Supplement of Atmos. Chem. Phys., 18, 12045–12059, 2018
https://doi.org/10.5194/acp-18-12045-2018-supplement

Atmospheric Chemistry and Physics
Open Access
EGU

Supplement of

Direct measurements of NO_3 reactivity in and above the boundary layer of a mountaintop site: identification of reactive trace gases and comparison with OH reactivity

Jonathan M. Liebmann et al.

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

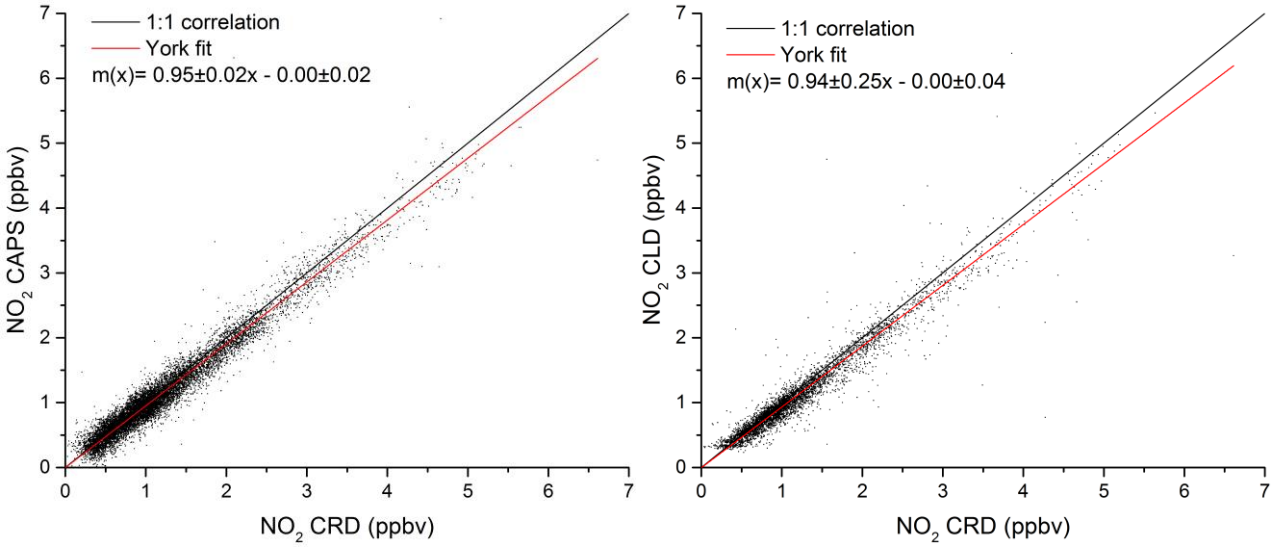

Figure S1: Comparison of CRD, CLD and CAPS measurements of NO_2.

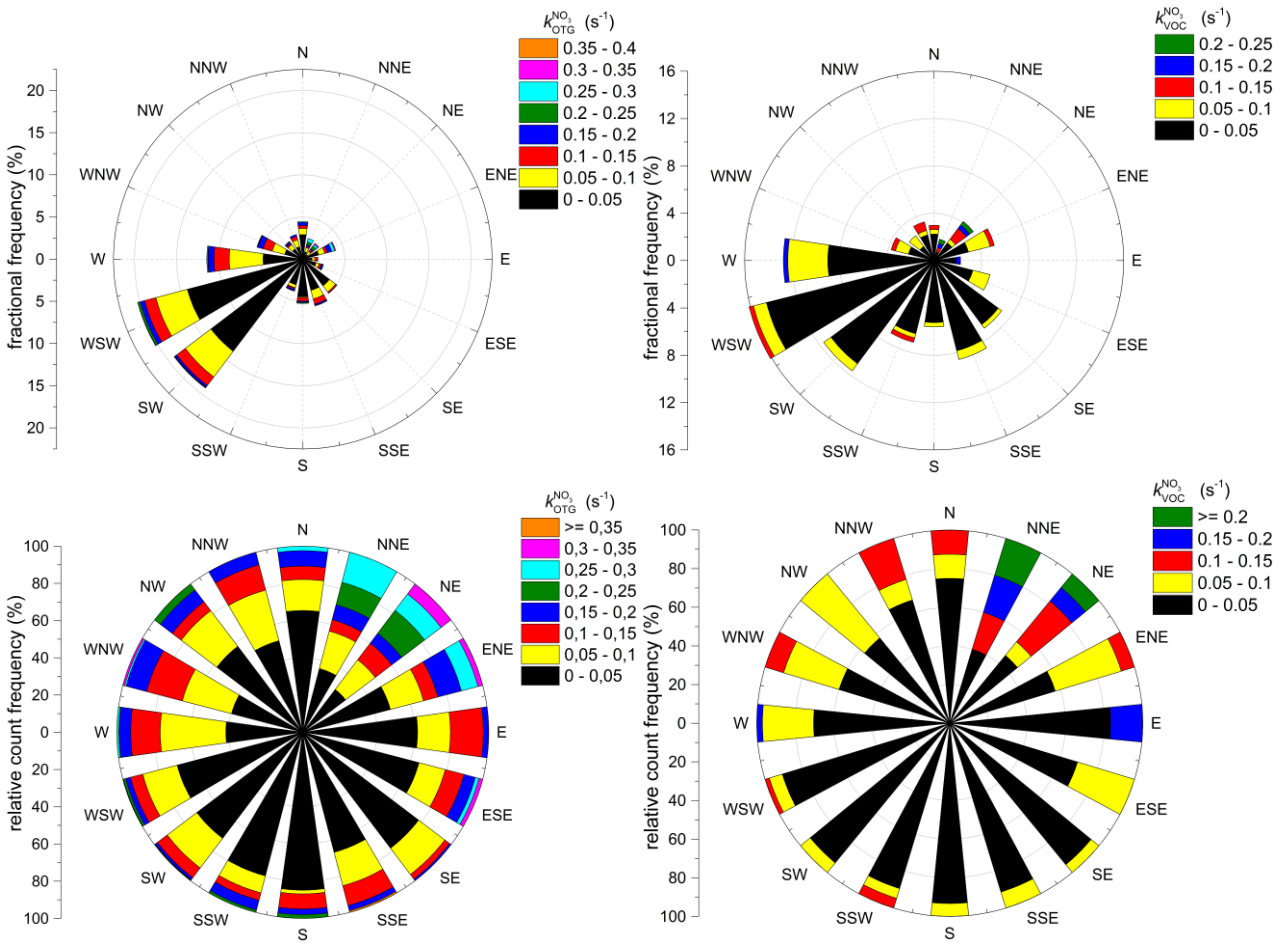

Figure S2: Upper panels: Wind rose of $k_{\mathrm{OTG}}^{\mathrm{NO_3}}$ and $k_{\mathrm{VOC}}^{\mathrm{NO_3}}$. Lower panels: Relative count frequency of $k_{\mathrm{OTG}}^{\mathrm{NO_3}}$ and $k_{\mathrm{VOC}}^{\mathrm{NO_3}}$.

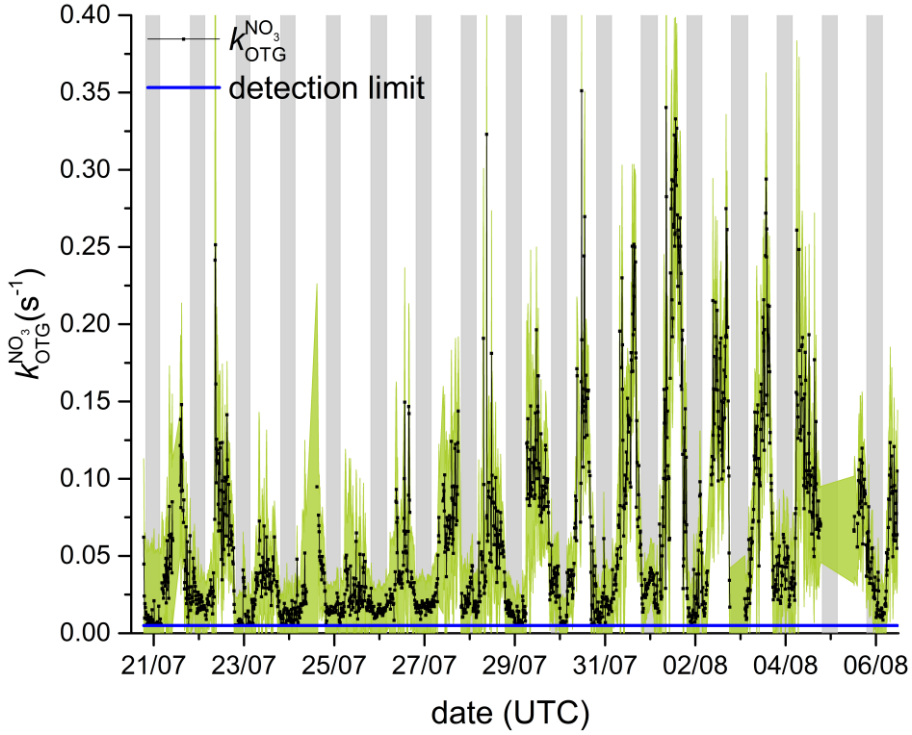

Figure S3: Measured NO_3-reactivity with corresponding uncertainty (green shaded area).

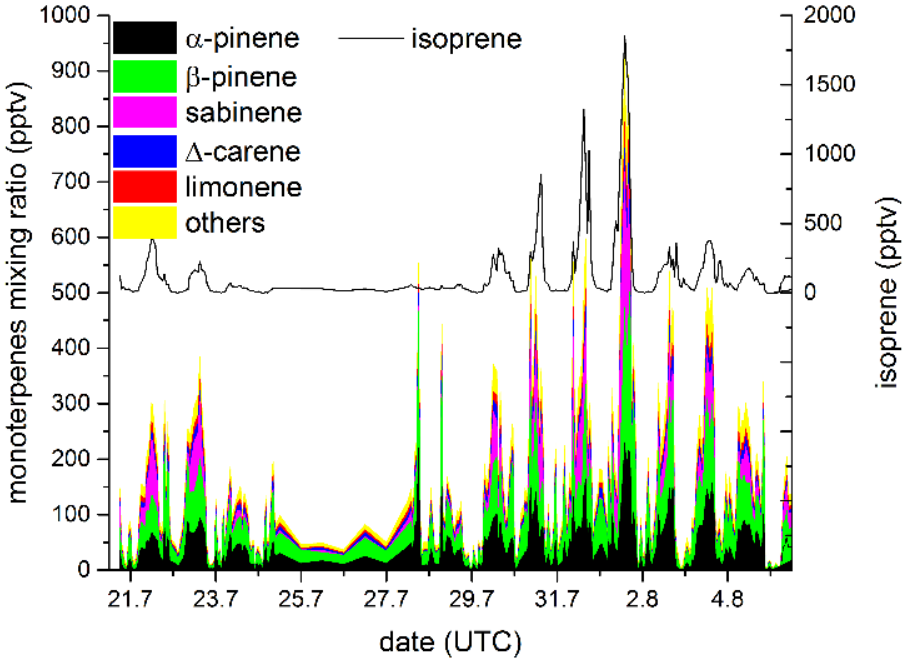

Figure S4: Overview of the measured BVOC mixing ratios. The term other includes terpinolene, β-phellandrene, α-terpinene, γ-terpinene, α—thujene and camphene. Myrcene and α–phellandrene were also measured but below the detection limit during the whole campaign. VOCs such as methanol, acetaldehyde, ethanol, acetone, methylethylketone and alkanes and aromatic compounds are not displayed as they did not contribute significantly to NO_3-reactivity.

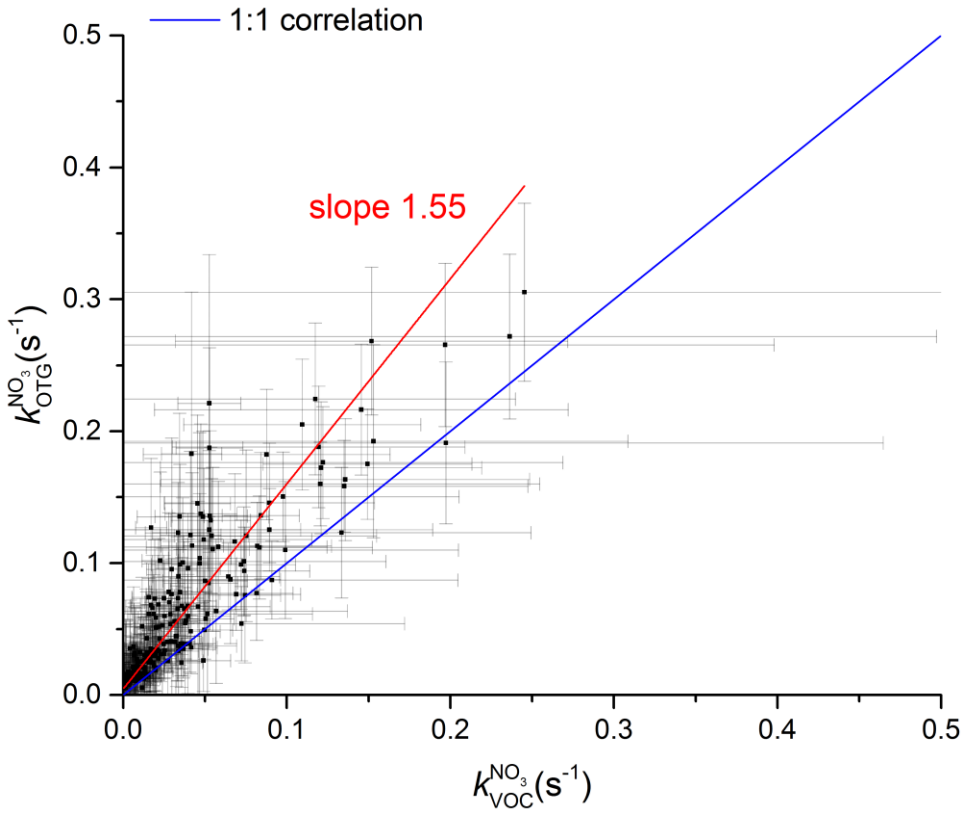

Figure S5: Plots of $k_{VOC}^{NO_3}$ versus $k_{OTG}^{NO_3}$. The 1:1 line is drawn in blue. The red line is the least-squares fit to the data (slope 1.55, intercept 0.005). The error bars shown for $k_{VOC}^{NO_3}$ were derived from uncertainties in the mixing ratios of the VOCs and the rate constant for the reaction with NO_3 as described in Section 3.2. The error bars shown for $k_{OTG}^{NO_3}$ were calculated as described in the text.

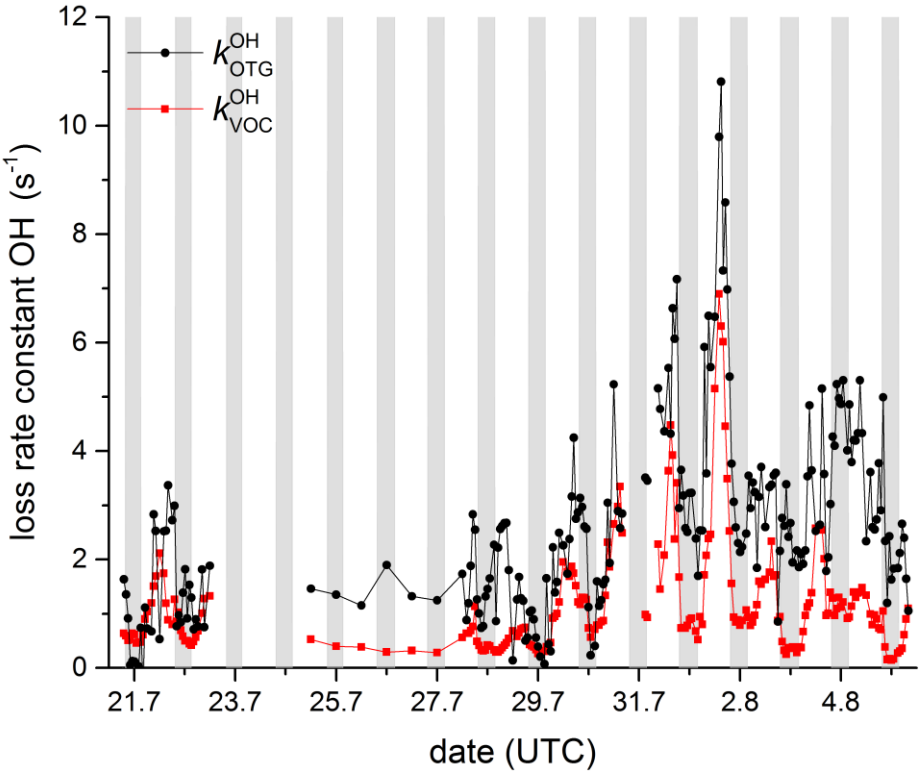

Figure S6: Comparison of k^{OH}_{OTG} and k^{OH}_{VOC}. The VOCs taken into consideration: Methylethylketone, α-pinene, acetaldehyde, acetone, acetylene, α-phellandrene, β-pinene, benzene, β-phellandrene, 2-butene, 2-pentene, ocimene, camphor, Δ-carene, methane, ethane, ethanol, ethane, ethylbenzene, eucalyptol, i-butane, i-butene, i-octane, i-pentane, isoprene, limonene, m-xylene, methanol, methyl cyclohexane, methyl cyclopentane, methyl pentane, myrcene, butane, heptane, hexane, nonane, octane, pentane, o-xylene, butane, 1-hexene, 1,3 butadiene, p-cymene, 1-pentene, propane, propene, propyne, sabinene, terpinolene, 3-methyl heptane,3-methyl pentane, toluene, trans 2-pentene, 1,2,3-trimethyl benzene, 1,3,5-trimethyl benzene, 1,2,4-trimethyl benzene, 2-methylhexane, 2,3-dimethyl butane and 2,3-dimethyl pentane.

OH-reactivity Null Measurement

In order to obtain OH-reactivity from CIMS measurements, the OH wall loss rate needs to be determined using zero (OH-reactivity) air. This null measurement was carried out before and after the campaign (17/7/2017 and 8/8/2017), along with the determination of the CIMS scaling factor of 11.1 ± 0.4 s^{-1}. The mean null value was measured as 1.04 ± 0.04, leading to wall loss rate of 11.5 ± 0.6 s^{-1} (wall loss rate = scaling factor x null value). This wall loss rate however led to implausible negative OH-reactivity measurement values during the campaign indicating that the null value was overestimated. This would be the case if the synthetic air contained OH reactants in sufficient quantity to result in non-null OH-reactivity. The null was measured using two separate synthetic air cylinders, which were both cross-referenced by synthetic air from two other cylinders. This however could not unequivocally confirm a difference between or high contamination level in the two synthetic air cylinders used for the null measurements. Therefore a different approach was used to determine the null for the intensive: Three nights were identified when the sampled air was from clean free tropospheric origin. It is here assumed that the measured inorganic and organic trace gases constitute the total OH-reactivity and missing reactivity is negligible. The selection of nights was achieved by visual inspection of ceilometer atmospheric backscatter data (https://www.dwd.de/DE/forschung/projekte/ceilomap/_ceilomap_node.html) filtering for periods with low backscatter as indicator of clean air. As second criterion was the absence of a gradient in CO_2 concentrations at the Hohenpeissenberg ICOS tower at heights 50, 93 and 131 m above the surface (https://www.icos-cp.eu/), indicating a well-mixed atmosphere not influenced by surface interaction. The timing of the three free troposphere periods, CIMS measurements, as well as the derived null values are summarized in Table S1, using the following Equation:

$$\mathrm{Null}_{\mathrm{FT\ derived}} = \frac{(\mathrm{scaling\ factor} * \ln(\frac{\mathrm{OH}_1}{\mathrm{OH}_2})_{\mathrm{CIMS}} - k_{OH\,\mathrm{calculated}})}{\mathrm{scaling\ factor}}$$

Using the mean derived null, CIMS wall loss rate k_w for this campaign is 9.2 ± 0.6 s^{-1}. The difference in the OH-reactivity measurements from the CIMS as a result of the free troposphere scaled null compared to the synthetic air null measurements is 2.3 ± 0.7 s^{-1}.

Table S1. Zero CIMS measurements scaled from nighttime free troposphere OH-reactivity

FT Time period	CIMS mean ($\ln(OH_1/OH_2)$)	Calculated OH-reactivity	Derived Null value
20/7/2017 23:06 – 21/7/2017 02:26	0.930 ± 0.078	1.37 ± 0.21	0.81 ± 0.08
28/7/2017 23:22 – 29/7/2017 00:42	0.949 ± 0.059	1.16 ± 0.17	0.84 ± 0.06
30.7. 2017 00:44 – 02:38	0.946 ± 0.051	1.36 ± 0.20	0.82 ± 0.05
			***Mean ±1 σ* = 0.82 ± 0.04**