Biogeosciences Discuss., 9, 13497–13536, 2012
www.biogeosciences-discuss.net/9/13497/2012/
doi:10.5194/bgd-9-13497-2012

Biogeosciences
Discussions

Seasonal measurements of total OH reactivity fluxes, total ozone loss rates and missing emissions from Norway spruce in 2011

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Received: 13 September 2012 – Accepted: 14 September 2012 – Published: 5 October 2012

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

Abstract

Numerous reactive volatile organic compounds (VOCs) are emitted into the atmosphere by vegetation. Most biogenic VOCs are highly reactive towards the atmosphere's most important oxidant, the hydroxyl (OH) radical. One way to investigate the chemical interplay between biosphere and atmosphere is through the measurement of total OH reactivity, the total loss rate of OH radicals. This study presents the first determination of total OH reactivity emission rates (measurements via the Comparative Reactivity Method) based on a branch cuvette enclosure system mounted on a Norway spruce (Picea abies) throughout spring, summer and autumn 2011. In parallel separate VOC emission rates were monitored by a Proton Transfer Reaction-Mass Spectrometer (PTR-MS), and total ozone (O_3) loss rates were obtained inside the cuvette. Total OH reactivity emission rates were in general temperature and light dependent, showing strong diel cycles with highest values during daytime. Monoterpene emissions contributed most, accounting for 56–69 % of the measured total OH reactivity flux in spring and early summer. However, during late summer and autumn the monoterpene contribution decreased to 11–16 %. At this time, a large missing fraction of the total OH reactivity emission rate (70–84 %) was found when compared to the VOC budget measured by PTR-MS. Total OH reactivity and missing total OH reactivity emission rates reached maximum values in late summer corresponding to the period of highest temperature. Total O_3 loss rates within the closed cuvette showed similar diel profiles and comparable seasonality to the total OH reactivity fluxes.

Total OH reactivity fluxes were also compared to emissions from needle storage pools predicted by a temperature-only dependent algorithm. Deviations of total OH reactivity fluxes from the temperature-only dependent emission algorithm were observed for occasions of mechanical and heat stress. While for mechanical stress, induced by strong wind, measured VOCs could explain total OH reactivity emissions, during heat stress they could not. The temperature driven algorithm matched the diel course much better in spring than in summer, indicating a different production and emission scheme

for summer and early autumn. During these times, unmeasured and possibly unknown primary biogenic emissions contributed significantly to the observed total OH reactivity flux.

1 Introduction

The Earth's atmosphere contains thousands of reactive biogenic volatile organic compounds (VOCs) (Goldstein and Galbally, 2007). These are important players for chemical processes consuming oxidants, forming products, radicals, and organic aerosol (Atkinson and Arey, 2003; Hoffmann et al., 1997; Williams et al., 2001; Pöschl et al., 2010). The reasons why vegetation emits VOCs so copiously (globally ca. 1.15 $\mathrm{Pg\,yr^{-1}}$, Guenther et al., 1995), are various and not yet fully understood (Kesselmeier and Staudt, 1999). Through photosynthesis plants convert light and carbon dioxide (CO_2) into energy and biomass. Based on this primary metabolism, vegetation forms, stores, transforms and releases a large variety of volatiles (such as isoprene, monoterpenes, sesquiterpenes or even diterpenes, e.g. Dudareva et al., 2006; Laothawornkitkul et al., 2009). Such emissions can be useful to the plant for signaling, attracting and guiding pollinators (Fehsenfeld et al., 1992), or reducing oxidant levels close to the plant (Jardine et al., 2012). Other compounds may be regarded as a reaction to stress, e.g. heat, drought, oxidant, mechanical, herbivores and pollution (Vickers et al., 2009; Niinemets, 2010; Loreto and Schnitzler, 2010). Oxygenated compounds such as formaldehyde, acetaldehyde, formic acid, acetic acid, acetone, methanol and methyl vinyl ketone (MVK) are also released (Kesselmeier et al., 1997; Rinne et al., 2007; Goldstein and Galbally, 2007; Jardine et al., 2012) but may be taken up by vegetation as well (e.g. Kesselmeier, 2001). Emissions of biogenic VOCs can be categorized into two groups: compounds which are emitted immediately following synthesis, and compounds which are released from storage pools (see Kesselmeier and Staudt, 1999). Isoprene and monoterpenes are synthesized and immediately released under light conditions if not stored in special organs such as resin ducts (coniferous trees) or glands (fragrant plants). This kind of VOC synthesis and emission can be simulated by a light and temperature related algorithm adapted by Guenther et al. (1993) and (1995). A simpler algorithm describes the release from storage organs exponentially depending on temperature only (Tingey et al., 1980; Guenther et al., 1993). This algorithm is often used to simulate the emission of monoterpenes stored in the resin ducts of coniferous needles or the light independent synthesis and release of sesquiterpenes. Oxygenated VOC species can be described by a light and temperature dependent algorithm due to the light regulated stomatal opening.

Several recent field studies have shown the importance of plant emissions for understanding the chemistry of the atmosphere and it's most important oxidant, the hydroxyl radical (OH) (e.g. Lelieveld et al., 2008; Heard and Pilling, 2003). Most biogenic VOCs are highly reactive towards OH and hence contribute significantly to its overall sink. The loss frequency of OH is termed total OH reactivity, and can be measured directly (using a pre-reactor and Proton Transfer Reaction-Mass Spectrometer – PTR-MS, or Laser Induced Fluorescence – LIF, e.g. Sinha et al., 2008; Kovacs and Brune, 2001) along with ambient OH radical concentrations, and levels of atmospheric trace gases such as VOCs and inorganics. Especially in forests, OH sources and sinks seem to be poorly understood. Field campaigns have found missing OH sources (e.g. Lelieveld et al., 2008; Hofzumahaus et al., 2009; Tan et al., 2001) as well as missing sinks (e.g. Di Carlo et al., 2004; Nölscher et al., 2012b) when comparing the production and loss terms for OH of commonly monitored atmospheric compounds. While theories have been developed to explain the observed high OH concentrations in forests based on the OH recycling potential (Peeters et al., 2009; Taraborrelli et al., 2012), the identity of the missing sinks, the missing OH reactivity, remains elusive. On the one hand the biosphere might directly emit missing OH reactive compounds. This hypothesis is supported by a terpene-like temperature dependency of missing OH reactivity (Di Carlo et al., 2004), the high unexplained fraction in biogenic environment (Lou et al., 2010), a typically biogenic diel variation and a positive flux from the forest canopy for high temperatures (Nölscher et al., 2012b). On the other hand, unknown and unmeasured oxidation products of biogenic VOCs are likely to contribute to the high missing OH reactivity in forests. This hypothesis is based on good model-measurement agreement at daytime when accounting for hydrocarbon oxidation products (Lou et al., 2010), and on first observations of branch level total OH reactivity. Kim et al. (2011) found no missing OH sinks when comparing total OH reactivity and VOC measurements within an enclosing branch system from four different tree species (red oak, white pine, beech, red maple).

This study presents first trans-seasonal total OH reactivity emission rate measurements from a branch enclosure system using the Comparative Reactivity Method (CRM). The cuvette was installed on a Norway spruce in its natural environment. Furthermore seasonal branch-level total ozone (O_3) loss rates have been investigated. The applied cuvette system enabled direct tree emission rates for VOCs to be examined via PTR-MS in parallel to total OH reactivity emissions. Fluxes for known Norway spruce emissions such as monoterpenes, acetone, isoprene, acetaldehyde and methanol (Cojocariu et al., 2004; Filella et al., 2007) could be characterized throughout the year 2011. Total OH reactivity emission rates were monitored in May/June and August/September. In this way the role of known VOCs as OH sinks could be determined. Additionally, the question whether biogenic emissions are a source of missing OH reactivity can be addressed directly and as a function of season.

2 Field site description and instrumentation

A mature Norway spruce (Picea abies, 80 yr old, 13 m tall, healthy), located at Kleiner Feldberg, Taunus, Germany (50°13′18″ N, 8°26′45″ E, 825 m a.s.l.), was selected for the installation of a branch enclosure system from which the measurements were made. The tree was part of a small stand of Norway spruce close to the top of the mountain. Norway spruce is the dominant tree in the Taunus region at higher altitudes (> 600 m). To the north and west of the site the land was predominantly covered with coniferous and mixed forest, with few roads or small towns. To the south of the site lies the heavily populated Rhein-Main area (pop. ca. 2 million) including a dense motorway system, the airport and large cities such as Frankfurt (ca. 25 km distant), Wiesbaden (ca. 30 km distant) and Mainz (ca. 40 km distant).

2.1 Branch level cuvette

In order to determine the nature and rate of direct emissions from Norway spruce, a dynamic branch enclosure system (Ruuskanen et al., 2005; Bourtsoukidis et al., 2012) was mounted on a branch 5 m above ground (Fig. 1). The branch enclosure system was a 15 l, cylindrical plexi-glass cuvette which absorbed UV radiation and hence limited photochemical reactions inside the cuvette. A lid for opening and closing the cuvette was operated automatically for the measurements in 20 min cycles, including a 3 min closure for emission rate observations. Temperature, ozone (O_3), carbon dioxide (CO_2) and photosynthetic active radiation (PAR) (for summer onward only) were continuously monitored inside the cuvette. During closures, humidity and temperature levels increased by not more than 10 % on average. CO_2 and O_3 decreased, with CO_2 values generally not falling below 250 ppmV. Hence, the branch did not show symptoms of being seriously impacted by the cuvette system, and therefore the emissions were considered to be natural. The measurement instruments were located directly underneath the tree within a van, and connected with 4.1 m long heated (70 °C) glass tubing to the cuvette. The residence time in the inlet was about 2 s. Biogenic VOCs were monitored by PTR-MS and total OH reactivity by a separate PTR-MS system using the Comparative Reactivity Method (Sinha et al., 2008).

2.2 Quantification of biogenic VOCs: PTR-MS

Measurements of VOC mixing ratios were made using a high sensitivity Proton Transfer Reaction-Mass Spectrometer (IONICON) (e.g. Lindinger et al., 1998). H_3O^+ ions are generated from water vapor in a hollow-cathode discharge source, and these protonate ambient gas molecules with higher proton affinity than water. This allows a wide range of gaseous organic compounds to be detected after acceleration through a drift tube and separation according to the mass-to-charge ratio (*m/z*) with a quadrupole mass spectrometer. In the set-up operated here, standard conditions were used for the drift tube voltage (600 V) and pressure (2.3 mbar). Optimization of the instrument resulted in sustained high sensitivity. More details of the PTR-MS configuration are presented in Bourtsoukidis et al. (2012). Amongst other VOCs (see Table 1) the sum of monoterpenes (*m/z* 137) and the sum of sesquiterpenes (*m/z* 205) were monitored and calibrated using gas standards (L4763, Ionimed analytic GmbH, Austria). Monoterpenes were calibrated with α-pinene, while for sesquiterpenes a permeation oven was used to produce stable β-caryophyllene concentrations (liquid β-caryophyllene standard: W225207, Sigma-Aldrich, Inc.).

2.3 Total OH reactivity measurements

Total OH reactivity (R_{total}) is the total loss rate of OH radicals due to atmospheric reactive molecules. It is defined as the sum of all single ambient compound reactivities, which can be calculated as product of the compound's concentration $[X]$ and reaction rate with OH ($k_{X+\text{OH}}$) (Eq. 1). If all atmospheric sink components of OH were known, the ambient concentration levels accurately measured and a rate coefficient determined, the calculation using Eq. (1) and the direct measurement of total OH reactivity would agree. The difference between calculated and directly measured total OH reactivity is termed missing OH reactivity.

$$R_{\text{total, calc}} = \Sigma\, k_{X_i+\text{OH}} \times [X_i] \qquad (1)$$

To date, total OH reactivity has been measured using three different techniques: (1) artificially generated OH in a flow tube reacts with the atmospheric composition and it's temporal decay is observed with Laser Induced Fluorescence (LIF) (e.g. Sadanaga et al., 2004); (2) a movable OH source in a flow tube reactor is used to vary reaction times of OH and the atmospheric constituents, and the OH signal is detected with LIF (e.g. Kovacs and Brune, 2001); (3) a competitive reaction between a reagent and OH alone, and then in the presence of atmospheric reactive molecules is observed by a suitable detector (e.g. Sinha et al., 2008). The last technique, termed Comparative Reactivity Method (CRM), was chosen in its latest configuration using a PTR-MS as detector (Nölscher et al., 2012a) for branch cuvette observations. It offers low sampling flow rates, a reasonably good time resolution (15 s), and good sensitivity for the expected high total OH reactivity levels (3–300 s^{-1}). The limit of detection for the CRM instrument operated during this campaign was 3–4 s^{-1} (2σ of the baseline noise), and the average overall uncertainty 16 %. This number is derived as propagation of errors and includes the uncertainties of the detector (PTR-MS, 5 %), the pyrrole gas mixture (5 %), error of rate coefficient (14 %), and flow variations (2 %).

2.4 VOC and total OH reactivity emission rate calculations

During closure, concentrations of continuously emitted species increased linearly in the cuvette. In the case of a single compound such as isoprene the rate of emission is normally expressed as the mass of species (ng) per unit needle dry weight ($g(dw)^{-1}$) per unit time (h^{-1}). While the system was closed ambient air was drawn into the cuvette and diluted the mixture (Ruuskanen et al., 2005). After correcting for the modest dilution effect of ambient air ($k_{dil} = (2.9 \pm 0.2) \times 10^{-3}\ s^{-1}$, see Bourtsoukidis et al., 2012), the data were fitted by a linear regression. Mono- and sesquiterpene emission rates from the branch enclosure have been reported in Bourtsoukidis et al. (2012).

Total OH reactivity emission rates (TOHRE) were obtained in similar fashion to those of the single compounds. Increasing reactive tree emissions during closure lead to an increasing total OH reactivity which is a property of the mixture's various component concentration levels and reaction rates with OH. Total OH reactivity emission rates were expressed as emitted total OH reactivity (R_{total} in s^{-1}) per unit needle dry weight ($g(dw)^{-1}$) per unit enclosure volume (m^{-3}) per unit time (s^{-1}). The resulting value for TOHRE has the dimensions ($s^{-2}\ g(dw)^{-1}\ m^{-3}$) and hence depends on the biomass (m_{bio}) and the volume of air enveloping the branch (V_{cuv}). As an example one cuvette closure is presented in Fig. 2.

$$\text{TOHRE} = \frac{dR_{\text{total}}}{dt} \times \frac{1}{m_{\text{bio}} \times V_{\text{cuv}}} \tag{2}$$

By including the CRM measured total OH reactivity ($R_{\text{total}} = R_{\text{total, meas}}$) in Eq. (2) the *measured* TOHRE was determined. It describes the flux of all OH reactive compounds being emitted from the examined Norway spruce branch. For comparison, the individual compounds measured by PTR-MS were singly transformed to OH reactivities and equivalently analyzed during cuvette closures. Inserting the single compound OH reactivity of e.g. isoprene ($R_{\text{total}} = R_{\text{isoprene}}$) in Eq. (2) leads to the isoprene OH reactivity emission rate (IOHRE). The sum of all single compound OH reactivities (Eq. 1) generates the total calculated total OH reactivity, which was processed in the same manner ($R_{\text{total}} = R_{\text{total, calc}}$) to determine the *calculated* TOHRE. Please note, that the dynamic cuvette system uses the increase in total OH reactivity (and PTR-MS compounds) during closure, due to the continuous tree emissions, to determine biogenic fluxes. This method differs from ambient total OH reactivity measurements and calculations which must take account of background values of species such as CO and NO_2. Significant fluxes of the two aforementioned species were not expected from the spruce branch cuvette as they are typically anthropogenic in character.

Typical for total OH reactivity measurements were 13–15 data points per closure. Cuvette closures with less than 8 data points and a fit quality R^2 worse than 0.1 were excluded from the analysis (overall 20 % of the data was lost). The uncertainty is dominated by the fit error of the slope, which was on average about 35 % of the measured value.

As an example of how single compound and total OH reactivity flux measurements may be combined spring, 26 May 2011 at 11:00 LT (local time, UTC + 3) is examined in more detail. A good match between measured and calculated TOHRE was observed. CRM measured for TOHRE a value of $0.29 \pm 0.10\,\text{s}^{-2}\,\text{g(dw)}^{-1}\,\text{m}^{-3}$ and the PTR-MS sum of all reactive VOC emissions led to a value of $0.28 \pm 0.10\,\text{s}^{-2}\,\text{g(dw)}^{-1}\,\text{m}^{-3}$. The highest emission rate at that time was found in the monoterpene signal which was about 452.7 ng $g(dw)^{-1}$ h^{-1}. In terms of OH reactivity, emissions of monoterpenes contributed with 0.19 ± 0.07 s^{-2} $g(dw)^{-1}$ m^{-3} to more than 50 % of the total measured signal of TOHRE. Due to its high reactivity, the isoprene OH reactivity emission rate is the second most important term for TOHRE with 0.05 ± 0.02 s^{-2} $g(dw)^{-1}$ m^{-3}, although the isoprene emission rate was 64.5 ng $g(dw)^{-1}$ h^{-1}. This is much less than the emission rates of acetone (285.3 ng $g(dw)^{-1}$ h^{-1}), methanol (224.6 ng $g(dw)^{-1}$ h^{-1}), acetaldehyde (105.7 ng $g(dw)^{-1}$ h^{-1}) and sesquiterpenes (104.4 ng $g(dw)^{-1}$ h^{-1}) which altogether have an OH reactivity emission of 0.03±0.01 s^{-2} $g(dw)^{-1}$ m^{-3} (11 % of measured TOHRE).

2.5 Total O_3 loss rates

Ozone was monitored continuously inside the cuvette. The opening and closing dynamic branch cuvette system allowed an estimate of total ozone loss rates (Altimir et al., 2002; Wieser et al., 2012). Following closure, ambient concentrations decreased due to loss processes inside the system. To some extent this loss processes were gas phase reactions of ozone with the doubly bonded and highly reactive biogenic VOCs. In addition ozone deposited on walls and plant surfaces, underwent surface reactions and was stomatally-uptaken (Loreto et al., 2001). The values calculated directly from the decrease of ozone in pptV per time (s^{-1}) during closures are a very simple estimate of the total O_3 loss rate due to all possible loss mechanisms inside the cuvette. It was assumed, that deposition to the cuvette walls is a constant loss. Depletion of ozone by reactive tree emissions and through stomatal uptake can be related to physiological parameters, which are main driving forces for these time scales (Kulmala et al., 1999; Kurpius and Goldstein, 2003). In this study we cannot separate the ozone loss due to deposition on surfaces, stomatal uptake, and the gas phase loss to biogenic emissions. Presented results have to be taken as qualitative guide to the total O_3 loss rates, which are compared in diel profiles and trends.

3 Results

Total OH reactivity emission (TOHRE) rates in the Norway spruce mounted cuvette, varied during spring, summer and early autumn 2011 between no detectable emissions and 15.69 s^{-2} $g(dw)^{-1}$ m^{-3}. These trans-seasonal data are presented in Fig. 3 alongside temperature, global radiation, wind speed and relative humidity. The two intensive measurement periods are separated visually into the first campaign (spring/early summer: 24 May–14 June 2011) and the second campaign (late summer/autumn: 12 August–7 September 2011) which was part of a comprehensive field campaign on top of Kleiner Feldberg (PARADE 2011). Covariation of TOHRE with temperature and light can be easily identified in Fig. 3. Clear diurnal trends were seen for most days, with higher TOHRE during daytime (campaign average: 0.63 ± 0.03 s^{-2} $g(dw)^{-1}$ m^{-3}) and lower values at night (campaign average: 0.32 ± 0.01 s^{-2} $g(dw)^{-1}$ m^{-3}). Exceptional for the year 2011 was the unseasonably warm and dry spring. Typical early summertime conditions (1–14 June 2011) with moderate ambient temperatures and low levels of soil moisture resulted in high TOHRE (on average 0.50 ± 0.02 s^{-2} $g(dw)^{-1}$ m^{-3}, Table 2). However, overall the summer was unusually rainy and cold (average ambient temperature in July was 12.2 °C, whereas 14.9 °C were typical for previous summers since 1997). The soil moisture during the second measurement period was significantly elevated in contrast to springtime and early summer. At the end of August (12 August–26 August 2011, within the second campaign) the temperature increased to high levels and highest TOHRE was measured (late summer average: 0.83 ± 0.07 s^{-2} $g(dw)^{-1}$ m^{-3}). On the 26 August 2011, meteorological conditions changed drastically becoming cold and wet, which coincided with a drop of all VOC emission rates as well as total OH reactivity fluxes. Vegetation experienced early autumn conditions at this time (27 August–7 September 2011). Lowest TOHRE was observed in early autumn with on average 0.16 ± 0.01 s^{-2} $g(dw)^{-1}$ m^{-3} for cold and rainy weather. The calculated TOHRE (from PTR-MS measured VOCs, as introduced in Sect. 2.4) generally showed analogous temporal trends but lower absolute values, with the best agreement to measured values in spring and the worst in late summer (summarized in Table 2).

3.1 VOC emission rates and OH reactivity contributions

Figure 4 presents the emission rates of the individually measured VOCs, and Fig. 5 the contribution of each compound to OH reactivity fluxes for both field campaigns in 2011. The strongest emissions from Norway spruce were monoterpenes, acetone, methanol and acetaldehyde, which is consistent with previous assessments (Filella et al., 2007; Schürmann et al., 1993; Grabmer et al., 2006). The composition of monoterpenes, which was analyzed via GC-MS in the laboratory from both needle and cartridge samples, was similar to summertime Norway spruce emissions measured elsewhere (e.g. Yassaa et al., 2012). Interestingly, the relative contribution of α-pinene and β-pinene did not change throughout the seasons, whereas limonene significantly increased in the second measurement period (Fig. 4). Unfortunately other speciated monoterpenes such as β-phellandrene, camphene and β-myrcene were not quantified during the second measurement period although the chromatogram clearly showed more peaks than could be identified. Similarly, the speciation data for sesquiterpenes were only available from springtime/early summer probes (35 % β-caryophyllene, 29 % α-farnesene, 18 % longicyclene, 3 % α-humulene, and some minor contributors). However, total monoterpenes and total sesquiterpenes were monitored continuously by the PTR-MS. Most of the VOC emission rates stayed relatively constant for the two observed intensive periods. Only the emission rates of total monoterpenes and acetaldehyde decreased significantly in late summer and autumn (Fig. 4), while sesquiterpenes were emitted in slightly higher ratios.

For total OH reactivity, it is not necessarily the most abundant biogenic VOC that is the most important since the compound's reaction rate with OH must be factored in. From Fig. 5 it is clear that the mixture of emitted monoterpenes on average contributed the most to calculated TOHRE rates. The reaction rate coefficient used for calculation of monoterpene OH reactivity emissions (MTOHRE) is a weighted average for compounds found in the springtime speciation ($k_{\mathrm{MT+OH}} = 1.22 \times 10^{-10}\,\mathrm{cm^3\,molecules^{-1}\,s^{-1}}$, Table 1). Since compounds were missing in the second speciation, no new reaction rate coefficient for summertime/autumn monoterpenes could be obtained. Assuming the mixture just contained the three measured compounds (α-pinene, β-pinene, limonene) a weighted reaction rate coefficient would be $k_{\mathrm{MT+OH}} = 1.09 \times 10^{-10}\,\mathrm{cm^3\,molecules^{-1}\,s^{-1}}$ which is less reactive but similar to the springtime-monoterpene reaction rate coefficient. The impact of various reaction rate coefficients is briefly discussed in Sect. 4.

Two more relevant compounds for TOHRE were isoprene and acetaldehyde. Isoprene OH reactivity emissions (IOHRE) were seasonally stable (see Table 2) and explained about 2–7 % of the measured TOHRE. Acetaldehyde OH reactivity emission (AOHRE) rates varied with the season, being highest in early summer (10 % of measured TOHRE). As monoterpene emissions showed a significantly lower level in late summer and autumn, their relative contribution to measured TOHRE became minor during this period (11–16 %). During spring, monoterpenes accounted for 69 %, and early summer for 56 %. Compounds such as methanol, nopinone and sesquiterpenes were only minor contributors to total OH reactivity fluxes.

3.2 Median diel profiles of measured, calculated TOHRE and total O_3 loss rates

The seasonal variation of measured and calculated TOHRE is given as diel median profiles in Fig. 6. Additionally, the ozone depletion inside the cuvette during closure was used as a proxy estimate of total O_3 loss rates and included for general comparison of diurnal trends, changing characteristics during seasons of emission rates, and total OH reactivity fluxes. When comparing the measured with the calculated TOHRE, on average missing emissions of OH reactive compounds could be found. These varied seasonally between on average $0.04\,\mathrm{s^{-2}\,g(dw)^{-1}\,m^{-3}}$ (relative missing fraction: 15 %) in spring and $0.7\,\mathrm{s^{-2}\,g(dw)^{-1}\,m^{-3}}$ (84 %) in late summer (Fig. 7).

During springtime measurements (24 May–31 May 2011), the TOHRE generally followed temperature, increasing around 07:00 LT (local time, UTC + 3), reaching maximum values between 09:00 and 16:00, and afterwards decreasing again. Calculated TOHRE in total was slightly lower than the measured median profile (although within the error bars). Total O_3 loss rates showed a different median variation throughout the day. It rapidly increased starting at 07:00 (in good agreement with temperature and radiation), reached a maximum at 09:00 (coincident with isoprene emission peak, maximal transpiration rates, and ahead of sesquiterpene emission peak) and then decreased in the course of the day.

Early summertime conditions (1 June–14 June 2011) led to elevated median measured and calculated TOHRE compared to spring. Daytime emissions started with the increase in temperature at 07:00 and returned to a stable, lower level at night. The gap between measurements and calculation (i.e. missing OH reactivity flux) was greater during daytime than at night (Figs. 6 and 7). Relatively low levels of total O_3 loss rates during day were characteristic for early summertime, closely following the calculated TOHRE median diel profile.

Much higher temperatures were characteristic for the observations made during late summer (12 August–26 August 2011). Here both, total OH reactivity emissions and the total ozone loss rates reached maximum median values (highest values during this study) in the afternoon of about $2.3\,\mathrm{s^{-2}\,g(dw)^{-1}\,m^{-3}}$ and $-111\,\mathrm{pptV\,s^{-1}}$, respectively. Total O_3 loss rates had maximum values at 13:00, two hours before measured and calculated TOHRE peaked. Coincident with the maximum total ozone loss rate inside the cuvette, missing TOHRE had a local minimum (Fig. 7). As observed in spring, as soon as temperature rose and radiation impinged on the cuvette, total O_3 loss rates increased rapidly. The general trend to high levels in late summer did not occur in the calculated total OH reactivity emissions. These showed even lower values than in spring and early summertime revealing high missing OH reactivity emissions.

The diel variation seen in spring and summertime for TOHRE was not as distinct in early autumn (27 August–7 September 2011). Measurements and calculations showed a consistent stable gap throughout the entire day. In contrast to total OH reactivity emissions, total O_3 loss rates varied throughout the day as before in late summer closely following temperature and radiation. The increase at 07:00 coincided with an increase in isoprene and sesquiterpene emissions and was followed by a decrease after 16:00 in the afternoon.

Summarized in Fig. 7 are the median profiles of spring, summer and autumn absolute missing TOHRE values. In late summer a significant fraction of the CRM measured total OH reactivity flux could not be explained when compared to the calculation based on individual PTR-MS measured species.

4 Discussion

The effect of seasonal trends, day-to-day variability, and rapidly changing environmental conditions on Norway spruce total OH reactivity emission rates are summarized in Fig. 8.

4.1 Comparison to a temperature dependent emission algorithm

Figure 8a presents an overview of the measured total OH reactivity emission rates alongside a solely temperature dependent model algorithm (Guenther et al., 1993, see Eq. 3). In this way a temperature-only dependent response of plant emissions (E) can be described. The algorithm has been used for modeling e.g. monoterpene emission rates from coniferous needle storage pools (e.g. Taipale et al., 2011) and has also proved to be effective in representing missing OH reactivity in the Michigan forest reasonably well (Di Carlo et al., 2004).

$$E = E_{\mathrm{S}} \exp^{(\beta(T - T_{\mathrm{S}}))} \tag{3}$$

A typical value for $\beta = 0.09\,\mathrm{K}^{-1}$ was chosen, the standard total OH reactivity emission rate E_{S} in Fig. 8a kept equal to $1\,\mathrm{s}^{-2}\,\mathrm{g(dw)}^{-1}\,\mathrm{m}^{-3}$. In this way, the general trend of a temperature-only driven emission rate could be compared qualitatively to the measured values of TOHRE. Additionally, the standard TOHRE factor E_{S} was calculated for each day through the linear fit between measured TOHRE and the un-scaled model values. As can be seen superimposed in Fig. 8a, slowly increasing values during early summer and a decrease in early autumn describe a seasonal trend of E_S. The temperature related model itself reflects the measured TOHRE throughout the observed period of the year reasonably well, emphasizing the temperature dependence of the observed TOHRE. Nevertheless, on several occasions TOHRE reveals different characteristics that the model does not resolve. Due to the seasonal trend in E_S, mean standard TOHRE factors of each season (spring, early summer, late summer, autumn) were used to scale the modeled values. The results are presented in Fig. 8b–e in four separate graphs representing each season. Each graph pictures TOHRE measured by CRM, calculated from PTR-MS results and the scaled model prediction for the observed time period. On the right hand axis different parameters are added for comparison.

During springtime observations the diurnal variation of measured and calculated TOHRE were in generally good agreement to the temperature dependent model. Two peaks stand out, which were found within the measurements and the calculation but not in the model. The high total OH reactivity emissions up to 1.5 and 2.7 $\mathrm{s^{-2}\,g(dw)^{-1}\,m^{-3}}$ could not be satisfactorily explained by the temperature-only dependent emissions. These high TOHRE events correspond to two peaks in the wind velocity. Wind speeds higher than 5.5 $\mathrm{m\,s^{-1}}$ are termed meteorologically as “moderate breeze” and are characterized by moving branches. It is likely that wind induced mechanical stress was a driving force in VOC and total OH reactivity emission fluxes from the Norway spruce branch on these two occasions. Similarly, ambient measurements of monoterpene levels in rural New Hampshire (USA) showed a high impact from storm events. Haase et al. (2011) observed that PTR-MS measured monoterpene mixing ratios increased on average by a factor of 93 % above pre-storm levels for heavy storms including high precipitation and sometimes hail. Interestingly in this study, monoterpene emission rates and TOHRE increased significantly for the examined Norway spruce during elevated wind velocities. No missing total OH reactivity flux was observed in these cases. From selected events throughout the two measurement intensives during 2011, total OH reactivity emissions generally rose by a factor of 6 (on average for wind speeds higher than 5.5 $\mathrm{m\,s^{-1}}$).

Emission rates in June, during early summer conditions, were generally higher than in spring. Increasing temperatures over the first five days in June enhanced both measured and calculated TOHRE. During daytime the measurements typically exceeded the values for TOHRE calculations. For one outstanding day (9 June 2011) measured TOHRE was significantly elevated when compared to PTR-MS measurements. This day was characterized by high temperature and low wind speeds. Windy days prior to this had caused spikes in calculated and measured TOHRE (similarly to the characterized event in spring), and perhaps even damaged the branch. Monoterpene emission rates closely followed the temperature-dependent pattern, whereas measured total OH reactivity emissions increased up to 4.2 $\mathrm{s^{-2}\,g(dw)^{-1}\,m^{-3}}$ on that day. One compound among the PTR-MS quantified VOCs showed the same behavior as TOHRE, which was benzene (Fig. 8c). Peak emission rates of 280 $\mathrm{ng\,g(dw)^{-1}\,h^{-1}}$ were reached while benzene average emission rates for the other three defined periods varied between 5.2 and 9.8 $\mathrm{ng\,g(dw)^{-1}\,h^{-1}}$. Benzenoids could be possibly emitted by plants following stress, although little is known about biochemical pathways of formation (Heiden et al., 1999; White et al., 2009; Dudareva et al., 2006). Other stress induced plant emissions e.g. methyl salicylate (MeSa), or higher mass oxygenated VOCs were not monitored and are therefore potential explanations for the high missing OH reactivity emission at that particular stress event.

While the scaled temperature driven model and total OH reactivity emissions agreed relatively well during the first measurement period, large discrepancies occurred during the second campaign. The mean emission factor during late summer was elevated by four outliers during this period. Hence, the modeled temperature dependence tends to overestimate the true emission rates. For comparison, the lower standard emission factor of the early summer is also included into the graph. For this period the comparison of measured and calculated TOHRE reveals remarkable discrepancies. The measurements by CRM seem significantly underestimated by the calculated TOHRE from PTR-MS results. Since it was cold and wet, low emission rates were expected until 21 August 2011. Afterwards temperature increased and reached the annual maximum (23 August 2011). Generally, humid and windy nights were followed by days with extremely high emissions of total OH reactivity (e.g. peak value for 23 August 2011: TOHRE = $13.6\,\mathrm{s^{-2}\,g(dw)^{-1}\,m^{-3}}$). The same behavior could be observed from total O_3 loss rates, which rose as well during daytime to high levels.

It seems that mechanisms that contributed to both, the production of OH reactive compounds and stimulation of ozone uptake or reactions, increased during daytime in late summer. The ratio of temperature driven pool emissions and de novo production with light and temperature seems to have changed, so that the temperature-only dependent model does not match the diel variation of TOHRE. The PTR-MS was not able to detect this increase in the emission rates of OH reactive VOCs both at night and daytime, which led to an average of 84 % missing OH reactivity emissions.

Meteorological characteristics changed markedly on 26 August 2011, but the gap between measured and calculated TOHRE remained high (on average 70 %, see also Table 2). Absolute values were found to be generally much lower due to cold and wet environmental conditions. Diel profiles were no longer pronounced, with less than 20 % variation between night and day which can also be noted from Fig. 6d. The measured total OH reactivity emission rates even stayed high for some nights (e.g. 1–3 September 2011). A similar trend was found for methanol emission rates which remained relatively high during the night compared to the monoterpene signal.

From springtime and early summer to late summer and early autumn, a clear change could be observed in measured TOHRE and total O_3 loss rates. By comparing to the temperature related emission model, diurnal trends in the observations could be generally well explained for the first measurement campaign, whereas the second dataset revealed large discrepancies. The emissions of most VOCs did not change throughout the year, although the signal of total monoterpenes, acetaldehyde decreased and total sesquiterpenes increased in late summer and autumn. Despite this, total OH reactivity emissions reached maximum values during late summer. Major contributions to total OH reactivity emissions at that time of the year remained unexplained. Interestingly, also the estimated total loss of ozone increased, giving evidence for either a higher rate of stomatal-uptake or the release of highly ozone reactive compounds. Possibly, both loss mechanisms are coupled which complicates the interpretation of this study's simplified approach.

4.2 A climatological perspective

It should be noted that from a climatological point of view the year 2011 was unusual in comparison to long-term meteorological observations. It had a cold and rainy summer with relatively low ozone mixing ratios (e.g. on average for July: $O_{3,ave}(2011) = 37.7\,\text{ppbV}$, $O_{3,ave}(1997\text{–}2011) = 48.8\,\text{ppbV}$). After the cold and rainy summer, for the second measurement period generally elevated soil moisture (by a factor of 2) and transpiration rates (by a factor of 1.6) have been observed when compared to the springtime measurements. In addition, during the measurement period in August 2011 sesquiterpene emission rates were significantly increased (from on average $46.7\,\text{ng}\,\text{g(dw)}^{-1}\,\text{h}^{-1}$ to $92.6\,\text{ng}\,\text{g(dw)}^{-1}\,\text{h}^{-1}$), subsequently decreasing to very low levels in autumn (on average $25.5\,\text{ng}\,\text{g(dw)}^{-1}\,\text{h}^{-1}$). This is indicative of a high activity (in terms of both the total OH reactivity emission rates and the ozone loss rates inside the cuvette system) of the tree during late summer, the period of the high missing OH reactivity flux.

Interestingly, highest total OH reactivity fluxes as well as peak ozone loss rates inside the cuvette coincided with the climatological, seasonal maximum of ambient ozone. It also has been found, that sesquiterpene emissions were triggered not only by temperature but also by atmospheric ozone levels (Bourtsoukidis et al., 2012).

4.3 Variation in mono- and sesquiterpene composition

One reason for the discrepancy between measurements and calculations in late summer and autumn TOHRE might be that the composition of mono- and sesquiterpenes seasonally changed which was not considered in the calculations (Sect. 3.1). This was tested with a range of rate coefficients based on previous studies of mono- and sesquiterpenes from Norway spruce (Kempf et al., 1996; Martin et al., 2003; Yassaa et al., 2012). Additionally, an exceptional high reaction rate coefficient for monoterpenes has been applied to TOHRE calculations from PTR-MS measurements. The gap between measured and calculated TOHRE remains, being decreased by less than 2 % for Yassaa et al. (2012) ($k_{\mathrm{MT}} = 1.3 \times 10^{-10}\,\mathrm{cm^3\,molecules^{-1}\,s^{-1}}$), Martin et al. (2003) ($k_{\mathrm{SQT}} = 2.2 \times 10^{-10}\,\mathrm{cm^3\,molecules^{-1}\,s^{-1}}$), and Kempf et al. (1996) ($k_{\mathrm{MT}} = 1.4 \times 10^{-10}\,\mathrm{cm^3\,molecules^{-1}\,s^{-1}}$). The unrealistic high rate coefficient ($k_{\mathrm{MT}} = 5.0 \times 10^{-10}\,\mathrm{cm^3\,molecules^{-1}\,s^{-1}}$) resulted in a missing OH reactivity emission rate of still 53 % in summer and 20 % in autumn, compared to originally 84 % (summer) and 70 % (autumn) (see Table 2). Therefore, it seems unlikely that variability in the mono- and sesquiterpene composition alone causes the high unexplained TOHRE in late summer and autumn. Additionally, it has to be noted, that uncalibrated and unidentified peaks in the analysis of the GC-MS chromatograms remained which leaves the estimate of the reaction rate coefficient somewhat uncertain, and provides direct evidence of unidentified contributors to total OH reactivity emissions.

4.4 Brief literature review

Evidence for a temperature related missing OH reactivity has been already reported in ambient air by Di Carlo et al. (2004) and Nölscher et al. (2012b). As presented in this study, the unexplained portion of total OH reactivity emission rates was high from Norway spruce emissions especially for high temperatures. Di Carlo et al. (2004) compared direct total OH reactivity measurements in the Michigan Forest from summer 2000 to BVOC measurements that were conducted two years earlier at the same site. The resulting “missing OH reactivity” showed terpene-like temperature dependency. Having included both, mono- and sesquiterpene direct emissions into the budget for total OH reactivity emission rates, a relatively large missing OH reactivity flux remains in this study for summer and early autumn. Despite a comprehensive set of atmospheric measurements during the HUMPPA-COPEC campaign 2010, high missing OH reactivity was found in summertime boreal forest (Nölscher et al., 2012b). Comparison of in and above canopy total OH reactivity measurements have indicated a biogenic origin of the highest unexplained total OH reactivity. This missing total OH reavtivity, occurring during prolonged periods of enhanced temperatures, was likely related to heat stress induced direct emissions and also to secondary oxidation products of various biogenically released compounds.

In contrast to these findings, Kim et al. (2011) reported that, based on alternate branch enclosure measurements of total OH reactivity, isoprene and selected mono- and sesquiterpenes, no missing OH reactivity was emitted directly from four observed tree species. No oxygenated species were included in Kim et al. (2011)’s total OH reactivity calculation, nor were they required to close the OH reactivity budget. In our study acetaldehyde was found to contribute significantly through spring, summer and autumn. In Kim et al. (2011) it is not clear whether the branch was impacted by the cuvette, and which compounds and reaction rate coefficients have been used for calculations. Such a good agreement of total OH reactivity measurements and calculations might be due to mechanical stress and the release of elevated monoterpene levels, as has been shown in this study. Furthermore, for the examined Norway spruce summertime exhibited the most missing total OH reactivity flux, whereas no missing OH reactivity from the four enclosed tree branches for measurements in July was found by Kim et al. (2011). Possibly, the species investigated did only emit isoprene, mono- and sesquiterpenes as significant contributors to total OH reactivity.

These contrasting studies emphasize the importance of further measurements of total OH reactivity in the atmosphere and also in closed systems such as branch cuvettes or plant chambers. Emission strength and composition may vary between species and individual plants, so that the completion of the current view requires more investigative field studies.

5 Summary and conclusions

Seasonal variation, diel behavior and the feedback to environmental stress of total OH reactivity emission (TOHRE) rates and total O_3 loss rates from Norway spruce were studied intensively for the first time. Direct measurements of total OH reactivity fluxes from a branch enclosure system via CRM could be compared to VOC emission rates determined simultaneously by a PTR-MS. TOHRE showed seasonal variability, being highest in late summer and lowest in early autumn. A clear temperature dependence was found when comparing the measured TOHRE to the temperature-only dependent algorithm for needle pool emissions of vegetation. Diel median profiles showed generally higher total OH reactivity flux by day than by night. Similarly, total O_3 loss rates increased during the daytime and stayed low at night. The total loss rate of ozone increased in late summer and autumn, which was consistent with the measured TOHRE (in late summer).

The predominant VOC emission measured by PTR-MS was the sum of monoterpenes. On average this accounted for 56–69 % of the measured TOHRE in spring and early summer, and for 11–16 % in late summer and early autumn. However, tests with previously reported typical compositions of mono- and sesquiterpenes emitted by Norway spruce did not significantly improve the mismatch. Besides monoterpenes, both isoprene and acetaldehyde contributed significantly to total OH reactivity emissions.

Fluxes of oxygenated compounds such as methanol showed a similar diel pattern to the measured TOHRE in late summer and autumn, when monoterpene emission rates drastically decreased compared to the growing season in May/June. It seems that instead, reactive compounds, not detected by PTR-MS, were produced and released by the Norway spruce during daytime. These were likely linked to total ozone loss rates that correlated well with temperature and light. Whether this was due to enhanced stomatal-uptake of ozone, surface reactions or total ozone reactivity caused by the tree emissions remains to be examined in future studies. However, enhanced transpiration rates and greater fluxes of total sesquiterpenes in late summer additionally support the hypothesis of higher daytime productivity of the examined Norway spruce.

In addition to seasonal and diurnal variation, environmental feedback impacted TOHRE from Norway spruce. Mechanical stress due to moderate to strong wind events led to elevated emissions of monoterpenes. Such wind events happen regularly in forested regions and their impact on monoterpene emissions has been already noted in several studies (Haase et al., 2011; Bamberger et al., 2011). Generally, in such wind events, both the calculated and the measured TOHRE increased significantly. Another feedback mechanism is stress related to heat. Surprisingly, benzene was found to correlate very well with the measured total OH reactivity emission for a hot day, for which the calculated TOHRE could not explain the observations by CRM. During this event the total OH reactivity emissions had a large unexplained fraction, which is likely to be caused by stress related compounds.

Although for springtime almost the entire signal of TOHRE could be explained by PTR-MS detected biogenic compounds (15 % missing total OH reactivity emissions), the fraction of unaccounted for total OH reactivity tree emissions increased in summer to 84 % and stayed high in autumn with 70 %. Light induced production and release of undetected highly reactive compounds add to the large fraction of unexplained total OH reactivity flux during the summer measurements from the Norway spruce branch enclosure. Peak total OH reactivity fluxes as well as highest estimated ozone loss rates inside the cuvette coincided with the maximum in the ten year average seasonal ozone profile. This study showed, that unmeasured and possibly unknown compounds, which are biogenically produced and released during daytime, contribute to the observed high missing fraction of OH reactivity generally reported from summertime observations in forested regions.

Acknowledgements. We are grateful for the supporting GC-MS analysis determined by W. Song, H. Hakola and H. Hellén. Many thanks for the technical support by T. Klüpfel and the entire PARADE-team. We acknowledge the use of the Taunus Observatory facilities of Goethe University, Frankfurt.

The service charges for this open access publication
have been covered by the Max Planck Society.

References

Altimir, N., Vesala, T., Keronen, P., Kulmala, M., and Hari, P.: Methodology for direct field measurements of ozone flux to foliage with shoot chambers, Atmos. Environ., 36, 19–29, doi:10.1016/S1352-2310(01)00478-2, 2002. 13506

Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem. Rev., 103, 4605–4638, doi:10.1021/cr0206420, 2003. 13499

Bamberger, I., Hörtnagl, L., Ruuskanen, T. M., Schnitzhofer, R., Müller, M., Graus, M., Karl, T., Wohlfahrt, G., and Hansel, A.: Deposition fluxes of terpenes over grassland, J. Geophys. Res.-Atmos., 116, 148–227, doi:10.1029/2010JD015457, 2011. 13519

Bourtsoukidis, E., Bonn, B., Dittmann, A., Hakola, H., Hellén, H., and Jacobi, S.: Ozone stress as a driving force of sesquiterpene emissions: a suggested parameterization, Biogeosciences Discuss., 9, 7661–7700, doi:10.5194/bgd-9-7661-2012, 2012. 13502, 13503, 13504, 13515

Calogirou, A., Jensen, N. R., Nielsen, C. J., Kotzias, D., and Hjorth, J.: Gas-phase reactions of nopinone, 3-isopropenyl-6-oxo-heptanal, and 5-methyl-5-vinyltetrahydrofuran-2-ol with OH, NO_3, and ozone, Environ. Sci. Technol., 33, 453–460, doi:10.1021/es980530j, 1999. 13527

Cojocariu, C., Kreuzwieser, J., and Rennenberg, H.: Correlation of short-chained carbonyls emitted from Picea abies with physiological and environmental parameters, New Phytol., 162, 717–727, doi:10.1111/j.1469-8137.2004.01061.x, 2004. 13501

Davis, M. E., Talukdar, R. K., Notte, G., Ellison, G. B., and Burkholder, J. B.: Rate Coefficients for the OH + pinonaldehyde ($C_{10}H_{16}O_2$) reaction between 297 and 374 K, Environ. Sci. Technol., 41, 3959–3965, doi:10.1021/es070048d, 2007. 13527

Di Carlo, P., Brune, W. H., Martinez, M., Harder, H., Lesher, R., Ren, X., Thornberry, T., Carroll, M. A., Young, V., Shepson, P. B., Riemer, D., Apel, E., and Campbell, C.: Missing OH reactivity in a forest: evidence for unknown reactive biogenic VOCs, Science, 304, 722–725, doi:10.1126/science.1094392, 2004. 13500, 13511, 13516

Dudareva, N., Negre, F., Nagegowda, D. A., and Orlova, I.: Plant volatiles: recent advances and future perspectives, Crit. Rev. Plant Sci., 25, 417–440, doi:10.1080/07352680600899973, 2006. 13499, 13513

Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A., Hewitt, C., Lamb, B., Liu, S., Trainer, M., Westberg, H., and Zimmerman, P.: Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry, Global Biogeochem. Cy., 6, 389–430, doi:10.1029/92GB02125, 1992. 13499

Filella, I., Wilkinson, M. J., Llusià, J., Hewitt, C. N., and Peñuelas, J.: Volatile organic compounds emissions in Norway spruce (Picea abies) in response to temperature changes, Physiol. Plantarum, 130, 58–66, doi:10.1111/j.1399-3054.2007.00881.x, 2007. 13501, 13508

Goldstein, A. H. and Galbally, I. E.: Known and unexplored organic constituents in the earth's atmosphere, Environ. Sci. Technol., 41, 1514–1521, doi:10.1021/es072476p, 2007. 13499

Grabmer, W., Kreuzwieser, J., Wisthaler, A., Cojocariu, C., Graus, M., Rennenberg, H., Steigner, D., Steinbrecher, R., and Hansel, A.: VOC emissions from Norway spruce (Picea abies L. [Karst]) twigs in the field – results of a dynamic enclosure study, Atmos. Environ., 40, Supplement 1, 128–137, doi:10.1016/j.atmosenv.2006.03.043, 2006. 13508

Guenther, A., Zimmermann, P., Harley, P., Monson, R., and Fall, R.: Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses, J. Geophys. Res., 98, 12609–12617, 1993. 13500, 13511

Guenther, A., Hewitt, C., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmermann, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873–8892, 1995. 13499

Haase, K. B., Jordan, C., Mentis, E., Cottrell, L., Mayne, H. R., Talbot, R., and Sive, B. C.: Changes in monoterpene mixing ratios during summer storms in rural New Hampshire (USA), Atmos. Chem. Phys., 11, 11465–11476, doi:10.5194/acp-11-11465-2011, 2011. 13512, 13519

Heard, D. E. and Pilling, M. J.: Measurement of OH and HO_2 in the troposphere, Chem. Rev., 103, 5163–5198, doi:10.1021/cr020522s, 2003. 13500

Heiden, A. C., Kobel, K., Komenda, M., Koppmann, R., Shao, M., and Wildt, J.: Toluene emissions from plants, Geophys. Res. Lett., 26, 1283–1286, doi:10.1029/1999GL900220, 1999. 13513

Hoffmann, T., Odum, J., Bowman, F., Collins, D., Klockow, D., Flagan, R., and Seinfeld, J. H.: Formation of organic aerosols from the oxidation of biogenic hydrocarbons, J. Atmos. Chem., 26, 189–222, 10.1023/A:1005734301837, 1997. 13499

Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.-C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S., Shao, M., Zeng, L., Wahner, A., and Zhang, Y.: Amplified trace gas removal in the troposphere, Science, 324, 1702–1704, doi:10.1126/science.1164566, 2009. 13500

Jardine, K. J., Monson, R. K., Abrell, L., Saleska, S. R., Arneth, A., Jardine, A., Ishida, F. Y., Serrano, A. M. Y., Artaxo, P., Karl, T., Fares, S., Goldstein, A., Loreto, F., and Huxman, T.: Within-plant isoprene oxidation confirmed by direct emissions of oxidation products methyl vinyl ketone and methacrolein, Glob. Change Biol., 18, doi:10.1111/j.1365-2486.2011.02610.x, 2012. 13499

Kempf, K., Allwine, E., Westberg, H., Claiborn, C., and Lamb, B.: Hydrocarbon emissions from spruce species using environmental chamber and branch enclosure methods, Atmos. Environ., 30, 1381–1389, doi:10.1016/1352-2310(95)00462-9, 1996. 13516

Kesselmeier, J.: Exchange of short-chain oxygenated volatile organic compounds (VOCs) between plants and the atmosphere: a compilation of field and laboratory studies, J. Atmos. Chem., 39, 219–233, 2001. 13499

Kesselmeier, J. and Staudt, M.: Biogenic volatile organic compounds (VOC): an overview on emission, Physiol. Ecol., J. Atmos. Chem., 33, 23–88, doi:10.1023/A:1006127516791, 1999. 13499

Kesselmeier, J., Bode, K., Hofmann, U., Mueller, H., Schaefer, L., Wolf, A., Ciccioli, P., Brancaleoni, E., Cecinato, A., Frattoni, M., Foster, P., Ferrari, C., Jacob, V., Fugit, J., Dutaur, L., Simon, V., and Torres, L.: Emission of short chained organic acids, aldehydes and monoterpenes from Quercus ilex L. and Pinus pinea L. in relation to physiological activities, carbon budget and emission algorithms, Atmospheric Environment, 31, Supplement 1, 119–133, doi:10.1016/S1352-2310(97)00079-4, 1997. 13499

Kim, S., Guenther, A., Karl, T., and Greenberg, J.: Contributions of primary and secondary biogenic VOC tototal OH reactivity during the CABINEX (Community Atmosphere-

Biosphere INteractions Experiments)-09 field campaign, Atmos. Chem. Phys., 11, 8613–8623, doi:10.5194/acp-11-8613-2011, 2011. 13501, 13517

Kovacs, T. A. and Brune, W.: Total OH loss rate measurement, J. Atmos. Chem., 39, 105–122, 2001. 13500, 13503

Kulmala, M., Hienola, J., Pirjola, L., Vesala, T., Shimmo, M., Altimir, N., and Hari, P.: A model for NO_x-O_3-terpene chemistry in chamber measurements of plant gas exchange, Atmos. Environ., 33, 2145–2156, doi:10.1016/S1352-2310(99)00069-2, 1999. 13506

Kurpius, M. and Goldstein, A.: Gas-phase chemistry dominates O3 loss to a forest, implying a source of aerosols and hydroxyl radicals to the atmosphere, Geophys. Res. Lett., 30, 0094–8276, doi:10.1029/2002GL016785, 2003. 13506

Laothawornkitkul, J., Taylor, J., Paul, N., and Hewitt, C. N.: Biogenic volatile organic compounds in the Earth system, New Phytol., 183, 27–51, doi:10.1111/j.1469-8137.2009.02859.x, 2009. 13499

Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737–740, 2008. 13500

Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS): medical applications, food control and environmental research, Int. J. Mass Spectrom., 173, 191–241, doi:10.1016/S0168-1176(97)00281-4, 1998. 13502

Loreto, F. and Schnitzler, J.-P.: Abiotic stresses and induced BVOCs, Trends Plant Sci., 15, 154–166, doi:10.1016/j.tplants.2009.12.006, 2010. 13499

Loreto, F., Mannozzi, M., Maris, C., Nascetti, P., Ferranti, F., and Pasqualini, S.: Ozone quenching properties of isoprene and its antioxidant role in leaves, Plant Physiol., 126, 993–1000, doi:10.1104/pp.126.3.993, 2001. 13506

Lou, S., Holland, F., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Häseler, R., Kita, K., Kondo, Y., Li, X., Shao, M., Zeng, L., Wahner, A., Zhang, Y., Wang, W., and Hofzumahaus, A.: Atmospheric OH reactivities in the Pearl River Delta – China in summer 2006: measurement and model results, Atmos. Chem. Phys., 10, 11243–11260, doi:10.5194/acp-10-11243-2010, 2010. 13500, 13501

Martin, D. M., Gershenzon, J., and Bohlmann, J.: Induction of volatile terpene biosynthesis and diurnal emission by methyl jasmonate in foliage of Norway spruce, Plant Physiol., 132, 1586–1599, doi:10.1104/pp.103.021196, 2003. 13516

Niinemets, U.: Mild versus severe stress and BVOCs: thresholds, priming and consequences, Trends Plant Sci., 15, 145–153, doi:10.1016/j.tplants.2009.11.008, 2010. 13499

Nölscher, A. C., Sinha, V., Bockisch, S., Klüpfel, T., and Williams, J.: A new method for total OH reactivity measurements using a fast Gas Chromatographic Photo-Ionization Detector (GC-PID), Atmos. Meas. Tech. Discuss., 5, 3575–3609, doi:10.5194/amtd-5-3575-2012, 2012. 13504

Nölscher, A. C., Williams, J., Sinha, V., Custer, T., Song, W., Johnson, A. M., Axinte, R., Bozem, H., Fischer, H., Pouvesle, N., Phillips, G., Crowley, J. N., Rantala, P., Rinne, J., Kulmala, M., Gonzales, D., Valverde-Canossa, J., Vogel, A., Hoffmann, T., Ouwersloot, H. G., Vilà-Guerau de Arellano, J., and Lelieveld, J.: Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010, Atmos. Chem. Phys., 12, 8257–8270, doi:10.5194/acp-12-8257-2012, 2012. 13500, 13516, 13517

Peeters, J., Nguyen, T. L., and Vereecken, L.: HOx radical regeneration in the oxidation of isoprene, Phys. Chem. Chem. Phys., 11, 5935–5939, doi:10.1039/B908511D, 2009. 13500

Pöschl, U., Martin, S. T., Sinha, B., Chen, Q., Gunthe, S. S., Huffman, J. A., Borrmann, S., Farmer, D. K., Garland, R. M., Helas, G., Jimenez, J. L., King, S. M., Manzi, A., Mikhailov, E., Pauliquevis, T., Petters, M. D., Prenni, A. J., Roldin, P., Rose, D., Schneider, J., Su, H., Zorn, S. R., Artaxo, P., and Andreae, M. O.: Rainforest aerosols as biogenic nuclei of clouds and precipitation in the Amazon, Science, 329, 1513–1516, doi:10.1126/science.1191056, 2010. 13499

Rinne, J., Taipale, R., Markkanen, T., Ruuskanen, T. M., Hellén, H., Kajos, M. K., Vesala, T., and Kulmala, M.: Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modeling, Atmos. Chem. Phys., 7, 3361–3372, doi:10.5194/acp-7-3361-2007, 2007. 13499

Ruuskanen, T., Kolari, P., Bäck, J., Kulmala, M., Rinne, J., Hakola, H., Taipale, R., Raivonen, M., Altimir, N., and Hari, P.: On-line field measurements of monoterpene emissions from Scots pine by proton-transfer-reaction mass spectrometry, Boreal Environ. Res., 10, 553–567, 2005. 13502, 13504

Sadanaga, Y., Yoshino, A., Watanabe, K., Yoshioka, A., Wakazono, Y., Kanaya, Y., and Kajii, Y.: Development of a measurement system of OH reactivity in the atmosphere by using a laser-induced pump and probe technique, Rev. Sci. Instrum., 75, 8, 2638–2655, doi:10.1063/1.1775311, 2004. 13503

Schürmann, W., Ziegler, H., Kotzias, D., Schönwitz, R., and Steinbrecher, R.: Emission of biosynthesized monoterpenes from needles of Norway spruce, Naturwissenschaften, 80, 276–278, doi:10.1007/BF01135913, 1993. 13508

Sinha, V., Williams, J., Crowley, J. N., and Lelieveld, J.: The Comparative Reactivity Method – a new tool to measure total OH Reactivity in ambient air, Atmos. Chem. Phys., 8, 2213–2227, doi:10.5194/acp-8-2213-2008, 2008. 13500, 13502, 13504

Taipale, R., Kajos, M. K., Patokoski, J., Rantala, P., Ruuskanen, T. M., and Rinne, J.: Role of de novo biosynthesis in ecosystem scale monoterpene emissions from a boreal Scots pine forest, Biogeosciences, 8, 2247–2255, doi:10.5194/bg-8-2247-2011, 2011. 13511

Tan, D., Faloona, I., Simpas, J., Brune, W., Shepson, P., Couch, T., Sumner, A., Carroll, M., Thornberry, T., Apel, E., Riemer, D., and Stockwell, W.: HO_x budgets in a deciduous forest: results from the PROPHET summer 1998 campaign, J. Geophys. Res.-Atmos., 106, 24407–24427, doi:10.1029/2001JD900016, 2001. 13500

Taraborrelli, D., Lawrence, M. G., Crowley, J. N., Dillon, T. J., Gromov, S., Grosz, C. B. M., Vereecken, L., and Lelieveld, J.: Hydroxyl radical buffered by isoprene oxidation over tropical forests, Nat. Geosci., 5, 190–193, doi:10.1038/ngeo1405, 2012. 13500

Tingey, D. T., Manning, M., Grothaus, L. C., and Burns, W. F.: Influence of light and temperature on monoterpene emission rates from slash pine, Plant Physiol., 65, 797–801, 1980. 13500

Vickers, C. E., Gershenzon, J., Lerdau, M. T., and Loreto, F.: A unified mechanism of action for volatile isoprenoids in plant abiotic stress, Nat. Chem. Biol., 5, 5, 283–291, doi:10.1038/nchembio.158, 2009. 13499

White, M. L., Russo, R. S., Zhou, Y., Ambrose, J. L., Haase, K., Frinak, E. K., Varner, R. K., Wingenter, O. W., Mao, H., Talbot, R., and Sive, B. C.: Are biogenic emissions a significant source of summertime atmospheric toluene in the rural Northeastern United States?, Atmos. Chem. Phys., 9, 81–92, doi:10.5194/acp-9-81-2009, 2009. 13513

Wieser, G., Matyssek, R., Götz, B., and Grünhage, L.: Branch cuvettes as means of ozone risk assessment in adult forest tree crowns: combining experimental and modelling capacities, Trees-Struct.Funct., 1–10, 2012. 13506

Williams, J., Pöschl, U., Crutzen, P. J., Hansel, A., Holzinger, R., Warneke, C., Lindinger, W., and Lelieveld, J.: An atmospheric chemistry interpretation of mass scans obtained from a proton transfer mass spectrometer flown over the tropical rainforest of Surinam, J. Atmos. Chem., 38, 133–166, doi:10.1023/A:1006322701523, 2001. 13499

Yassaa, N., Song, W., Lelieveld, J., Vanhatalo, A., Bäck, J., and Williams, J.: Diel cycles of isoprenoids in the emissions of Norway spruce, four Scots pine chemotypes, and in Boreal forest ambient air during HUMPPA-COPEC-2010, Atmos. Chem. Phys., 12, 7215–7229, doi:10.5194/acp-12-7215-2012, 2012. 13508, 13516

Table 1. PTR-MS measured and calibrated VOCs, and the applied rate coefficients used for OH reactivity calculations. The reaction rate coefficients were taken from the IUPAC preferred values except for nopinone which was measured by Calogirou et al. (1999) and pinonaldehyde (Davis et al., 2007).

PTR-MS mass	compound	rate coefficient (cm^3 $molecules^{-1}$ s^{-1})
m/z 33	methanol	9.00×10^{-13}
m/z 42	acetonitrile	2.20×10^{-14}
m/z 45	acetaldehyde	1.50×10^{-11}
m/z 47	ethanol	3.24×10^{-12}
m/z 59	acetone	2.19×10^{-13}
m/z 69	isoprene	1.00×10^{-10}
m/z 79	benzene	1.28×10^{-12}
m/z 137*	total monoterpenes	1.22×10^{-10}
m/z 139	total nopinone	1.70×10^{-11}
m/z 155	linalool	1.59×10^{-10}
m/z 169	pinonaldehyde	3.46×10^{-11}
m/z 205*	total sesquiterpenes	1.69×10^{-10}

* weighted rate coefficients used according to GC-MS composition analysis (see Sect. 3.1).

Table 2. Average values for meteorological parameters, total OH reactivity emissions (TOHRE), the single compound total OH reactivity emissions of monoterpenes (MTOHRE), isoprene (IOHRE) and acetaldehyde (AOHRE) and the unknown fraction of TOHRE (missing TOHRE). Data is averaged for the entire measurement period (all), for 24 May–31 May 2011 (spring), 1 June–14 June 2011 (early summer), 12 August–26 August 2011 (late summer) and 27 August–7 September 2011 (early autumn).

	all	spring	early summer	late summer ^{c}	early autumn ^{c}
temperature (°C)^a	15.0 ± 0.1	13.5 ± 0.2	15.1 ± 0.2	17.9 ± 0.2	13.0 ± 0.2
relative humidity (%)^a	76.0 ± 0.4	63.8 ± 1.0	72.1 ± 0.7	81.2 ± 0.7	83.6 ± 0.7
wind speed ($\mathrm{m\,s^{-1}}$)^a	2.8 ± 0.03	2.9 ± 0.06	3.3 ± 0.08	2.4 ± 0.05	2.4 ± 0.05
soil moisture^a	74.2 ± 0.6	52.1 ± 0.2	45.2 ± 0.08	97.6 ± 0.3	104.3 ± 0.3
ambient ozone (ppbV)^a	45.2 ± 0.3	50.3 ± 0.6	49.5 ± 0.5	44.4 ± 0.6	37.0 ± 0.5
total ozone loss rate ($\mathrm{pptV\,s^{-1}}$)^a	−31.2 ± 0.7	−27.0 ± 1.2	−21.6 ± 0.6	−40.9 ± 1.6	−36.9 ± 1.9
TOHRE (measured) ($\mathrm{s^{-2}\,g(dw)^{-1}\,m^{-3}}$)^a	0.4868 ± 0.0206	0.2715 ± 0.0127	0.5033 ± 0.0205	0.8260 ± 0.0722	0.1639 ± 0.0063
TOHRE (calculated) ($\mathrm{s^{-2}\,g(dw)^{-1}\,m^{-3}}$)^a	0.1961 ± 0.0121	0.2310 ± 0.0165	0.3661 ± 0.0338	0.1286 ± 0.0066	0.0484 ± 0.0020
MTOHRE (calculated) ($\mathrm{s^{-2}\,g(dw)^{-1}\,m^{-3}}$)^b	0.1453 (30 %)	0.1874 (69 %)	0.2806 (56 %)	0.0870 (11 %)	0.0268 (16 %)
IOHRE (calculated) ($\mathrm{s^{-2}\,g(dw)^{-1}\,m^{-3}}$)^b	0.0189 (4 %)	0.0186 (7 %)	0.0275 (5 %)	0.0189 (2 %)	0.0089 (5 %)
AOHRE (calculated) ($\mathrm{s^{-2}\,g(dw)^{-1}\,m^{-3}}$)^b	0.0230 (5 %)	0.0142 (5 %)	0.0491 (10 %)	0.0105 (1 %)	0.0074 (5 %)
missing TOHRE ($\mathrm{s^{-2}\,g(dw)^{-1}\,m^{-3}}$)^b	0.2907 (60 %)	0.0405 (15 %)	0.1372 (27 %)	0.6974 (84 %)	0.1155 (70 %)

[a] average ± standard error

[b] average (relative contribution to measured TOHRE)

[c] average (applied monoterpene and sesquiterpene composition ratios of springtime GC-MS analysis)

Fig. 1. Cuvette set-up in the field on Kleiner Feldberg, Taunus, Germany: The enclosure system was fixed at a Norway spruce branch. The instruments (Sensors, PTR-MS, CRM) were located in the van underneath to keep inlet lines short. For 17 min the lid was kept open to allow contact with the natural atmospheric environment and closed automatically for 3 min.

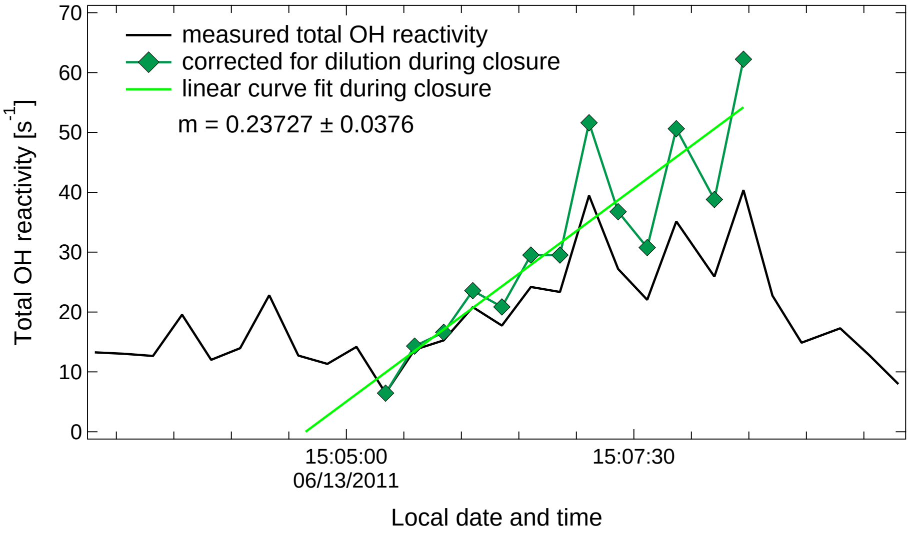


Fig. 2. Example for total OH reactivity emission (TOHRE) calculation: The originally measured total OH reactivity (black line) varied for open cuvette measurements between 10–20 s^{-1}, during closure it increased to 40 s^{-1}. The dilution during cuvette closure due to leaking in of atmospheric air suppresses the measured total OH reactivity stronger the longer the system is closed. A dilution correction is applied (green markers) before fitting the closure data with a linear regression line (green line). Slopes, uncertainty of the slopes, and fit quality are obtained for each closure.

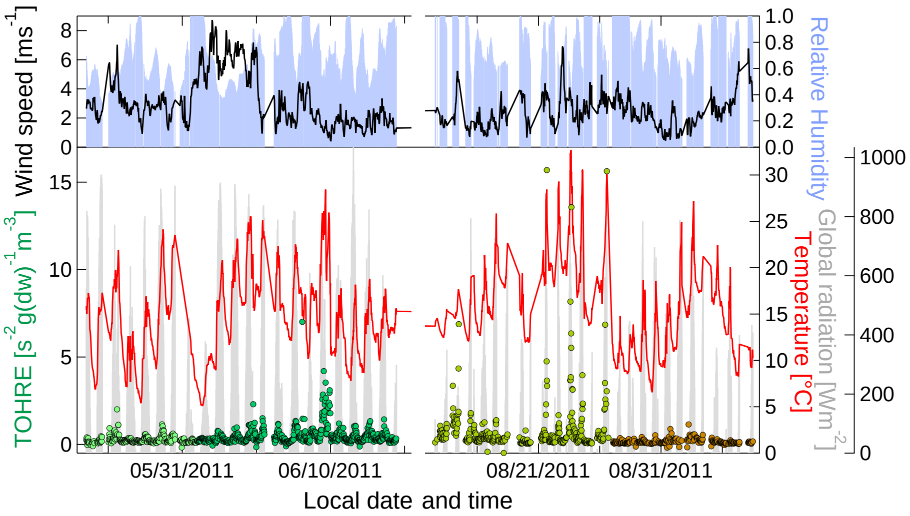


Fig. 3. Overview of the entire data set: Total OH reactivity emissions (TOHRE, green markers) were measured from 24 May to 14 June 2011 and 12 August to 7 September 2011 covering the seasonal impact from spring to early autumn. Temperature inside the cuvette (red line) and global radiation from a co-located mast (grey area) showed high variability throughout the measurement period as well as wind speed (black line, top panel) and relative humidity (blue area, top panel).

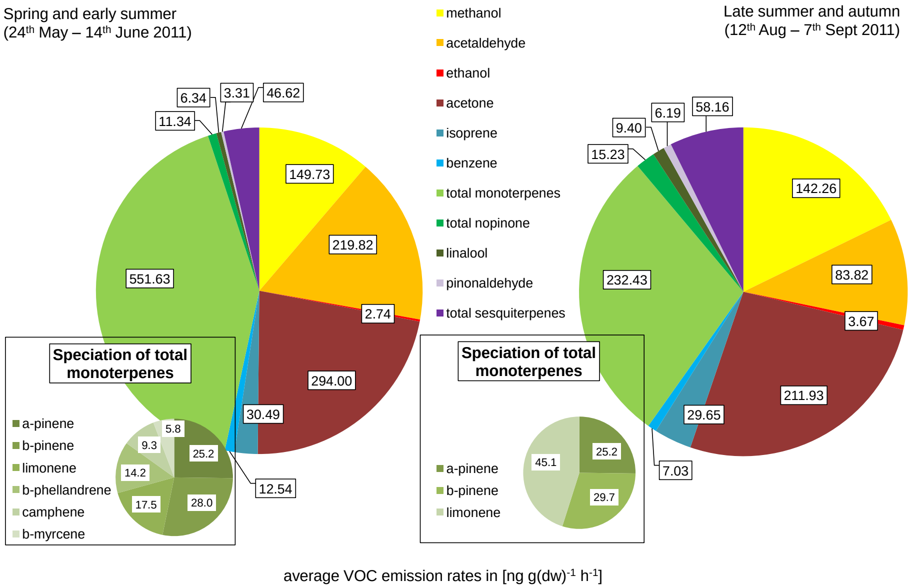
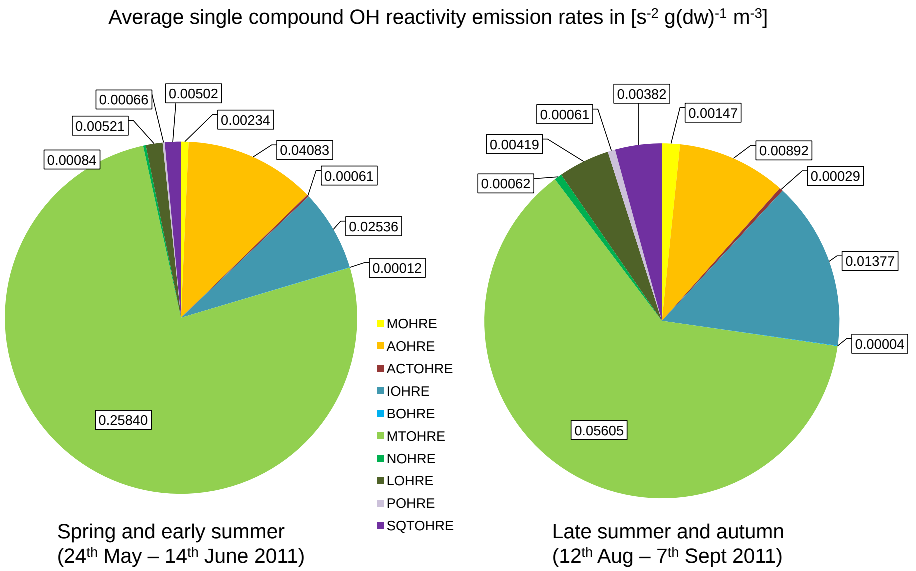


Fig. 4. The composition of biogenic VOC emissions and monoterpenes specified by GC-MS for both measurement periods **(a)** springtime and early summer, **(b)** late summer and autumn. Average emission rates are given in ng g(dw)$^{-1}$ h^{-1}, the speciation is the relative contribution of single monoterpenes to the measured sum by PTR-MS.



Spring and early summer
(24th May – 14th June 2011)

Late summer and autumn
(12th Aug – 7th Sept 2011)

Fig. 5. Average contribution of PTR-MS measured compounds to total OH reactivity emission rates (calculated). Single compound OH reactivity emissions (OHRE) are calculated from the measured concentration levels and the reaction rate coefficients given in Table 1. The following compounds were included in the budget: methanol (MOHRE), acetaldehyde (AOHRE), acetone (ACTOHRE), isoprene (IOHRE), benzene (BOHRE), total monoterpenes (MTOHRE), total nopinone (NOHRE), linalool (LOHRE), pinonaldehyde (POHRE), total sesquiterpenes (SQTOHRE).

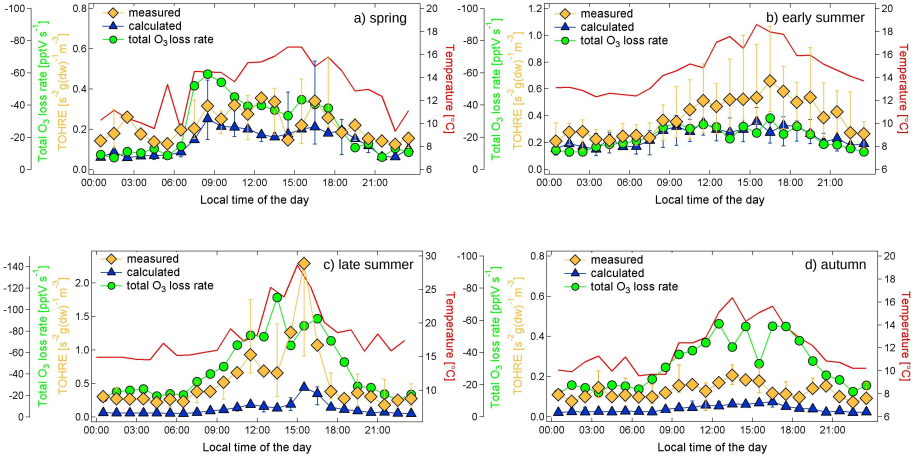


Fig. 6. Median diel profiles for four periods **(a)** spring, **(b)** early summer, **(c)** late summer, **(d)** autumn of total OH reactivity emissions (TOHRE) which were measured by CRM (orange markers) and calculated from PTR-MS data (blue markers) and of the observed total ozone loss rate (green markers). Additionally, the median temperature profile is included (red line). Uncertainties of the hourly median are given for measured and calculated TOHRE as 75 and 25 percentiles.

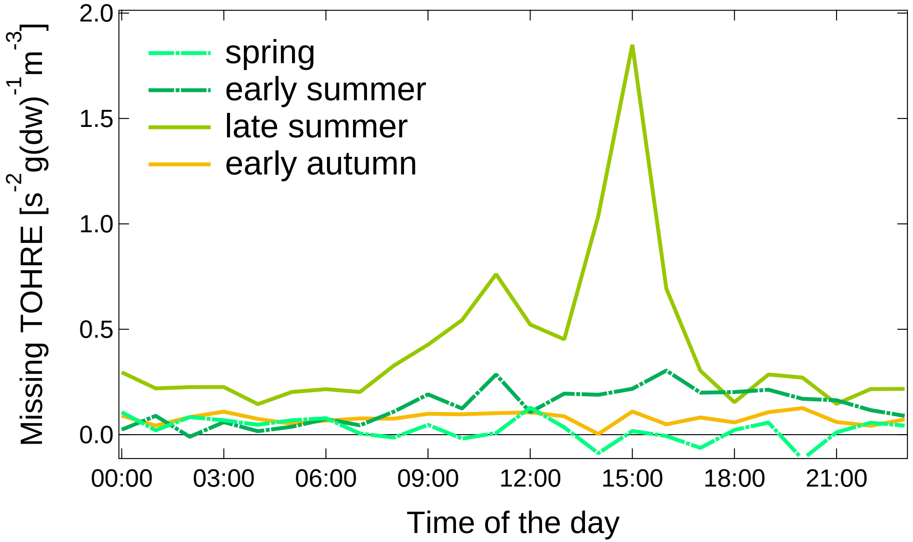


Fig. 7. Missing TOHRE as median diel profile for spring, early summer, late summer and early autumn. Missing total OH reactivity fluxes describe the unknown or unmeasured difference which was found by comparing calculated and measured TOHRE.

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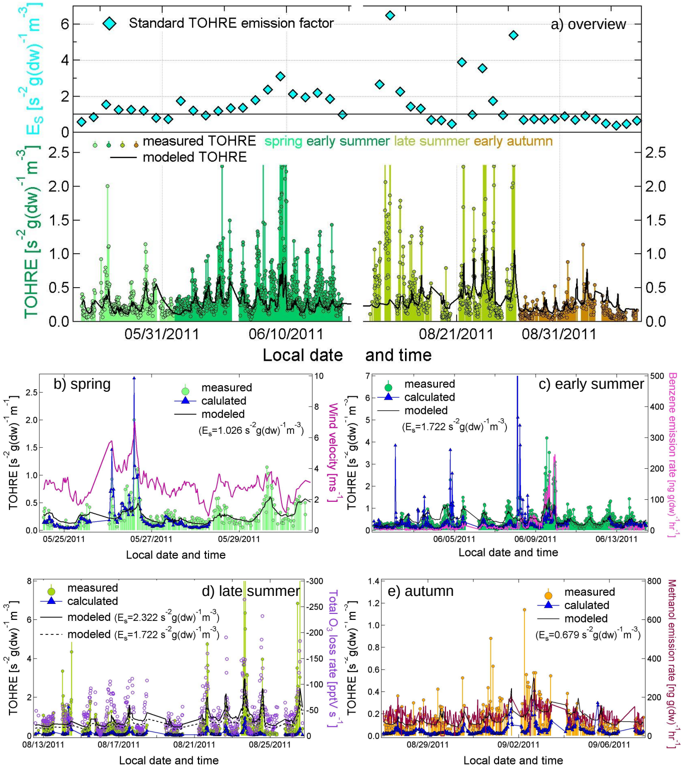

Fig. 8. Overview for model, calculation and measurement comparison of TOHRE: **(a)** The entire campaign has been modeled (black line) using an unscaled temperature-only dependent algorithm to compare to measured TOHRE (markers on sticks), superimposed the daily standard total OH reactivity emission factor is pictured. Each of the other graphs **(b–e)** presents measured, calculated and modeled TOHRE as well as one parameter such as wind velocity, benzene emission rates, total O_3 loss rate and methanol emission rates.