

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

**Summertime total
OH reactivity**

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Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010

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Received: 2 March 2012 – Accepted: 5 March 2012 – Published: 14 March 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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12, 7419–7452, 2012

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Abstract

Ambient total OH reactivity was measured at the Finnish boreal forest station SMEAR II in Hyytiälä (Latitude 61°51' N; Longitude 24°17' E) in July and August 2010 using the Comparative Reactivity Method (CRM). The CRM – total OH reactivity method – is a direct, in-situ determination of the total loss rate of hydroxyl radicals (OH) caused by all reactive species in air. During the intensive field campaign HUMPPA-COPEC 2010 (Hyytiälä United Measurements of Photochemistry and Particles in Air – Comprehensive Organic Precursor Emission and Concentration study) the total OH reactivity was monitored both inside (18 m) and directly above the forest canopy (24 m) for the first time.

The comparison between these two total OH reactivity measurements, absolute values and the temporal variation have been analyzed here. Stable boundary layer conditions during night and turbulent mixing in the daytime induced low and high short-term variability, respectively. The impact on total OH reactivity from biogenic emissions and associated photochemical products was measured under “normal” and “stressed” (i.e. prolonged high temperature) conditions. The advection of biomass burning emissions to the site caused a marked change in the total OH reactivity vertical profile. By comparing the OH reactivity contribution from individually measured compounds and the directly measured total OH reactivity, the size of any unaccounted for or “missing” sink can be deduced for various atmospheric influences. For “normal” boreal conditions a missing OH reactivity of 58 %, whereas for “stressed” boreal conditions a missing OH reactivity of 89 % was determined. Various sources of not quantified OH reactive species are proposed as possible explanation for the high missing OH reactivity.

1 Introduction

Boreal forests are among the largest terrestrial ecosystems on Earth covering 15 million km² (FAO, 2010). Vegetation is a significant source of reactive biogenic volatile organic compounds (BVOCs) (Guenther et al., 1995) including a hemiterpene (iso-

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prene), monoterpenes (e.g. α -pinene) and sesquiterpenes (e.g. α -farnesene) (Fehsenfeld et al., 1992; Kesselmeier and Staudt, 1999). These various reactive emissions represent a strong potential sink for the main tropospheric oxidant, the hydroxyl radical (OH). Moreover, these species also react in the atmosphere with ozone (O₃) or nitrate radicals (NO₃) (Atkinson and Arey, 2003). The resulting photochemical products can influence ambient ozone, contribute to particle formation and growth processes, and therefore impact air quality and climate.

Biogenic volatile organic compounds are produced in plant organs and released depending on physical (e.g. mechanical and meteorological stimuli) and physiological (e.g. natural respiration) processes. It has been established that the chemical composition of the BVOCs and the emission rates are highly dependent on the plant species (Niinemets et al., 2004; Laothawornkitkul et al., 2009; Yassaa et al., 2012). In warmer regions, e.g. the tropics, isoprene is the strongest BVOC emission (Guenther et al., 2006) while in temperate and boreal regions monoterpenes, such as α -pinene, β -pinene and Δ -3-carene, predominate (Williams et al., 2007; Rinne et al., 2009). Monoterpene emissions are mainly temperature dependent, because resin duct storage pools in which the terpenes are located release these chemicals primarily according to the ambient temperature (Tingey et al., 1980; Guenther et al., 1993). Some monoterpene emissions are also driven by light (Shao et al., 2001; Ghirardo et al., 2010) when de novo biosynthesis is initiated. Another factor influencing plant emissions is the reaction to stress (Niinemets, 2010; Loreto and Schnitzler, 2010), including physical damage (Juuti et al., 1990; Yassaa and Williams, 2007; Haase et al., 2011), herbivoral attack (Wu and Baldwin, 2010), drought and heat (Rennenberg et al., 2006).

Total OH reactivity presents an excellent way to investigate the exchange and balance between atmosphere and biosphere, in terms of both the chemical composition and the budget of the atmosphere's primary oxidant (OH). It is defined as the total OH loss rate calculated as the sum of all sink terms due to OH reactive species X_{*j*}, which depends on their ambient concentrations [X_{*j*}] and the respective reaction rate

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coefficients $k_{\text{OH}+\text{X}_i}$.

$$R_{\text{total}} = \sum k_{\text{OH}+\text{X}_i} \times [\text{X}_i] \quad (1)$$

Alternatively, total OH reactivity can be measured directly (Kovacs and Brune, 2001; Sadanaga et al., 2004; Sinha et al., 2008) and compared to the calculated total OH reactivity as in Eq. (1). Previous studies have shown that this comparison can reveal gaps in the general understanding of local atmospheric chemistry, in particular of unquantified OH radical sinks. Especially in forested regions total OH reactivity has been observed to be significantly higher than expected from measurements of individual species. Thus, in ambient air there is often a “missing”, and hence unexplained fraction of OH reactivity. Di Carlo et al. (2004) observed for two campaigns in the Michigan forest (northern hardwood forest) 1998 and 2000 an exponential dependence between temperature and missing OH reactivity. It was therefore suggested that unmeasured, terpene-like BVOCs contributed to this missing OH sink. In contrast, Ren et al. (2006) found similar absolute total OH reactivity, but no missing OH reactivity at a comparable forest site. In the tropical rainforest direct total OH reactivity measurements have indicated a significant missing fraction of total OH reactivity (Sinha et al., 2008; Ingham et al., 2009). Similarly, Sinha et al. (2010) found within the canopy of a boreal forest 50 % missing OH reactivity which did not correlate significantly with light or temperature. These results and other total OH reactivity measurements of forest field campaigns are summarized in Table 1.

Several hypotheses have been developed over the last decade concerning the identity and nature of the missing OH reactivity. In addition to unmeasured primary emissions suggested by Di Carlo et al. (2004), a significant contribution from secondary products has been proposed (Lou et al., 2010; Taraborrelli et al., 2012). A strong contribution to ambient missing OH reactivity from secondary oxidation products appears to be supported by branch enclosure measurements that showed no missing fraction in primary emissions (Kim et al., 2011). However, accounting for the reaction products of previously measured compounds at the Hyttiälä site (boreal forest) using Chemical

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Master Mechanism modeling did not explain the discrepancy between calculated and directly measured total OH reactivity (Mogensen et al., 2011).

In this study total OH reactivity measurements for a boreal forest during summer are presented. Measurements were taken both within the canopy (where primary emissions likely predominate) and above the canopy (with a higher fraction of photooxidation products). Ambient conditions varied between unusually hot periods, periods influenced by biomass burning and typical summertime boreal forest meteorological conditions. Simultaneous comprehensive observations of ambient gas-phase compounds and aerosols, allowed the missing OH reactivity at the Hyytiälä field station SMEAR II to be examined in detail through a comparison with concurrently measured primary emissions and secondary products.

2 Experimental

For the HUMPPA-COPEC campaign in summer 2010 the total OH reactivity instrument was installed at the SMEAR II station in Hyytiälä, Finland. Measured at the same site were precursors such as anthropogenic and biogenic VOCs, their oxidation products, and the main oxidants OH, O₃ and NO₃ as well as aerosol distributions, other inorganic chemical constituents, and meteorological parameters.

2.1 Measurement site in Hyytiälä

Boreal forest surrounds the Hyytiälä SMEAR II station which has been set up to routinely monitor ecological, meteorological and plant physiological parameters as well as gas-phase chemistry, new particle formation and aerosol growth throughout the year. In summer 2010 an additional tower (HUMPPA-COPEC tower) was built to house further photochemical instrumentation. A comprehensive description of the measurement site, typical vegetation and land-use characteristics, campaign instrumentation and meteorological parameters are described elsewhere (Williams et al., 2011).

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The height of the predominantly Scots pine canopy is around 20 m from the ground, the trees being approximately 50 yr old. Two inlet lines of identical length were positioned adjacent to the forest at 18 m and 24 m on the HUMPPA-COPEC tower within a small clearing to provide air samples from within and above canopy.

2.2 Comparative reactivity method – a total OH reactivity instrument

During HUMPPA-COPEC 2010 the total OH reactivity was measured directly using a modified version of the Comparative Reactivity Method (CRM) described by (Sinha et al., 2008). Total OH reactivity can be determined based on competitive reactions between OH and a selected reagent, which is not present in ambient air, and other atmospheric reactive compounds. The reagent (pyrrole in this case) is diluted with zero air, introduced into a Teflon coated glass reactor and detected with a Proton Transfer Reaction Mass Spectrometer (PTR-MS). Next, OH is produced by photolyzing water vapor (humidified nitrogen) and mixed into the reactor. The initial pyrrole concentration (C1) is reduced by the amount of generated OH radicals, which can be seen in the detector's signal (C2). By exchanging zero air with ambient air, atmospheric reactive molecules enter the reactor and react with OH. The competitive reaction between those atmospheric molecules and pyrrole for OH results in a higher amount of detectable pyrrole molecules (C3). The following equation provides the total OH reactivity in air R_{air} .

$$R_{\text{air}} = C1 \times k_{\text{pyr}+\text{OH}} \times \frac{(C3-C2)}{(C1-C3)} \quad (2)$$

Where $k_{\text{pyr}+\text{OH}}$ is the rate coefficient of pyrrole with OH. The reaction rate of pyrrole with OH has recently been measured (Dillon et al., 2012). The rate coefficient used here ($1.2 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$) corresponds to the temperature and pressure regime of the reactor. Corrections for the influence of humidity to the PTR-MS sensitivity (Sinha et al., 2009), pseudo-first order conditions and dilution are applied. Although these

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corrections are small in comparison to the overall signal, they are essential for the reliable quantification of the total OH reactivity by this method. The data has been averaged into 5 min intervals. The threshold for NO interference has been previously determined to be 10 ppbV in ambient air (Sinha et al., 2008). Since NO levels detected were lower than 0.4 ppbV for the entire field campaign no significant interference on the CRM measurements occurred and no correction was needed. The instrument switched between the above and in canopy inlet lines (both 30 m length) in a 20 min cycle. The dwell time for an air sample in these lines was ± 23 s. The residence time for the reactor was less than 10 seconds, the PTR-MS sampling time 12 s.

In comparison to the system described by Sinha et al. (2008), the set-up used here is more fully automated. To avoid humidity effects in the reactor, meaning different water levels in measurement (C3) and baseline (C2) leading to different OH concentrations, a catalytic converter was used to generate zero air with ambient humidity. The catalytic converter effectively converted VOC mixtures to $\text{CO}_2 + \text{H}_2\text{O}$. However, the resulting water vapor was minor in comparison with ambient humidity levels. A pump, which has been installed downstream of the reactor (in contrast to the previously described set-up (Sinha et al., 2008)), draws the ambient air samples into the reactor. This way the atmospheric air sample entered the reactor without passing through a pump beforehand, eliminating possible OH reactivity loss due to removal of OH reactive compounds in the pump. Temperature and pressure in the reactor as well as ambient temperature, pressure and humidity were recorded during the entire campaign and used for OH reactivity calculations. The detection limit was found to be $3\text{--}4\text{ s}^{-1}$ with respect to the 2σ of the baseline pyrrole concentration level (C2). Errors in the detector (5 %), rate coefficient (14 %), gas standard (5 %) and dilution (2 %) lead to an overall uncertainty of 16 %. A detailed description of the modified instrument and the applied corrections is given in Nölscher et al. (2012).

In order to check the accuracy of the system, standard-tests were regularly performed throughout the campaign as well as in subsequent experiments (Jülich, September 2010; Paris (COMPOH), June 2011). Both propane and propene standards were

introduced and the measured OH reactivity matched the expected value within the respective uncertainties (Fig. 1). The results showed good linearity in all tests over a long time period and the atmospherically relevant total OH reactivity regime.

3 Results

In the course of the campaign, the site was impacted by a variety of emission sources including the surrounding forest, transported biomass burning pollutants, and occasional urban influences. The campaign can be subdivided into three parts based on the meteorological conditions and total OH reactivity characteristics (see Fig. 2). Prior to the start of the campaign the forest had been exposed to unusually high temperature conditions (14–30 °C) for several weeks and showed symptoms of heat (but not drought) stress (Bäck et al., 2012). The regime “**stressed boreal**” (18/07/2010–25/07/2010) was defined as the period of the elevated temperature extending into the field campaign. Within this period, boreal forest emissions were mixed with anthropogenic pollutants transported by south-westerly winds. At the end of this period wind from the north brought clean, cool air to the measurement site for circa 2 days. Under these conditions the minimum anthropogenic influence was detected. The second regime, named “**transported pollution**”, was defined for 26/07/2010–29/07/2010. Within this time wildfire pollution plumes from Russia were advected to the measurement site (Williams et al., 2011). Strongly enhanced mixing ratios of biomass burning tracers, such as CO (peak concentration: 438 ppbV) and acetonitrile (peak concentration: 551 pptV), were used to define the **transported pollution** period. A HYSPLIT-back-trajectory analysis indicated wildfires 400 km east of Moscow as the source burning region. Local temperatures remained high throughout this period (14–32 °C). Following this period, at the beginning of August (01/08/2010–07/08/2010) temperatures varied between 14–27 °C and wind directions changed between south-west and south-east. The meteorological conditions here are comparable to previous summertime observations (2007: 8–24 °C, 2008: 6–24 °C, 2009: 12–22 °C – Williams et al., 2011) and

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hence this regime is termed "**normal boreal**". Since the conurbations Tampere and Helsinki lie to the south-west and St Petersburg to the south-east it is likely that this **normal boreal** regime represents a boreal forest signal with occasional anthropogenic influence. It should be noted that peak ozone concentrations (50–76 ppbV) were always coupled with southerly winds. Therefore the potential for ozonolysis products was higher during these periods. Storms and precipitation events happened more frequently during the **normal boreal** regime compared to the beginning of the campaign.

3.1 In canopy – above canopy comparison of total OH reactivity

Using total OH reactivity measurements at both heights, a deviation from equal OH reactivity between above (R_{above}) and in (R_{in}) canopy OH reactivity can be calculated.

$$\Gamma = \frac{R_{\text{above}}}{R_{\text{in}}} - 1 \quad (3)$$

Equal total OH reactivity above and in the canopy lead to a value $\Gamma = 0$. When OH reactivity in the canopy is higher than above, Γ is negative. For higher OH reactivity above the canopy, Γ is positive. Figure 2 also presents the in canopy – above canopy comparison Γ for the entire measurement period. The green colored bars indicate OH reactivity was higher in the canopy (negative values), the bars are blue when total OH reactivity was higher above the canopy (positive values). The previously characterized regimes show distinct differences: predominantly green during **stressed boreal**, predominantly blue during **transported pollution** and mixed for the **normal boreal** regime.

3.2 Missing OH reactivity

In addition to direct measurements from the CRM instrument, total OH reactivity was calculated using single compound measurements. Summing up each of the single compound OH reactivities (Eq. 1) leads to the total calculated OH reactivity. The difference

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between this calculated and the directly measured total OH reactivity provides the missing OH reactivity.

Single compound measurements from a GC-MS instrument drawing air on the same inlet line as the CRM (HUMPPA-COPEC tower), PTR-MS vertical gradient measurements from the SMEAR II meteo tower, Fast GC-MS observations from SMEAR II meteo tower, and other measurements from nearby towers (less than 200 m distant) associated with the SMEAR II station were used to calculate a theoretical value for total OH reactivity above the canopy. For the purpose of this calculation it is assumed that all measurements are co-located. Overall 35 compounds contributed to the total calculated OH reactivity. Compounds, method, location and the applied rate coefficients are listed in Table 2.

In Fig. 3 the above canopy measured total OH reactivity (marked in blue), the calculated OH reactivity (red) and the missing fraction (color-coded by itself) are included. The missing fraction indicates how much of the measured OH reactivity remains unexplained by the calculated OH reactivity. Clearly, the sum of these 35 compounds was less than the total measured OH reactivity for most of the time. Only 17 % of all results are found to have lower than 50 % missing fraction of total OH reactivity. Also included in Fig. 3 is the overall uncertainty (grey shaded) of the calculated OH reactivity. This is estimated as the root square propagation of the uncertainties in the reaction rate coefficients and the single compound measurements.

3.3 Characteristics of boreal summertime OH reactivity

A detailed analysis of the results in terms of absolute values, in canopy – above canopy comparison (Γ) and missing OH reactivity for all previously characterized regimes is given in the following paragraphs:

Whole campaign: Results for the entire HUMPPA-COPEC campaign (18/07/2010–09/08/2010) are illustrated in Figs. 2 and 3 and summarized in Table 3. Total OH reactivity was observed to vary between values at the limit of detection (3 s^{-1}) and 76 s^{-1} .

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The ambient air temperature, which is also shown in Fig. 2, fluctuated during summer 2010 between 10–32 °C.

Mean results for the entire campaign do not show a significant difference between in and above canopy measured total OH reactivity. Within the canopy $12.4 \pm 0.1 \text{ s}^{-1}$ was detected and $11.5 \pm 0.1 \text{ s}^{-1}$ above the canopy. Slightly positive values were found on average for Γ (0.13 ± 0.01). The large range of total OH reactivity over the campaign is apparent in high standard deviations, around 10 s^{-1} . High short-term variability was noted in the BFORM campaign during summer 2008 at the same measurement site (Sinha et al., 2010). In HUMPPA-COPEC the measured total OH reactivity in summer 2010 shows a diel pattern in short-term variability when calculating the relative standard deviation (RSD) (standard deviation over mean value) for night and day (30 min mean values). Daytime total OH reactivity measurements above the canopy showed an overall high variability ($\text{RSD}_{\text{day}} = 1.22$). A lower short-term variability ($\text{RSD}_{\text{night}} = 0.84$) was found during the night.

For the entire measurement period the calculated OH reactivity (sum of measured compound contributions, see Sect. 3.2) is on average $2.2 \pm 0.01 \text{ s}^{-1}$. Here CO (0.406 s^{-1}), methane (0.280 s^{-1}) and acetaldehyde (0.248 s^{-1}) are the most dominant contributors. Biogenic emissions like isoprene (0.222 s^{-1}), Δ -3-carene (0.130 s^{-1}), α -pinene (0.101 s^{-1}) and methanol (0.073 s^{-1}) also contributed significantly to the calculated OH reactivity along with NO_2 (0.096 s^{-1}) and HCHO (0.098 s^{-1}). From Fig. 3 it is clear that the calculated OH reactivity does not reflect the high variability of the measured total OH reactivity. Since the calculated OH reactivity remains broadly constant, the trend of the missing total OH reactivity is similar to the measured.

Stressed boreal regime: This regime represents the boreal forest under conditions of prolonged heat stress (see Sect. 3). Wind speeds were lower than 6 m s^{-1} which enhances the impact of local forest sources on the measurement site. Measured total OH reactivity in the canopy reached 76 s^{-1} for high temperatures and southerly winds, and dropped below detection limit (3 s^{-1}) for low temperatures and northerly winds. On

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average the measured total OH reactivity was highest during this period (in canopy: $30.7 \pm 0.4 \text{ s}^{-1}$, above canopy: $23.6 \pm 0.3 \text{ s}^{-1}$, Table 3).

During this period 90 % of the Γ values (on average $\Gamma = -0.21 \pm 0.01$) are negative and the total OH reactivity observed in the canopy is elevated compared to the above canopy OH reactivity. This indicates that the direct biogenic emissions have likely had a strong impact on total OH reactivity at this time. The diel median profile of Γ , absolute values and missing fraction of OH reactivity are presented in Fig. 4 (left panel). In canopy total OH reactivity was higher than measured above canopy during daytime. In contrast to Γ , the diel profile of total OH reactivity observations was highest during nighttime. This is in good agreement with measured diel cycles of monoterpenes which are major primary biogenic emissions of the boreal forest (Fig. 5, second row). These show minimum values during daytime and elevated concentrations during the night due to suppressed turbulent mixing. The minimum measured total OH reactivity could be found in the morning hours (08:00 [UTC+2]). This agrees well with the minimum missing fraction of total OH reactivity which is 60 % in the morning hours as the stable nocturnal boundary layer breaks up and mixing into a higher residual boundary layer starts (Fig. 4). In general at the beginning of the campaign, during **stressed boreal** conditions (see also Table 3), the highest fraction of missing OH reactivity was observed. In this period 89 % are missing or unaccounted for, meaning that barely 10 % of the measured total OH reactivity can be explained by other ambient observations.

Transported pollution regime: During biomass burning influence, on average the above canopy OH reactivity was higher ($13.0 \pm 0.2 \text{ s}^{-1}$) than within the canopy ($10.9 \pm 0.2 \text{ s}^{-1}$). Exceptional were days with unusually high temperatures (up to 32°C), when in canopy measurements were higher with maximum values of 39 s^{-1} . Accordingly, Γ was found to be predominantly positive (on average 0.35 ± 0.02) (Figs. 2 and 4). For 81 % of the measurements in this period, the measured total OH reactivity above the canopy was higher than within the canopy. The higher OH reactivity above the canopy level was likely due to the myriad transported pollutants from biomass burning. The diel profile of total OH reactivity for this regime (Fig. 4, medium panel) has a maximum

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in the late afternoon, in contrast to the **stressed boreal** regime. However, similar to the **stressed boreal** regime, the minimum in measured OH reactivity occurs in the morning. On average the unexplained fraction of OH reactivity is 73%, the closest agreement being at 09:00–12:00 [UTC+2] with only 30% missing.

5 Since pyrrole is known to be produced by biomass burning (Karl et al., 2007; Yokelson et al., 2007) it is important to exclude possible interferences for CRM measurements in this period. During the biomass burning influenced period in summer 2010 at the Hyytiälä measurement site, a second PTR-MS observing $m/z = 68$ and frequent tests with a GC-PID, configured to measure pyrrole, both found no detectable pyrrole
10 in ambient air.

Normal boreal regime: Total OH reactivity varied from the limit of detection (3 s^{-1}) to 30 s^{-1} (with one exceptional peak up to 67 s^{-1}) within this period. On average in canopy measurements showed slightly higher ($7.8 \pm 0.2 \text{ s}^{-1}$) OH reactivity than above the canopy ($6.8 \pm 0.2 \text{ s}^{-1}$). Hence, Γ (on average 0.13 ± 0.01) fluctuated around 0 and
15 showed no consistent vertical distribution in total OH reactivity. In comparison to the previously discussed **stressed boreal** and **transported pollution** regime, the **normal boreal** forest shows less diel variation in total OH reactivity (Fig. 4). These results are consistent with in canopy measurements during summer 2008 at the same site (Sinha et al., 2010).

20 The overall short-term variability in total OH reactivity changed significantly, as can be seen in Fig. 4 (right panel), from 21:00–12:00 [UTC+2] (relatively quiescent, $\text{RSD}_{\text{night}} = 0.61$) to 14:00–19:00 (highly variable, $\text{RSD}_{\text{day}} = 1.22$). During the night the stable nocturnal boundary layer confines the weak forest emissions and the signal shows little short-term variability. In the daytime, frequent and effective mixing processes and turbulence bring down less reactive air into the forest canopy to mix with the strong
25 emissions, causing rapid variations in the total OH reactivity.

During **normal boreal** conditions an average missing fraction of 58% was observed. No significant trend in the missing fraction of total OH reactivity and high short-term variability were seen during this period.

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During HUMPPA-COPEC 2010 the missing OH reactivity was consistently high (58–89%). This suggests that the total sink of OH was not well characterized despite the comprehensive suite of atmospheric measurements at the HUMPPA-COPEC campaign (see Table 2). A summary of the missing OH reactivity fraction for three characteristic regimes as a function of time of the day can be found in Fig. 6. Remarkably high is the missing fraction of total OH reactivity found above canopy during the influence of prolonged high temperatures (on average 89%) and low wind speeds, hence local **stressed boreal** conditions (orange line). During the **transported pollution** period (black line), on average 73 % missing total OH reactivity was observed above the canopy. **Normal boreal** conditions (green line), with moderate temperatures and changable winds, led to on average 58 % unexplained total OH reactivity. For the **stressed boreal** and the **transported pollution** periods, total OH reactivity was best accounted for by individual measurements during the morning hours (05:30–10:30 [UTC+2]) and worst in the late afternoon (13:00–18:00 [UTC+2]). In the morning, the stable nocturnal boundary layer broke up and air entrained from the residual layer and then the free troposphere (Nilsson et al., 2001). The measured total OH reactivity could be accounted for up to 70 %. In the **normal boreal** forest conditions, more mixing occurred due to frontal passages and no diel variation could be observed. One low missing total OH reactivity event was observed during this period (01:00 [UTC+2]). This corresponded to an occasion when exceptionally high monoterpene mixing ratios were measured at the site. The event was associated with emissions from a local saw mill. Since monoterpenes dominated the emissions and were measured at the site, this had the effect of reducing the missing fraction of total OH reactivity.

In order to understand the origin of the boreal summertime missing OH reactivity, tracers representative of primary biogenic emissions, directly processed photochemical products and transported pollutants are compared. Figure 5 presents diel median values of temperature, photosynthetically active radiation (PAR) and O₃ mixing ratios

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in the first row for the three defined regimes (**stressed boreal, transported pollution, normal boreal**). Light levels reached a maximum at 12:00 [UTC+2], whereas the temperature maximum was in the late afternoon (16:00 [UTC+2]). The second row of Fig. 5 focuses on median primary emissions. As boreal forest strongly emits monoterpenes, Δ -3-carene is presented as a typical boreal primary emission. Isoprene is shown on the same graph. Both species are very reactive to OH and hence important for total OH reactivity. The diel development of ambient monoterpene mixing ratios depends on the direct emission strength, the lifetime due to oxidants and dynamical processes. For all shown periods in the campaign ambient levels of monoterpenes are higher during the night due to a small temperature-coupled release from the trees, a shallow stable nocturnal boundary layer (ca. 200–400 m) and low levels of oxidants. A decrease in the morning (06:30–08:30 [UTC+2]) was coupled to mixing of clean residual air and increasing oxidants (see O_3 in Fig. 5). Minimum ambient mixing ratios during daytime are caused by dilution through turbulent mixing into a larger boundary layer (ca. 900–2000 m) and a higher oxidation capacity of the atmosphere. This is despite the trees emitting monoterpenes at higher rates during the day because of high temperatures and light (Eerdekens et al., 2009; Yassaa et al., 2012). Highest ambient mixing ratios of isoprene are found in the afternoon (16:00–18:00 [UTC+2]). This is because isoprene emission is coupled to both temperature and light (Guenther et al., 2006).

In the third row of Fig. 5, two types of secondary products are shown. Primary biogenic emissions are effectively oxidized into secondary products once they are exposed to the atmosphere. The boreal forest provides a low NO_x environment where oxidation products like peroxides (from OH oxidation during day), aldehydes and organic acids (O_3 oxidation during night and day) can form (Atkinson and Arey, 2003). During the HUMPPA-COPEC campaign, some secondary products have been found to peak during daytime, coincident with the highest temperature, insolation and oxidants levels. The median PAN mixing ratio is given as example of a secondary product in Fig. 5. Other secondary compounds peak during the night due to reaction processes in the stable nocturnal boundary layer with O_3 or NO_3 yielding compounds such as pinic acid,

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which is presented here. Coupling and feedback between dynamical diel processes and chemistry is discussed further in Ouwersloot et al. (2012).

In the **normal boreal** forest primary biogenic emissions peak at different times of the day (Fig. 5, right panel). In terms of total OH reactivity, high monoterpene levels by night and elevated isoprene by day act to stabilize total OH reactivity throughout the day. Secondary products also exhibit maxima, both by day and night. For example pinic acid peaks at night, showing similar diel profile as its precursor monoterpene (Fig. 5). In contrast peak concentrations of PAN were measured around midday. The diel profile of the missing total OH reactivity fraction during the **normal boreal** forest period shows high variability and no diel dependency (Fig. 4, right panel). It is likely that the missing contributors are of both primary and secondary origin.

In addition to total OH reactivity provided by the **normal boreal** forest, biomass burning plumes impacted the **transported pollution** period. Secondary products, such as PAN (Fig. 5, middle panel) were elevated in concentration and peaked in the afternoon. Since this coincides temporally with the measured total OH reactivity diel median profile (Fig. 4, middle panel), it is likely that the multitude of unmeasured secondary products contribute significantly to the 73 % average missing total OH reactivity during this period. As the stable nocturnal boundary layer breaks up in the morning (07:00–10:00 [UTC+2]) both absolute measured total OH reactivity and missing fraction decrease. This is despite total OH reactivity being measured as higher above the canopy for most of the **transported pollution** regime (Fig. 4, middle panel). Possibly, vertical mixing of air masses with different characteristics, such as the residual layer (containing low reactivity levels) and free tropospheric air (affected by measured transported pollutants) influenced the total OH reactivity instrument during this period.

The missing total OH reactivity was significantly enhanced for **stressed boreal** conditions. While in the **normal boreal** forest period 58 % was missing, during heat-stress it was 89 %. During the long heat-stress period for HUMPPA-COPEC 2010 parallel enclosure studies showed that the emission rates increased and the composition became more diverse (Yassaa et al., 2012). No ambient air measurements of these reactive

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primary emissions or their secondary products were available, although they are likely contributors to missing total OH reactivity. This contention is supported by elevated total OH reactivity inside the canopy and the diel profile, which compares well with the profile of monoterpenes and their products (Figs. 4 and 5, left panel).

Overall, total OH reactivity measurements in the summertime boreal forest showed impact of chemical and dynamical processes. Diel boundary layer height development, local meteorological conditions and long range transport were reflected in short-term variability, vertical distribution, measured and missing total OH reactivity. The best agreement between calculated and measured total atmospheric OH reactivity was found under **normal boreal** forest conditions. A mixture of boreal primary biogenic emissions, photooxidation products and occasional anthropogenic pollutants likely contributed to the missing fraction of total OH reactivity of on average 58 %. This is comparable to the values obtained by Sinha et al. (2010), for the same site. Transported biomass burning secondary products enhanced the average missing total OH reactivity to 73 %. It should be noted, that in the HUMPPA-COPEC campaign 2010 organic peroxides, multifunctional compounds and organic nitrates were not quantified. Even more total OH reactivity was missing (on average 89 %) in the **stressed boreal** forest. High emissions of various stress-induced compounds (e.g. sesquiterpenes, aldehydes) and their large number of photooxidation products were not quantified in the atmosphere. The in canopy – above canopy comparison of total OH reactivity suggests, that under these heat-stress conditions enhanced and more diverse primary biogenic emissions, and their secondary products, contribute strongly to the high missing OH reactivity.

Acknowledgements. The entire HUMPPA-COPEC team is grateful for the support of the Hyytiälä site engineers and staff. Support of the European Community – Research Infrastructure Action under the FP6 “Structuring the European Research Area” Programme, EUSAAR Contract No. RII3-CT-2006-026140 is gratefully acknowledged. Special thanks to Thomas Klüpfel and Rolf Hofmann for technical support, Laurens Ganzeveld, Domenico Taraborrelli and Jaana Bäck for helpful discussions.

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Table 1. Total OH reactivity field studies in forest environments, typical measured values, the mean missing (unexplained) fraction and a hypothesis to explain this missing OH reactivity.

Publication	OH reactivity [s^{-1}]	Missing fraction ^a	Hypothesis
Di Carlo et al. (2004) PROPHET Northern Michigan, mixed forest ^b Summer 1998/2000	1–12	temp. dependent	unmeasured terpene-like emissions
Ren et al. (2006) PMTACS-NY Whiteface Mountain, mixed forest ^b Summer 2002	2–12	0 %	no significant missing OH reactivity
Sinha et al. (2008) GABRIEL Surinam, tropical forest Summer 2005	28–72	70 %	unmeasured compounds
Ingham et al. (2009) OP-3 Borneo, tropical forest Spring 2008	10–60	50 %	unmeasured direct biogenic emissions and isoprene oxidation products
Sinha et al. (2010) BFORM Hyytiälä, boreal forest Summer 2008	5–12	50 %	primarily unmeasured direct biogenic emissions

^a Note that the missing fraction of total OH reactivity depends on the available single compound's measurements.

^b Inconsistent results in missing OH reactivity were found although the measurement sites were similar. The PROPHET mixed forest is characterized by northern hardwood, mixed aspen, bog conifers, pines and red oaks. The PMTACS-NY mixed forest is composed of hardwood and conifer species with birch, sugar maple, beech, some red spruce and balsam fir. It was suggested that there is a significant difference in BVOC emissions between these two sites (Ren et al., 2006).

Table 2. Compounds, instruments and locations of the measurements which have been used for the calculation of total OH reactivity. The rate coefficients were taken from the literature and listed here in $\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$.

Compound	Method	Location	rate coefficient		
α -pinene ^a	GC-MS	HUMPPA-COPEC tower	5.30×10^{-11}		
β -pinene ^b			7.43×10^{-11}		
Δ -3-carene ^b			8.80×10^{-11}		
isoprene ^a			1.00×10^{-10}		
β -myrcene ^c			3.34×10^{-10}		
benzene ^a			1.19×10^{-12}		
m-xylene ^b			2.31×10^{-11}		
p-xylene ^b			1.43×10^{-11}		
ethylbenzene ^b			7.00×10^{-12}		
methanol ^a	PTR-MS	SMEAR II meteo tower	9.00×10^{-13}		
acetonitrile ^a			2.20×10^{-14}		
acetaldehyde ^a			1.50×10^{-11}		
formic acid ^a			4.50×10^{-13}		
acetone ^a			1.80×10^{-13}		
MVK/MACR ^a			3.00×10^{-11}		
MEK ^a			1.20×10^{-12}		
toluene ^a			5.60×10^{-12}		
iso-butan ^b			Fast GC-MS	SMEAR II meteo tower	2.10×10^{-12}
n-butane ^b					2.35×10^{-12}
iso-pentane ^b	3.60×10^{-12}				
n-pentane ^b	3.70×10^{-12}				
methane ^a	GC-FID	SMEAR II meteo tower	6.40×10^{-15}		
NO ₂ ^c			BLC+CLD CLD	HUMPPA-COPEC tower	1.10×10^{-11}
NO ^a	1.29×10^{-11}				
O ₃ ^a	UV absorption		7.30×10^{-14}		
CO ^a			VUV absorption	1.44×10^{-13}	
H ₂ O ₂ ^a	Dual enzyme		1.70×10^{-12}		
HCHO ^a			Hantzsch	8.50×10^{-12}	

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Table 2. Continued.

Compound	Method	Location	rate coefficient
SO ₂ ^a	Smear II	SMEAR II meteo tower	1.30×10^{-12}
pinonic acid ^c	APCI-IT-MS		1.04×10^{-11}
pinic acid ^c			8.70×10^{-12}
HONO ^a	Marga		6.00×10^{-12}
MHP ^b	HPLC	HUMPPA-COPEC tower	5.50×10^{-12}
PAA ^c	CIMS		1.88×10^{-12}
PAN ^a			3.00×10^{-14}

^a iupac preferred value; ^b Atkinson and Arey 2003; ^c others: β -myrcene (Hites and Turner, 2009), NO₂ (Mollner et al., 2010), pinonic & pinic acid (Vereecken and Peeters, 2002), PAA (Jenkin et al., 1997).

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Table 3. Characteristic regimes during HUMPPA-COPEC 2010, average values for total OH reactivity measured in the canopy (18 m) and above the canopy (24 m), the mean in canopy – above the canopy comparison Γ , average calculated and missing OH reactivity and the average missing fraction of total OH reactivity. Uncertainties are given as standard error.

	Whole campaign	Stressed boreal	Transported pollution	Normal boreal
measured OH reactivity (in canopy)	$(12.4 \pm 0.1) \text{ s}^{-1}$	$(30.7 \pm 0.4) \text{ s}^{-1}$	$(10.9 \pm 0.2) \text{ s}^{-1}$	$(7.8 \pm 0.2) \text{ s}^{-1}$
measured OH reactivity (above canopy)	$(11.5 \pm 0.1) \text{ s}^{-1}$	$(23.6 \pm 0.3) \text{ s}^{-1}$	$(13.0 \pm 0.2) \text{ s}^{-1}$	$(6.8 \pm 0.2) \text{ s}^{-1}$
Γ	0.13 ± 0.01	-0.21 ± 0.01	0.35 ± 0.02	0.13 ± 0.01
calculated OH reactivity (above canopy)	$(2.2 \pm 0.01) \text{ s}^{-1}$	$(2.0 \pm 0.02) \text{ s}^{-1}$	$(2.8 \pm 0.02) \text{ s}^{-1}$	$(2.0 \pm 0.01) \text{ s}^{-1}$
missing OH reactivity (above canopy)	$(8.9 \pm 0.1) \text{ s}^{-1}$	$(21.6 \pm 0.3) \text{ s}^{-1}$	$(10.3 \pm 0.2) \text{ s}^{-1}$	$(4.8 \pm 0.2) \text{ s}^{-1}$
missing fraction (above canopy)	68 %	89 %	73 %	58 %

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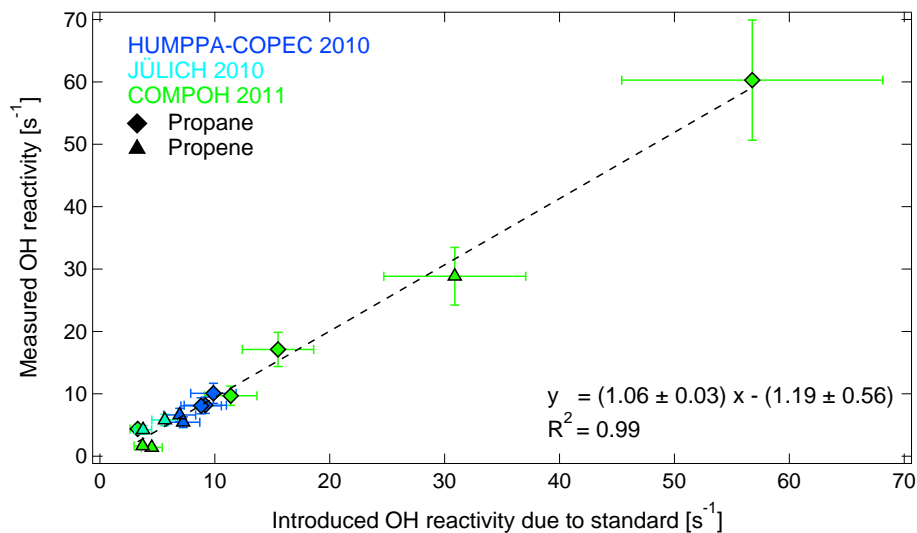


Fig. 1. Standard tests with propane and propene at different days for the HUMPPA-COPEC campaign (summer 2010), experiments in Jülich (autumn 2010) and the COMPOH campaign in Paris (spring 2011). Given is a linear fit, with slope and the quality of the fit.

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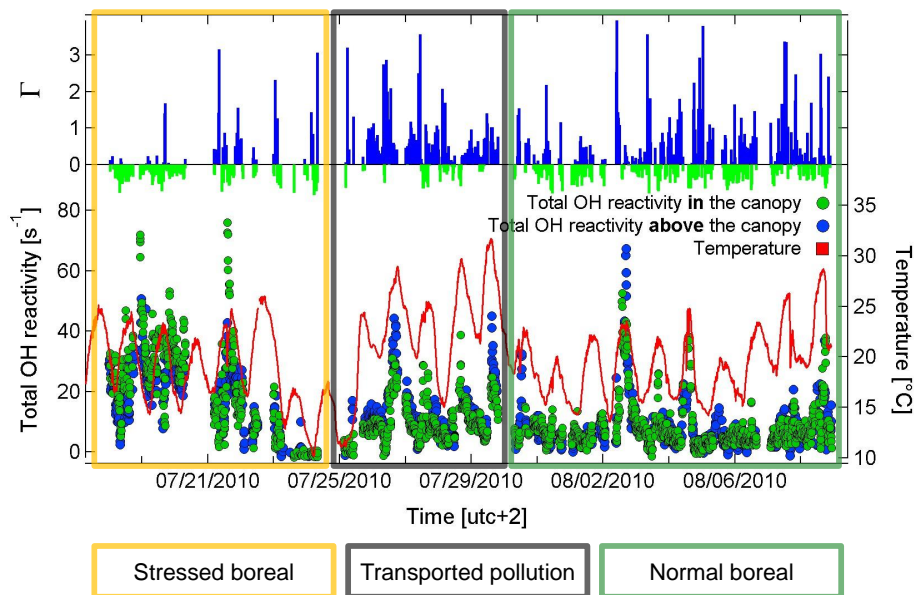


Fig. 2. Overview of total OH reactivity measurements in (green markers) and above (blue markers) the canopy, temperature (red) and superimposed (green and blue bars) the in canopy – above canopy comparison of total OH reactivity Γ . Three periods of different influences and conditions are defined, marked and labeled.

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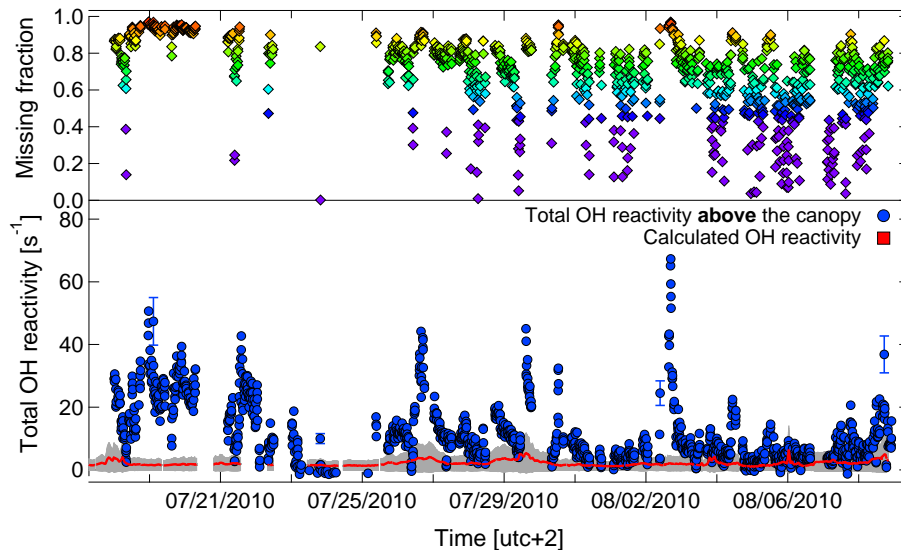


Fig. 3. Overview of total OH reactivity measurements above the canopy (blue markers), calculated OH reactivity (red) and superimposed the missing fraction of total OH reactivity (color-coded by itself). High missing fraction indicates a high percentage of unaccounted for OH reactivity when comparing single compound ambient measurements to the results of CRM. Error bars in grey show the uncertainty in the total OH reactivity calculation.

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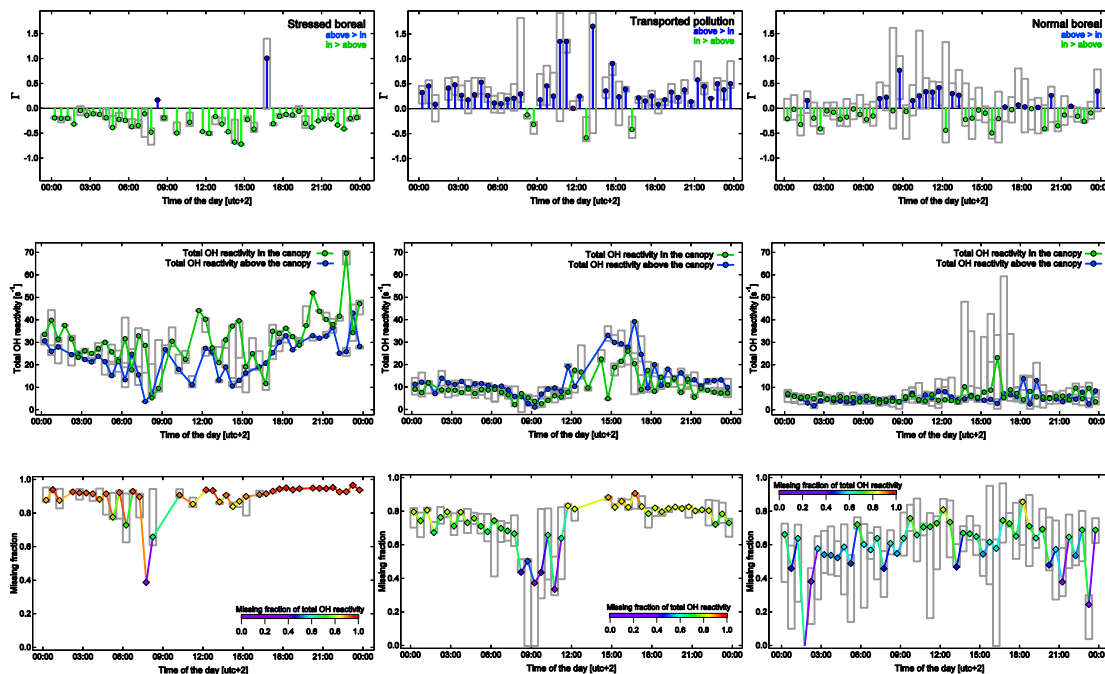


Fig. 4. Median diel variation for Γ , total OH reactivity measurements (in and above canopy) and missing fraction. Three characteristic regimes are shown: stressed boreal, transported pollution and normal boreal.

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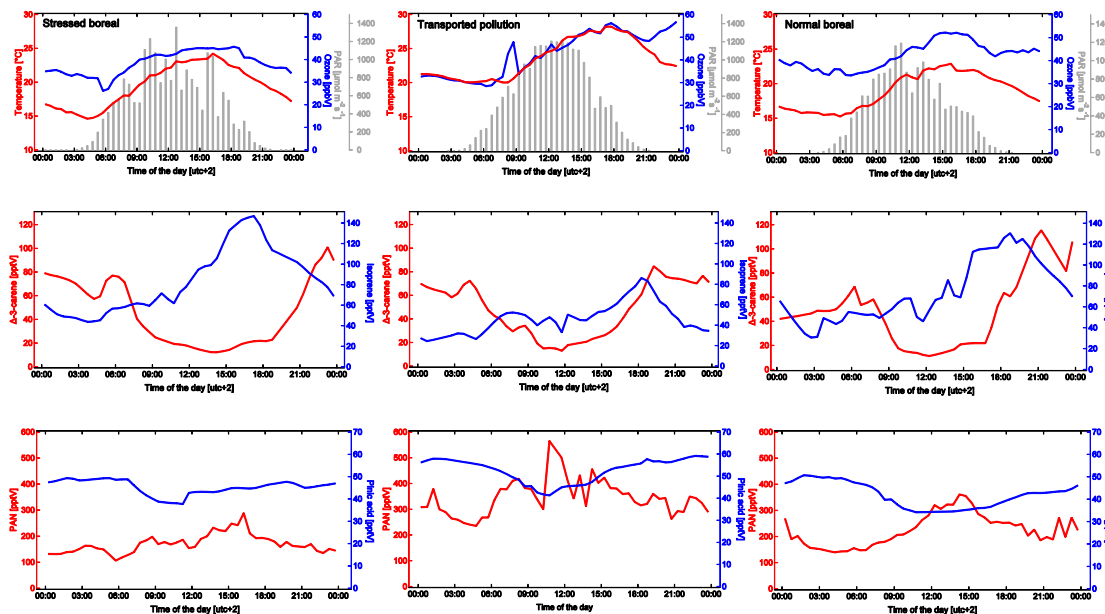


Fig. 5. Median diel variation for several measured parameters during HUMPPA-COPEC 2010 in stressed boreal, transported pollution and normal boreal forest conditions. Temperature, O_3 mixing ratios and PAR are presented in the first row for all regimes. The second row pictures the diel variation of primary biogenic emissions (Δ -3-carene and isoprene) and the lowermost row shows secondary products such as PAN and pinic acid.

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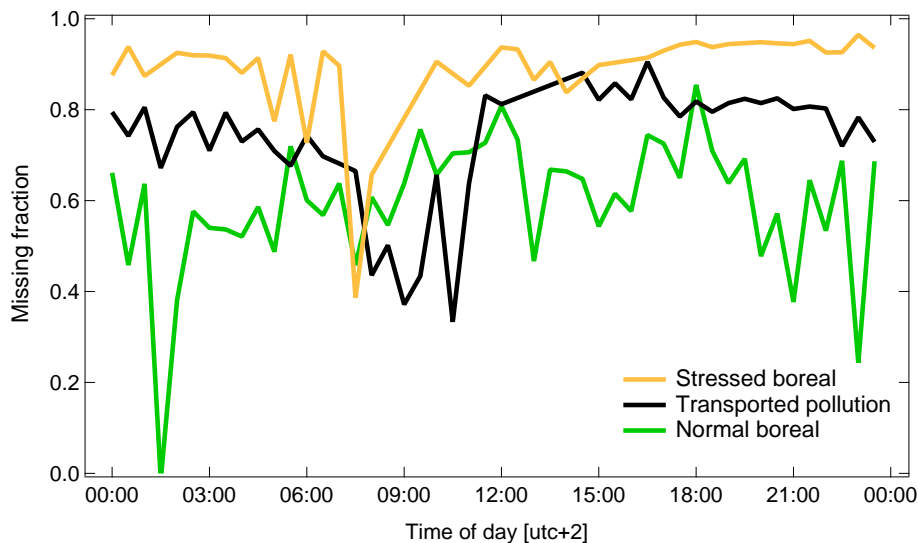


Fig. 6. Summary of missing fraction of total OH reactivity for all characteristic regimes as diel median profile: normal boreal (green), transported pollution (black), stressed boreal (orange).

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