

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

Gunnar W. Schade · Sheena J. Solomon ·
Ebba Dellwik · Kim Pilegaard ·
Annette Ladstätter-Weissenmayer

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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. Fluxes of methanol were bidirectional: Emission occurred during both day and night with highest fluxes ($0.2 \text{ mg C m}^{-2} \text{ h}^{-1}$) during a warm period; deposition occurred dominantly at daytime. Confirming previous branch-level measurements on beech, the forest's monoterpene emissions ($0\text{--}0.5 \text{ mg C m}^{-2} \text{ h}^{-1}$), and in-canopy mixing ratios showed a diurnal cycle consistent with light-dependent emissions; a result contrasting temperature-only driven emissions of most conifer species. Also emitted was

acetone, but only at ambient temperatures exceeding 20°C . Slow deposition dominated at lower temperatures. Our in-canopy gradient measurements contrast with 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 (OVOCs). Instead, their gradients were flat and only small deposition velocities ($<0.2 \text{ cm s}^{-1}$) were observed to the onsite soil. However, as methanol soil uptake was consistent and possibly related to soil moisture, more measurements are needed to evaluate its soil sink strength. In turn, as canopy scale fluxes are net fluxes with stomatal emissions from photosynthesizing leaves potentially affecting non-stomatal oxygenated VOC uptake, only independent, controlled laboratory experiments may be successful in separating gross fluxes.

Keywords Beech forest · VOCs · Flux · PTR-MS · Deposition

G. W. Schade (✉)
Department of Atmospheric Sciences,
Texas A&M University, 3150 TAMU,
College Station, TX 77843, USA
e-mail: schade@ariel.met.tamu.edu

G. W. Schade · S. J. Solomon ·
A. Ladstätter-Weissenmayer
Institute of Environmental Physics, University of Bremen,
Otto-Hahn-Allee 1, 28359 Bremen, Germany

E. Dellwik · K. Pilegaard
Biosystems Department, Risø National Laboratory
for Sustainable Energy, Technical University
of Denmark—DTU, PO Box 49, 4000 Roskilde, Denmark

Introduction

Since the mid-1990s 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 et al. 2006) through their abundance in rural and remote areas of the troposphere, including

the free troposphere (Dufour et al. 2007; Fall et al. 2001; Karl et al. 2003; Lewis et al. 2005; Riemer et al. 1998; Schade and Goldstein 2001, 2006; Singh et al. 2000, 2004).

Based on recent budget estimates (Galbally and Kirstine 2002; Jacob et al. 2002, 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. 2001b, c, Karl et al. 2002, 2003; Kirstine et al. 1998; Schade and Goldstein 2001; Spirig et al. 2005; Warneke et al. 1999, 2002). However, the magnitudes of these sources as a function of ecosystem type, as well as the dependences of emissions on physical and biological drivers remain subjects 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 1 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, stomatal opening, and temperature (Brunner et al. 2007; Custer and Schade 2007; Folkers et al. 2008; Hüve et al. 2007; Karl et al. 2003, 2004, 2005a; 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. Lastly, Jacob et al. (2005) inferred both wet and dry deposition (corresponding to 0.2 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 (Brunner et al. 2007; Custer and Schade 2007; Karl et al. 2004, 2005a; 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 ± 0.14 cm s⁻¹ for methanol, a similar value for acetaldehyde, and a slightly lower value of 0.14 cm s⁻¹ for acetone. Calculated deposition velocities ranged up to 1 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*), Karl et al. (2005a) 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. Similar to their rain forest study, Karl and coworkers (Karl et al. 2005a) found typical deposition velocities of 0.3 cm s⁻¹ for methanol and acetaldehyde (max 1 cm s⁻¹ for methanol) in this pine forest, and 0.1 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 cm s⁻¹) with the exception of MEK (Karl et al. 2005a).

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 investigated 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 cm s⁻¹ for 10–20% 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 cm s⁻¹. In both cases simultaneous acetone

deposition velocity was a factor of 2–5 lower (Schade and Custer, in prep.).

To address both the plant source and potential in- and sub-canopy sinks for a common ecosystem in temperate, central Europe, 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 (“[Measurement setup](#)” section) as well as concentration gradients from inside the beech canopy towards the ground. Springtime was chosen with the expectation of observing larger methanol fluxes as a result of leaf development (“[VOC concentrations and fluxes](#)” section). Above to below canopy gradients were measured to address the distribution of sources and sinks within the forest (“[Canopy gradients](#)” section), and soil chamber tests were run to evaluate the soil sink strength (“[Soil chamber flux measurements](#)” section).

Measurement setup

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 area (Pilegaard et al. 2001, 2003). The groves 100–300 m (~4 ha), and 500–750 m (~3 ha) SE of the site, and 250–400 m SW of the site (~3 ha) are most relevant for flux interpretation. The forest soil is a typical Cambisol (sandy loam to loam, O + A horizon 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 m² 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).

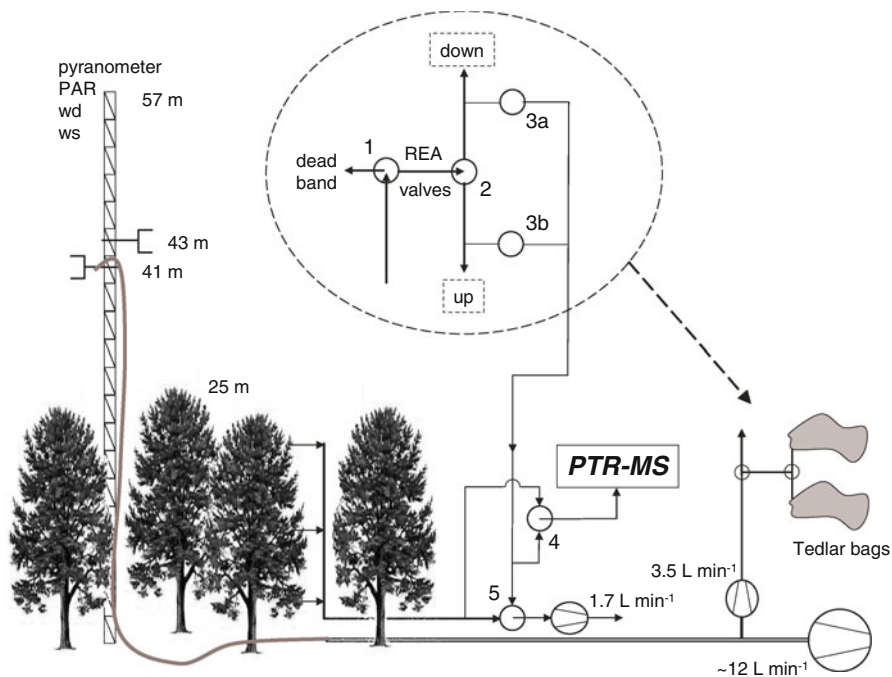
At the site itself a lattice mast extends to more than twice the average beech canopy height (24–25 m) and carries all the micrometeorological flux instrumentation. Next to it is a scaffold walk-up tower with several platforms (3 m × 3 m), which extends into the canopy up to 24 m. An extensive set of instruments monitors above canopy turbulence, and energy and CO₂ fluxes. They are supplemented by below canopy measurements of radiation and temperature, and soil energy and trace gas fluxes (Ambus et al. 2001; Janssens and Pilegaard 2003; Pihlatie et al. 2005; Pilegaard et al. 2001, 2003, 2006). 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 and 1.5 km to the WSW and WNW, respectively.

Sampling setup

A schematic of the setup is shown in Fig. 1. Ambient air sampling was conducted from 4 heights: 41, 22, 14, 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 (described 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 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

Fig. 1 Experimental setup at the Soroë 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



trailer. All three gradient inlets terminated in PTFE normally closed isolation valves (BiochemValve Inc. model 075T, not shown in Fig. 1). Sample air from the gradient was acquired with another Teflon-coated membrane pump (same KNF model N 86 KTDC B) restricted to 1.7 l min^{-1} flow.

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 out of the REA reservoirs or from the gradient sampling line and pump it towards the methanalyzer. A small subsample ($50\text{--}100 \text{ ml min}^{-1}$) 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 and $<10 \text{ s}$ 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 4 Hz on the PTR-MS instrument. The acetone peak shape was Gaussian and unaffected by the amount of acetone in

the balloon. Assuming an instantaneous release of acetone during the balloon burst, the observed peak broadening served as a gauge of low pass filtering by the transfer line.

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 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. We estimated from the balloon burst experiments and from daily flow measurements in the main line that the entered lag times were uncertain to $\pm 1 \text{ s}$ ($<10\%$), which can lead to a possible underestimation of the calculated β -factor of up to 20% (Schade and Goldstein 2001). For this particular setup, we chose the discrimination factor b 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 out of a filled bag at 1.75 l min^{-1} , which led to a chosen b ranging from 0.8 to 0.9 for filling the bags at 3.5 l min^{-1} 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 as on tower gradient), through which the reservoirs were emptied directly after the sampling period from 0 to 30 min into the hour.

The CR23Xs 8 control ports were programmed to switch all PTFE valves such that each hour was divided into five 12-min segments: The downdraft reservoir was measured from 30 to 42 min, followed by the updraft reservoir from 42 to 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 deadband 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 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 confirmed by switching the bags; they still showed a slight bias (<0.1 ppb offset on a scatter plot) 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 $81 + 137$. 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 (10–30%) 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, similar to previous interpretations (Beauchamp et al. 2008; Wang et al. 1996). Similar to our observation, the recent work by Beauchamp and coworkers (Beauchamp et al. 2008) found that short-term storage ($<1 \text{ h}$) did not seem to have large effects. However they observed the importance of VOC bag-to-ambient gradients, and also the temperature effect. While the ventilation-driven, rapid temperature 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. Nevertheless, as the bag effect was seemingly not different between the bags and we found no other measured variable that correlated with the effect, we treated the bag effect as stochastic. We then accounted for up- versus down-bag offsets using the comparison measurements, and report the calculated fluxes from the REA sampling system.

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 Ionicon 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 to 2.6×10^6 cps during the study with a typically $<5\%$ contribution from the monitored first water cluster at

m/z 37. Inflow to the heated Silcosteel line of the instrument was regulated to $<100 \text{ ml min}^{-1}$ 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 to twice 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 (cations; dwell time in s) 21 (0.05),

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 2007).

Typical background count rates observed during the field study ranged from 100 cps for m/z 33, to less than 1 cps for m/z 137, and all reported mixing ratios have been adjusted for these count rates assuming complete oxidative VOC removal in the catalyst. Together with the counting statistics, they suggested detection limits of 0.1 ppb or better for all species except methanol (0.3 ppb). These and all other quantifications were based on first principle volume mixing ratio (VMR) calculations using

$$VMR_m = \left(1/k_{mt} \times \ln \left(\frac{CR_{21}/\Gamma_{21}}{CR_{21}/\Gamma_{21} + (CR_m - CR_{bg,m})/\Gamma_m} \right) \right) / VMR_t \quad (1)$$

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 (cations; 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 from many tree species. Lastly, masses 61

with ion count rates CR (in cps), mass spectral transmittance ratios Γ given by the manufacturer, reaction rate constants k_m given by Zhao and Zhang (2004), a reaction time t of 0.11 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).

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

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

Beta was calculated from the measured buoyancy flux and mean sonic virtual temperature during sampled up- and downdrafts by inverting Eq. 2 (Katul et al. 1996; Schade and Custer 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 together with uncertainties of 10% each in β and σ_w served to estimate a determination limit for the measured fluxes. Additional quality control included the removal of periods when a bag was obviously leaky and after a new bag had been installed, measured friction velocity was smaller than 0.2 m s^{-1} , or rain had influenced the measurements. Additional uncertainty arises from possible low pass filtering in the tubing and from possible sample carry-over in a reservoir. Due to the strong similarity of our setup with that of Karl and coworkers (Karl et al. 2002), we can estimate from their results (Fig. 6 in (Karl et al. 2002)) that the former effect, namely flux losses in our sampling line ($Re > 5,000$) due to dampening of high frequency concentration fluctuations, was likely always $<10\%$. This was confirmed by using the shape of the acetone spikes from the balloon bursts to create a low pass filter function, subsequently used to degrade the sonic temperature signal. Buoyancy fluxes calculated using the degraded temperature time series were always within 10% of fluxes using the original signal. The latter effect, namely that part of an air sample from the previous half hour remained in the bag when a new sample was collected, would act as a low pass filter on the calculated flux timeline. Again, the effect is likely very small, because the setup was such that each bag was commonly emptied before the completion of its 12-min period, and when not, the remaining sample volume was very small ($\sim 1 \text{ l}$, i.e. $<5\%$ of total), thereby not affecting the next sample significantly.

Soil-atmosphere VOC exchange measurements

Soil enclosure tests were carried out on 4 days during the second part of the campaign to evaluate the soil exchange behavior of VOCs. A cylindrical plexiglass 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, in prep.). It has several access ports and is 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 line was inserted through one of the side access ports extracting air at $<50 \text{ ml min}^{-1}$ 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 $\sim 5 \text{ min}$, (2) placement of the chamber onto its Plexiglas bottom to measure the chamber effect for 5–10 min, and (3) placement of the chamber onto different soil surface locations surrounding the measurement trailer for 10–15 min each. Data were analyzed following King (1999), based on work by Conrad and Seiler (Conrad and Seiler 1985) on carbon monoxide consumption in soils. Deposition velocity v_{dep} was calculated from

$$v_{dep} = \frac{H}{t} \times \ln \left(\frac{VMR_t - VMR_{eq}}{VMR_o - VMR_{eq}} \right) \quad (3)$$

In Eq. 3, H is the height of the chamber, t is incubation time, and VMR_{eq} is the concentration at the time of equilibrium. Using Eq. 3 assumes simultaneous sources (E) and sinks ($v_{dep} \times VMR_t$) in the soil, with production of zero and consumption of first order in concentration. While such behavior has been documented extensively for CO (King 1999), there is no such documentation 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 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 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, in prep.).

VOC concentrations and fluxes

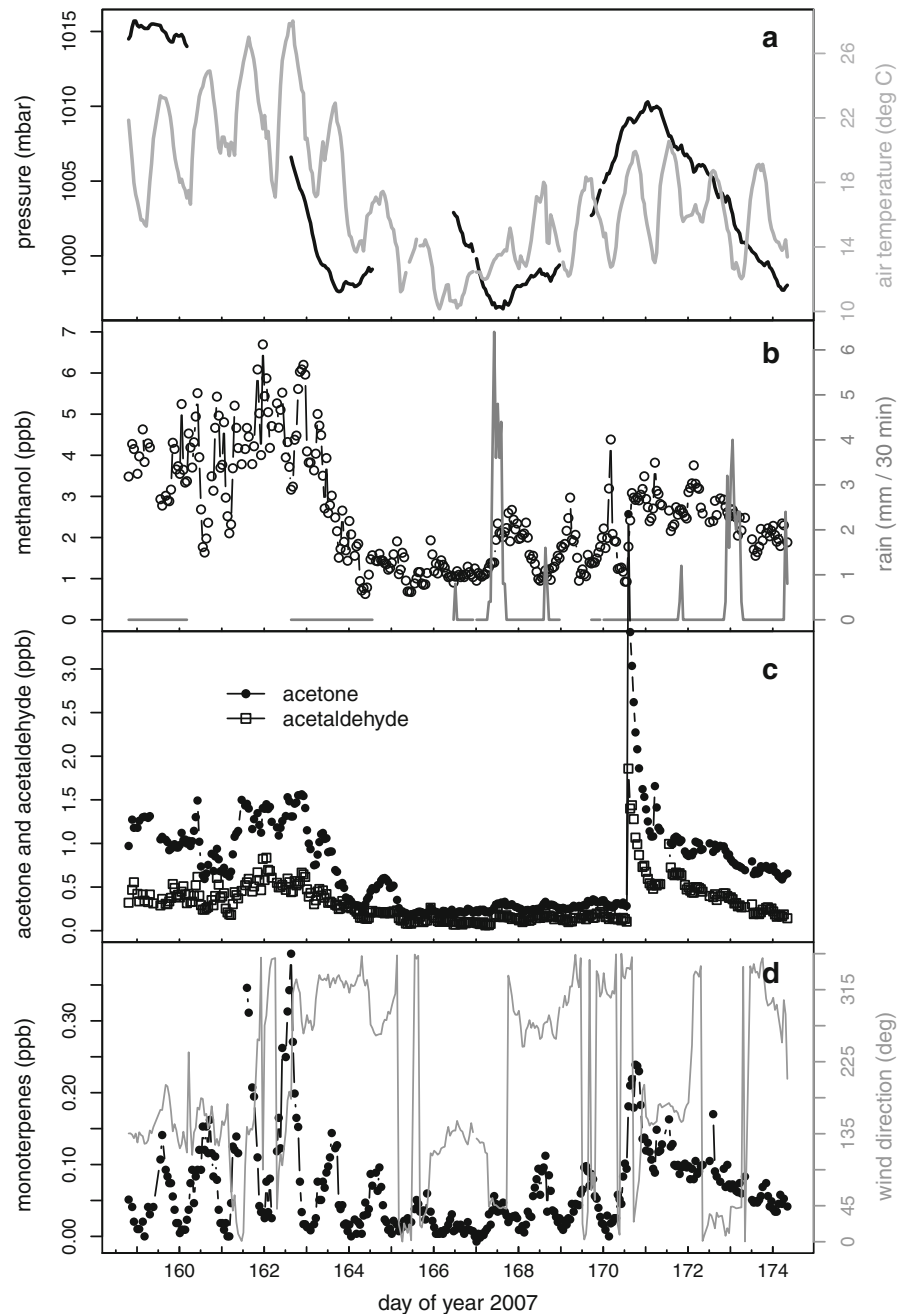
VOC measurements were performed from 6 June to 23 June 2007. Meteorological data and measured methanol and other VOC mixing ratios are shown in

Fig. 2a–d. Highest abundances coincided with south-easterly flows and warm temperatures, caused by typical blocking high pressure over Scandinavia in early June. A cold front passage during the night of DOY 163/164 (June 12/13) 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 DOY 172/173 (21/22 June) causing another drop in VOC abundances.

More remarkable than the synoptic patterns were the diurnal cycle of monoterpenes during the early

Fig. 2 Time series of meteorological parameters and trace gas mixing ratios measured in the canopy space



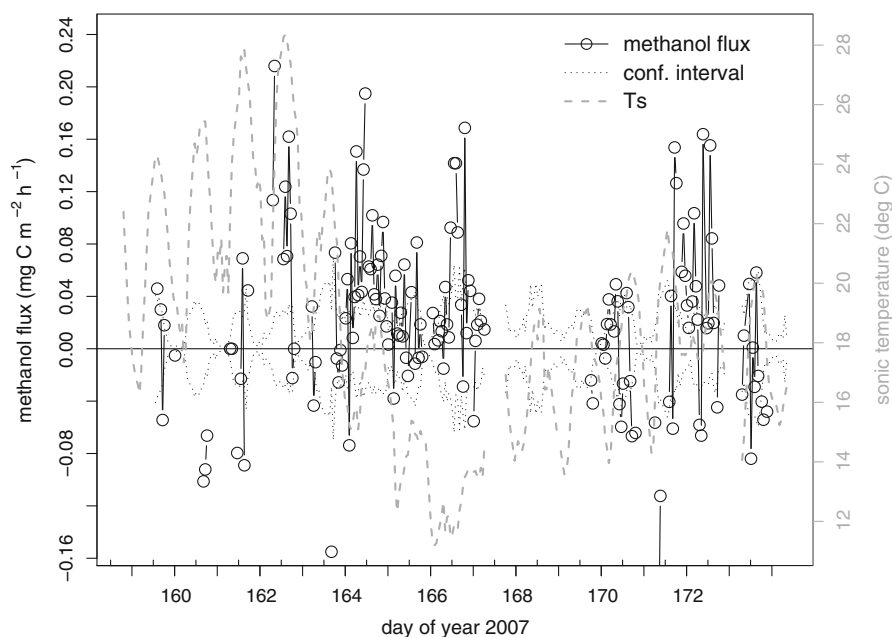
warm phase (Fig. 2d) and the simultaneous increase of several m/z values concurrent with a wind direction shift on DOY 170 (Fig. 2c). Investigations the following day revealed that hay fields just outside the forest and as close as 1 km to the SE of the site had recently been mowed leaving the hay to dry onsite. Previous laboratory and field measurements (Davison et al. 2008; de Gouw et al. 1999, 2000; Fall et al. 2001; Karl et al. 2001a, b, c; Karl et al. 2005a, b; Olofsson et al. 2003; Warneke et al. 2002) 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. methylbutanal), 73 (MEK), and 81 (here: hexenals (Fall et al. 1999)) 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, namely that onsite monoterpene abundance maximizes during the day, is consistent with recent gas-chromatographic work showing that monoterpene emissions from European beech, dominated by sabinene, are light-dependent (Dindorf et al. 2006; Schuh et al. 1997). 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 several days, followed by a drop later in the campaign (e.g. DOY 169 and 170). This is contrasting to the observations by Karl and coworkers (Karl et al. 2004, 2005a). 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 ($<0.3 \text{ m}^2 \text{ m}^{-2}$). Hence, the potentially most intensive methanol emission period was likely missed. In addition, observed methanol fluxes did not follow a clear diurnal cycle on many days, with the exception of the period of and

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



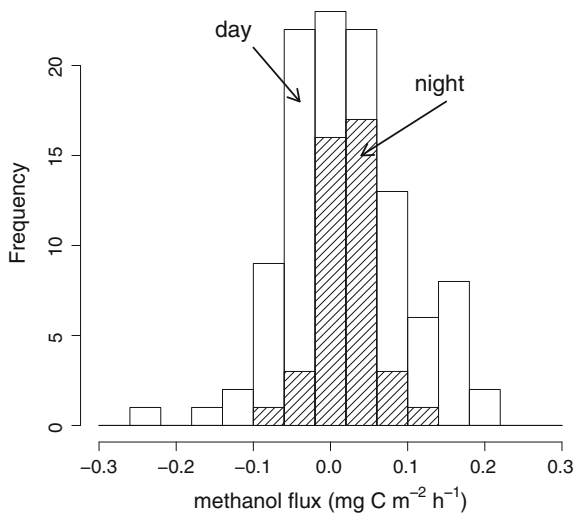


Fig. 4 Histograms of daytime and nighttime methanol fluxes. *Central bar* captures nearly all non-significant fluxes ($\pm 0.02 \text{ mg C m}^{-2} \text{ h}^{-1}$)

following the warmest day (DOY 162, 11 June), on which the highest fluxes occurred in the early afternoon. Also during this period, elevated morning emissions (08:00 h standard time) were more common. Figure 4 shows the distribution of daytime and nighttime methanol fluxes. The daytime flux distribution displayed a maximum near zero with tails at both the emission and deposition ends. Nighttime fluxes were fewer due to the turbulence criterion, but displayed a mean emission flux and a near-normal distribution (median = mean). Median 10:00 to 16:00 h methanol fluxes before DOY 167 (16 June) were $0.06 \text{ mg C m}^{-2} \text{ h}^{-1}$, but dropped to $<0.01 \text{ mg C m}^{-2} \text{ h}^{-1}$ after DOY 167. Median midnight to 06:00 h methanol fluxes for the whole period were $0.02 \text{ mg C m}^{-2} \text{ h}^{-1}$ and remained unchanged. In addition, only 4 out of 33 measurements during these nighttime hours were towards the canopy suggesting a small but consistent late night source.

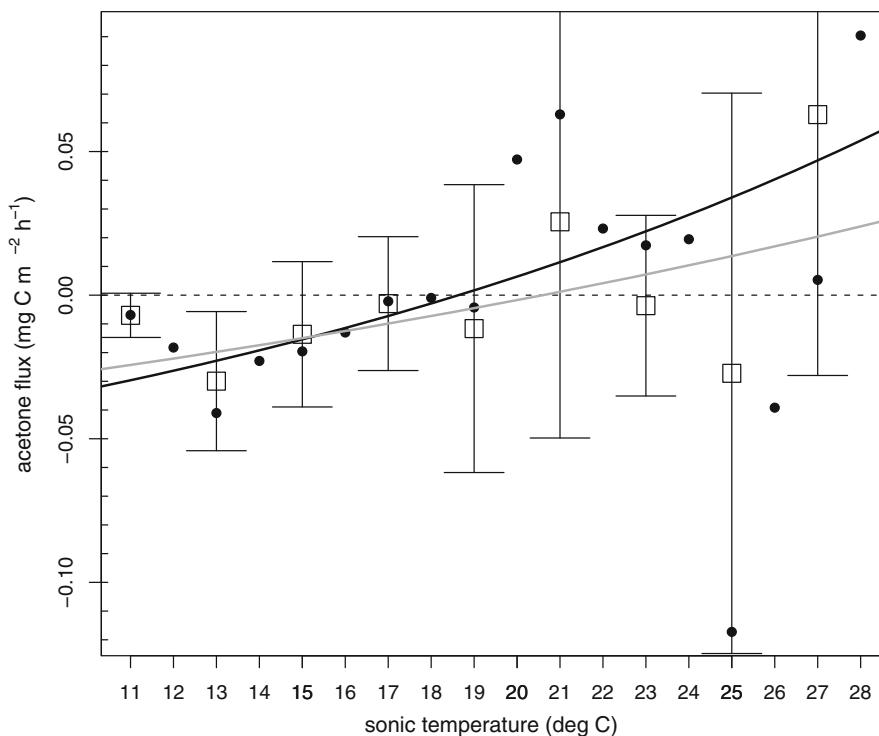
We can compare some aspects of our results to the controlled measurements on beech seedlings by Hüve et al. (2007). At the end of their experiment when leaf expansion had not yet ceased, these authors recorded a daytime methanol emission rate of approximately $0.22 \text{ nmol m}^{-2} \text{ s}^{-1}$, and a several times higher rate at night. Our median, LAI-adjusted 10:00 to 16:00 h flux of approximately $0.3 \text{ nmol m}^{-2} \text{ s}^{-1}$ for the first period is surprisingly similar to the seedling value. However, our median nighttime fluxes as well as the

second period daytime fluxes were three to six times lower. Possible explanations may lie in the age of the beech trees, particularly the lack of stomatal control in the beech seedlings versus the strong stomatal control of the mature trees at the Soroe site as evident from near zero water vapor fluxes during virtually all nights for which data is available.

Measured negative methanol fluxes (deposition) were not strongly correlated with any other measured parameter. We merely found a tendency of deposition fluxes to increase with ambient mixing ratio as might be expected. A resistant regression (minimizing the sorted squared residuals) to all negative flux values versus the in-canopy mixing ratios suggested an exchange velocity of $-1.1 \pm 0.9 \text{ cm s}^{-1}$. This is comparable to the upper limits reported by Karl and coworkers (Karl et al. 2004, 2005a) for the maximum LAI region of a tropical and a pine forest, respectively. However, the uncertainty of this value is high and therefore its significance low.

Other OVOC fluxes were generally lower than those of methanol, with exceptions after the wind shift on DOY 170 (19 June), which we attribute to the nearby hay field mowing (“Canopy gradients” section). Similar to methanol, acetone fluxes were found to be 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, shown in Fig. 5, were significantly correlated ($r^2 = 0.53$, $P < 0.01$) with ambient temperature, similar to previous studies (e.g. Schade and Goldstein 2001). We cannot exclude the possibility that acetone is chemically produced below the inlet, particularly as a result of very fast sabinene-OH chemistry (Atkinson et al. 1990; Carrasco et al. 2006; Hakola et al. 1994; Reissell et al. 1999). The resulting upward acetone flux could contribute a significant fraction to the measured total. The temperature dependence factor evaluated from Fig. 5 (using both regressions) was $0.04 \pm 0.02 \text{ K}^{-1}$, the standard emission $0.05 \pm 0.02 \text{ mg C m}^{-2} \text{ h}^{-1}$ ($22 \text{ ng m}^{-2} \text{ s}^{-1}$) at 30°C . This is significantly less than previously found for pine forests (Janson et al. 1999; Karl et al. 2005a; Schade and Goldstein 2001), but comparable to Norway spruce needle measurements (Grabmer et al. 2006; Janson and de Serves 2001). A compensation-point equivalent temperature of approximately 20°C resulted from the temperature-dependence (Fig. 5), but a

Fig. 5 Acetone flux as a function of sonic virtual temperature. *Closed circles* show 1-degree, open squares 2-degree binned average fluxes, error bars show ± 1 standard deviation ($N = 6\text{--}31$). The *solid black and grey lines* are weighted log-linear regressions to the *circles and squares*, respectively



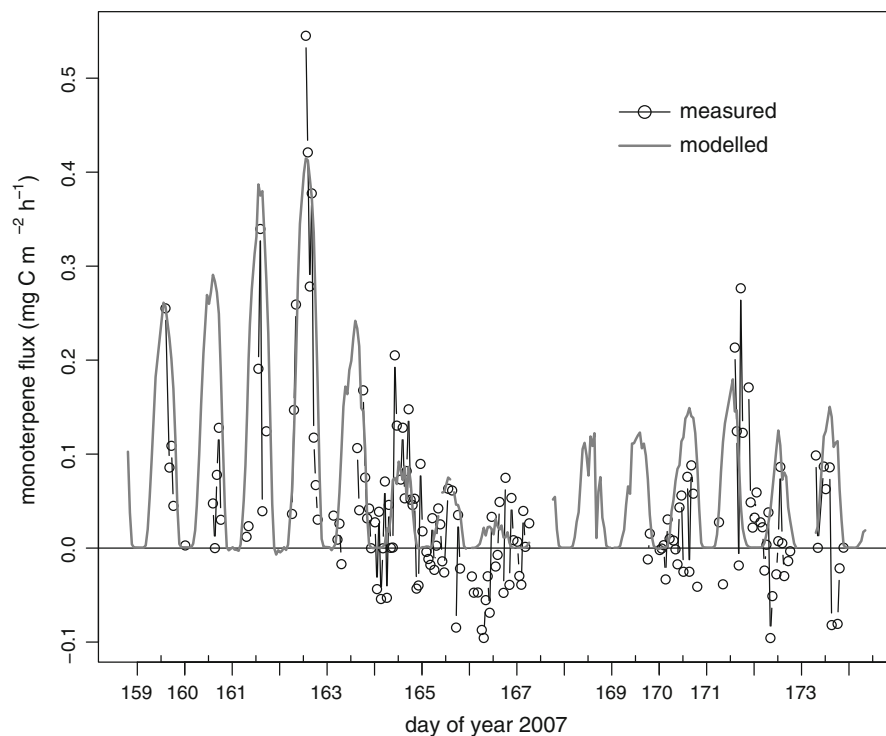
correlation of deposition fluxes with ambient mixing ratios of acetone was not found. Acetone abundance was generally below 1 ppb under these conditions, which suggests that its deposition depends on more factors than just abundance.

We also analyzed the flux data for m/z 45 (acetaldehyde) and m/z 73 (MEK), but the results showed mostly insignificant fluxes when compared to the error estimate from the bag intercomparison samples. Still, when considering the largest bag differences found in each case, exchange velocities of several centimeters per second can be calculated. Hence, our flux measurement method is not appropriate to determine small VOC fluxes.

Monoterpene fluxes from European beech have been measured by Schuh et al. (1997), and were recently reevaluated by Holzke et al. (2006) and Dindorf et al. (2006) on trees in northern Germany. All these authors found substantial, light-driven emissions and a high variability of standard emission factors (at $1,000 \mu\text{mol m}^{-2} \text{s}^{-1}$ PAR and 30°C). Our own measurements, shown in Fig. 6, confirm the diurnal cycle of emissions with maximum fluxes on the warmest, cloud-free days of the campaign. To compare to the previously published leaf and branch

chamber emission data, we carried out a series of model runs using the light- and temperature dependence model given by Holzke et al. (2006). We assumed a three-layer canopy top ($>14 \text{ m agl}$) with LAI values of $1\text{--}1.5 \text{ m}^{-2} \text{ m}^{-2}$ each as estimated from the sub-canopy PAR gradients, uniform canopy temperatures equal to the sonic virtual temperature, and an ellipsoidal leaf angle distribution with a twice as high portion of horizontally oriented leaves. LAI and standard emission factor were treated as variables, but remained the same for all layers. Accepting a deviance of a factor of two between model and measurements resulted in possible standard emission factors between 0.10 and $0.38 \text{ mg C m}^{-2} \text{ h}^{-1}$ ($0.2\text{--}0.8 \text{ nmol m}^{-2} \text{ leaf area s}^{-1}$). The best match was achieved for a standard emission factor of $0.19 \text{ mg C m}^{-2} \text{ h}^{-1}$ (leaf area), and the resulting emissions curve is included in Fig. 6. The results compare well with typical values given by Holzke et al. (2006), and are strongly driven by the high flux data on days with good fetch conditions, such as early in the campaign. Somewhat more limited fetch conditions for beech at this site occur under SE winds (Dellwik and Jensen 2005). Under these conditions up to half the flux footprint (calculated using the parameterized model

Fig. 6 Measured and modeled total monoterpene flux, using a standard emission of $0.19 \text{ mg C m}^{-2} \text{ h}^{-1}$. Gaps in model data are due to unavailability of meteorological data



of Kljun et al. (2004)) may contain the nearest conifer grove, and we note that higher than expected monoterpene mixing ratios and fluxes occurred on DOY 166 and the night of DOY 171/172.

Although in good agreement with expectation from enclosure measurements, our results contrast with those 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, α -pinene, β -pinene, and limonene, which are typical pine forest monoterpenes, while beech emissions were dominated by sabinene in past studies (Dindorf et al. 2006; Holzke et al. 2006; Schuh et al. 1997). Although part of the monoterpene composition difference may be explained by sabinene decomposition on the trap during storage (Dindorf et al. 2006), this cannot account for the large abundance differences. As we found no record of forest activities during 1996, such as logging, that would result in large monoterpene emissions we can only speculate that their setup at 31 m height was strongly influenced by nearby emissions from the large conifer patch to the SE, which was one dominant wind direction during their study days. Footprint analysis shows that

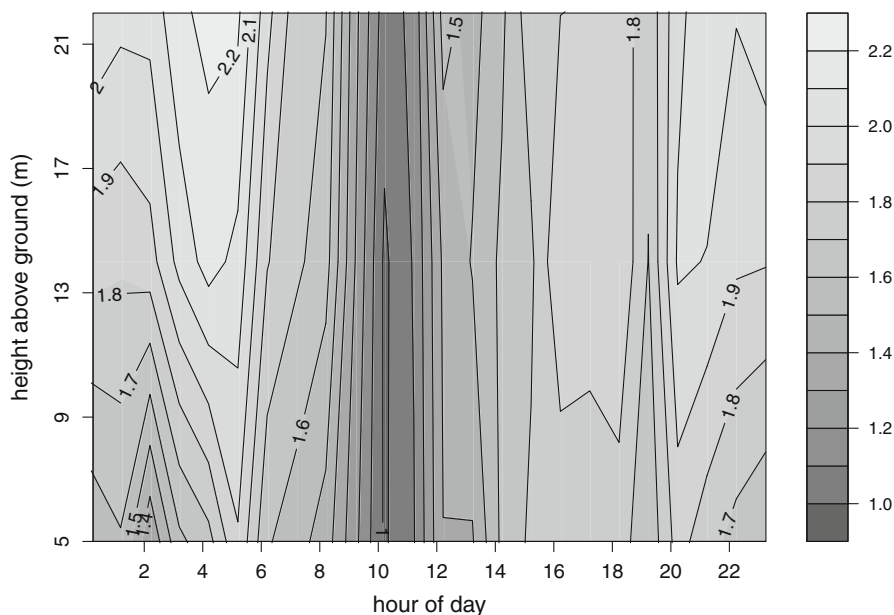
approximately 50% of the 6 and 7 June 1996 footprints encompassed the nearest conifer area, which, together with higher temperatures during these measurements, may have contributed to the higher monoterpene abundances and fluxes.

Canopy gradients

To compare in-canopy with above canopy fluxes, the storage term was calculated from the gradient measurements. Storage term fluxes for all 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. 2005a), 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 7 shows interpolated mean methanol mixing ratios as a function of height and time of day

Fig. 7 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

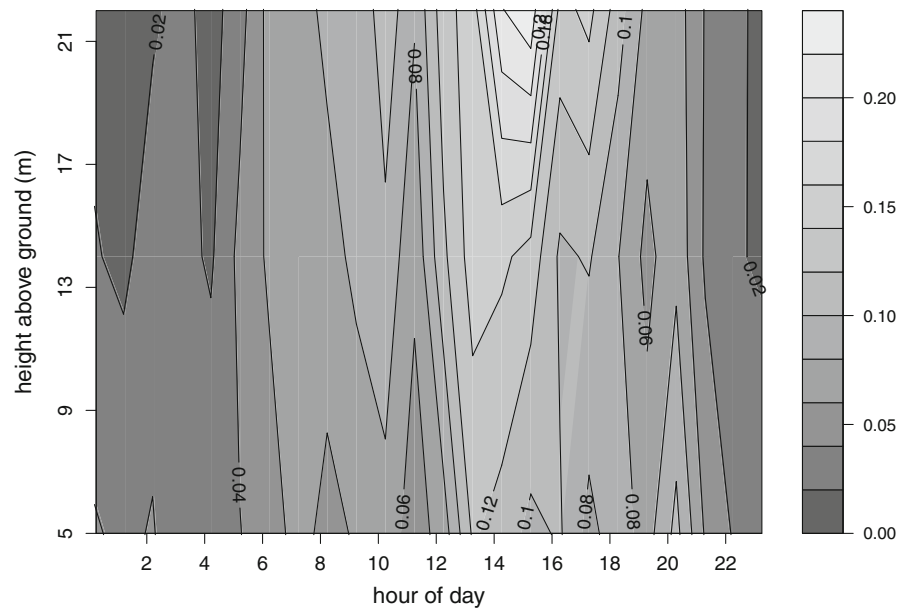


during the cooler part of the campaign: Mixing ratios were higher at night with a maximum in the early morning hours, and displayed nighttime vertical gradients of up to 0.04 ppb m^{-1} , while daytime mixing ratios were flat. While in principle consistent with the nighttime canopy emissions under reduced turbulence as discussed above, regional advection over the forest from other sources could also produce such a pattern (see below). In fact, the morning drop of ambient methanol mixing ratios of up to 20% per hour seen in Fig. 7 was observed for nearly all VOCs measured. As it was observed less frequently during the early June warm period, we interpret the drop as down-mixing of clean marine background air from the residual layer, particularly 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.

The gradient graph for monoterpenes, Fig. 8, shows the opposite diurnal development compared to methanol: maximum mixing ratios and vertical gradients in the early afternoon as expected from light and temperature-driven emissions in the canopy. In this case, the gradient measurements are consistent with the findings in the previous section. The observed methanol gradients cannot support the estimated exchange velocity of -1.1 cm s^{-1} , because we lack an additional unbiased above-canopy mixing ratio

measurement. However, we found a weak correlation between the u^* -normalized 14–22 m methanol gradient and the above-canopy net methanol deposition flux, which would be expected for a deposition into the canopy assuming that this process also creates a mixing ratio minimum at the 22 m level with respect to the sub-canopy measurements at 14 m. Hence, the methanol gradient measurements generally support an uptake in the canopy when above-canopy fluxes were negative. The gradient measurements of other VOC species presented a less clear picture. For instance, we observed generally very small gradients ($<0.2 \text{ ppb}$; noise level from toluene gradient: $<0.03 \text{ ppb}$) for acetone and acetaldehyde. Nevertheless, especially the 5–14 m gradients increased significantly after a heavy rain on DOY 167 (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. Due to a record warm spring and a lack of rain since mid May, unusually low spring soil moisture ($<20\%$) (Dellwik 2003; Pilegaard 2001) was recorded before the rain. Combined

Fig. 8 Same as Fig. 6 but for monoterpenes before DOY 165



with the observed effect of soil moisture on soil respiration at this site (Janssens and Pilegaard 2003) we speculate that soil microbial activity may have been low before the rain, so soil deposition of OVOCs may have been low as well.

A second major change to the measured gradients was observed after the wind direction shift on DOY 170, which 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. 9. 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 pre-wind shift 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. 9). On the other hand, the same analysis for methanol (data not shown), which was not strongly affected by the DOY 170 wind shift, suggested a compensation point between 1 and 1.5 ppb.

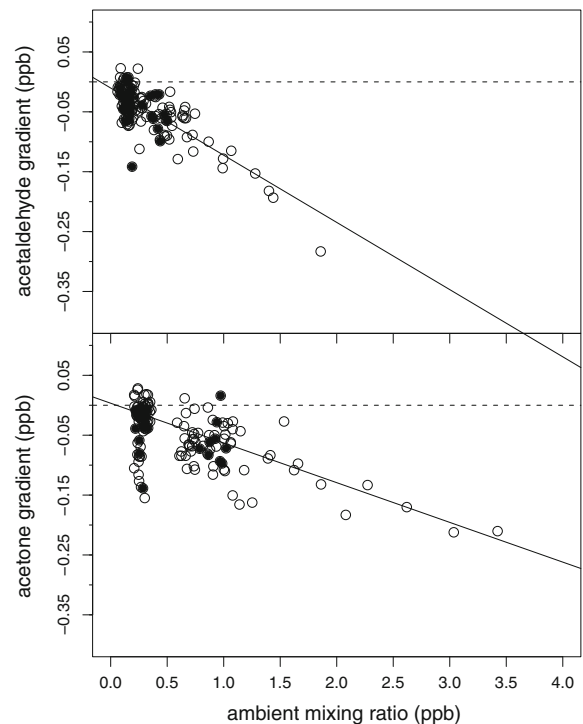


Fig. 9 Relationship between acetaldehyde (*top*) and acetone (*bottom*) mixing ratios and their respective below canopy 5–14 m gradients after the 16 June rain event. *Open circles* depict all data, *closed circles* only data after DOY 172, when mixing ratios had dropped back to ‘normal’ after the wind shift 2 days earlier

Soil chamber flux measurements

During the last four mornings of the campaign, the gradient sampling line to the PTRMS was moved to the flux chamber for a series of soil trace gas exchange tests within an approximate 5 m distance from the instrument trailer. The same data acquisition program as for the gradient measurements was applied. A time series data example for methanol is shown in Fig. 10. We investigated count rates at both m/z 32 ($^{16}\text{O}_2^+$) and m/z 37 (first water cluster), both used as a measure of possibly varying m/z 33 background, to determine whether the observed drops in m/z 33 were indeed caused by soil consumption. Higher humidity in the chamber could suppress the drift tube O_2^+ abundance, but when observed the effect was found to explain at most 10% of the m/z 33 decrease. Generally, no changes in humidity or O_2^+ count rates were observed between ambient ground level and chamber enclosure readings, while drops in m/z 33 count rates were always observed. Nevertheless, we cannot completely rule out that changes in background count rates may have contributed to the observed variability of several VOCs. In addition, because only a limited number of enclosure tests

were performed, and because the soil in the tested area may have been disturbed by foot traffic, the results should be viewed with some caution.

We found that methanol uptake dominated for this location, and was generally consistent from 1 day to the next. We pooled similar tests and summarized the calculated exchange velocities in Table 1. Soil temperatures during all these tests, measured by the main system several meters away, were between 13 and 14°C. Soil moisture (between 0 and 16 cm depth), inferred from previous relations between soil moisture and precipitation (Pilegaard et al. 2001), increased from ~25% (DOY 171) to ~31% (DOY 174).

With few exceptions the calculated exchange velocities for the remaining VOC were insignificant, but allowed upper estimates of $\pm 0.1 \text{ cm s}^{-1}$. Due to the consistency between this relatively slow soil exchange and the observed weak gradients toward the ground it appears unlikely that exchange velocities were significantly higher at other soil locations in this forest. Although more measurements are needed to confirm exchange fluxes of this soil, some general tendencies were observed: the beech litter heap showed emissions of m/z 69 and 71 similar to observations by Warneke and coworkers (1999); the

Fig. 10 Methanol measurements during a series of soil incubation tests on DOY 172 (21 June). *Solid lines* depict the concentration development by a linear model for production by the chamber itself, or following an exponential decay model approaching steady state equilibrium in the chamber (King 1999)

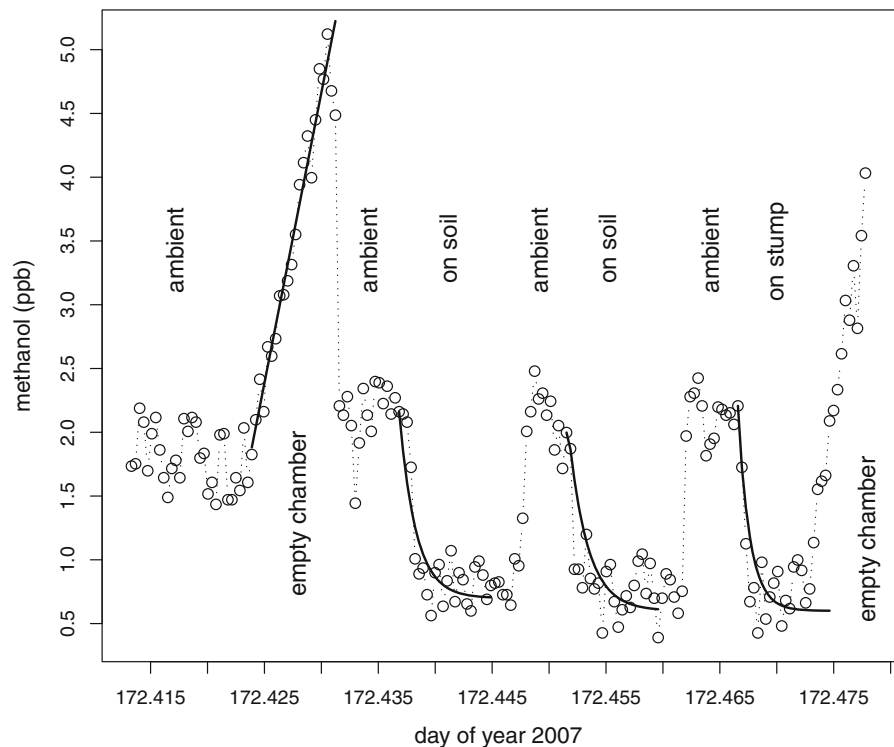


Table 1 Exchange velocities to the onsite soil in cm s^{-1}

Mass (VOC)	Soil (N = 5–11) ^a	Beech litter ^b	Mineral soil ^b	Stump with moss (N = 1–2)
m/z 33 (methanol)	-0.16 ± 0.05	-0.1	-0.26	-0.2
m/z 45 (acetaldehyde)	-0.08 ± 0.02	-0.05	-0.04	-0.13
m/z 59 (acetone)	(0.1) ^c	NA ^c	NA	NA
m/z 61 (acetic acid)	(0.1)	-0.16	-0.4	NA
m/z 73 (MEK)	(0.1)	NA	NA	-0.08

Soil temperatures were between 13 and 14°C during all incubations

^a Error = 1 sd; samples include incubations of soil only and soil with small plants

^b 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”)

^c A number in parenthesis is an upper limit of absolute exchange velocity estimated from the data; NA not applicable (1 sd > median)

mineral soil from which the litter horizon had been removed and the tree stump with moss showed slightly higher deposition velocities for methanol. Mass 33 (methanol) was always found to be produced by the chamber and taken up in subsequent soil enclosure tests (Fig. 10). We also found a tendency towards lower equilibrium methanol count rates in the chamber as soil humidity increased. However, this effect may have been at least in part due to very high ambient humidity levels rather than microbial activity. Large ambient humidity levels can lower methanol background counts (de Gouw and Warneke 2007), and this effect may be inferred from the calculated methanol ground-level mixing ratios, which were significantly lower than the respective 5 m gradient level data on the last 2, wet days. Hence, the ground-level methanol abundances may have been underestimated on those days.

Conclusions

Our canopy flux and gradient measurements complement recent laboratory and field enclosure measurements on methanol and monoterpene emissions, respectively, from European beech. Our above-canopy monoterpene flux and canopy-gradient findings confirmed previous laboratory and field enclosure studies, showing that monoterpenes emissions from beech are light-dependent. Our methanol flux measurements showed indications of nighttime emissions, but results were less clearcut as the data did not confirm the large nighttime emissions found in a

recent seedling study. Strong stomatal control of leaf trace gas exchange in mature trees and the timing and duration of our study probably affected this result.

There is increasing interest in methanol sinks as well, and we have studied its ambient mixing ratios, in-canopy gradients, and soil exchange rates at the Soroe site to compare to previous studies. We found indications for methanol uptake by the forest canopy when ambient mixing ratios were elevated, generally weak gradients towards the surface, and relatively low soil deposition rates. These findings are in contrast to much larger deposition rates found in a rainforest and a pine forest. They demonstrate that global deposition rates should not be inferred from just a few field studies (e.g. Jacob et al. 2005). We suggest that dedicated, controlled fumigation experiments should be performed to determine the different roles of gross emission and deposition, as well as possible compensation points for various ecosystem components.

A similar conclusion holds for the other OVOC species we analyzed, such as acetone, acetaldehyde, and MEK. Like methanol fluxes, also acetone fluxes were found to be bidirectional. However, despite a relationship with ambient temperatures, its biosphere–atmosphere exchange pattern remained elusive, its fluxes lower than observed in previous research (Janson and de Serves 2001; Schade and Goldstein 2001). We conclude that temperature alone should not be used to extrapolate biospheric acetone emissions, neither for acetaldehyde and MEK. We infer from the measured sub-canopy vertical distributions in this ecosystem that their exchange fluxes must have been

very small because of the absence of strong gradients for these OVOCs. This was supported by the soil exchange flux tests.

Overall, the soil exchange flux survey showed slow deposition rates to the soil surface for all OVOCs measured (Table 1), consistent with the general absence of strong gradients below the canopy. Observed tendencies suggesting differences between plant litter and mineral soil OVOC exchange and possible effects of soil microbial activity, suggest that soils may generally act as OVOC sinks. Future measurements should include soil fumigation tests and soil respiration measurements to evaluate the soil VOC exchange further.

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