Direct measurement of NO$_3$ reactivity in a boreal forest

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Supplementary Information

Technical description of the GC-AED

A Gas Chromatograph equipped with an Atomic Emission Detector (GC-AED) was deployed in the field for the first time to perform in-situ gas phase VOC measurements. The set-up consisted of cryogenic pre-concentrator (Entech 7200) system with three liquid nitrogen cooled traps, coupled with an Agilent 7890B GC and a new Joint Analytical Systems third generation AEDIII detector (JAS, Moers, Germany).

In the Entech pre-concentration system, at first water is removed within an empty Silonite™ D coated 1/8" (0.32 cm) stainless steel tube trap held at -50 °C which thereafter is heated to 10°C while forward flushed with 50 ml He towards the main Silonite™ D Tenax® packed enrichment trap cooled to -60°C where the VOC trapping takes place. The volatiles are then refocused into a smaller dead volume for split-less injection (Silonite™ D coated 1/32", 0.08 cm diameter stainless steel tubing) at -180°C. After thermal release the collected VOC sample passes through an insulated and heated transfer line (110°C) into the GC.

The AED operates by atomizing all compounds eluting from the GC column (Supelco SPB-624 60 m column, 3.5 mL min^{-1} He as carrier gas, 34 min GC run) within a helium plasma. The element specific characteristic emission lines (e.g. for carbon, sulfur, bromine, iodine, nitrogen etc.) which occur at specific wavelengths are focused onto the entrance slit of the spectrometer. In the spectrometer, a high-resolution flat field grating is used to disperse the atomic emission light spectrum in the wavelength range of 160-209 nm onto two flat plane back thin CCD chips, where the wavelength dependent spectra are simultaneously recorded in the full range. All the transfer lines of the coupled system are insulated, heated and monitored at set values.

The GC-AED was installed at the Hyytiälä site, within an air-conditioned measurement container (25°C). Ambient air was sampled from the center of the common inlet also used by the NO_3 reactivity instrument. A 15 m insulated and heated (10°C above ambient) ½" (1.27 cm) PFA Teflon tubing was used as a GC-AED system inlet line with a flowrate of 20 L min^{-1} (transmission time 3.3 s). The ambient air was filtered using 5.0 µm PTFE (47 mm in diameter) membrane filters (Sartorius Stedim GmbH, Göttingen, Germany) which were changed every 5 days.

GC-AED was calibrated *in-situ* with an 84-component gravimetrically prepared gas-phase calibration reference standard with a stated accuracy of better than ±5% (Apel-Riemer Environmental, Inc., Florida, USA). The average total uncertainty of the species measured from repeated calibration standard measurements combined with the flow measurements and calibration standard uncertainty was calculated 14%. Since monoterpenes were an important part of this campaign α-pinene, Δ-3-carene, β-pinene, camphene and d-limonene were all calibrated individually, despite it being possible to derive ambient concentrations via the carbon signal alone. Detection limits for the monoterpene species were 1.0, 0.9, 0.4, 0.5 and 0.3 pptv respectively.
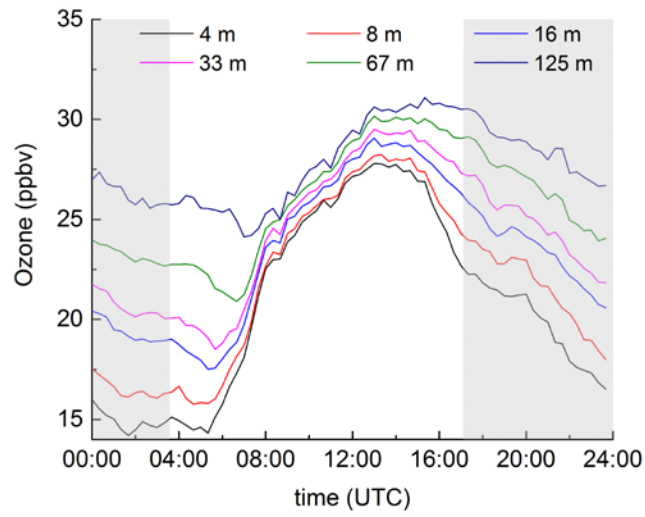
Figure S1: The campaign averaged, diel variation of ozone at different heights (4 m to 125 m) as measured at the SMEAR II tower. The largest day/night differences are observed for the lower levels.
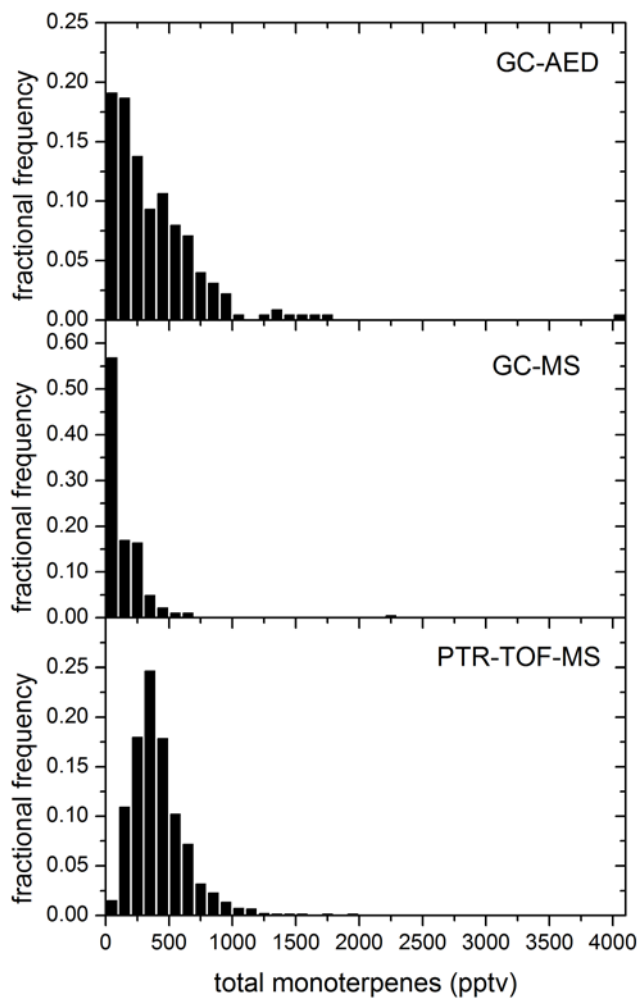
Figure S2: Histograms highlighting differences in the total mono-terpene mixing ratios measured using different instruments at different locations.
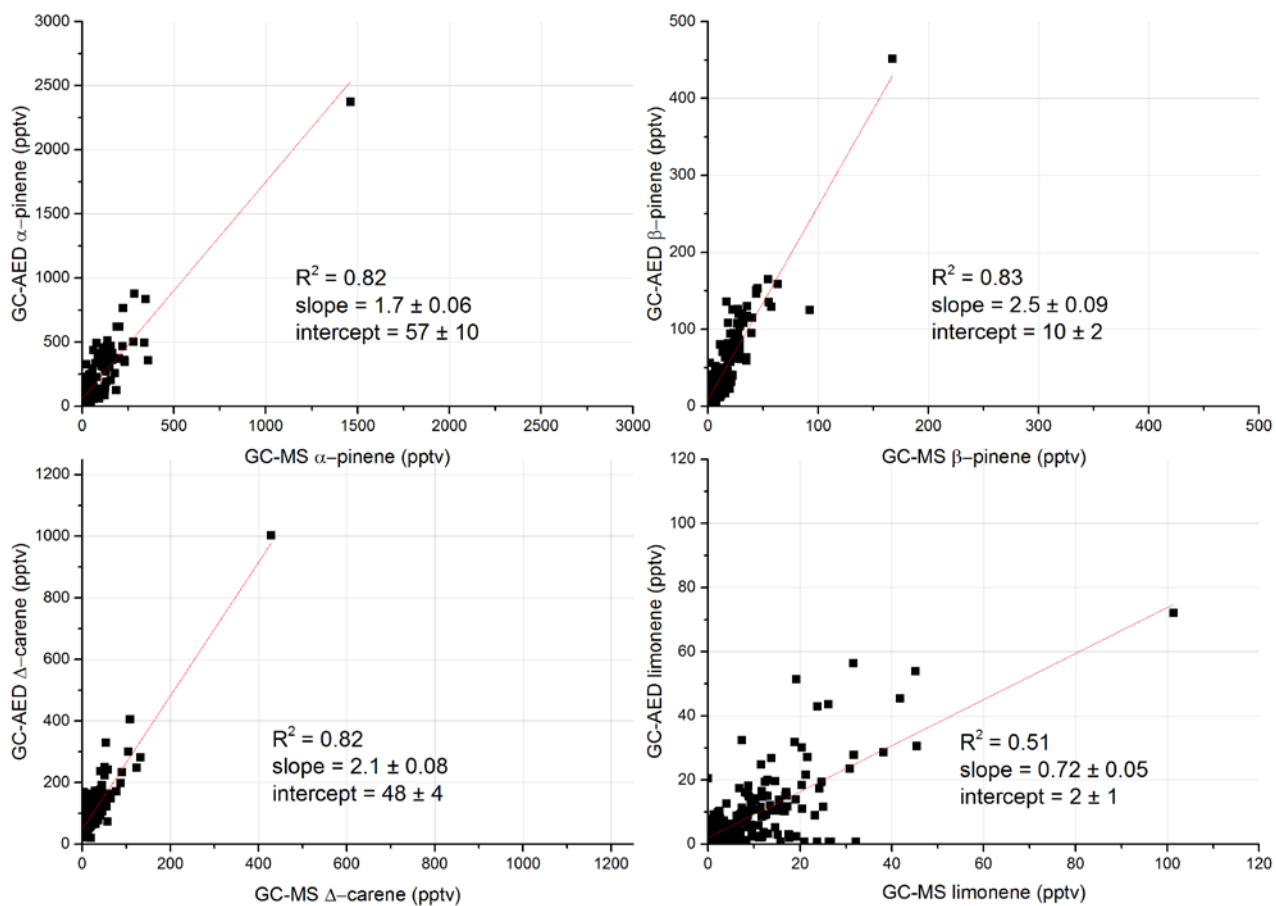
Figure S3: Comparison of individual monoterpenes measured by GC-AED and GC-MS.
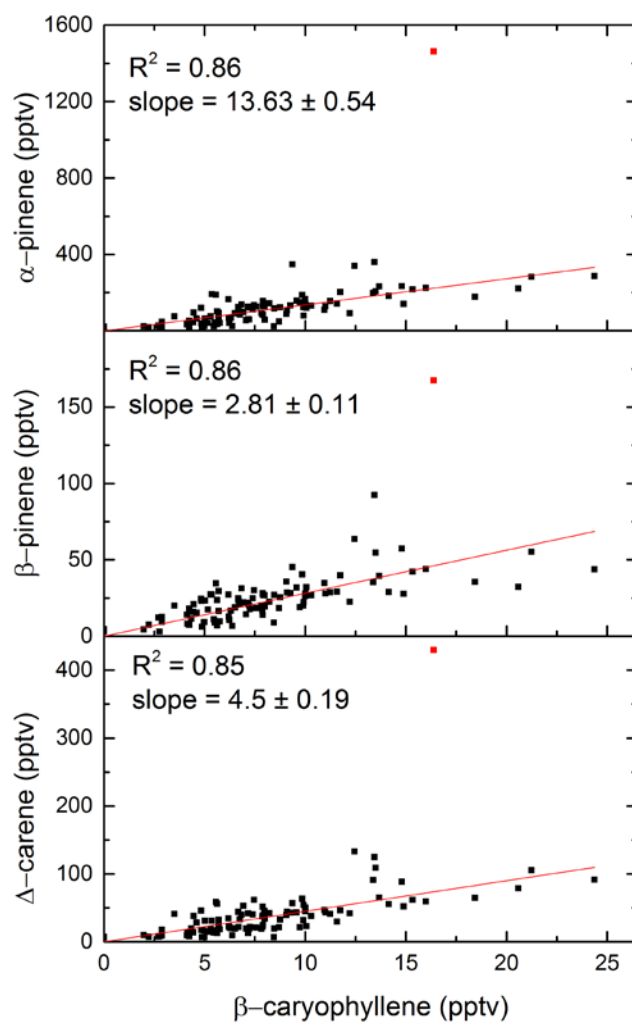
Figure S4: Correlation of *β*-caryophyllene with monoterpenes.
Red lines are proportional fits to the data.
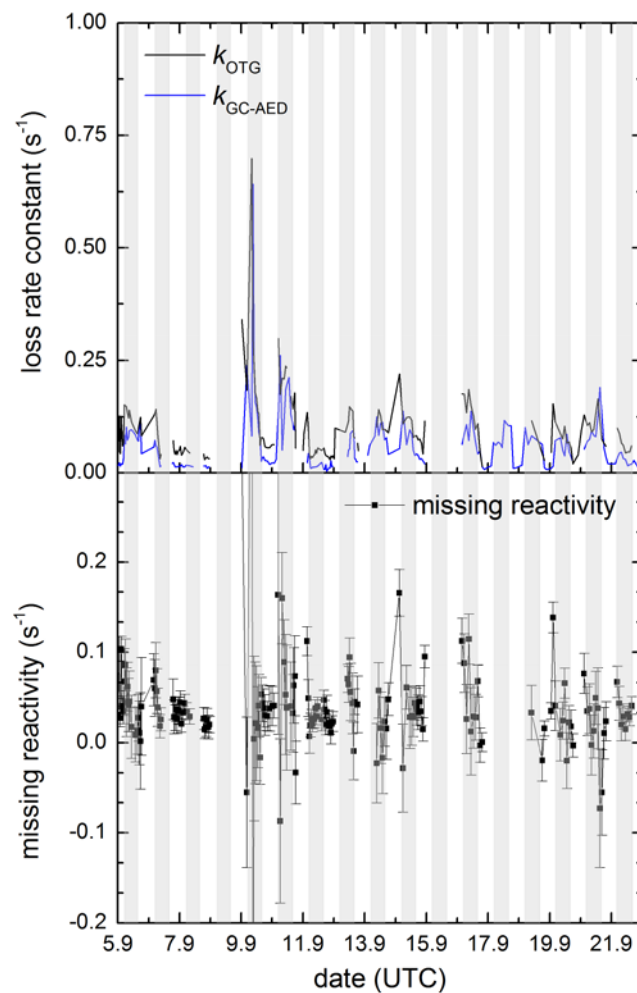
Figure S5: Upper panel: time series of k_{OTG} and $k_{GC\text{-}AED}$. Lower panel: Missing reactivity ($k_{OTG} - k_{GC\text{-}AED}$) with total uncertainty.
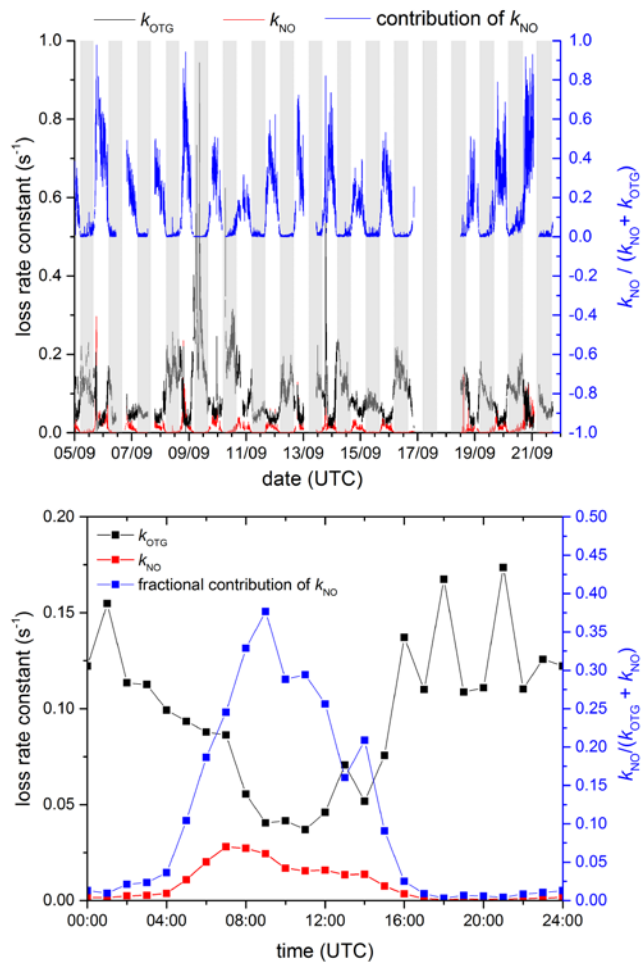
Figure S6: Upper panel: Time series of the loss rate constant for NO$_3$ due to reaction with NO (k_{NO}) and k_{OTG} and the fractional contribution of NO (k_{NO}) to the overall, chemical loss of NO$_3$ (k_{NO} + k_{OTG}). Lower panel: Same parameters averaged over the campaign.