



# Direct measurement of NO<sub>3</sub> radical reactivity in a boreal forest

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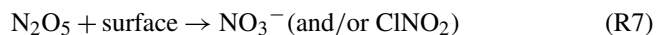
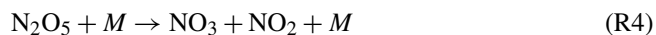
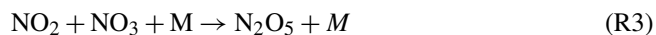
**Abstract.** We present the first direct measurements of NO<sub>3</sub> reactivity (or inverse lifetime, s<sup>−1</sup>) in the Finnish boreal forest. The data were obtained during the IBairn campaign (Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen budget) which took place in Hyytiälä, Finland during the summer/autumn transition in September 2016. The NO<sub>3</sub> reactivity was generally very high with a maximum value of 0.94 s<sup>−1</sup> and displayed a strong diel variation with a campaign-averaged nighttime mean value of 0.11 s<sup>−1</sup> compared to a daytime value of 0.04 s<sup>−1</sup>. The highest nighttime NO<sub>3</sub> reactivity was accompanied by major depletion of canopy level ozone and was associated with strong temperature inversions and high levels of monoterpenes. The daytime reactivity was sufficiently large that reactions of NO<sub>3</sub> with organic trace gases could compete with photolysis and reaction with NO. There was no significant reduction in the measured NO<sub>3</sub> reactivity between the beginning and end of the campaign, indicating that any seasonal reduction in canopy emissions of reactive biogenic trace gases was offset by emissions from the forest floor. Observations of biogenic hydrocarbons (BVOCs) suggested a dominant role for monoterpenes in determining the NO<sub>3</sub> reactivity. Reactivity not accounted for by in situ measurement of NO and BVOCs was variable across the diel cycle with, on average, ≈ 30 % “missing” during nighttime and ≈ 60 % missing during the day. Measurement of the NO<sub>3</sub> reactivity at various heights (8.5 to 25 m) both above and below the canopy, revealed a strong nighttime, vertical gradient with maximum values closest to the ground. The gradient disappeared during the daytime due to efficient vertical mixing.

## 1 Introduction

Biogenic and anthropogenic volatile organic compounds (VOCs) have a significant impact on air quality and human health and knowledge of their tropospheric lifetimes, determined by the oxidizing capacity of the lowermost atmosphere, is a prerequisite to predicting future atmospheric composition and climate change (Lelieveld et al., 2008). Recent estimates (Guenther et al., 2012) suggest that about 1000 Tg of biogenic volatile organic compounds (BVOCs), are emitted annually by vegetation. The boreal forest covers an area of ≈ 15 million km<sup>2</sup> worldwide, which is comparable to that covered by tropical rainforest (Eerdekens et al., 2009). Forests emit large amounts of unsaturated hydrocarbons in the form of the terpenoids such as, isoprene (2-methylbuta-1,3-diene, C<sub>5</sub>H<sub>8</sub>), monoterpenes (C<sub>10</sub>H<sub>16</sub>), and sesquiterpenes (C<sub>15</sub>H<sub>24</sub>) that have a significant impact on HO<sub>x</sub> (HO + HO<sub>2</sub>) and NO<sub>x</sub> (NO + NO<sub>2</sub>) budgets (Hakola et al., 2003; Tarvainen et al., 2005; Holzke et al., 2006; Lappalainen et al., 2009) and the formation of secondary organic particle (Hallquist et al., 2009).

Along with the reaction with O<sub>3</sub>, BVOCs are oxidized in the troposphere by reactions with OH and NO<sub>3</sub> radicals. OH radical-induced oxidation mainly takes place during daytime with the NO<sub>3</sub> radical (formed by reaction of O<sub>3</sub> with NO<sub>2</sub>, Reaction R1) accounting for the major fraction of radical-induced loss of BVOC at nighttime (Wayne et al., 1991; Atkinson, 2000; Atkinson and Arey, 2003a, b; Brown and Stutz, 2012; Mogensen et al., 2015; Ng et al., 2017; Liebmann et al., 2017). The rapid photolysis of NO<sub>3</sub> by sunlight

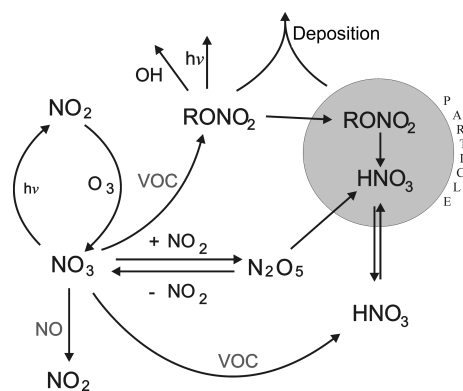
(Reactions R5, R6) and reaction with NO (Reaction R2) typically reduces its lifetime to a few seconds during daytime. At nighttime, reaction of NO<sub>3</sub> with NO<sub>2</sub> results in thermal equilibrium between NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> (Reactions R3, R4).



Reactions (R1) to (R6) do not represent a reduction of NO<sub>x</sub> as no reactive nitrogen species are removed from the gas phase. However, heterogeneous uptake of N<sub>2</sub>O<sub>5</sub> to particles (R7) and the reaction of NO<sub>3</sub> with BVOCs (forming either HNO<sub>3</sub> or organic nitrates, see below) both result in the transfer of gas-phase NO<sub>x</sub> to particulate forms, thus reducing the rate of photochemical O<sub>3</sub> formation from NO<sub>2</sub> photolysis (Dentener and Crutzen, 1993).

In forested environments at low NO<sub>x</sub> the lifetime of NO<sub>3</sub> with respect to chemical losses during the temperate months will generally be driven by the terpenoids (isoprene, monoterpenes, and sesquiterpenes), the reaction proceeding via addition to the carbon–carbon double bond to form nitrooxyalkyl peroxy radicals. The peroxy radicals react further (with HO<sub>2</sub>, NO, NO<sub>2</sub>, or NO<sub>3</sub>) to form multi-functional peroxides and organic nitrates, which can contribute to the generation and growth of secondary organic aerosols (Ehn et al., 2014; Fry et al., 2014; Ng et al., 2017; Liebmann et al., 2017) or be lost by deposition. The main processes outlining the role of NO<sub>3</sub> in removing NO<sub>x</sub> from the atmosphere are summarized in Fig. 1. Clearly, the lifetime of NO<sub>3</sub> with respect to reaction with BVOCs (the subject of this article) determines the relative rate of formation of inorganic nitrate via heterogeneous processes (HNO<sub>3</sub>) and organic nitrates, which have different lifetimes with respect to chemical and depositional loss and thus different efficiencies of NO<sub>x</sub> removal. It also indirectly determines the rate of generation of reactive chlorine (in the form of ClNO<sub>2</sub>) resulting from the heterogeneous reactions of N<sub>2</sub>O<sub>5</sub> with chloride containing particles (Osthoff et al., 2008; Thornton et al., 2010; Phillips et al., 2012, 2016; Ammann et al., 2013).

Reactivity measurements have previously been applied to assess the overall loss rates of the OH radical in the boreal forest and to test for closure in its budget (Hens et al., 2014). In forested environments, the measured reactivity has generally been found to be significantly higher than that calculated from summing up reactivity due to individual reactive trace gases, (Sinha et al., 2010; Nölscher et al., 2012, 2016) resulting in an apparent “missing reactivity”. In a similar vein, O<sub>3</sub> flux measurements in Californian pine forests required monoterpene emissions that were 10 times higher



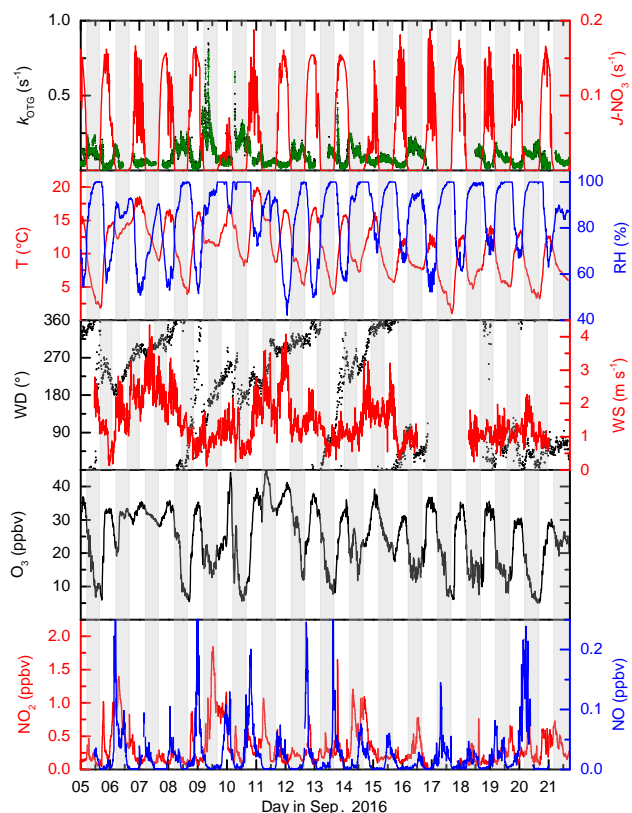
**Figure 1.** Gas-phase formation and loss of tropospheric NO<sub>3</sub> indicating processes which transfer reactive nitrogen to the particulate phase. RONO<sub>2</sub> are alkyl nitrates. VOC is volatile organic compound.

than measured in order to explain the O<sub>3</sub> losses (Goldstein et al., 2004). These studies argue for the presence of monoterpenes/sesquiterpenes that are not detected by standard instruments used to measure BVOCs. Direct measurements of NO<sub>3</sub> reactivity were not available until very recently (Liebmann et al., 2017); hence the reactivity of NO<sub>3</sub> has traditionally been calculated from concentration measurements by assuming balanced production and loss terms (stationary state, see Sect. 3.4), or from measurements of the VOCs that contribute to its loss and the known rate constant for reaction of each VOC with NO<sub>3</sub>. The first method may break down when stationary state is not achieved (Brown et al., 2003). For example, Sobanski et al. (2016b) observed much lower stationary-state loss rates of NO<sub>3</sub> compared to those calculated from measured VOC mixing ratios in a forested/urban location. It was therefore concluded that this was mainly the result of sampling from a low-lying residual layer with VOC emissions that were too close to the sampling point for NO<sub>3</sub> concentrations to achieve stationary state. The second method relies on comprehensive measurement and accurate quantification of all VOCs that react with NO<sub>3</sub>, which, in a chemically complex environment such as a forest, may not always be possible.

In this paper we describe direct, point measurements of NO<sub>3</sub> reactivity in ambient air in the boreal forest of southern Finland and analyse the results using ancillary measurements of NO<sub>x</sub>, NO<sub>3</sub>, O<sub>3</sub>, and biogenic hydrocarbons as well as meteorological parameters.

## 2 Measurement site and instrumentation

The IBAIRN campaign took place in September 2016 in the boreal forest at Hyytiälä, Finland. September marks the transition from late summer to autumn at Hyytiälä, with the number of daylight hours at the site changing from ≈ 14 to 11.5 from the beginning to the end of September, with the



**Figure 2.** Overview of measurements during IBARN. The grey shaded regions represent nighttime. The uncertainty in  $k_{\text{OTG}}$  is given by the green shaded region. Measurements were obtained from the common inlet at a height of 8.5 m apart from the NO<sub>3</sub> photolysis rate (taken from a height of 35 m on an adjacent tower), wind direction (WD) and wind speed (WS) (both at 16.5 m on the 128 m tower). A time series of  $k_{\text{OTG}}$  is given in log scale in the Supplement (Fig. S1).

first widespread ground frost occurring close to the end of the campaign. The relative humidity within the canopy frequently reached 100 % at nighttime, though there was little rainfall during the study period. By the end of the campaign, the initially green leaves of deciduous trees had turned brown and fresh needle/leaf litter was accumulating on the forest floor. The daily profiles of temperature, relative humidity and the NO<sub>3</sub> photolysis rate constant ( $J_{\text{NO}_3}$ ) are displayed in Fig. 2.

### 2.1 SMEAR II site

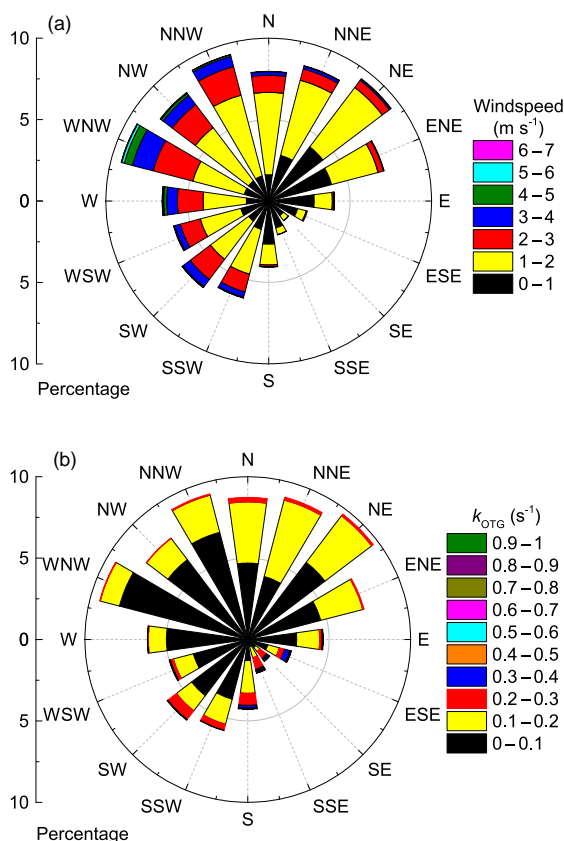
The measurements presented here were conducted at the “Station for Measuring Forest Ecosystem-Atmosphere Relations II” (SMEAR II) in Hyytiälä (61°51′N, 24°17′E) in southern Finland at 180 m above sea level (Hari and Kulmala, 2005). This site has been the focus of intensive research investigating BVOCs (Rinne et al., 2005; Holzke et al., 2006; Hakola et al., 2009; Lappalainen et al., 2009;

Aaltonen et al., 2011) and their influence on O<sub>3</sub> reactivity (Mogensen et al., 2015; Zhou et al., 2017), OH reactivity (Sinha et al., 2010; Nölscher et al., 2012) and simulations on NO<sub>3</sub> lifetimes (Hakola et al., 2003; Peräkylä et al., 2014). SMEAR II is located 49 km north-east of Tampere (pop. ≈ 226 000; 430 inh. km<sup>-2</sup>) and 88 km south-west of Jyväskylä (pop. ≈ 137 000; 120 inh. km<sup>-2</sup>). Anthropogenic influence at the site is generally low, especially when the wind comes from the sparsely populated northern sector. Operations of a sawmill, a wood mill, and a pellet factory in Korkeakoski, 5 km southeast of Hyytiälä, can result in elevated levels of monoterpenes at SMEAR II (Eerdekens et al., 2009; Liao et al., 2011; Williams et al., 2011; Hakola et al., 2012). Furthermore, pollution from forest management as well as minor influences from nearby settlements with low population densities are possible.

Figure 2 shows the local wind speed and wind direction at a height of 16 m (close to the top of the canopy) during the campaign. The wind rose in Fig. 3a indicates that the prevailing wind was from the north-west and north-east sectors (≈ 60 % of the time) compared to 28 % from the southern sector, of which only ≈ 8 % came from the south-east. Nonetheless, two isolated plumes from Korkeakoski were evident as greatly increased values of the NO<sub>3</sub> reactivity and BVOC levels, as discussed later. In general wind speeds at a height of 16 m were low, favouring a stable boundary layer during nighttime. Wind speed, wind direction, temperature, precipitation, and relative humidity were monitored at various heights on the 128 m SMEAR II tower. Details regarding these and other supporting measurements made at this site can be found elsewhere (Hari and Kulmala, 2005; Hari et al., 2013). The vegetation at the site consists mostly of Scots pine (*Pinus sylvestris*, > 60 %) with occasional Norway spruce (*Picea abies*), aspen (*Populus sp.*) and birch (*Betula sp.*). The most common vascular plants are lingonberry (*Vaccinium vitis-idaea* L.), bilberry (*Vaccinium myrtillus* L.), wavy hair grass (*Deschampsia flexuosa* (L.) Trin.) and heather (*Calluna vulgaris* (L.) Hull.). The ground is covered with common mosses as such as Schreber’s big red stem moss (*Pleurozium schreberi* (Brid.) Mitt.) and a dicranum moss (*Dicranum Hedw. sp.*). The canopy height is ≈ 20 m with an average tree density of 1370 stems (diameter at breast height > 5 cm) per hectare (Ilvesniemi et al., 2009).

### 2.2 NO<sub>3</sub> reactivity measurement

NO<sub>3</sub> reactivity was measured using an instrument that was recently described in detail by Liebmann et al. (2017). Initially, 40 to 60 pptv of synthetically generated NO<sub>3</sub> radicals (Reaction R1) were mixed with either zero air (ZA) or ambient air in a cylindrical flow-tube thermostatted to 21 °C. After a reaction time of 10.5 s, the remaining NO<sub>3</sub> was detected by cavity-ring-down spectroscopy (CRDS) at 662 nm. The measurement cycle was typically 400 s for synthetic air



**Figure 3.** (a) Wind rose coloured according to wind speed. (b) Wind rose coloured according to  $k_{\text{OTG}}$ .

and 1200 s for ambient air, with intermittent signal zeroing (every  $\approx 100$  s) by addition of NO.

The observed loss of NO<sub>3</sub> in ambient air compared to ZA was converted to a reactivity via numerical simulation of a simple reaction scheme (Liebmann et al., 2017) using measured amounts of NO, NO<sub>2</sub>, and O<sub>3</sub>. The parameter obtained,  $k_{\text{OTG}}$ , is a loss rate constant for NO<sub>3</sub> from which contributions from NO and NO<sub>2</sub> have been removed, and thus refers to reactive loss to organic trace gases (OTGs) only. Throughout the article, NO<sub>3</sub> reactivity and  $k_{\text{OTG}}$  are equivalent terms, with units of s<sup>-1</sup>. The dynamic range of the instrument was increased to 0.005–45 s<sup>-1</sup> by automated, dynamic dilution of the air sample, the limit of detection being defined by the stability of the NO<sub>3</sub> source. Online calibration of the reactivity using an NO standard was performed every 2 h for 10 min. The uncertainty of the measurement was between 0.005 and 0.158 s<sup>-1</sup>, depending mainly on dilution accuracy, NO levels, and the stability of the NO<sub>3</sub> source (Liebmann et al., 2017).

The instrument was operated in a laboratory container located in a gravel-bedded clearing in the forest. Air samples were drawn at a flow rate of 2900 standard cubic centimetres per minute (sccm) through a 2  $\mu$ m membrane filter (Pall Teflo) and 4 m of PFA tubing (6.35 mm OD) from the centre

of a high-flow inlet ( $\varnothing = 15$  cm, flow = 10 m<sup>3</sup> min<sup>-1</sup>) which sampled at a height of 8 m, 3 m above the roof of the container and circa 8 m away from the forest edge. Several instruments sampled from the high-flow and we refer to this as the “common inlet”. Relative humidity and temperature were monitored in the common inlet using standard sensors (1st Innovative Sensor Technology, HYT939,  $\pm 1.8$  % RH). Vertical profiles of NO<sub>3</sub> reactivity (8.5 to 25 m) were measured by attaching 30 m of PFA tubing directly to the flow tube and raising/lowering the open end (with membrane filter) using a rope hoist attached to a 30 m tower about 5 m from the container.

### 2.3 NO, NO<sub>2</sub>, O<sub>3</sub>, and NO<sub>3</sub> measurements

NO was sampled from the common inlet using a modified commercial chemiluminescence detector (CLD 790 SR) based on the reaction between NO and O<sub>3</sub> (ECO Physics, Dürnten, Switzerland). The detection limit for NO was 5 pptv for an integration period of 5 s, the total uncertainty ( $2\sigma$ ) was 20 % (Li et al., 2015). Ozone was measured by two instruments based on optical absorption, both sampling from the common inlet. These were a 2B-Technology, Model 202 and a Thermo Environmental Instruments Inc., Model 49 both with detection limits of  $\approx 1$  ppb. The two instruments had uncertainties (provided by manufacturer) of 5 and 2 % respectively. Agreement between the two O<sub>3</sub> measurements was excellent (slope =  $1.000 \pm 0.001$ , offset of  $-0.21$  ppbv,  $R^2 = 0.98$ ). Vertical profiles in O<sub>3</sub> (up to 125 m) were made using a TEI 49 C analyser sampling from inlets at various heights on a tower located 130 m north–north-west of the measurement container. NO<sub>2</sub> and NO<sub>3</sub> were measured from the common inlet using a multi-channel, thermal dissociation-cavity ring down spectrometer (TD-CRDS) recently described in detail by (Sobanski et al., 2016a). NO<sub>3</sub> radicals were detected at 662 nm with a detection limit of 1.3 pptv (1 min averaging) and an uncertainty of 25 %. NO<sub>2</sub> was detected at 405 nm with an uncertainty of 6 % and a detection limit of 60 pptv (1 min averaging).

### 2.4 VOC measurements

Three different instruments were used to monitor VOCs, including (1) a gas chromatograph equipped with an atomic emission detector (GC-AED) which sampled from the common inlet; (2) a thermal desorption gas chromatograph with mass spectrometric detection (GC-MS) sampling about 1.5 m above the ground and  $\approx 10$  m away from the reactivity measurements; and (3) a proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS) located about 170 m away in dense forest and sampling at a height of  $\approx 2.5$  m above the ground.

### 2.4.1 GC-AED

The GC-AED consisted of a cryogenic pre-concentrator coupled to an Agilent 7890B GC and an atomic emission detector (JAS AEDIII, Moers, Germany). The GC-AED sampled air through a 15 m long, 1/2" (1.27 cm) outer diameter PFA Teflon tube (flow rate = 20 L min<sup>-1</sup>, transmission time 3.3 s) which was heated to ≈ 10 °C above ambient. The instrument 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 to be 14 %.  $\alpha$ -pinene,  $\Delta$ -3-carene,  $\beta$ -pinene, camphene, and *d*-limonene were all calibrated individually. Detection limits for the monoterpene species were 1.0, 0.9, 0.4, 0.5, and 0.3 pptv respectively. As this is the first deployment of this instrument, more details are provided in the Supplement: a full description will be the subject of an upcoming publication.

### 2.4.2 GC-MS

The GC-MS was located in a container in a gravel-bedded clearing about 4 m from the edge of the forest and ≈ 30 m away from the common inlet. Air samples were taken every other hour (30 min sampling time) at a height of 1.5 m by drawing air at 1 L min<sup>-1</sup> through a 1 m long fluorinated ethylene propylene (FEP) inlet (inner diameter 1/8 inch). Ozone was removed via a heated (120 °C) stainless steel tube (Hellén et al., 2012). VOCs were collected from a 40 mL min<sup>-1</sup> subsample flow into the cold trap (Tenax TA/Carbopack B) of the thermal desorption unit (TurboMatrix, 650, Perkin-Elmer) connected to a gas chromatograph (Clarus 680, Perkin-Elmer) with HP-5 column (60 m, inner diameter 0.25 mm, film thickness 1 µm) coupled to a mass spectrometer (Clarus SQ 8 T, Perkin-Elmer). The instrument was used for measurements of isoprene, monoterpenes, and aromatic hydrocarbons and was calibrated for all individual compounds using liquid standards in methanol solutions, which were injected into the Tenax TA/Carbopack B adsorbent tubes and analysed with the same method as the air samples. Detection limits for monoterpenes ( $\alpha$ -pinene, camphene,  $\beta$ -pinene, 3 $\Delta$ -carene, myrcene, *p*-cymene, limonene, 1,8-cineol, and terpinolene) were 0.2–1.2 pptv and for  $\beta$ -caryophyllene 0.8 pptv. The average total uncertainty (10 % for all monoterpenes and  $\beta$ -caryophyllene) was calculated from the reproducibility of the calibrations, uncertainty of the standard preparation and the uncertainty in the sampling flow.

### 2.4.3 PTR-TOF-MS

The PTR-TOF-MS (PTR-TOF 8000, Ionicon Analytic GmbH) measures whole VOC spectra in real time (Jordan et al., 2009; Graus et al., 2010) with mass resolution of 4500 (full width at half maximum). The instrument was located in the main cottage, approximately 170 m away from the common inlet. Ambient air was sampled from 2.5 m above the ground, using a 3.5 m long (4 mm inner diameter) PTFE sampling air at 20 L min<sup>-1</sup>. A subsample flow of 1 L min<sup>-1</sup> was passed via 10 cm of PTFE tubing (1.6 mm inner diameter), by way of a three-way valve and 15 cm of PEEK tubing (1 mm inner diameter) to the PTR-TOF-MS. The raw data was collected with 10 s resolution. The instrument measured total monoterpenes at  $m/z = 137$  and isoprene at  $m/z = 69$ , which were calibrated with a gas standard (Apel Riemer Environmental Inc., USA) containing isoprene and  $\alpha$ -pinene. The calibration set up and routine are described in detail in Schallhart et al. (2016). The campaign average limit of detection (LOD, 3 $\sigma$ , 10 min time resolution) was 5.5 and 3.2 pptv for isoprene and monoterpenes respectively.

## 3 Results and discussion

NO<sub>x</sub> mixing ratios were generally low during the campaign with NO<sub>2</sub> between 0.1 to 1.84 ppbv with a campaign average of 0.32 ppbv showing little variation across the diel cycle. The mean daytime NO mixing ratio was 43 pptv while nighttime NO was close to or below the limit of detection (≈ 5 pptv) and its contribution to the loss of NO<sub>3</sub> was generally insignificant (see below). Ozone mixing ratios showed large day/night differences with daily maxima between 30 and 40 ppbv, whilst nighttime values were as low as 5–10 ppbv. Possible reasons for the large changes in O<sub>3</sub> across the diel cycle are addressed in Sect. 3.1.

### 3.1 NO<sub>3</sub> reactivity and nighttime loss of O<sub>3</sub>

NO<sub>3</sub> reactivity was measured from 5 September 12:00 UTC to 22 September 05:30 UTC; the 1 min averaged time series of  $k_{\text{OTG}}$  is displayed in Fig. 2. The overall uncertainty in  $k_{\text{OTG}}$  is given by the green, shaded region. NO<sub>3</sub> photolysis and reaction with NO result in concentrations that are generally below the detection limit of modern instruments during daytime and steady-state calculations of NO<sub>3</sub> reactivity are lower limit estimates. In contrast, our direct approach allows us to derive and analyse daytime values of  $k_{\text{OTG}}$  as long as NO<sub>x</sub> measurements are available (see above). Figure 2 indicates that, in general, the NO<sub>3</sub> reactivity was highest at nighttime; the maximum observed values in  $k_{\text{OTG}}$  was 0.94 s<sup>-1</sup>, (at 21:00 UTC on 9 September) implying a lifetime of just 1 s and a very reactive air mass at this time. The mean nighttime value of  $k_{\text{OTG}}$  was ≈ a factor ten lower at 0.11 s<sup>-1</sup>, the daytime mean even lower at 0.04 s<sup>-1</sup>. Broadly speaking, the nighttime NO<sub>3</sub> lifetimes during IBAIRN were very short



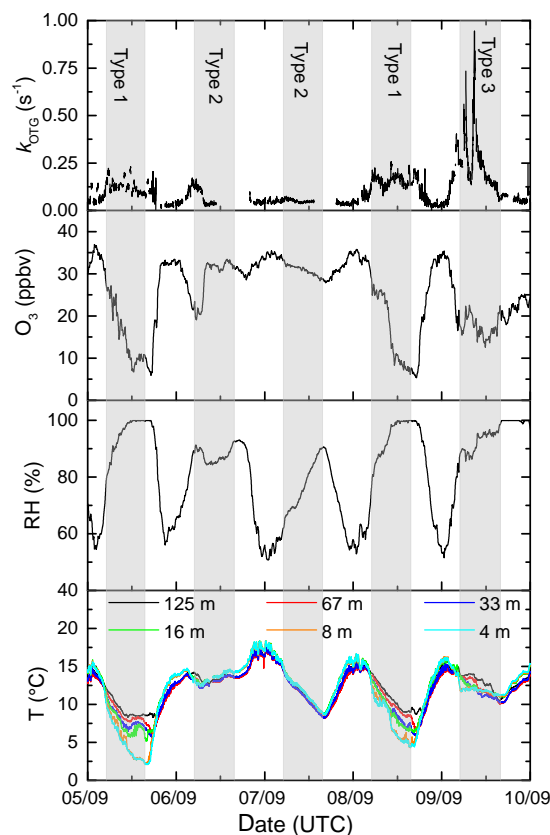
( $\approx 10$  s on average) compared to previous indirect, ground level measurements in other locations where several groups have reported lifetimes of hundreds to thousands of seconds (Heintz et al., 1996; Allan et al., 1999; Geyer et al., 2001; Aldener et al., 2006; Ambrose et al., 2007; Brown et al., 2009; Crowley et al., 2010, 2011; Sobanski et al., 2016b). Our short NO<sub>3</sub> lifetimes are, however, compatible with the very low NO<sub>3</sub> mixing ratios observed in forested regions with high rates of emission of biogenic trace gases (Gölz et al., 2001; Rinne et al., 2012; Ayres et al., 2015).

Figure 3b illustrates the dependence of  $k_{\text{OTG}}$  on wind direction. Air masses from the northern sector were generally associated with lower reactivity ( $< 0.2 \text{ s}^{-1}$ ) whereas all incidents of reactivity larger than  $0.3 \text{ s}^{-1}$  were associated with air masses from the SE sector. Enhanced reactivity from the south-east may be caused by emissions from the sawmill at Korkeakoski (Eerdekens et al., 2009), or a local woodshed storing freshly cut timber about 100 m away from the containers. This may have been compounded by the lower than average wind speeds associated with air masses from the south-east, which reduced the rate of exchange between the nocturnal boundary layer and above canopy air, effectively trapping ground-level emissions into a shallow boundary layer. Emissions from the sawmill reaching the site on the night of the 9–10 September provided a useful test of our method at high reactivity.

In order to examine the difference in daytime and nighttime NO<sub>3</sub> reactivity and also explain the large nighttime variability in  $k_{\text{OTG}}$  we categorize the nights into three broad types: (1) nights with strong temperature inversion where the NO<sub>3</sub> reactivity was greatly increased compared to the previous or following day, (2) nights without temperature inversion with comparable (usually low) daytime and nighttime NO<sub>3</sub> reactivity, and (3) events with unusually high NO<sub>3</sub> reactivity. Figure 4 shows an expanded view of  $k_{\text{OTG}}$  over a five day/night period (5–10 September) in which all three types are represented. It also plots the temperature at different heights as well as the RH and O<sub>3</sub> measured in the common inlet at 8.5 m height.

### 3.1.1 Type 1 and type 2 nights

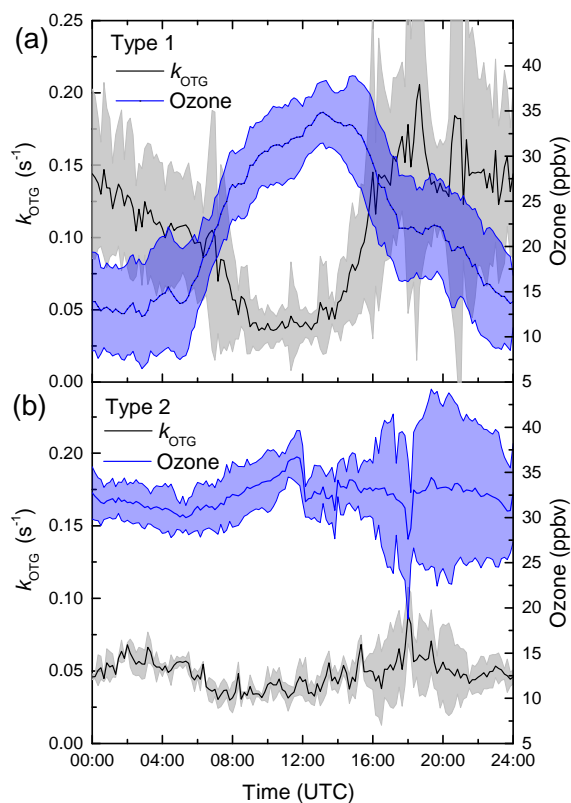
Within this 5-day period, the nights on which the reactivity was high relative to the day (type 1) are the 5–6 and 8–9. These nights are characterized by large depletion in O<sub>3</sub>, a significant temperature inversion of 5–7 °C between heights of 8 and 128 m, and a relative humidity of 100 % directly after sunset. In contrast, two interspersed nights with comparable reactivity to daytime values (6–7, 7–8, type 2) display much weaker (if any) nighttime loss of O<sub>3</sub> compared to levels during the previous day, no significant temperature inversion and a relative humidity less than 100 %. The observations within this period can be extended to all campaign days. Figure 5 presents the diel cycle of  $k_{\text{OTG}}$  and O<sub>3</sub> mixing ratios separated into nights of type 1 (with temper-



**Figure 4.** Expanded view of five campaign days illustrating the three types (1–3) of night encountered. Type 1 has a strong vertical gradient in temperature ( $T$ ) and significant O<sub>3</sub> loss with relative humidity (RH) at 100 %. Type 2 (no temperature inversion), has little or no O<sub>3</sub> loss. Type 3 is influenced by emissions from the Korkeakoski sawmill.

ature inversion) and type 2 (no temperature inversion). The shaded regions represent the variability of the measured values. During 24 h periods in which the night was characterized by strong temperature inversion (panel (a) in Fig. 5), the O<sub>3</sub> mixing ratios display a large diel variation, with a maximum of 35 ppbv at about 13:00 UTC dropping rapidly to a minimum of  $\approx 13$  ppb between midnight and sunrise at around 05:00 UTC. O<sub>3</sub> depletion due to its slow reaction with NO<sub>2</sub> (present at maximum 2 ppbv at night) does not contribute significantly to its loss even if all resultant NO<sub>3</sub> reacts to form organic nitrates rather than to form N<sub>2</sub>O<sub>5</sub> and re-release NO<sub>x</sub>.

The O<sub>3</sub> mixing ratio shows an inverse diel profile to the NO<sub>3</sub> reactivity raising the possibility that the rapid loss of ozone is linked to high NO<sub>3</sub> reactivity; the large values of  $k_{\text{OTG}}$  and rapid O<sub>3</sub> depletion observed on nights with a significant temperature inversion are clear indicators that nighttime boundary layer dynamics plays a key role in controlling both the NO<sub>3</sub> reactivity and O<sub>3</sub> loss. A strong nocturnal temperature inversion will weaken the mixing within or ventila-



**Figure 5.** Diel profiles of  $k_{OTG}$  (black line) and  $O_3$  (blue line) on two different types of days/nights. (a) Type 1 (strong nighttime temperature inversion). (b) Type 2, (no temperature inversion). The shaded areas represent  $2\sigma$  uncertainty and indicate variability over the diel cycle.

tion of the lowermost boundary layer causing a build-up of reactive, biogenic emissions in the lower layer, and also prevent down-mixing of drier,  $O_3$ -rich air leading to the apparent higher loss rate of  $O_3$  and higher relative humidity. The strong anti-correlation between  $k_{OTG}$  and  $O_3$  may also provide a clue to the origin of the  $O_3$  loss. Whilst the generally high  $NO_3$  reactivity can, to a large extent, be explained by the presence of reactive trace gases (see Sect. 3.2), the precipitous loss of  $O_3$  on several nights when  $k_{OTG}$  was high (see Figs. 2 and 4) may have components of both dry deposition and gas-phase reactions.

The campaign averaged, diel variation of ozone at different heights (4 to 125 m) as measured at the SMEAR II tower (Fig. S2 of the Supplement) indicate that the most rapid losses of ozone are at the lowest heights, around and below the canopy. Ozone is generally removed from the lower troposphere by both stomatal and non-stomatal deposition, the latter involving loss to surfaces and soil. The reactive, gas-phase loss mechanisms of  $O_3$  and  $NO_3$  are in some ways similar, as both react with NO to form  $NO_2$ , or with unsaturated VOCs by addition to the double bond. We estimated the loss rate constant for  $O_3$  due to its reaction

with terpenes using approximate ambient mixing ratios from 20:00 to 00:00 UTC on the 20 September for *d*-limonene (20 pptv),  $\alpha$ -pinene (400 pptv),  $\Delta$ -carene (100 pptv), and  $\beta$ -pinene (100 pptv) and using literature rate constants for the  $O_3$  + terpene reactions. The calculated  $O_3$  loss (only 2 % from 20:00 to 00:00 UTC) is clearly insufficient to explain the IBAIRN observations. We also note that the presence of high concentrations of terpenes when the site was impacted by the Korkeakoski sawmill resulted in the largest  $NO_3$  reactivity observed, but did not lead to large  $O_3$  losses (Fig. 4). As leaf stomata are closed during nighttime, the decrease in  $O_3$  can be attributed either to non-stomatal deposition or chemical sinks due to reaction with reactive biogenic trace gases (not the measured monoterpenes) and NO. Previous studies of  $O_3$  loss in forests have highlighted the potential role of unidentified, reactive organic compounds (Kurpius and Goldstein, 2003; Goldstein et al., 2004; Holzinger et al., 2006; Rannik et al., 2012). In contrast to monoterpenes, which react only slowly with  $O_3$  (rate constants are  $\approx 10^{-16}$ – $10^{-17}$   $cm^3$  molecule $^{-1}$  s $^{-1}$ ), sesquiterpenes can react rapidly; for example, for  $\beta$ -caryophyllene the rate coefficient is  $k_{O_3} = 1.2 \times 10^{-14}$   $cm^3$  molecule $^{-1}$  s $^{-1}$  (IUPAC, 2017). The presence of sesquiterpenes would therefore provide an explanation for the observations of high  $NO_3$  reactivity and rapid  $O_3$  loss. We examine the potential role of sesquiterpenes in more detail in Sect. 3.2 where the contribution of measured terpenoids to  $NO_3$  reactivity is discussed. We also note that recent modelling studies using Hyytiälä data (Chen et al., 2018; Zhou et al., 2017) conform that  $O_3$  depletion events are associated with the formation of a shallow boundary layer and high relative humidity. Zhou et al. (2017) conclude that chemical reaction plays only a minor role in ozone loss processes during the night, which was suggested to be dominated by deposition to wet surfaces at relative humidity > 70 %, which is in accord with laboratory investigations (Sun et al., 2016).

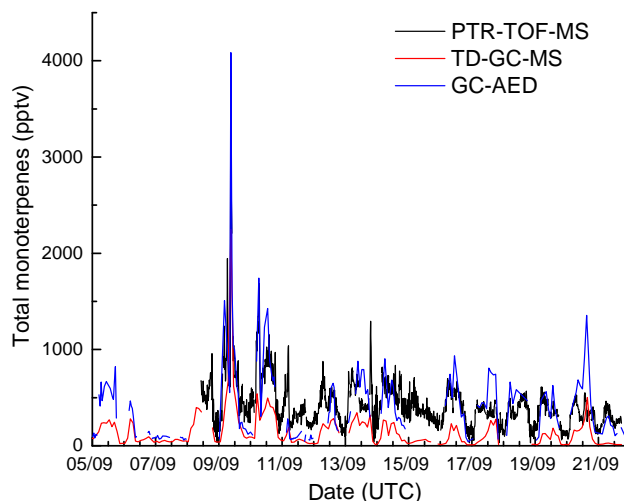
### 3.1.2 Type 3 nights

The period between the evening and midnight on the 9 September is an example of a type 3 night, with extremely high  $NO_3$  reactivity, which was not accompanied by significant  $O_3$  depletion, temperature inversion or a RH of 100 %. The apparently anomalously high reactivity on this night can be traced back to a change in wind direction, which swept from easterly to southerly during this period, bringing air that was impacted by monoterpene emissions from the sawmill in Korkeakoski. High mixing ratios of terpenoids in air masses that have passed over the sawmill have been documented frequently (Eerdekens et al., 2009; Sinha et al., 2010; Liao et al., 2011; Hakola et al., 2012; Nölscher et al., 2012). Other occurrences of sawmill contaminated air during IBAIRN were on the 10 September from 18:40 to 19:00 UTC and on the 14 September from 06:30 to 08:00 UTC, HYSPLIT back-trajectories (GDAS global, 0.5°), indicating that

the air mass passed over Korkeakoski  $\approx 0.5$  h prior to reaching the SMEAR II site.

### 3.2 Comparison of $k_{\text{OTG}}$ with NO<sub>3</sub> reactivity derived from VOC measurements

In this section we compare  $k_{\text{OTG}}$  with NO<sub>3</sub> reactivity calculated from ambient VOC mixing ratios. During IBAIRN, three instruments (GC-MS, GC-AED, and PTR-TOF) measuring VOCs were deployed (see Sect. 2.5 for details). As the PTR-TOF reports only a summed mixing ratio of all monoterpenes,  $\Sigma\text{MT}(\text{PTR-TOF})$ , we first generated an equivalent parameter for the two GCs,  $\Sigma\text{MT}(\text{GC-MS})$  and  $\Sigma\text{MT}(\text{GC-AED})$ . For the GC-MS,  $\alpha$ -pinene,  $\beta$ -pinene,  $\Delta$ -carene, *d*-limonene, camphene, myrcene, and terpinolene were considered whereas for the GC-AED,  $\alpha$ -pinene,  $\beta$ -pinene,  $\Delta$ -carene, camphene, and *d*-limonene were taken into account. The  $\Sigma\text{MT}$  data are displayed as a time series in Fig. 6, which indicates large differences between the three measurements as highlighted in Fig. S3 of the Supplement). While the  $\Sigma\text{MT}(\text{GC-AED})$  and  $\Sigma\text{MT}(\text{PTR-TOF})$  data are in reasonable agreement, especially when mixing ratios were large, the values reported by the GC-MS are consistently and significantly lower (factor 2 to  $> 10$ ) than those of the others instruments. The time dependent variability in the differences in  $\Sigma\text{MT}$  reported by the GC-MS, GC-AED, and PTR-TOF is a strong indication that the cause is most likely related to instrument location and inhomogeneity in terpene emissions within the forest. Whilst the GC-AED sampled from the common inlet at a height of 8.5 m, which was also used for the NO<sub>3</sub> reactivity measurements, the inlet of the GC-MS was  $\approx 10$  m away and sampled 1.5 m above the gravel covered clearing, very close to the side of the container which housed the instrument. The PTR-TOF-MS was located roughly 170 m away in a wooden cottage directly surrounded by dense forest and sampled close to the forest floor at a height of  $\approx 1.5$  m. With very low within-canopy wind speeds, especially during nighttime, both horizontal as well as vertical mixing in the forest and in the clearing are weak so that each VOC measurement may, to some extent, reflect the mixture and total amount of BVOCs that are very locally emitted. This aspect was examined by comparing individual monoterpenes measured by the GC-MS and the GC-AED. The results, presented as correlation plots for 4 monoterpenes in Fig. S4 of the Supplement, show that the monoterpene ratios measured by the two instruments (GC-AED/GC-MS), were variable with values of  $1.69 \pm 0.06$  for  $\alpha$ -pinene,  $2.51 \pm 0.09$  for  $\beta$ -pinene,  $4.29 \pm 0.21$  for  $\Delta$ -carene, and  $0.45 \pm 0.03$  for *d*-limonene. A similar picture emerges for isoprene, for which the GC-AED measured mixing ratios that were a factor 2–5 larger than measured by the GC-MS. The variable relative concentrations of monoterpenes reported by each instrument is further evidence of the inhomogeneity of emissions within the forest and also the influence of different tree chemotypes within single tree-



**Figure 6.** Time series of total monoterpenes from GC-AED (black), GC-MS (red), and PTR-TOF-MS (blue). The data are reproduced as histograms in Fig. S3 of the Supplement.

families in Hyytiälä, which can exhibit vastly different emission rates of various monoterpenes (Bäck et al., 2012; Yassaa et al., 2012).

For the purpose of comparing our point measurements of  $k_{\text{OTG}}$  with NO<sub>3</sub> reactivity calculated from BVOC measurements, we restricted our analysis to the data set obtained by the GC-AED, which sampled from the same inlet. Nonetheless, when comparing measured NO<sub>3</sub> mixing ratios with those calculated from NO<sub>3</sub> reactivity and its production term (see Sect. 3.4) we use both GC-based datasets.

The loss rate constant,  $k_{\text{OTG}}$ , represents chemical reactions of [NO<sub>3</sub>] with all organic trace gases present, and can be compared to the loss rate constant ( $k_{\text{GC-AED}}$ ) obtained from the concentrations of VOCs in the same air mass as measured by the GC-AED, and the rate coefficient for reaction with NO<sub>3</sub>:

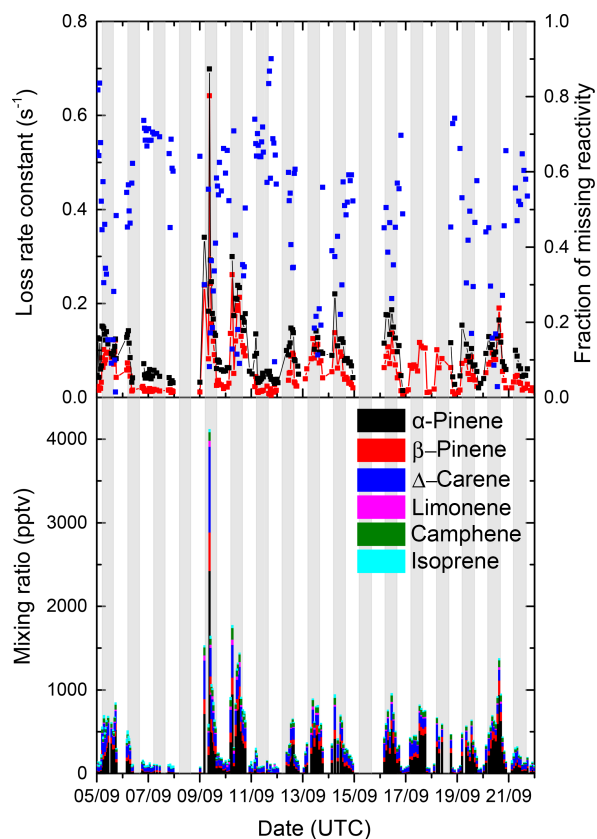
$$k_{\text{GC-AED}} = \sum k_i [C_i], \quad (1)$$

A difference in the values of  $k_{\text{OTG}}$  and  $k_{\text{GC-AED}}$  is defined as missing reactivity ( $\text{s}^{-1}$ ):

$$\text{missing reactivity} = k_{\text{OTG}} - k_{\text{GC-AED}}; \quad (2)$$

where  $[C_i]$  is the measured VOC concentration and  $k_i$  the corresponding rate constant. The rate constants used in these calculations of  $k_{\text{GC-AED}}$  were taken from the IUPAC evaluation (IUPAC, 2017). Figure 7 (lower panel) shows the concentrations of the monoterpenes as measured by the GC-AED. The dominant monoterpene was  $\alpha$ -pinene followed by  $\Delta$ -carene,  $\beta$ -pinene, *d*-limonene, and camphene. The GC-AED also detected myrcene and linalool and some other terpenes but the very low mixing ratios meant that none of them contributed significantly to NO<sub>3</sub> loss.

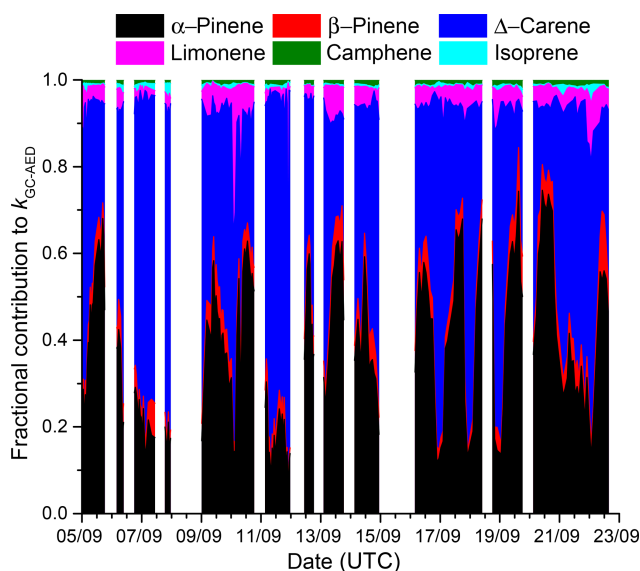




**Figure 7.** Upper plot: comparison of  $k_{\text{GC-AED}}$  (red data points) and measured  $\text{NO}_3$  reactivity ( $k_{\text{OTG}}$ , black data points). The fractional missing reactivity (blue data points) was calculated as  $(k_{\text{OTG}} - k_{\text{GC-AED}})/k_{\text{OTG}}$ . Lower plot: mixing ratios of individual monoterpenes as measured by the GC-AED and their contribution to the  $\text{NO}_3$  reactivity. The grey shaded areas represent nighttime.

In Fig. 7 (upper panel) we overlay the time series of  $k_{\text{OTG}}$  and  $k_{\text{GC-AED}}$ . For clarity of presentation we have omitted to plot the overall uncertainty of each measurement, which was calculated as described previously (Liebmann et al., 2017) and is plotted in Fig. S6 of the Supplement. The correlation between  $k_{\text{OTG}}$  and  $k_{\text{GC-AED}}$  is displayed as Fig. S7 of the Supplement and indicates, on average, that measured organics accounted for  $\approx 70\%$  of the total  $\text{NO}_3$  reactivity.

The uncertainty associated with  $k_{\text{GC-AED}}$  was calculated by propagating uncertainty in the mixing ratios of the individual terpenes (14 %, mainly resulting from uncertainty in the calibration standard and the calibration reproducibility) and assuming 15 % uncertainty in the rate coefficients for reactions of  $\text{NO}_3$  with each terpene. The values of  $k_{\text{OTG}}$  and  $k_{\text{GC-AED}}$  do not agree within their combined uncertainties, indicating that the missing reactivity calculated in Eq. (3) is statistically significant. Figure 8 plots the time series of the fractional contribution to  $k_{\text{GC-AED}}$  made by monoterpenes detected by the GC-AED. The GC-AED derived  $\text{NO}_3$  reactivity is dominated by  $\alpha$ -pinene and  $\Delta$ -carene and to a lesser

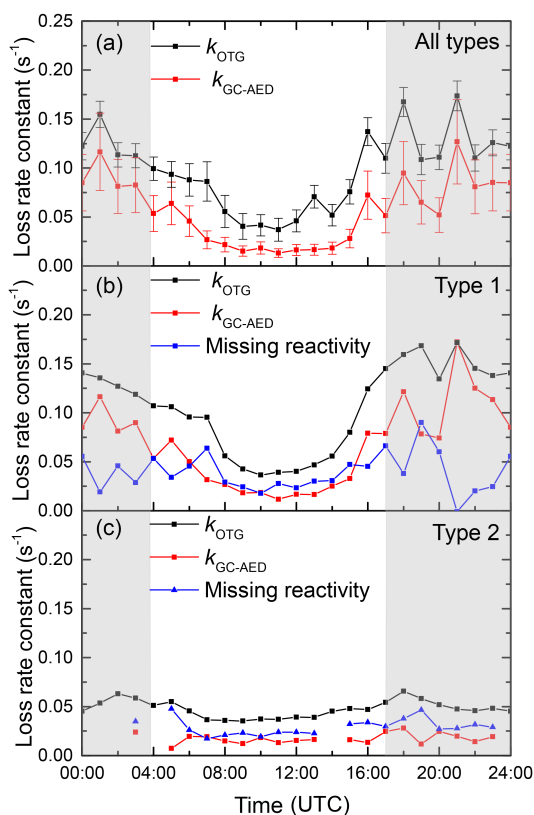


**Figure 8.** Fractional contribution of individual monoterpenes (measured by the GC-AED) to  $k_{\text{GC-AED}}$  indicating the dominant role of  $\alpha$ -pinene and  $\Delta$ -carene.

extent *d*-limonene, with minor contributions from  $\beta$ -pinene, camphene, and isoprene.

In Fig. 9 we plot the diel profiles of  $k_{\text{OTG}}$  and  $k_{\text{GC-AED}}$  ( $\text{s}^{-1}$ ) averaged for the whole campaign. To do this, we interpolated the values of  $k_{\text{OTG}}$ , obtained with 60 s time resolution averaged to 900 s data onto the low-time resolution ( $\approx 60$  min) GC-AED dataset. In the lower panels of Fig. 9 we plot two separate diel profiles, separating the data into nights with (middle panel) and without (lower panel) strong temperature inversion. The missing reactivity (in  $\text{s}^{-1}$ ) across the entire diel profile is between  $\approx 0.02$  and  $0.07$ , the larger value encountered during nighttime. In contrast, the fraction of missing reactivity within the campaign averaged diel cycle was observed during daytime ( $\approx 60\%$ ), with only 30 % missing at nighttime. The lowermost panel of Fig. 9 highlights the fact that  $k_{\text{OTG}}$  was lower during campaign day/night periods with no temperature inversion and shows that it is roughly constant across the diel cycle. Likewise, the diel cycle in the reactivity attributed to the monoterpenes is also constant, with a missing reactivity of between  $0.02$  and  $0.04 \text{ s}^{-1}$ . A different picture emerges for the diel cycle considering only the days/nights with strong temperature inversion. On average, we see a much higher nighttime reactivity, which is tracked in its diel profile by that calculated from the measured monoterpenes. In this case, the missing reactivity is generally higher and more variable, with values between  $0$  and  $0.1 \text{ s}^{-1}$ .

Although statistically significant, the fraction of reactivity missing is much smaller than that reported for OH at this site (Nölscher et al., 2012) whereby up to 90 % of the observed reactivity was unaccounted for when the forest was under stress due to high temperatures. For OH, the fractional



**Figure 9.** (a) Campaign averaged diel cycle of NO<sub>3</sub> reactivity ( $k_{\text{OTG}}$ ) and the reactivity calculated from the monoterpenes reported by the GC-AED. The error bars represent the overall uncertainty in each parameter and not variability. Panels (b) and (c) show data from type 1 nights (significant nocturnal temperature inversion) and type 2 nights (weak or no nocturnal temperature inversion) respectively.

missing reactivity was also greatest when the overall reactivity was high, which is in contrast with the situation for NO<sub>3</sub> where missing reactivity was highest when the overall reactivity was low (i.e. during daytime). The OH radical reacts with most hydrocarbons and many inorganic trace gases and may be considered unselective in its reactivity, whereas NO<sub>3</sub> is a more specific oxidant of VOCs, its reactions in the forest dominated by addition to unsaturated VOCs or reaction with NO.

As the nighttime mixing ratios of NO were low (< 5 pptv apart from the night 20–21 September when a mixing ratio of  $\approx 25$  pptv was measured), its contribution to the overall nighttime loss of NO<sub>3</sub> was insignificant. Figure S8 of the Supplement indicates that, averaged over the entire campaign, NO accounted for less than 2 % of the reactive loss of NO<sub>3</sub> at night. A different picture emerges for daytime, for which the campaign averaged contribution of NO to the overall chemical reactivity of NO<sub>3</sub> peaked at 40 % at about 10:00 UTC. However, even during daytime, the average missing reactivity of  $0.025 \text{ s}^{-1}$  (Fig. 9) would require an

extra 40 pptv of NO to account for it, which is clearly not within the total uncertainty of the NO measurement.

A more plausible explanation for the missing NO<sub>3</sub> reactivity is incomplete detection of all reactive BVOCs by the GC-AED, which does not report mixing ratios of some hydrocarbons such as 2-methyl-3-buten-2-ol, *p*-cymene, and 1,8 cineol, which the GC-MS showed to be present. The GC-MS mixing ratios of these species (which react slowly with NO<sub>3</sub>) were however too low for them to contribute significantly, even taking into account the potentially larger concentrations at the common inlet.

We also consider the potential role of sesquiterpenes. Mixing ratios of  $\beta$ -caryophyllene reported by the GC-MS were generally low, with a maximum value of 25 pptv. However, the rate coefficient reported (Shu and Atkinson, 1995) for the reaction of NO<sub>3</sub> with  $\beta$ -caryophyllene is large ( $1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and sesquiterpenes at levels of 10 s of pptv can contribute significantly to NO<sub>3</sub> loss rates. Like monoterpenes, the emissions of sesquiterpenes are driven by temperature, with tree emissions most important during the hottest months (Duhl et al., 2008). Whilst previous studies at this site (Hakola et al., 2006) found no correlation between the  $\beta$ -caryophyllene and monoterpene emissions of an enclosed Scots pine branch, we find that  $\beta$ -caryophyllene mixing ratios (reported by the GC-MS) are correlated with those of several monoterpenes measured by the same instrument. This is illustrated in Fig. S5 of the Supplement which indicates  $\beta$ -caryophyllene/monoterpene ratios ( $\alpha$ -pinene  $\beta$ -pinene and  $\Delta$ -carene) of  $0.061 \pm 0.002$  ( $R^2$  0.86),  $0.294 \pm 0.011$  ( $R^2$  0.86), and  $0.181 \pm 0.007$  ( $R^2$  0.84), respectively. As the monoterpenes and sesquiterpenes have very different lifetimes with respect to chemical loss, we have excluded the sawmill impacted data (red data point) as sesquiterpenes are unlikely to survive the  $\approx 0.5$  h. transport time from Korkeakoski due to their rapid reaction with O<sub>3</sub>. The high levels of  $\beta$ -caryophyllene measured may indicate that the source during IBARN is unlikely to be Scots pine, the emissions from which are strongly temperature dependent during the summer months but low and independent of temperature in September (Hakola et al., 2006).

A rough estimate of the  $\beta$ -caryophyllene mixing ratio at the common inlet may be obtained from the GC-AED measurement of  $\alpha$ -pinene and the  $\alpha$ -pinene/ $\beta$ -caryophyllene ratios measured by the GC-MS (see above). The resulting  $\beta$ -caryophyllene mixing ratios lie between 10 and 60 pptv, which, based on a rate constant of  $1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , results in a contribution to NO<sub>3</sub> reactivity of up to  $0.03 \text{ s}^{-1}$ . As  $\beta$ -caryophyllene emissions from pine tree needles reveals a strong temperature dependence (Hakola et al., 2006) it seems unlikely that this is an important source of  $\beta$ -caryophyllene during the relatively cold September nights of the IBARN campaign and its emissions from other sources, especially those at ground level including soil may be more important (Insam and Seewald, 2010; Penuelas et al., 2014).

In summary, the BVOC measurements indicate that NO<sub>3</sub> reactivity in this boreal environment is dominated by reaction with monoterpenes with, on average, 70 % of the reactivity during nighttime and 40 % of the reactivity during daytime explained by  $\alpha$ - and  $\beta$ -pinene,  $\Delta$ -carene, limonene, and camphene. Unidentified monoterpenes/sesquiterpenes are likely to account for a significant fraction of the VOC-derived missing reactivity.

### 3.3 NO<sub>3</sub> levels: measurements versus calculations using production and loss terms

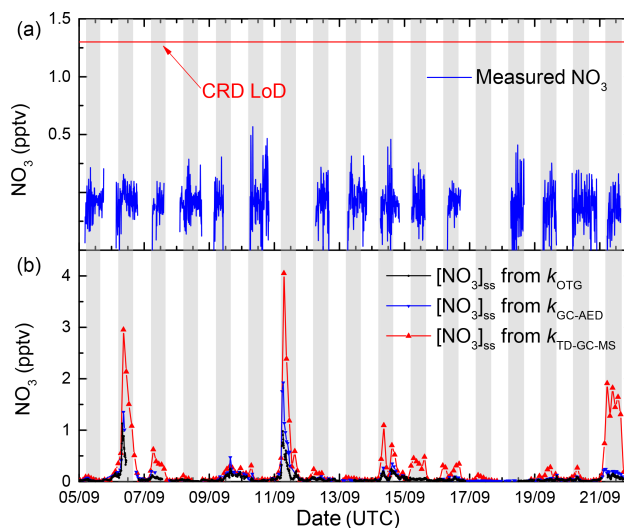
Previous estimates of NO<sub>3</sub> reactivity (often reported as its inverse lifetime) have relied on NO<sub>3</sub> concentration measurements and the assumption that the production and loss of NO<sub>3</sub> are in stationary state. By combining  $k_{\text{OTG}}$  and other loss processes such as photolysis and reaction with NO with the NO<sub>3</sub> production term, we can also calculate the NO<sub>3</sub> concentration:

$$[\text{NO}_3]_{\text{ss}} = \frac{\text{NO}_3 \text{ production rate}}{\text{NO}_3 \text{ loss rate}} = \frac{[\text{O}_3][\text{NO}_2]k_1}{([k_{\text{OTG}}] + [J_{\text{NO}_3}] + [\text{NO}]k_2)}, \quad (3)$$

where  $k_1$  is the rate constant ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for reaction of NO<sub>2</sub> with O<sub>3</sub> and  $k_2$  is the rate constant ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for the reaction of NO<sub>3</sub> with NO and  $J_{\text{NO}_3}$  is its photolysis rate constant ( $\text{s}^{-1}$ ).  $J_{\text{NO}_3}$  was calculated from actinic flux measurements (spectral radiometer, Metcon GmbH; Meusel et al., 2016) and NO<sub>3</sub> cross sections/quantum yields from an evaluation (Burkholder et al., 2016). This expression does not consider indirect loss of NO<sub>3</sub> via heterogeneous loss processes of N<sub>2</sub>O<sub>5</sub>, which, given the high levels of BVOC (short NO<sub>3</sub> lifetimes) and low aerosol surface area, cannot contribute significantly.

Figure 10 plots the time series of measured NO<sub>3</sub> mixing ratios (1 min averages, blue lines) for the entire campaign, which indicates that NO<sub>3</sub> was always below the detection limit of 1.3 pptv, which is defined by variation in the zero-signal rather than random noise (Sobanski et al., 2016a). The fact that the measured NO<sub>3</sub> mixing ratios are slightly negative (by  $\approx 0.2$  pptv) is due to a few percent NO<sub>2</sub> contamination of the NO sample used to zero the NO<sub>3</sub> signal. We also plot the time series (black line) of the stationary state NO<sub>3</sub> mixing ratios,  $[\text{NO}_3]_{\text{ss}}$ , calculated according to (Eq. 3). The low NO<sub>x</sub> levels and moderate O<sub>3</sub> levels combine to result in a weak production rate for NO<sub>3</sub> of less than  $0.03 \text{ pptv s}^{-1}$  for the entire campaign resulting in predicted levels of  $[\text{NO}_3]_{\text{ss}}$  of less than 0.2 pptv. On two nights, higher mixing ratios close to 1 pptv (nights of 6–7 and 10–11) are predicted, a result of elevated production rates due to higher NO<sub>2</sub> levels.

The advantages of directly measured  $k_{\text{OTG}}$  rather than reactivity calculations based on measurements of reactive trace gases is illustrated by plotting the predicted NO<sub>3</sub> levels based on the reactive hydrocarbons reported by the GC-AED and



**Figure 10.** Stationary state NO<sub>3</sub> mixing ratios calculated from the production term ( $k_1[\text{NO}_2][\text{O}_3]$ ) and using either  $k_{\text{OTG}} + k_2[\text{NO}] + J_{\text{NO}_3}$  (b, black line),  $k_{\text{GC-MS}} + k_2[\text{NO}] + J_{\text{NO}_3}$  (b, red line), or  $k_{\text{GC-MS}} + k_2[\text{NO}] + J_{\text{NO}_3}$  (b, blue line) as loss terms. For comparison, the measured NO<sub>3</sub> mixing ratios are also plotted (a, blue line) as well as the 1.3 pptv limit of detection (horizontal red line).

GC-MS, i.e. use of  $k_{\text{GC-MS}}$  and  $k_{\text{GC-AED}}$  rather than  $k_{\text{OTG}}$ . Use of the GC-MS data, which reported the lowest levels of biogenic hydrocarbons, would lead to the prediction of measurable amounts (up to 4 pptv) of NO<sub>3</sub> on several nights, contradicting our NO<sub>3</sub> measurements and previous reports (Rinne et al., 2012) of very low NO<sub>3</sub> levels at this site.

### 3.4 Vertical gradient in NO<sub>3</sub> reactivity

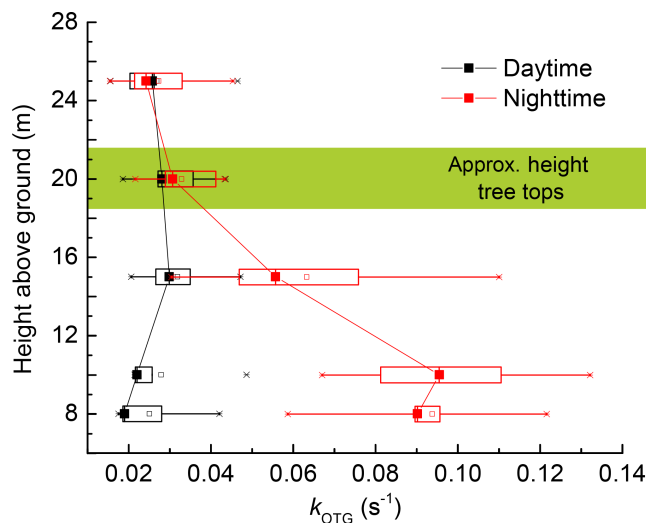
Both column and point measurements of tropospheric NO<sub>3</sub> indicate a strong vertical gradient in its mixing ratio with significantly elevated levels aloft (Aliwell and Jones, 1998; Allan et al., 2002; von Friedeburg et al., 2002; Stutz et al., 2004; Brown et al., 2007a, b; Brown and Stutz, 2012). The NO<sub>3</sub> gradient is the result of lower production rates close to the ground, where O<sub>3</sub> levels are depleted due to deposition and also lower loss rates aloft as the concentration of reactive trace gases from ground level emissions decreases with altitude. High resolution data (Brown et al., 2007b) indicate that the largest gradient in NO<sub>3</sub> concentration is often found in the lowermost 50 m. Nighttime monoterpene mixing ratios in forested, boreal regions have been found to display a vertical gradient, with highest mixing ratios at lower levels (Holzinger et al., 2005; Rinne et al., 2005; Eerdekens et al., 2009). This is a result of direct emissions, such as monoterpenes from the trees at canopy level; and emissions of monoterpenes and sesquiterpenes from rotting leaf litter into a shallow, stratified boundary layer, suggesting that reactive species close to the ground will dominate in con-

trolling the NO<sub>3</sub> lifetime and thus mixing ratio (Aaltonen et al., 2011). We explored this by measuring  $k_{\text{OTG}}$  at various heights above ground, including measurements from a few metres below the canopy, to a few metres above the tree tops. Altogether we recorded 14 vertical profiles on the 18 September 2016, five obtained during the daytime (10:15–05:15 UTC) and nine obtained at nighttime (16:00–24:00 UTC).

Figure 11 displays the averaged nighttime and daytime values of  $k_{\text{OTG}}$  recorded at 8.5, 12.0, 17.0, 22.0, and 27.0 m. The total time to take a single profile was < 15 mins. During the day (black data points), we find no significant vertical gradient in NO<sub>3</sub> reactivity, which was roughly constant at  $\approx 0.03 \text{ s}^{-1}$ . In contrast, the average nighttime vertical profile (red data points) reveals a strong gradient in  $k_{\text{OTG}}$  with the highest values slightly below canopy height (8.5 to 12.5 m) with a rapid decrease above. At 20 m and above, daytime and nighttime values of  $k_{\text{OTG}}$  were comparable. These observations are qualitatively consistent with gradients in monoterpene mixing ratios in this forest (Rinne et al., 2005) and with the conclusion of Mogensen et al. (2015), who considered NO<sub>3</sub> reactions with monoterpenes and sesquiterpenes emitted from Scots pines at canopy height for the exceptionally warm summer of 2010. The modelled, nighttime vertical gradient in NO<sub>3</sub> described by Mogensen et al. (2015) displays a maximum at 12 m but differs from the measured gradient from IBAIRN in that lower reactivity was modelled at the lowest heights, which may be expected as the model considered only emissions of reactive BVOCs from trees and not from ground sources. In contrast to the vertical gradient measured during IBAIRN, the modelled NO<sub>3</sub> reactivity showed highest values during daytime, coincident with the maximum NO mixing ratio (Mogensen et al., 2015) but was generally lower than our measured values. Mogensen et al. (2015) indicate that the model is likely to underestimate the NO<sub>3</sub> reactivity due to compounds that cannot be measured by GC-MS as well as by the unknown products of their oxidation.

The increase in  $k_{\text{OTG}}$  below the canopy may be caused by ground level emissions of reactive trace gases from tree and plant debris or other flora (mosses, lichens) at forest-floor level.  $\alpha$ -pinene and  $\Delta^3$ -carene, emissions from ground level may vary with litter quality and quantity, soil microbial activity and the physiological stages of plants (Warneke et al., 1999; Insam and Seewald, 2010; Aaltonen et al., 2011; Penuelas et al., 2014). Previous work in the tropical forest has indicated that sesquiterpenes concentrations can peak at ground level rather than within the canopy (Jardine et al., 2011), although the applicability of this result to the boreal forest is unclear.

We conclude that high rates of emission of reactive gases into the stratified nocturnal boundary layer along with ventilation and dilution above canopy height result in strong nocturnal gradients in NO<sub>3</sub> reactivity. During the daytime, efficient turbulent mixing removes the gradient. We did not obtain a vertical profile of  $k_{\text{OTG}}$  on a night when the tempera-



**Figure 11.** Vertical profiles of NO<sub>3</sub> reactivity ( $k_{\text{OTG}}$ ) on 17–18 September 2016. The data represent the average of five profiles during the day and nine profiles during the night.

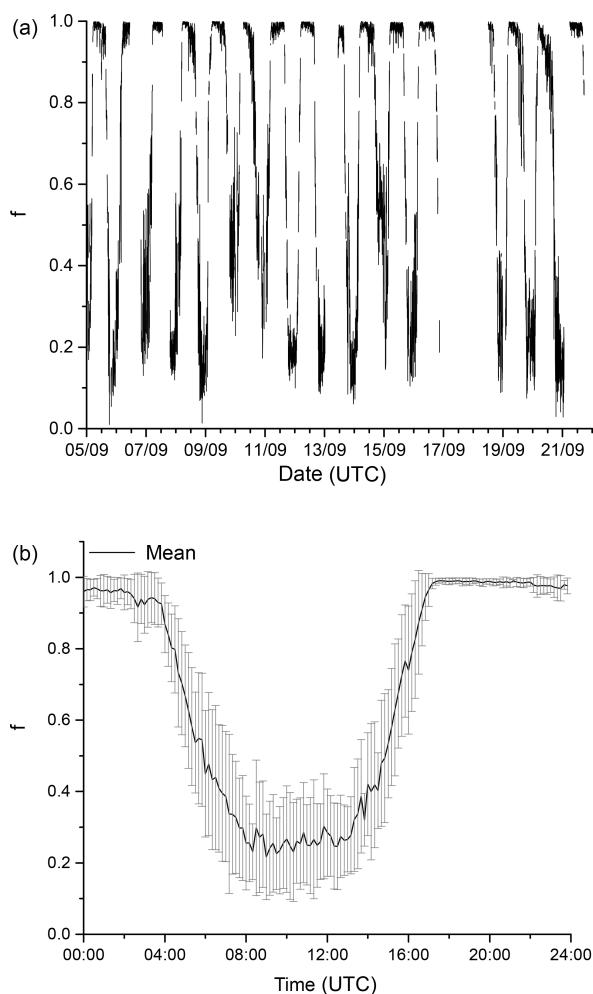
ture inversion was absent, but expect it would be significantly weaker, as is the gradient in O<sub>3</sub> on such nights.

### 3.5 High NO<sub>3</sub> reactivity and its contribution to NO<sub>x</sub> loss

The high reactivity of NO<sub>3</sub> towards organic trace gases in the boreal environment means that other loss processes, including formation of N<sub>2</sub>O<sub>5</sub> or reaction with NO are suppressed. To a first approximation we can assume that, at nighttime, in the absence of NO and sunlight, each NO<sub>3</sub> radical formed in the reaction of NO<sub>2</sub> with O<sub>3</sub> will react with a biogenic hydrocarbon, resulting in formation of an organic nitrate at a yield of between 20 and 100 %, depending on the identity of the organic reactant (Ng et al., 2017). The large values for  $k_{\text{OTG}}$  obtained during the day mean that a significant fraction of the NO<sub>3</sub> formed can be converted to organic nitrates rather than result in re-formation of NO<sub>2</sub> via reaction with NO or photolysis. The fraction,  $f$ , of NO<sub>3</sub> that will react with organic trace gases is given by

$$f = \frac{k_{\text{OTG}}}{([k_{\text{OTG}}] + [J_{\text{NO}_3}] + [\text{NO}]k_2)}. \quad (4)$$

Figure 12 illustrates the time series (upper plot) and the campaign averaged diel cycle (lower plot) for  $f$  which varies between  $\approx 0.1$  and 0.4 at the peak of the actinic flux, the variation is largely caused by day-to-day variability in insolation. As the spectral radiometer was located at a height of 35 m,  $J_{\text{NO}_3}$  will be slightly overestimated around midday as light levels within the canopy are lower. The overestimation will be magnified during the early morning and late afternoon when the forest is in shade at lower levels but the spectral radiometer is not. The daytime values for  $f$  are thus



**Figure 12.** The fraction,  $f$ , of the total NO<sub>3</sub> loss with organic trace gases as a time series (a) and as a campaign averaged, diel cycle (b) where  $f = k_{\text{OTG}}/(k_{\text{OTG}} + J_{\text{NO}_3} + k_{\text{NO}})$ .

lower limits. With typical daytime NO levels of 50–100 pptv, the term  $[\text{NO}]k_2$  contributes  $\approx 0.03\text{--}0.06\text{ s}^{-1}$  to NO<sub>3</sub> loss, whereas  $J_{\text{NO}_3}$  has maxima of close to  $0.1\text{ s}^{-1}$  each day. For comparison daytime values of  $k_{\text{OTG}}$  of  $\approx 0.05\text{ s}^{-1}$  were often observed (Fig. 2).

The diel cycle for  $f$  shows that even at the peak of the actinic flux, on average circa 20 % of the NO<sub>3</sub> formed will react with an organic trace gas rather than be photolysed or react with NO in this environment. This implies that, in the summer–autumn boreal forest, NO<sub>3</sub> reactions may represent a significant loss of NO<sub>x</sub> not only during the nighttime but over the full diel cycle, with a significant enhancement in the daytime production of alkyl nitrates, generally assumed to proceed only via reactions of organic peroxy radicals with NO.

## 4 Conclusions

The first direct measurements of NO<sub>3</sub> reactivity to organic trace gases ( $k_{\text{OTG}}$ ) in the boreal forest indicate that NO<sub>3</sub> is very short lived in this environment with lifetimes generally less than 10 s, mainly due to reaction with monoterpenes. The highest NO<sub>3</sub> reactivities were encountered during nights with strong temperature inversions and a relative humidity of 100 %, and were accompanied by rapid O<sub>3</sub> depletion, together highlighting the important role of nocturnal boundary layer dynamics in controlling canopy-level NO<sub>3</sub> reactivity. The daytime reactivity was sufficiently large that reactions of NO<sub>3</sub> with organic trace gases could compete with photolysis and the reaction with NO, so that NO<sub>3</sub>-induced losses of NO<sub>x</sub> and the formation of organic nitrates was significant. Measurements of the vertical profile in NO<sub>3</sub> reactivity indicate a strong gradient during nighttime, with the highest reactivity observed below canopy height, highlighting a potential role for emissions of reactive trace gases from the forest floor. The hydrocarbons measured did not fully account for the observed NO<sub>3</sub> reactivity, indicating the presence of unsaturated organic trace gases that were not identified, sesquiterpenes being potential candidates.

**Data availability.** The IBAIRN data will be released at the end of 2018 when they can be obtained on request (via John Crowley) from the owners.

**Supplement.** The supplement related to this article is available online at: <https://doi.org/10.5194/acp-18-3799-2018-supplement>.

**Competing interests.** The authors declare that they have no conflict of interest.

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