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**Beech forest VOC
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Interactive Discussion

Methanol and other VOC fluxes from a Danish beech forest during springtime

G. W. Schade[1,2], S. J. Solomon[2], E. Dellwik[3], K. Pilegaard[3], and
A. Ladstätter-Weissenmayer[2]

[1]Dept. Atmos. Sci., Texas A&M Univ., 3150 TAMU, College Station, TX 77843, USA
[2]IUP, University of Bremen, Otto-Hahn-Allee 1, 28359 Bremen, Germany
[3]Biosystems Department, Risø National Laboratory for Sustainable Energy, Technical
University of Denmark – DTU, P.O. Box 49, 4000 Roskilde, Denmark

Abstract

In-canopy mixing ratio gradients and above-canopy fluxes of several volatile organic compounds (VOCs) were measured using a commercial proton transfer reaction mass spectrometer (PTR-MS) in a European beech (*Fagus sylvatica*) forest in Denmark. Emission fluxes of methanol occurred dominantly late at night, which was supported by highest mixing ratios in the crown region, and is in line with recent controlled laboratory experiments. Also confirming previous measurements, monoterpene emissions showed a diurnal cycle consistent with light-dependent emissions, supported by highest mixing ratios in the canopy space during early afternoon. Also emitted was acetone, but only at ambient temperatures exceeding 20°C. Deposition dominated at lower temperatures. Deposition fluxes occurred also for methanol but seemingly as a result of high ambient methanol mixing ratios. Our in-canopy gradient measurements contrasted earlier results from tropical and pine forest ecosystems in that they did not show this beech ecosystem to be a strong sink for oxygenated VOCs. Instead, their gradients were flat and only small deposition velocities ($<0.1\,\mathrm{cm\,s^{-1}}$) were observed to the onsite soil. However, as soil uptake was consistent and appeared to be related to soil moisture, more measurements are needed to evaluate the soil sink strength. In turn, as canopy scale fluxes are net fluxes with emissions from photosynthesizing leaves affecting potential oxygenated VOC uptake, only independent, controlled laboratory experiments may be successful in separating stomatal from non-stomatal fluxes, and emission from deposition.

1 Introduction

Since the mid-nineties interest in Oxygenated Volatile Organic Compounds (OVOCs) has increased. It is now widely recognized that OVOCs, particularly acetone and methanol, can play significant roles in atmospheric chemistry (Folberth et al., 2006; Folkins and Chatfield, 2000; Lary and Shallcross, 2000; Singh et al., 1995; Sommariva

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et al., 2006) through their abundance in rural and remote areas of the troposphere, including the free troposphere (Fall et al., 2001; Riemer et al., 1998; Schade and Goldstein, 2001, 2006; Singh et al., 2000; Singh et al., 2004; Karl et al., 2003;Lewis et al., 2005; Dufour et al., 2007).

Based on recent budget estimates (Galbally and Kirstine, 2002; Jacob et al., 2002; Jacob et al., 2005), the emissions of methanol and acetone are likely dominantly of biogenic rather than anthropogenic origin, and numerous measurements have confirmed both green plant and litter sources (Brunner et al., 2007; Cojocariu et al., 2004; Custer and Schade, 2007; De Gouw et al., 2000; Fukui and Doskey, 1998; Janson and de Serves, 2001; Karl et al., 2001a, 2001b, 2002, 2003; Kirstine et al., 1998; Schade and Goldstein, 2001; Spirig et al., 2005; Warneke et al., 1999; Warneke et al., 2002). However, the magnitudes of these sources as a function of biome, as well as the dependences of emissions on physical and biological drivers remain subject of debate.

Compared to most other OVOCs, green plant emissions of methanol are now relatively well understood. Methanol has a comparatively long lifetime of approximately one week, and can serve as a significant source of HO_x in the free and upper troposphere (e.g. Tie et al., 2003). Plant emissions probably comprise two thirds of total emissions to the troposphere (Galbally and Kirstine, 2002; Jacob et al., 2005). Production most likely originates in the demethylation of pectin during plant cell wall expansion (Fall and Benson, 1996; Galbally and Kirstine, 2002; Hüve et al., 2007), and emissions are controlled by growth rate and status, stomatal opening, and temperature (Folkers et al., 2008; Hüve et al., 2007; Custer and Schade, 2007; Brunner et al., 2007; Karl et al., 2004, 2004, 2005; Schade and Goldstein, 2001). Another important source is the photochemical production of methanol from methane under very low NO_x conditions, which leads to a tropospheric background concentration of approximately 0.4 ppb (Schade and Goldstein, 2006). The major sink of methanol is through reaction with the hydroxyl radical. In addition, Jacob et al. (2005) inferred both wet and dry deposition (corresponding to $0.2\,\mathrm{cm\,s^{-1}}$) sinks to balance the global methanol budget using the GEOS-CHEM model.

OVOC deposition is difficult to separate from the net fluxes that are commonly observed above canopy. For example, several authors (Custer and Schade, 2007; Brunner et al., 2007; Karl et al., 2004, 2005; Spirig et al., 2005) found either occasional or regular deposition fluxes during their field studies but generally not during daytime. Assuming that methanol emissions are regulated by stomatal conductance in most plants, deposition to plant surfaces may only be observable at night. In a recent rainforest study, Karl et al. (2004) inferred nighttime sub-canopy deposition rates by a storage term analysis and combining gradient measurements with a model. They found an average deposition velocity of $0.27 \pm 0.14 \, \text{cm s}^{-1}$ for methanol, a similar value for acetaldehyde, and a slightly lower value of $0.14 \, \text{cm s}^{-1}$ for acetone. Calculated deposition velocities ranged up to $1 \, \text{cm s}^{-1}$ for methanol and appeared to maximize just below the LAI maximum in the upper canopy of the rainforest ecosystem. In another, detailed laboratory and field study on loblolly pine (*Pinus taeda*), the same authors confirmed that the flux of several OVOCs, including methanol, acetaldehyde, acetone, and methyl ethyl ketone (MEK), is bidirectional, and deposition can typically be observed below the canopy at night, but also during the day (Karl et al., 2005). Similar to their rain forest study, Karl and coworkers (Karl et al., 2005) found typical deposition velocities of $0.3 \, \text{cm s}^{-1}$ for methanol and acetaldehyde (max. $1 \, \text{cm s}^{-1}$ for methanol) in this pine forest, and $0.1 \, \text{cm s}^{-1}$ for acetone, all maximizing in the pine canopy LAI maximum. They also reported the inferred deposition in the lowest layer of their study, seemingly corresponding to soil uptake. These values were typically lower ($<0.2 \, \text{cm s}^{-1}$) with the exception of MEK (Karl et al., 2005).

While it remains unclear what processes are responsible for uptake in a canopy, trace gas uptake in soils is generally microbially mediated. Uptake rate is affected by physical parameters such as soil texture and water filled pore space, which control the diffusion rate to active microorganism sites in the soil (e.g. Smith et al., 2003; Yonemura et al., 2000). If OVOCs are consumed by microorganisms, the uptake rate is likely first order in atmospheric concentration and can be assessed via enclosure measurements. For example, Schade and Custer (2005) used a soil chamber over an

agricultural soil to observe methanol uptake. Measured deposition velocities ranged from 0.05 to $0.3\,\mathrm{cm\,s^{-1}}$ for 10 to 20% volumetric soil moisture. Concurrent eddy covariance measurements at the same site before crop development showed deposition velocities after a rain event to range from 0.1 to $0.4\,\mathrm{cm\,s^{-1}}$. In both cases simultaneous acetone deposition velocity was a factor of 2–5 lower (Schade and Custer, 2008[1]). Although their PTR-MS measured abundance were seemingly misinterpreted, the flux results of Asensio (Asensio et al., 2007) for a Mediterranean soil are in accordance with these data.

To address both the plant source and potential in- and sub-canopy sinks for a common European ecosystem, we carried out a field measurement campaign at a well-studied beech forest in Denmark (Soroe) in 2007. We measured both above-canopy fluxes with a relaxed eddy accumulation technique (Sect. 2) as well as concentration gradients from inside the beech canopy towards the ground. Springtime was chosen with the expectation to observe larger methanol fluxes as a result of leaf development (Sect. 3). Above to below canopy gradients were measured to address the distribution of sources and sinks within the forest (Sect. 4), and soil chamber tests were run to evaluate the soil sink strength (Sect. 5).

2 Measurement setup

2.1 Field site

The Soroe field site has been extensively described by Pilegaard et al. (2003) and is used as a carbon flux monitoring site within the CarboEuroflux network, as well as a soil nitrogen flux site. Several tower platforms were set up in a mature European beech (*Fagus sylvatica* L.) forest (*Lille Bøgeskov*). The forest is relatively small and managed, containing several groves of conifers comprising 20% of the total footprint

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[1]Schade, G. W. and Custer, T. G.: VOC exchange fluxes of an agricultural soil, Atmos. Environ., in preparation, 2008.

area (Pilegaard et al., 2001, 2003). The groves 100 m to 300 m (∼4 ha), and 500 m to 750 m (∼3 ha) SE of the site, and 250 m to 400 m SW of the site (∼3 ha) are most relevant for flux interpretation. The forest soil is a typical brown earth (sandy loam to loam, O+A layer depth of 10–40 cm) with a carbon content of 200 t ha^{-1}, and a pH of 4–
6 in the upper 15 cm (Ambus et al., 2001). Spring leaf-out of the beech trees generally occurs in May, but LAI increases have been observed after June. Plant canopy analyzer data revealed that peak canopy leaf area index (end July) was approximately 5 m^2 m^{-2} (Pilegaard et al., 2003). Turbulence measurements indicated roughness length and displacement heights of 1.8 and 20.6 m, and suggested a shallow roughness sub-layer
(Dellwik and Jensen, 2000, 2005).

At the site itself a lattice mast extends to more than twice the average beech canopy height (25 m) and carries all the micrometeorological flux instrumentation. Next to it is a scaffold walk-up tower with several platforms (3 m×3 m), which extends into the canopy up to 24 m. An extensive set of instruments monitors above canopy turbulence,
and energy and CO_2 fluxes. They are supplemented by below canopy measurements of radiation and temperature, and soil energy and trace gas fluxes (Pilegaard et al., 2001a, 2001b, 2003, 2006; Janssens and Pilegaard, 2003; Pihlatie et al., 2005; Ambus et al., 2001). Instrumentation for in-situ trace gas measurements is housed in a trailer approximately 10 m SE from the towers, which is supplied with line power. The
trailer has a small air conditioner and natural ventilation through windows to reduce temperature fluctuations.

Site access is provided by a forest road, off from a minor land road (<20 cars per hour during the day) that traverses the forest in E-W direction approximately 150 m north of the towers. The nearest anthropogenic VOC sources are the city of Sorø,
6 km to the SW, and a major E-W highway (E20) 4 km to the S. Other possible OVOC sources include two animal farms (Ngwabie et al., 2007) 1 km and 1.5 km to the WSW and WNW, respectively.

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2.2 Sampling setup

Ambient air sampling was conducted from 4 heights: 41 m, 22 m, 14 m, and 5 m. A sonic anemometer (CSAT3, Campbell Sci., UK) was installed on a cross beam at 41 m extending towards the west from the lattice mast. An 8 mm ID PTFE sampling line for
above-canopy sampling ran from the sonic down into the instrument shed, where it was converted to a 6.35 mm ID PFA line connected to two membrane pumps in series (Rietschle Thomas model LM22) drawing air at 11.5–12 L min^{-1}. Another 3.5 L min^{-1} of this main line flow was routed through a Teflon-coated membrane pump (KNF model N86 KTDC B), which served to fill the relaxed eddy accumulation (REA) reservoirs (de-
scribed below). The canopy to sub-canopy setup consisted of an independent 4.3 mm ID PFA sampling line that was run up the scaffold tower to 22 m. At 5 m and 14 m above ground, additional ~5 m of the same PFA lines were TEE'd off towards the west side of the scaffold, away from the trailer. All three gradient inlets terminated in PTFE normally closed isolation valves (BiochemValve Inc. model 075T). Sample air from the gradient
was acquired with another Teflon-coated membrane pump (KNF model N 86 KTDC B) restricted to 1.7 L min^{-1} flow. A schematic of the setup is shown in Fig. 1.

The acquired air samples were routed to two instruments: the "methanalyzer", a commercial wet-chemical formaldehyde analyzer equipped with a homemade methanol-to-formaldehyde converter (Solomon et al., 2005), and a commercial PTR-
MS instrument (de Gouw et al., 2003). The second Teflon-coated membrane pump was used to acquire sample air from either the REA reservoirs or the gradient sampling line and pump it towards the methanalyzer. A small subsample (50–100 mL min^{-1}) was extracted from this flow ahead of the pump through a few meters of 1.6 mm ID PFA line to the PTR-MS instrument (Fig. 1). Line volume and flow considerations suggested that
lag times between entering the tubes and arriving at the REA valves or instruments were 11 s and <10 s for the above-canopy and gradient lines, respectively. The former was confirmed at the start of the campaign by popping acetone-spiked balloons next to the anemometer while following mass 59 at 20 Hz on the PTR-MS instrument.

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2.3 Sonic data acquisition and REA sampling

The sonic anemometer's analog output data were saved on a CR23X data logger (Campbell Sci., UK). The measured vertical wind speed w was processed by the logger to calculate running means of w and σ_w (Schade and Goldstein, 2001). The properly lagged, instantaneous w was then evaluated against $w \pm b \times \sigma_w$ to decide which REA valve should be opened towards filling the respective up- and downdraft reservoirs (fixed lag times between 10.5 and 12 s were entered into the data logger, using 11 s more than 95% of the time). The discrimination factor b was chosen according to the desired total volume that was needed to supply the methanalyzer with a sufficiently large sample. In our case, this volume was approximately 21 L for a 12-min sampling time at 1.75 L min^{-1}, which led to a chosen b ranging from 0.8 to 0.9 under the local turbulence conditions. High-speed 3-way Teflon isolation valves (BiochemValve model 075T) were installed as REA valves (Fig. 1 inset). The first valve decided between sampling and dumping (deadband), the second whether the sample should enter the up- or downdraft reservoir (Baker et al., 1999). Each reservoir entry was also equipped with an additional TEE towards a 2-way PTFE valve (same model than on tower gradient), through which the reservoirs were emptied directly after the sampling period from 0–30 min into the hour.

The CR23X's 8 control channels were programmed to switch all PTFE valves such that each hour was divided into five 12-min measuring periods: The downdraft reservoir was measured from 30–42 min, followed by the updraft reservoir from 42–54 min, followed by the gradient inlets top to bottom. Hence, the reservoirs were emptied as soon as possible after filling to minimize bag effects. In addition, the CR23X performed a reservoir comparison every 13 h, or by user intervention, via sampling dead-band air alternately into both reservoirs.

In this study, 25 L standard Tedlar® bags with polypropylene fittings (SKC via Analyt-MTC GmbH, Germany) were used as reservoirs. We filled and emptied the bags three times with ambient air before usage in the setup. They were hung up under a table

during sampling to avoid kinking, and leaky bags – as indicated by a significant flow from a visually empty bag – were replaced as soon as possible. A total of five bags were used during this study. Although a bag that had been repeatedly filled and emptied many times did not seem to show any significant differences in the selected count
5 rates on the PTR-MS when comparing air measured during filling the bag with subsequent out-of-the-bag air, several effects observed during the campaign lead us to conclude that these bags should be avoided for certain VOCs without future intensive testing: Several measured m/z values (33, 43, 45, 61, 59, 81+137) that correspond to atmospheric VOCs showed elevated values from newly installed bags, which we con-
10 firmed by switching the bags; they still showed a slight bias (<0.1 ppb) towards higher values from older bags filled with above canopy (41 m) air as compared to the top gradient level (22 m, in-canopy), which was influenced neither by a bag nor by a pump. Under ordinary circumstances this would suggest a deposition to the canopy. However, this is unprecedented for monoterpenes, which showed this effect on m/z 81+137.
15 Rather, a bag effect is supported by the observation that a rapid temperature change to the bags (−5 K), induced by the opening of the trailer door in the early morning, led to a significant drop of count rates (10% to 30%) during the bag measurement (not during the gradient measurement). We interpret this as either a temperature-driven desorption of volatiles from or diffusion through the bag-walls. While such rapid temperature
20 changes did not occur at other times of the day, they suggest possible biases of certain VOC mixing ratios even for the short storage times used in this study. Therefore, we report in-canopy in lieu of above-canopy mixing ratios. However, as the bag effect was not significantly different between the bags, and we account for up- versus down-bag offsets using the comparison measurements, we also report the observed fluxes from
25 the REA sampling system.

2.4 Analytical instruments and data handling

Two instruments were used to observe VOC mixing ratios in this study: the methanalyzer described by Solomon et al. (2005) and our 2003 model PTR-MS (Custer and

Schade, 2007). As the methanalyzer showed an unusually slow response time and rapid signal degradation in the field, its data will not be discussed here. The PTR-MS, described in more detail by de Gouw et al. (2003) and evaluated for VOC measurements by Warneke et al. (2003) and Hayward et al. (2002), was an ideal tool for this study. We operated the drift tube at 2 mbar pressure, 40°C, and a 125 Td drift field. Parent H_3O^+ ion counts assessed at m/z 21 ranged from 1.7×10^6 cps to 2.6×10^6 cps during the study with at most a 5% contribution from the monitored first water cluster at m/z 37. Inflow to the heated Silcosteel line of the instrument was regulated to <100 mL min^{-1} to avoid pressure cycling effects.

Two multiple ion detection programs were run on the PTR-MS using its accompanying Balzers Quadstar 422 software for sequencing. Each program sequence measured several m/z values during each approximate 30-s cycle, then cycled for 23 times on the bags, or 71 times on the gradient. Additionally, "background" counts were evaluated once a day by routing the sample through a heated platinum catalyst (de Gouw et al., 2003) for a complete gradient time measurement (36 min). The first program contained m/z values (dwell time in s) 21 (0.05), 25 (1), 30 (0.1), 31 (2), 32 (0.05), 33 (2), 37 (0.05), 41 (2), 42 (2), 43 (2), 45 (2), 59 (2), 61 (2), 69 (2), 71 (2), 73 (2), 81 (2), 93 (2), and 137 (2). The second program contained m/z values (dwell time in s) 21 (0.05), 25 (1), 32 (0.05), 33 (5), 37 (0.05), 45 (5), 59 (5), 69 (5), 73 (2), 81 (2), 93 (2), and 137 (2), focusing on longer counting of masses that are most commonly observed for dominant atmospheric VOC species. Monitoring of m/z 93 was changed to m/z 79 half way through the campaign. As recently reviewed by de Gouw and Warneke (2007), mass (m/z) 33, corrected for its oxygen isotope abundance, is generally assigned to methanol, while m/z 45 and 59 are assigned to acetaldehyde and acetone, respectively. Mass 69 is most often assigned to isoprene (C_5H_8), a highly reactive VOC; its first oxidation products methacrolein and methyl vinyl ketone (C_4H_6O) are observed at m/z 71. Mass 73 is commonly assigned to methyl ethyl ketone (C_4H_8O, MEK); masses 93 and 79 are almost exclusively due to atmospheric toluene (C_7H_8) and benzene (C_6H_6), used as car traffic tracers. Masses 81 and 137 are generally assigned

to monoterpene fragments ($C_6H_9^+$) and unfragmented monoterpenes ($C_{10}H_{16}$; Lee et al., 2005), commonly emitted conifer species. Lastly, masses 61 and 43 (and 41) are often associated with acetic acid and its fragments, but share at times large interferences as especially m/z 43 is a common fragment (de Gouw and Warneke,
5 2007).

Typical background count rates observed during the field study ranged from 85 for m/z 33, to less than 1 for m/z 137, and all reported mixing ratios have been adjusted for these count rates assuming complete VOC removal in the catalyst. Together with the counting statistics, they suggested detection limits of better than 0.05 ppb for all species
10 in the second program, and $\sim$0.1 ppb for the same species using the first program. These and all other quantifications were based on first principle volume mixing ratio (VMR) calculations using

$$VMR_m = (-1/k_m t \times \ln(\frac{CR_{21}/\Gamma_{21}}{CR_{21}/\Gamma_{21} + (CR_m - CR_{bg,m})/\Gamma_m}))/VMR_t \qquad (1)$$

with ion count rates CR, mass spectral transmittance ratios Γ given by the manufac-
15 turer, reaction rate constants k_m given by Zhao and Zhang (2004), a reaction time t of 11 ms, and the molecular density in the drift tube (VMR_t). Hence, mixing ratios and flux values have an estimated relative error of at least 30% mostly due to uncertainties in the ion-molecule reaction rates and the transmittance factors (Ammann et al., 2004; de Gouw and Warneke, 2007).
20 Recorded count rates were split into their subsections of measurement, and means, medians and standard deviations were calculated excluding the first and last minutes of measurements. Bag differences were calculated in ppb and converted to fluxes using the REA formula

$$F_{VOC} = \beta \times \sigma_w \times (VMR_{up} - VMR_{down}). \qquad (2)$$

25 Beta was calculated from the measured buoyancy flux and mean sonic virtual temperature during sampled up- and downdrafts by inverting Eq. (2) (Schade and Custer,

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2004; Schade and Goldstein, 2001). To correct for bag offsets, a virtual "bag flux" time series, created from a smooth spline interpolation of all bag comparison samples while taking account of times when the bags had been switched, was subtracted. Ninety five percent confidence limits around this series served as determination limits for the
5 measured fluxes. Additional quality control included the removal of periods after a new bag had been installed, measured friction velocity was smaller than $0.2\,\mathrm{m\,s^{-1}}$, or rain had influenced the measurements.

2.5 Soil-atmosphere VOC exchange measurements

Soil enclosure tests were carried out on four days during the second part of the cam-
10 paign to evaluate the deposition velocity of VOCs. A cylindrical plexiglas chamber with a diameter of 20 cm, a height of 35 cm, and two snap-in Plexiglas lids was used for this purpose (Schade and Custer, 2008[1]). It is ventilated through several access ports and aspirated by a small 12-V, high volume flow fan offset from the top lid and blowing downwards. The chamber was placed directly on flat ground. A 1.3 mm ID sampling
15 line was inserted through one of the side access ports extracting air at $<50\,\mathrm{mL\,min^{-1}}$ towards the PTR-MS. Each test cycle included (1) ambient air monitoring with the lid and fan on but the chamber lying on its side for ∼5 min, (2) placement of the chamber onto its Plexiglas bottom to measure the chamber effect for 5–10 min, and (3) place-ment of the chamber onto different soil surface locations surrounding the measurement
20 trailer for 10–15 min each. Data were analyzed following King (1999), based on work by Conrad and Seiler (1985) on carbon monoxide consumption in soils. Deposition velocity v_{dep} was calculated from

$$v_{\mathrm{dep}} = H/t \times \ln\left(\mathrm{VMR}_t - \mathrm{VMR}_{eq}/\mathrm{VMR}_o - \mathrm{VMR}_{eq}\right). \tag{3}$$

In Eq. (3), H is the height of the chamber, t is incubation time, and VMR_{eq} is the
25 concentration at the time of equilibrium. Using Eq. (3) assumes simultaneous sources (E) and sinks ($v_{\mathrm{dep}} \times \mathrm{VMR}_t$) inside a statically operated chamber, with production of zero and consumption of first order in concentration. While such behavior has been

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documented extensively for CO (King, 1999), this is not the case for VOCs. However, regarding sources we found that nearly all OVOCs monitored with this chamber showed a zero order production rate as the chamber effect. We have also previously shown that methanol emissions from a hot topsoil (Schade and Custer, 2004) were independent
5 of concentration. Regarding consumption, we follow the guideline that soil microbial uptake is generally first order in concentration, and so is time development towards Henry equilibrium.

Note that chamber operation can be viewed essentially as static (as opposed to dynamic, meaning flow-through) because the extracted flow is very small compared to
10 the chamber volume and incubation times were smaller than 15 min. In equilibrium, trace gas consumption and production are equal. Therefore, if the production rate E is assumed to equal the chamber effect, v_{dep} can also be estimated from E/VMR_{eq}. In our case, the chamber effect for most OVOCs was so significant that its equation with E seemed justified (Schade and Custer, 2008[1]).

15 ## 3 VOC concentrations and fluxes

VOC measurements were performed from 6 June to 23 June 2007. Measured methanol and other VOC mixing ratios are shown in Fig. 2a–d. Highest abundances coincided with southeasterly flows and warm temperatures, caused by typical blocking high pressure over Scandinavia in early June. A cold front passage during the night
20 of 12/13 June (DOY 163/164) caused temperatures and VOC mixing ratios to drop to typical background values (Schade and Goldstein, 2006) as a clean subarctic air mass was established. The following week brought very unstable weather conditions due to a near stationary warm front over Denmark with frequent rain events. Finally, a front connected to an Atlantic cyclone passed the site during the night of 21/22 June (DOY
25 172/173) causing another drop in VOC abundances.

More remarkable than the synoptic patterns were the diurnal cycle of monoterpenes during the early warm phase (Fig. 2d) and the simultaneous increase of several *m/z*

values concurrent with a wind direction shift on DOY 170 (Fig. 2c). Investigations the following day revealed that hay fields just outside the forest and as close as 1 km to the SE had recently been mowed leaving the hay to dry onsite. Previous laboratory and field measurements (Davison et al., 2008; Karl et al., 2001a, 2001b, 2001c, 2005; Olofsson et al., 2003; Warneke et al., 2002; de Gouw et al., 1999, 2000; Fall et al., 2001) have shown that cut-induced VOC emissions ("wound" emissions) can be substantial and are dominated by OVOCs. Observed increases at masses 33 (methanol), 45 (acetaldehyde), 59 (acetone), 69 (e.g. methyl butanal), 73 (MEK), and 81 (hexenals) together with SE wind directions are consistent with the cutting source, and confirm typical agricultural activities as significant OVOC sources in rural areas.

The former finding that onsite monoterpene abundance maximizes during the day is consistent with the recent discovery that monoterpene emissions from European beech are light-dependent (Dindorf et al., 2006). Measured monoterpene abundance was, however, much lower than reported by Gallagher and coworkers (Gallagher et al., 2000) for the same site in June 1996.

A closer look at the diurnal cycle of methanol mixing ratios revealed generally higher and invariant or slowly increasing values at night as compared to daytime. Morning bursts were observed on many days, followed by a drop later in the campaign (e.g. DOY 169 and 170). This is sharply contrasting the observations by Karl and coworkers (Karl et al., 2004, 2005), but consistent with recent laboratory measurements showing that beech leaf expansion and methanol emissions occur dominantly at night (Hüve et al., 2007), with only a moderate morning emission peak as a result of stomatal opening. The commonly observed mixing ratio drops after sunrise are likely due to dilution with air from aloft as a result of boundary layer rise. The opposite is true in the evenings before sunset, when higher mixing ratios may have been caused by ongoing emissions into a shallow surface layer (Schade and Goldstein, 2001).

Measured methanol fluxes are shown in Fig. 3. Significant emission fluxes above the canopy were observed during the whole campaign. Unfortunately, campaign start was delayed by several weeks, missing the leaf-out period in May. An analysis of the

onsite PAR measurements above the canopy and at three levels below the canopy top (19, 14, and 5 m) showed that two thirds of onsite LAI are above 19 m but any LAI increases during June 2007 at the tower itself were negligible ($<0.3\,\mathrm{m}^2\,\mathrm{m}^{-2}$). Hence, the potentially most intensive methanol emission period was likely missed. In addition, observed methanol fluxes did not follow a clear diurnal cycle on most days, and high emissions coincided with elevated temperatures only during and after the hottest day (DOY 162, 11 June 2007). Due to lack of sufficient turbulence the expected nighttime emissions were less frequently observed. However, as shown in Figure 4, median turbulent nighttime fluxes were dominantly upward while a larger number of daytime fluxes were downward or insignificantly different from neutral (Fig. 3). This appears to confirm the recently published laboratory data on beech methanol emissions by Hüve and coworkers (Hüve et al., 2007). At the end of their experiment when leaf expansion had not yet ceased, these authors recorded a daytime methanol emission rate of approximately $0.01\,\mathrm{mg\,C\,m}^{-2}\,\mathrm{h}^{-1}$, and a several times higher rate at night. Our median daytime flux of $0.08\,\mathrm{mg\,C\,m}^{-2}\,\mathrm{h}^{-1}$ for temperatures above 20°C and light levels above $500\,\mu\mathrm{mol\,m}^{-2}\,\mathrm{s}^{-1}$ PAR, is broadly consistent with this value considering the high variability in our field measurements, and potential effects from tree age and LAI in the field. However, there is insignificant evidence from our data that nighttime methanol emissions of beech may still be higher than daytime emissions at this stage of leaf development in the field.

Similar to previous studies, we also observed deposition fluxes, shown in Figs. 3 and 4. Deposition generally occurred during daytime for temperatures below 21°C. When observed, deposition was significantly ($p=0.016$) correlated with ambient mixing ratios and a robust regression to the data exceeding the determination threshold (Fig. 3) suggested a deposition velocity of $1.1\pm0.5\,\mathrm{cm\,s}^{-1}$. This is comparable to the upper limits reported by Karl and coworkers (Karl et al., 2004, 2005) for the maximum LAI region, but also bears a large uncertainty. Its significance will be discussed further in Sect. 4.

Other OVOC fluxes were generally lower than those of methanol. Both acetaldehyde

and MEK showed largely insignificant fluxes when compared to the error estimate from the bag intercomparison samples. Exceptions were observed after the wind shift on DOY 170, which we attribute to the nearby hay field mowing (Sect. 4). This was also true for acetone. Unlike acetaldehyde and MEK though, acetone fluxes were generally significant. Similar to methanol, its fluxes were bidirectional: Emissions were observed on the two warmest days (DOY 161, 162), while deposition was observed for most of the remaining period until the DOY 170 wind shift. Aggregated acetone fluxes were significantly correlated (r^2=0.55, p=0.02) with ambient temperature as in previous studies, exhibiting a temperature dependence factor of 0.04±0.01 K^{-1}, and a standard emission of 0.054 mg C m^{-2} h^{-1} (24 ng m^{-2} s^{-1}) at 30°C. This is significantly less than previously found for pine forests (Karl et al., 2005; Schade and Goldstein, 2001; Janson et al., 1999), but comparable to Norway spruce needle measurements (Grabmer et al., 2006; Janson and de Serves, 2001). A compensation-point equivalent temperature of ~20°C resulted from the temperature-dependence, but a correlation of deposition fluxes with ambient mixing ratios of acetone was not found. Acetone abundance was generally below 1 ppb under these conditions, which suggests that its deposition depends on more factors than just abundance.

Monoterpene fluxes from European beech have recently been studied by Holzke et al. (2006) and Dindorf et al. (2006) on trees in northern Germany. Though emissions were previously thought to be very small, these authors found substantial, light-driven emissions and a high variability of standard emission factors (at 1000 μmol m^{-2} s^{-1} PAR and 30°C). Our own measurements, shown in Fig. 5, confirm the diurnal cycle of emissions with maximum values on the warmest, cloud-free days of the campaign. Included is a model output assuming the light- and temperature dependence given by Holzke et al. (2006), a three-layer canopy top with LAI equal to 1 m^{-2} m^{-2} each, uniform canopy temperatures, and an ellipsoidal leaf angle distribution with a higher portion of horizontally oriented leaves. Model runs that matched the measurements within a factor of two resulted in standard emission factors ranging from 0.10 to 0.37 mg C m^{-2} h^{-1} (0.2 to 0.8 nmol m^{-2} s^{-1}), comparing well with typical values given

by Holzke et al. (2006). Hence, despite the limited fetch conditions for beech at this site (Dellwik and Jensen, 2005), our measurements are highly consistent with previous results from enclosure measurements on trees that grew in a similar climate. Both these and our results are, however, in obvious disagreement with the results of Gallagher and coworkers (Gallagher et al., 2000). These authors found five to ten times larger monoterpene mixing ratios and fluxes at the Soroe site in 1996. In addition, their fluxes were dominated by Δ-3-carene, β-pinene, α-pinene, and limonene, which are typical pine forest monoterpenes, while beech emissions in Germany were always dominated by sabinene (Dindorf et al., 2006; Holzke et al., 2006). Though Gallagher and coworkers also found sabinene, we speculate that their setup at 31 m height was strongly influenced by nearby emissions from the conifer patches inside the forest, approximately 100–400 m to the SE, which was the dominant wind direction during their study days.

4 Canopy gradients

To compare in-canopy with above canopy fluxes, the storage term was calculated from the gradient measurements. Similarly to the example for methanol, shown in Fig. 4, storage term fluxes for all other VOCs were found to be very small. Significant contributions occasionally occurred at nighttime, particularly for methanol in the early morning hours up to sunrise. Thus, contrary to results from Karl and coworkers for a pine forest ecosystem (Karl et al., 2005), only small effects of in-canopy fluxes were observed in this European beech forest.

The measured within (22 m) to sub canopy (5 m) gradients generally showed decreasing VOC mixing ratios towards the ground. This was most prominent for methanol and the monoterpenes emitted in the canopy. Figure 6 shows interpolated mean methanol mixing ratios as a function of height and time of day: Mixing ratios were higher at night with a maximum in the early morning hours, and displayed nighttime vertical gradients of up to 0.04 ppb m^{-1}, while daytime mixing ratios were flat. This picture is

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consistent with canopy emissions occurring dominantly at night as discussed above, with the additional effect of reduced turbulence. The equivalent graph for monoterpenes, Fig. 7, shows the opposite diurnal development: maximum mixing ratios and vertical gradients in the early afternoon due to light and temperature-driven emissions in the canopy. Hence, in both these cases, our gradient measurements support the conclusions from the previous section.

The gradient measurements cannot, unfortunately, support or reject the above estimated deposition velocity for methanol of approximately $1\,cm\,s^{-1}$. Even for a boundary layer depth of only 100 m, ambient mixing ratios would only change by 3.6% per hour, which could not be resolved with our measurements. Although ambient mixing ratios generally dropped in the morning by up to 20% per hour during the latter part of the campaign (Fig. 6), this trend was observed for nearly all VOCs measured. As it was not observed during the early June warm period, we interpret the drop as down-mixing of clean marine background air from the residual layer under northerly wind directions. This is supported by the fact that both sensible heat flux and friction velocity maximized around noon, the same time mixing ratios started to increase again.

Aside from the species emitted by the beech canopy, the gradient measurements of other VOC species presented a less clear picture. For instance, we observed very small gradients (<0.2 ppb; noise level from toluene gradient: <0.03 ppb) for acetone and acetaldehyde. Nevertheless, especially the 5–14 m gradients increased significantly after a heavy rain on 16 June, for both these compounds and methanol. Although there was a generally positive covariance between sup-canopy friction velocity and sub-canopy gradient magnitude (data not shown), the observation that the 5–14 m gradients were weak the nights before the rain and large the nights thereafter, suggest a significant influence on the gradient as a result of soil deposition. As we will show in the next section, the soil at this site was indeed a sink for OVOCs in the second half of June. However, the unusually low soil moisture at this time of year (<20%) (Dellwik, 2003; Pilegaard, 2001) due to a record warm spring and a lack of rain since mid May, combined with the observed effect of soil moisture on soil respiration at this site

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(Janssens and Pilegaard, 2003) suggests that soil microbial activity may have been low before the rain, wherefore soil deposition of OVOCs may have been so as well.

A second major change to the measured gradients was observed after the wind direction shift on DOY 170 that brought higher OVOC mixing ratios to the site. Particularly the marked increase in acetaldehyde and acetone (Fig. 2) was correlated with strong gradients towards the surface, depicted in Fig. 8. As the source of the drastic mixing ratio increase was right outside the forest, there is a dynamical explanation for this relationship, namely the horizontal advection over the forest alongside a limited vertical exchange due to the forest's canopy. As source strength decreased, so did the apparent gradient. However, as part of the gradient was retained, even during daytime, after mixing ratios had returned to previous conditions, a deposition flux to the onsite soil seems likely. The surprising finding is that there did not appear to be a compensation point for this uptake (Fig. 8). On the other hand, the same analysis for methanol, which was not strongly affected by the DOY 170 wind shift, suggested a compensation point between 1 and 1.5 ppb (data not shown), further discussed below.

5   Soil chamber flux measurements

During the last four mornings of the campaign, the gradient sampling line to the PTR-MS was moved to the flux chamber for a series of tests within an approximate 5 m distance from the instrument trailer. Therefore the results of these tests should be viewed with some caution because the soil in this area may have been disturbed by foot traffic. Nevertheless, our results for this soil type were consistent from one day to the next. Table 1 summarizes observed deposition velocities under different manipulations. Soil temperature, measured by the main system several meters away was between 13 and 14°C during all our tests. Although soil moisture was not measured at this time, it can be inferred from previous relations between soil moisture and rain (Pilegaard et al., 2001) to have increased from ∼25% (DOY 171) to ∼31% (DOY 174).

Results were pooled due to the small amount of samples, with a standard deviation

between samples similar to that of the individual incubations as evaluated from linear least squares fits to Eq. (3). Nearly all deposition velocities were $<0.1\,\mathrm{cm\,s}^{-1}$, so it comes to no surprise that the gradient measurements did not resolve a stronger gradient towards the surface in this environment. Nonetheless, some general tendencies were observed: the beech litter heap showed emissions of *m/z* 61, 69, and 73, and higher deposition rates for acetone. The mineral soil from which the litter had been removed and the tree stump with moss showed slightly higher deposition fluxes for methanol. Mass 61 showed both uptake and emission, and mass 69 was nearly always emitted, at particularly large rates from the litter heap, similar to observations by Warneke et al. (1999).

Methanol was always found to be produced by the chamber and taken up in subsequent soil incubations. The ambient mixing ratios during these were generally close to 2 ppb (Fig. 2) with a low of 1.5 ppb on the last day (DOY 174). However, equilibrium mixing ratios with the soil under the chamber continuously dropped from 1.5 ppb on DOY 171 to 0.5 ppb on DOY 174, seemingly parallel to increasing soil moisture as a result of overnight rains (Fig. 2). Therefore, it appears that deposition velocity was limited by diffusion into the soil, while the compensation point may have been driven by the soil's microbial activity, which is strongly dependent on soil moisture at the soil temperatures we measured (Janssens and Pilegaard, 2003). The alternative would be Henry equilibrium. However, as the amount of methanol deposited to the soil during the four measurement days was more than doubled while soil water was not, and equilibrium levels were maintained despite the chamber's own emissions, Henry equilibrium was likely not solely responsible for the deposition flux.

6 Conclusions

Our canopy flux and gradient measurements confirmed recent laboratory and field enclosure measurements on methanol and monoterpene emissions, respectively, from European beech. Methanol appears to be emitted dominantly at night, while

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monoterpenes are emitted at daytime as their production in *Fagus sylvatica* leaves is light dependent. As a result canopy mixing ratios were highest at night for methanol, and during daytime for the monoterpenes. Methanol deposition to the canopy was observed as well, particularly when its ambient mixing ratios were high. However, our
5 data set is too small to conclude that the calculated deposition velocity from this relationship is representative for this or similar forests. Our result of $\sim 1\,\mathrm{cm\,s^{-1}}$ was within the range of previously determined values. If methanol dry deposition to canopies were occurring at that velocity ubiquitously, this process would be a more important sink then previously thought. On the other hand, our reported fluxes and previously published
10 canopy and enclosure based methanol fluxes likely already incorporate a non-stomatal deposition, realizing that reported fluxes are usually net fluxes. Thus, budget models cannot constrain the individual flux terms but rather the net fluxes (e.g. Jacob et al., 2005). More fumigation experiments will be needed to determine the possibly different roles of gross emission and deposition, as well as possible compensation points.

15   The other VOC species we focused on in this article include acetaldehyde, acetone, and MEK. Neither of them showed a clear-cut emission or deposition pattern. The measured vertical distributions confirmed this via the absence of strong gradients for these OVOCs. Similarly, soil exchange fluxes were highly variable, occasionally showing emissions. For acetone, despite a relationship with ambient temperatures, its
20 biosphere-atmosphere exchange pattern remains elusive. In this beech ecosystem, it was dominantly emitted above $\sim 20°C$, and deposited below. In other ecosystems acetone was still emitted at much lower temperature (Janson and de Serves, 2001; Schade and Goldstein, 2001), wherefore temperature alone should not be used to extrapolate biospheric acetone emissions.

25   In general, deposition to the soil surface was observed for all OVOCs measured but at significantly lower rates then previously found, and consistent with the absence of strong gradients below the canopy. We also found no single ambient mixing ratio compensation point with the soil for any of the OVOCs. Rather it appeared that increasing soil moisture with its influence on soil microbial activity may have affected the mixing

ratio equilibrium. Future measurements should therefore include fumigation tests and soil respiration measurements.

Our results confirm that the biosphere-atmosphere exchange of oxygenated VOCs is highly complex. While the role of soils is likely that of a small, microbiologically driven sink, green plants act as overall net sources, at least for methanol. However, though the production mechanism for methanol (and other OVOCs) in leaves may be the same throughout the plant kingdom, its diurnal and seasonal patterns alongside differing plant physiologies can strongly affect emissions to the atmosphere. At the same time oxygenated VOC deposition occurs, possibly down both stomatal and non-stomatal pathways. As canopy flux measurements result only in net fluxes to the atmosphere, controlled enclosure studies alongside carefully devised field measurements appear necessary to shed more light on these complex carbon exchanges.

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Table 1. Deposition velocities to the onsite soil in $\mathrm{cm\,s^{-1}}$. Soil temperatures were between 13 and 14°C during all incubations.

mass (VOC)	soil (N=7–13)[1]	beech litter[2]	mineral soil[2]	stump with moss
m/z 33 (methanol)	0.06±0.03	0.07	0.09	0.14
m/z 45 (acetaldehyde)	0.03±0.02	0	0	0.03
m/z 59 (acetone)	0.03±0.03	0.13	0.07	NA[3]
m/z 61 (acetic acid)	0.02±0.03	NA	NA	0.05
m/z 73 (MEK)	0.05±0.03	NA	NA	0.05

[1] error=1 sd; samples include incubations of soil only and soil with small plants
[2] litter was completely removed from a second soil spot and piled; the chamber was then moved to this second spot for another incubation test ("mineral soil")
[3] NA=not applicable (either due to emission or a very low regression coefficient)
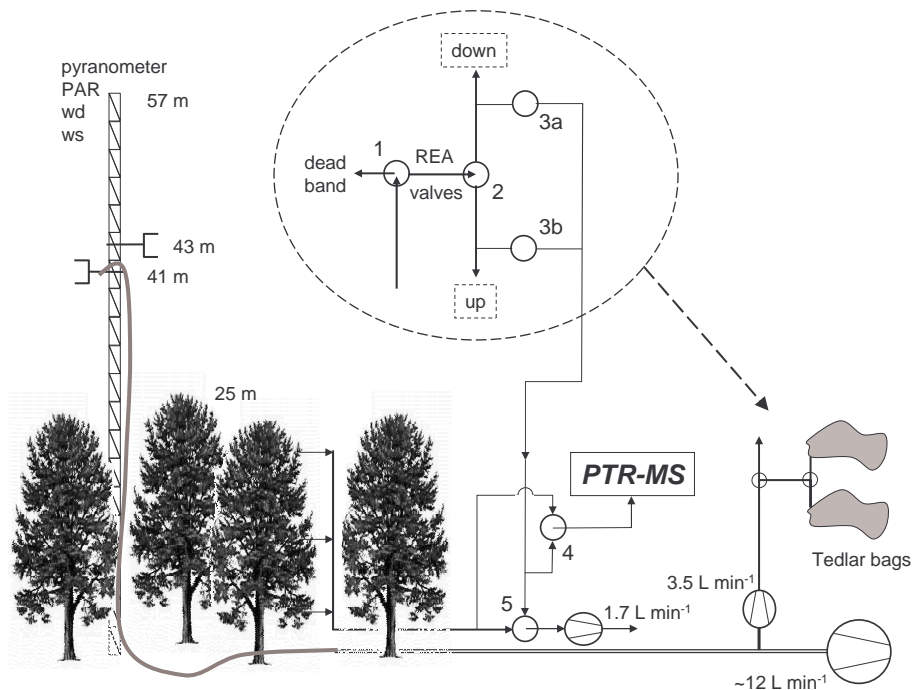
Fig. 1. Experimental setup at the Soroe field site (not to scale). Inset magnifies REA setup for the bag sampling. Circles with numbers mark the high speed PTFE valves. Valves 1 and 2 decided between sampling or not, and into which bag, respectively. Valves 3a and 3b are used to access the bag samples consecutively, and Valve 4 allowed the PTR-MS to switch between the bag samples and the gradient.
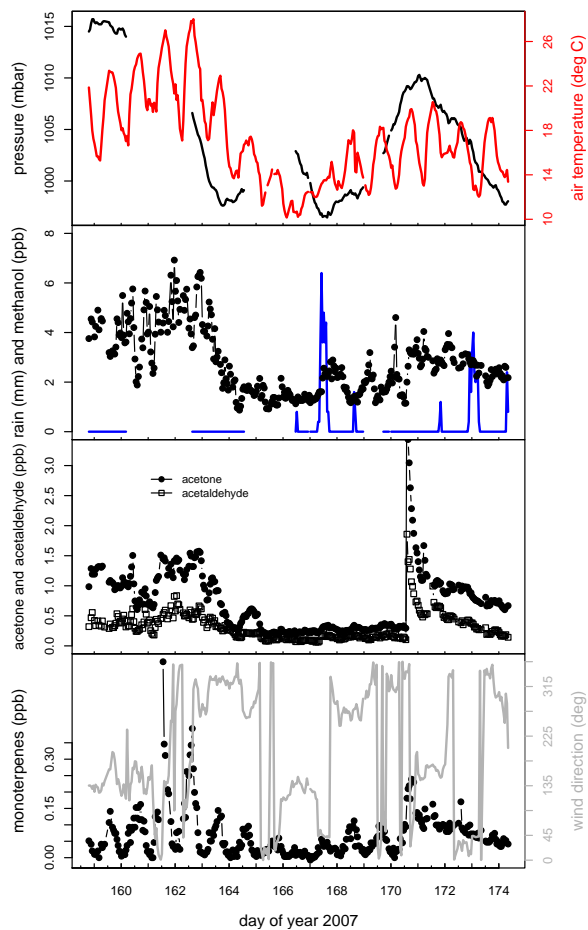
Fig. 2. Time series of meteorological parameters and trace gas mixing ratios measured in the canopy space.

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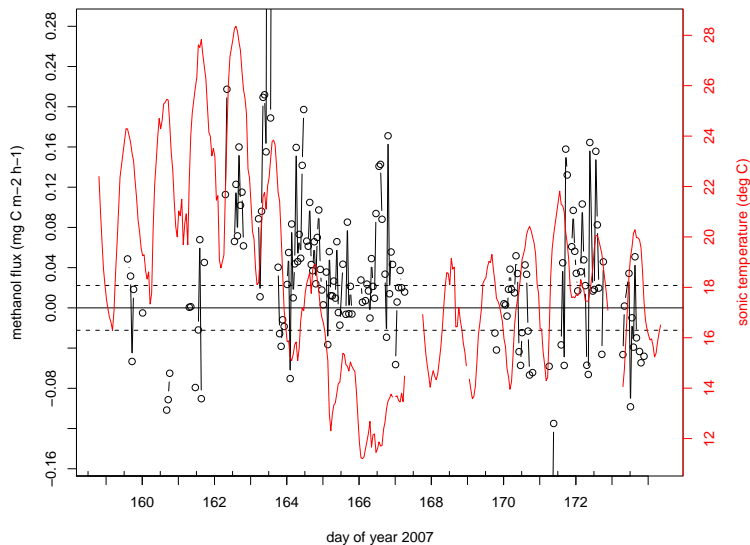
Fig. 3. Time series of sonic virtual temperature and calculated half-hourly methanol fluxes. Dotted line marks 95% confidence level based on the bag intercomparison samples.
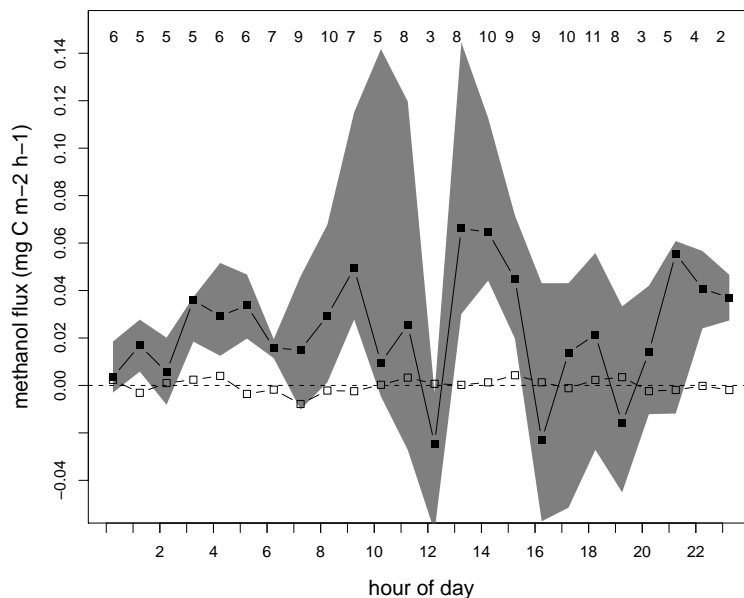
Fig. 4. Aggregated median (closed squares) and interquartile range (gray swath) of diurnal methanol fluxes. Series of numbers on top denotes the available samples per hour; open squares depict median diurnal cycle of calculated storage flux.
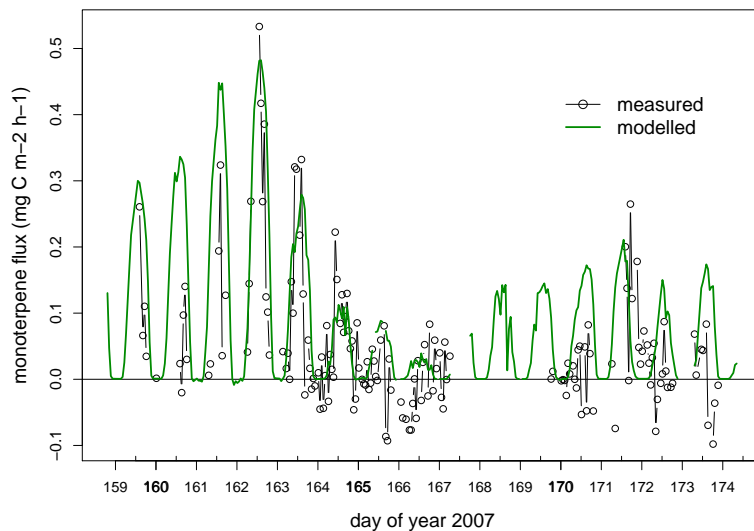
Fig. 5. Measured and modeled total monoterpene flux, using a standard emission of $0.2\,\text{mg C m}^{-2}\,\text{h}^{-1}$. Gaps in model data are due to unavailability of meteorological data.
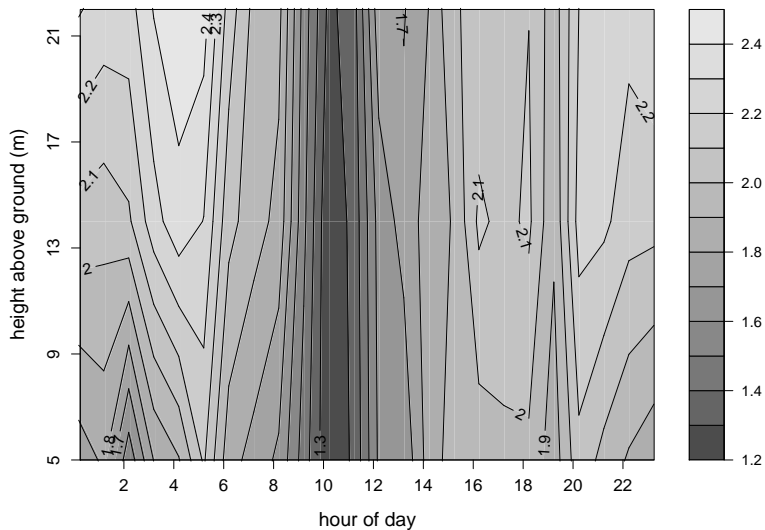
Fig. 6. Interpolated mean methanol mixing ratios as a function of time of day and height above ground inside the beech forest. Only measurements after DOY 164 are shown to avoid averaging skewed distributions.
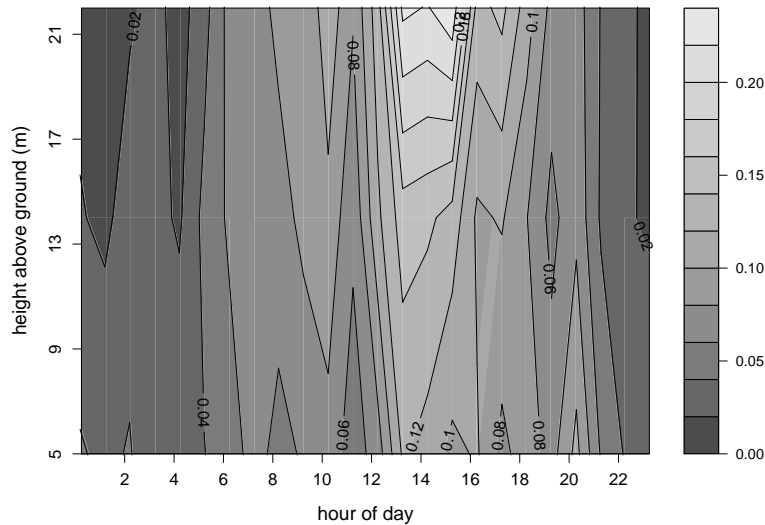
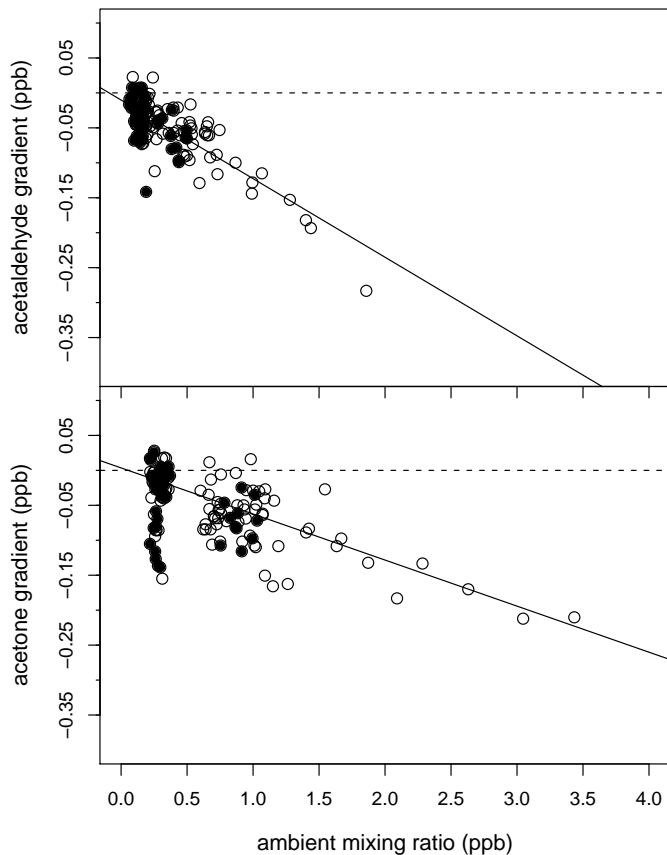**Fig. 7.** Same as Fig. 6 but for monoterpenes before DOY 165.

Fig. 8. Relationship between acetaldehyde (top) and acetone (bottom) mixing ratios and their respective below canopy gradients after the 16 June rain event. Open circles depict all data, closed circles only data after DOY 172, when mixing ratios had dropped back to "normal" after the wind shift two days earlier.