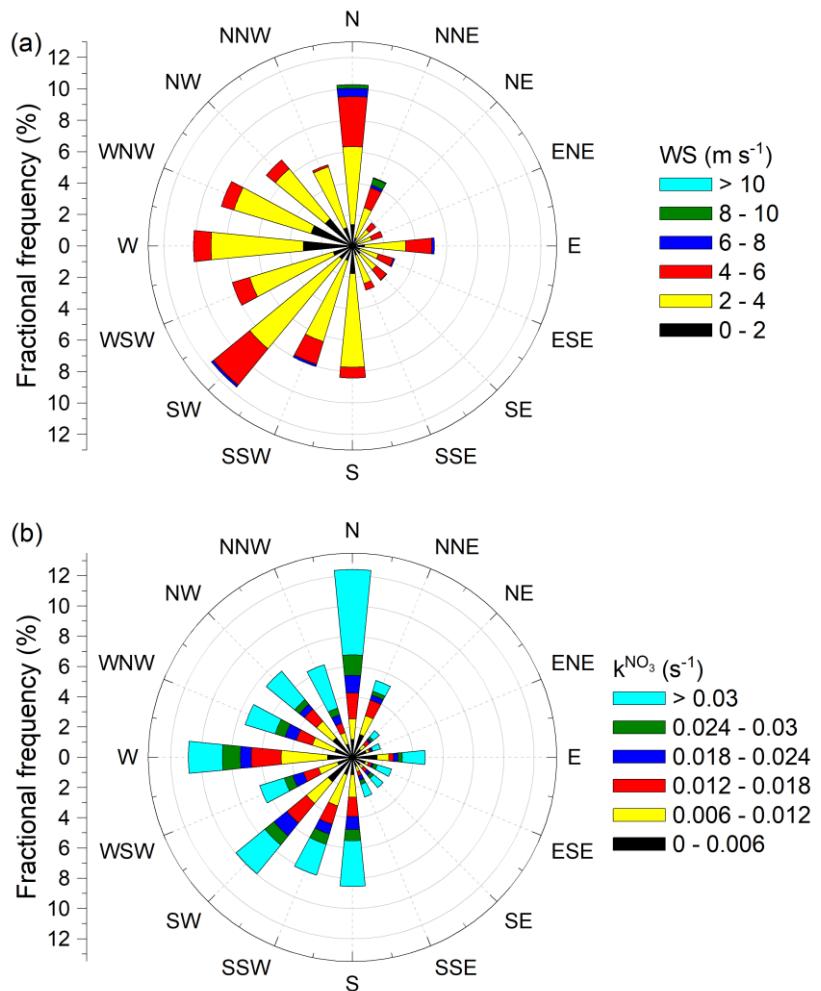


Figure S3: Wind rose of (a) wind speed and (b) NO_3 reactivity measured during the TO2021 campaign.

S4 VOC measurements

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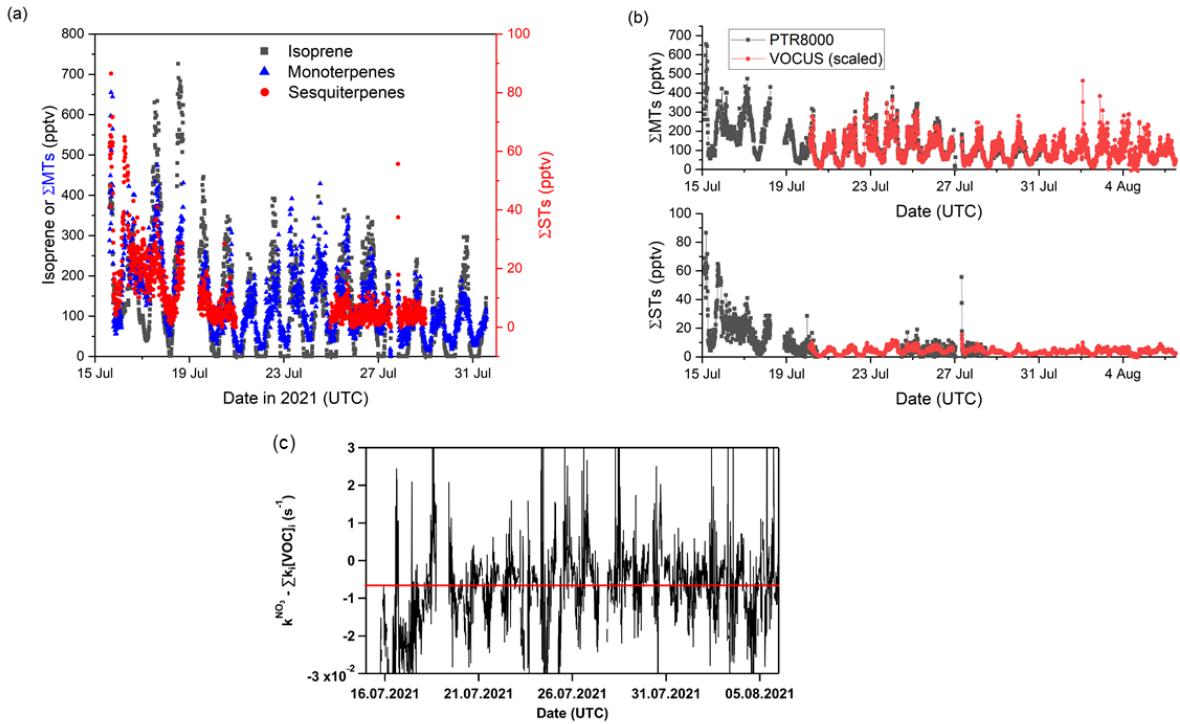


Figure S4: (a) Time-trace of PTR-MS measurements (PTR8000) of isoprene (black squares, left axis), the sum of monoterpenes (Σ MTs, blue triangles, left axis) and the sum of sesquiterpenes (Σ STs, red circles, right axis) during the second half of the TO2021 campaign. Major ticks mark 00:00 UTC. (b) Time-series of monoterpene signals ($m/z = 137.132$, upper panel) and sesquiterpene signals ($m/z = 205.195$, lower panel) from the VOCUS data (red) scaled with a constant factor for each mass to the calibrated data from the PTR8000 setup (black). (c) Time-series of the difference (black solid line) between directly measured NO_3 reactivity (k^{NO_3}) and $\sum k_i [VOC]_i$. The red solid line represents the median (-0.0066 s^{-1}) of the difference.

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45 S5 Nighttime NO: Model calculation and correlation plots

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* NIGHTTIME NO EMISSION SIMULATION ;  

* ======  

variable N2O5 NO3 NO2 O2 ;  

* -----;  

50 * INITIAL CONCENTRATIONS ;  

* -----;  

parameter T 284.6 ;  

parameter O3i 6137372069288.082 ;  

parameter NOi 1E-99 ;  

55 parameter P 688 ;  

parameter M ;  

parameter k1 ;  

parameter k2 ;  

parameter k3 ;  

60 parameter k4 ;  

parameter k5 ;  

parameter KVOC ;  

parameter KVOCi 0.03561 ;  

parameter NO ;  

65 parameter <5> INPARAM ;  

parameter varia press temp ozone EM ;  

parameter kdep 1.5E-5 ;  

* -----;  

* ;  

70 COMPILE GENERAL ;  

M = P * 3.24E16 * (298/T) ;  

** ;  

COMPILE INITIAL ;  

NO = NOi ;  

75 O3 = O3i ;  

KVOC = KVOCi ;  

** ;  

COMPILE EQUATIONS ;  

* -----;  

80 % k1 : N2O5 = NO3 + NO2 ;  

% k2 : NO2 + NO3 = N2O5 ;  

% k3 : NO + NO3 = NO2 + NO2 ;  

% k4 : NO2 + O3 = NO3 + O2 ;  

% k5 : NO + O3 = NO2 + O2 ;  

85 % KVOC : NO3 = ;  

% kdep : NO2 = ;  

* -----;  

*Rate equations ;  

k1 = ((1.3e-3*(T/300)-3.5*exp(-11000/T))*M*  

90 (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

```

```

95 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
    ; IUPAC
100 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 ;
105 open 20 "forFAC.dat" old ;
    ** ;
    COMPILE BLOCK 3 ;
    PSTREAM 3 ;
    ** ;
110 COMPILE BLOCK 4 ;
    READ 20 INPARAM <5> ;
    varia = INPARAM<0> ;
    press = INPARAM<1> ;
    temp = INPARAM<2> ;
115 ozone = INPARAM<3> ;
    EM = INPARAM<4> ;
    P = press ;
    T = temp ;
120 NO = EM ;
    O3 = ozone ;
    KVOC = varia ;
    ** ;
    PSTREAM 3 7 ;
125 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 ;
130    ** ;
    *hmax 0.1 ;
    BEGIN ;
    STOP ;

```

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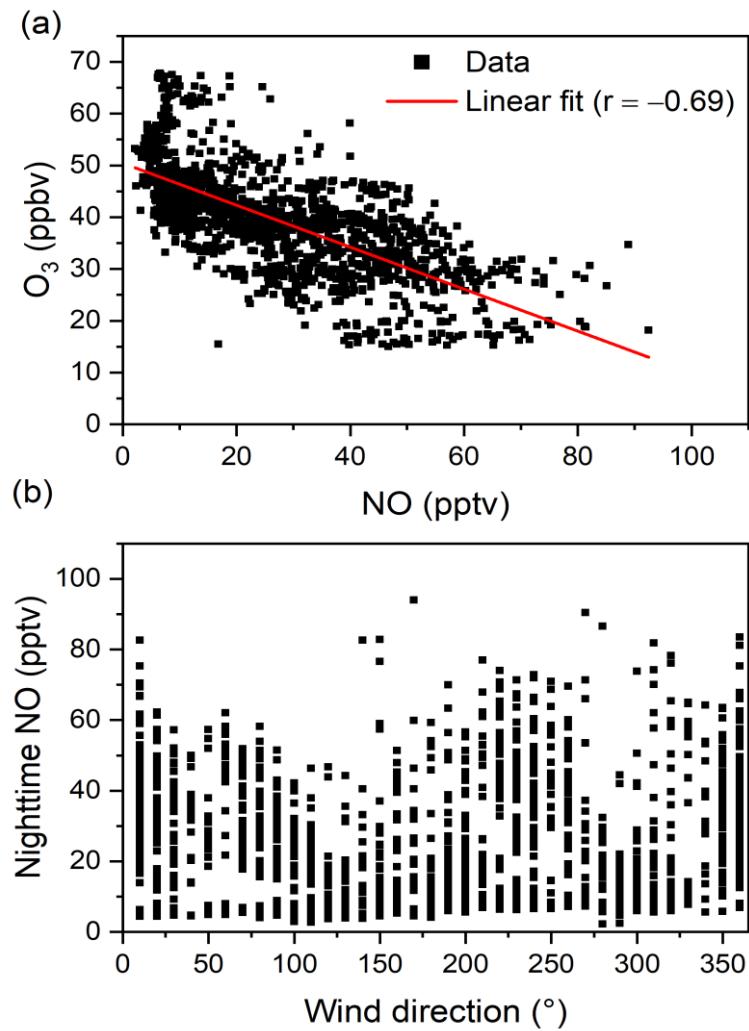
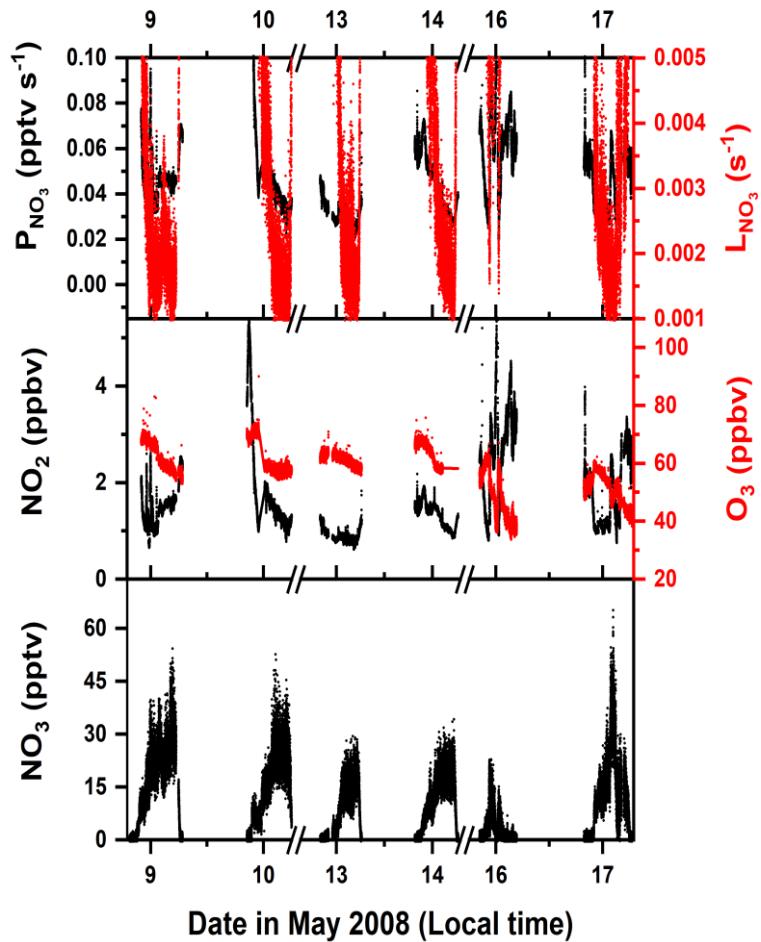


Figure S5: (a) Nighttime NO mixing ratios plotted against O_3 . The red line represents a linear, least-squares fit (correlation coefficient r is -0.69). (b) Dependence of nighttime NO mixing ratios on the wind direction.

S6 Previous measurements on the Kleiner Feldberg

Table S1: Overview of the key parameters of the set-ups deployed to measure NO₂, O₃ and NO₃ mixing ratios during the TO2008, PARADE, INUIT and NOTOMO campaign on the Kleiner Feldberg.

Campaign (Reference)	NO ₂	O ₃	NO ₃
	LOD (Uncertainty)		
	Method; Reference		
TO2008 (Crowley et al., 2010)	80 pptv (10%) CLD; Crowley et al., 2010	2 ppbv (5%) UV, Crowley et al., 2010	1-2 pptv (15%) CRDS; Schuster et al. 2009
PARADE (Sobanski et al., 2016b)	30 pptv (6%) CRDS; Thieser et al., 2016	1 ppbv (5%) UV; Drewnick et al., 2012	2 pptv (15%) CRDS; Schuster et al., 2009
INUIT (Sobanski et al., 2017)	30 pptv (6%) CRDS; Thieser et al., 2016	1 ppbv (5%) UV; Drewnick et al., 2012	2 pptv (15%) CRDS; Schuster et al., 2009
NOTOMO	60 pptv (6.5%) CRDS; Sobanski et al., 2016a	2 ppbv (2%) UV; Sobanski et al., 2016b	1.5 pptv (25%) CRDS; Sobanski et al., 2016a



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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).

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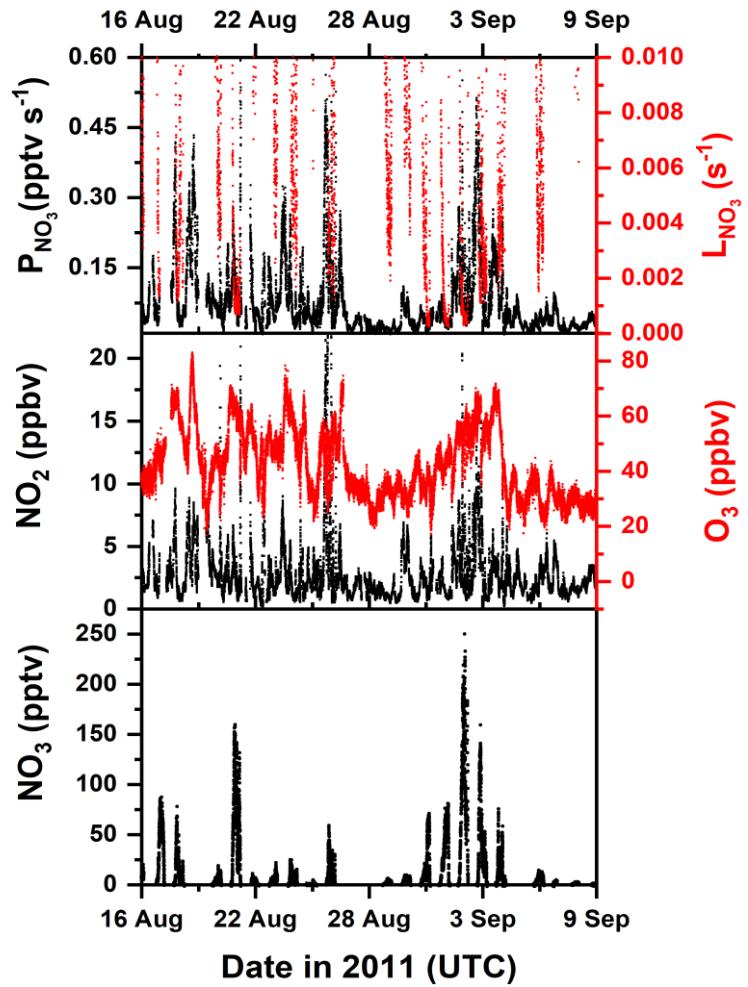
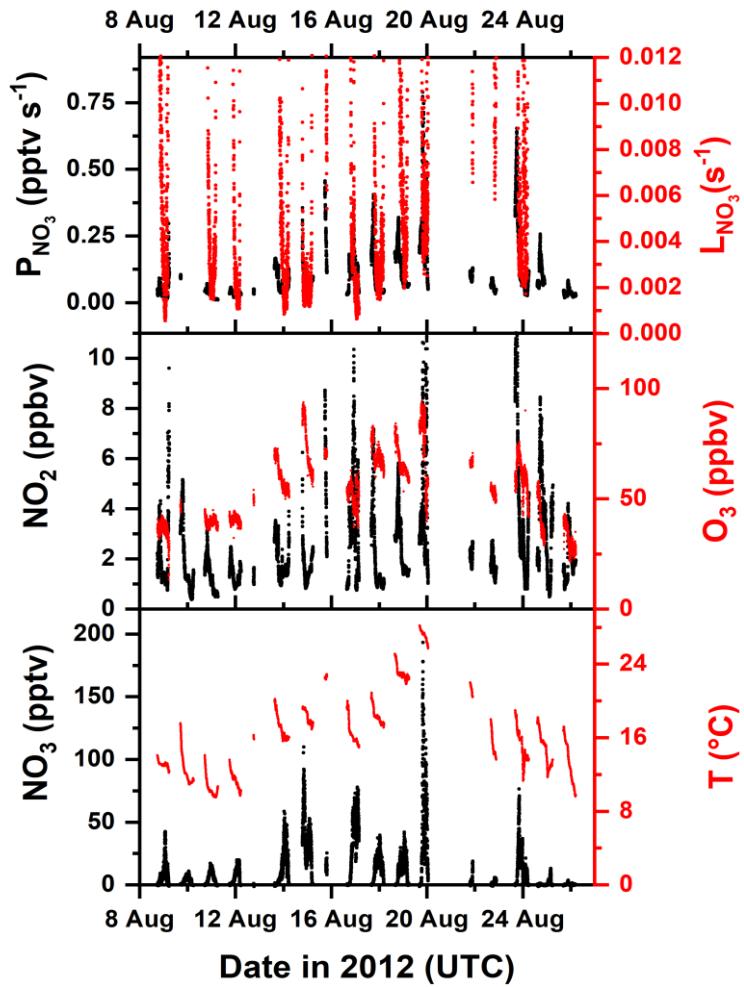
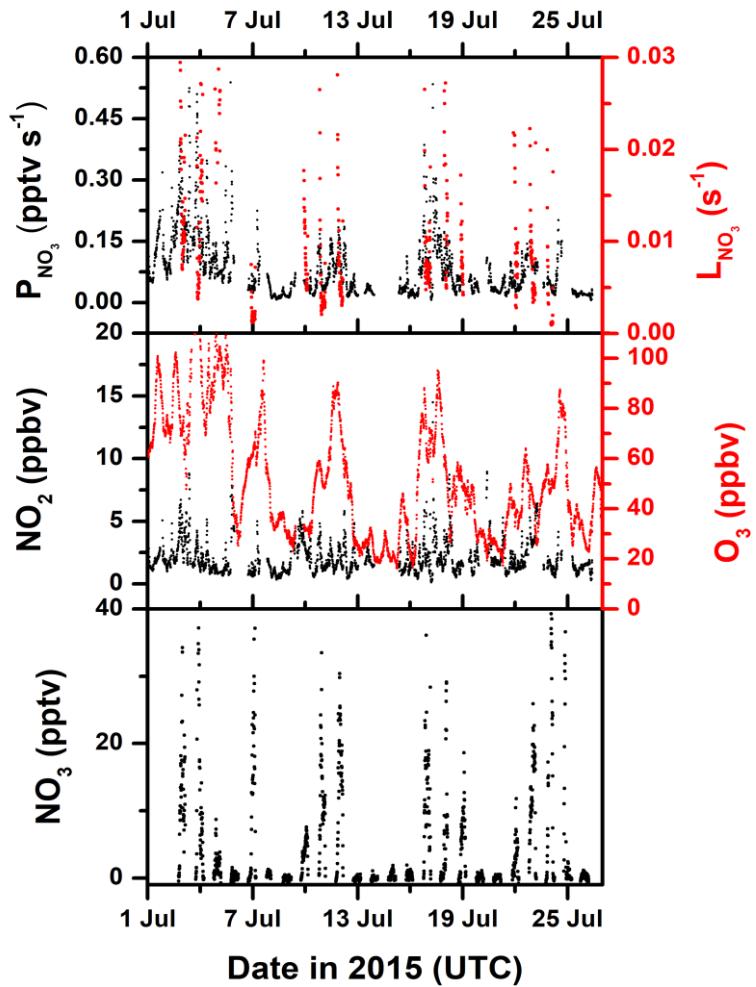


Figure S7: Time-series of NO_3 , NO_2 and O_3 mixing ratios as well as NO_3 production and loss rates during the PARADE campaign. Major ticks represent 00:00 UTC. Data was published in Sobanski et al. (2016b).



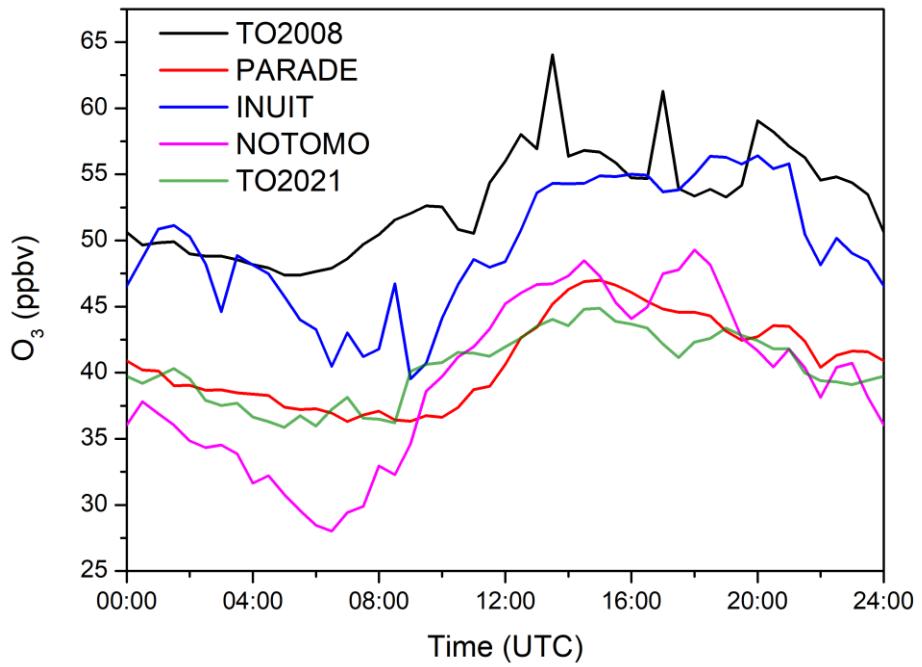
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Figure S8: Time-series of temperature, NO_3 , NO_2 and O_3 mixing ratios as well as NO_3 production and loss rates during the INUIT campaign. Major ticks represent 00:00 UTC.



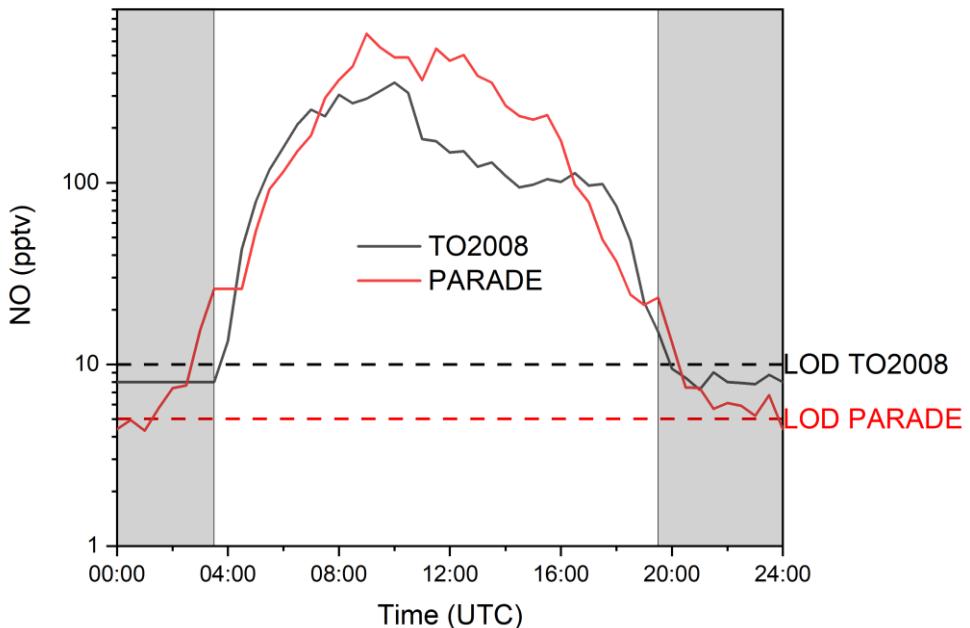
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Figure S9: Time-series of NO_3 , NO_2 and O_3 mixing ratios as well as NO_3 production and loss rates during the NOTOMO campaign. Major ticks represent 00:00 UTC. Data was published in Sobanski et al. (2017).



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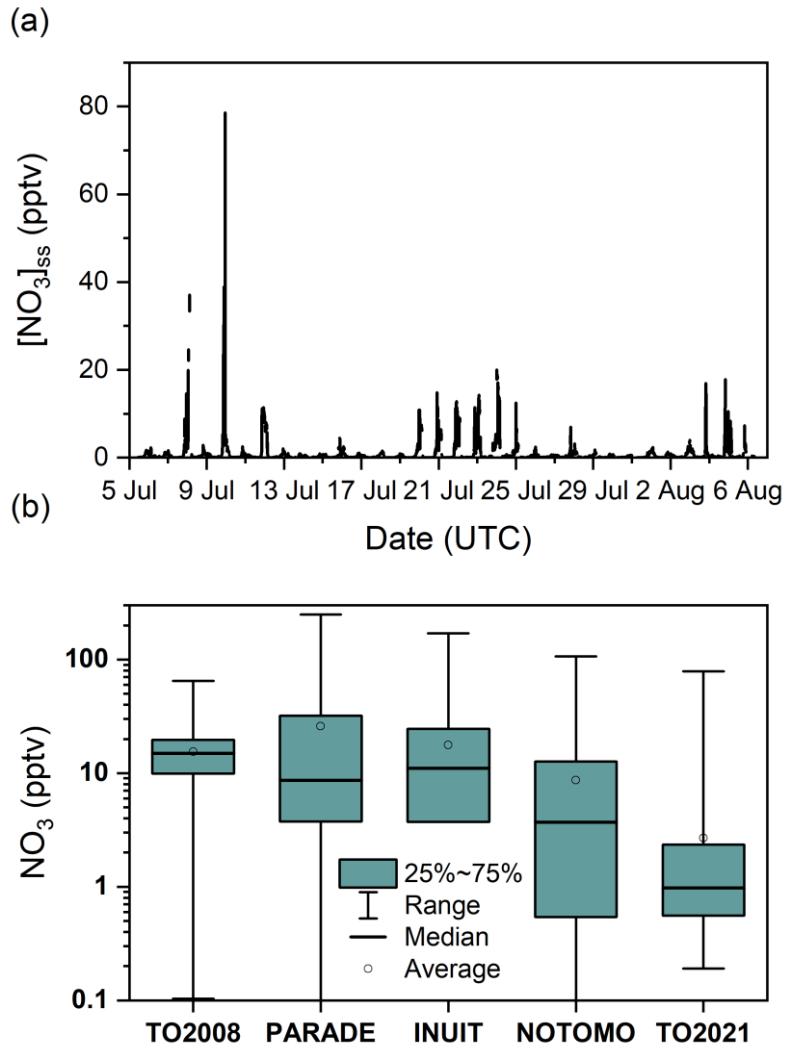
Figure S10: Median diel cycles of O₃ mixing ratios measured during TO2008, PARADE, INUIT, NOTOMO and TO2021.



180 **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.

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195 **Figure S12:** (a) Calculated NO₃ mixing ratios according to Eq. (4) for TO2021 with values for $k^{NO_3} < LOD$ set to 0.002 s⁻¹. (b) Same as Fig. 13c in the main text but using nighttime NO₃ mixing ratios as in Fig. S12a.

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References

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