DISJUNCT EDDY COVARIANCE MEASUREMENTS OF VOLATILE ORGANIC COMPOUND FLUXES USING PROTON TRANSFER REACTION MASS SPECTROMETRY

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Abstract

Volatile organic compounds (VOCs) are emitted into the atmosphere from natural and anthropogenic sources, vegetation being the dominant source on a global scale. Some of these reactive compounds are deemed major contributors or inhibitors to aerosol particle formation and growth, thus making VOC measurements essential for current climate change research. This thesis discusses ecosystem scale VOC fluxes measured above a boreal Scots pine dominated forest in southern Finland. The flux measurements were performed using the micrometeorological disjunct eddy covariance (DEC) method combined with proton transfer reaction mass spectrometry (PTR-MS), which is an online technique for measuring VOC concentrations.

The measurement, calibration, and calculation procedures developed in this work proved to be well suited to long-term VOC concentration and flux measurements with PTR-MS. A new averaging approach based on running averaged covariance functions improved the determination of the lag time between wind and concentration measurements, which is a common challenge in DEC when measuring fluxes near the detection limit. The ecosystem scale emissions of methanol, acetaldehyde, and acetone were substantial. These three oxygenated VOCs made up about half of the total emissions, with the rest comprised of monoterpenes. Contrary to the traditional assumption that monoterpene emissions from Scots pine originate mainly as evaporation from specialized storage pools, the DEC measurements indicated a significant contribution from de novo biosynthesis to the ecosystem scale monoterpene emissions.

This thesis offers practical guidelines for long-term DEC measurements with PTR-MS. In particular, the new averaging approach to the lag time determination seems useful in the automation of DEC flux calculations. Seasonal variation in the monoterpene biosynthesis and the detailed structure of a revised hybrid algorithm, describing both de novo and pool emissions, should be determined in further studies to improve biological realism in the modelling of monoterpene emissions from Scots pine forests. The increasing number of DEC measurements of oxygenated VOCs will probably enable better estimates of the role of these compounds in plant physiology and tropospheric chemistry.

Keywords: disjunct eddy covariance, lag time determination, long-term flux measurements, proton transfer reaction mass spectrometry, Scots pine forests, volatile organic compounds

Contents

List of publications

This thesis consists of an introductory review and five research articles. In the review, these papers are cited according to their Roman numerals.

I **Taipale, R.**, Ruuskanen, T. M., Rinne, J., Kajos, M. K., Hakola, H., Pohja, T., and Kulmala, M.: Technical Note: Quantitative long-term measurements of VOC concentrations by PTR-MS – measurement, calibration, and volume mixing ratio calculation methods, Atmos. Chem. Phys., 8, 6681–6698, 2008.

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

III **Taipale, R.**, Ruuskanen, T. M., and Rinne, J.: Lag time determination in DEC measurements with PTR-MS, Atmos. Meas. Tech., 3, 853–862, 2010.

IV Ghirardo, A., Koch, K., **Taipale, R.**, Zimmer, I., Schnitzler, J.-P., and Rinne, J.: Determination of *de novo* and pool emissions of terpenes from four common boreal/alpine trees by $^{13}CO_2$ labelling and PTR-MS analysis, Plant Cell Environ., 33, 781–792, 2010.

V **Taipale, R.**, Kajos, M. K., Patokoski, J., Rantala, P., Ruuskanen, T. M., and Rinne, J.: Role of de novo biosynthesis in ecosystem scale monoterpene emissions from a boreal Scots pine forest, Biogeosciences Discuss., 7, 8019–8040, 2010.

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1   Introduction

Vegetation emits large amounts of volatile organic compounds (VOCs) into the atmosphere. Oceans, biomass burning, and human activity are other major sources of these reactive compounds. VOCs are also formed in the atmosphere as reaction products of other organic compounds. Global biogenic VOC emissions ($\sim$ 1150 Tg (C) per year) are estimated about ten times higher than anthropogenic emissions, although in urban areas the human impact often dominates (Piccot et al., 1992; Guenther et al., 1995).

The largest VOC sources are tropical, temperate, and boreal forests. Examples of significant biogenic compounds found so far are terpenoids (isoprene, monoterpenes, and sesquiterpenes) and some oxygenated compounds like methanol, acetaldehyde, acetone, methacrolein, methyl vinyl ketone, methyl ethyl ketone, and methylbutenol. Since the first reported measurements by Isidorov et al. (1985), numerous studies, including this thesis, have focused on VOC emissions from the Eurasian boreal zone, nowadays recognized as an important but still poorly characterized source. The main findings and future directions of research on boreal VOC emissions have been recently reviewed by Rinne et al. (2009).

The reasons for plant VOC emissions are somewhat unclear and under debate (e.g. Sharkey and Singsaas, 1995; Pẽnuelas and Llusià, 2004; Owen and Pẽnuelas, 2005). The known ecological functions of biogenic VOCs include pollination, seed dispersal, defence against herbivores and pathogens, plant-to-plant signalling, allelopathy, and protection against abiotic stress (for reviews see, e.g. Yuan et al., 2009; Loreto and Schnitzler, 2010). Various algorithms have been developed to describe terpenoid emissions from different plant species (e.g. Tingey et al., 1980; Guenther et al., 1991, 1993, 2006; Schuh et al., 1997; Shao et al., 2001; Niinemets et al., 2002; Bäck et al., 2005; Schurgers et al., 2009). These algorithms connect emissions with a varying number of biological, environmental, and physico-chemical factors (Niinemets et al., 2010a,b). They have been the basis for regional and global emission inventories, both for terpenoids and some oxygenated compounds (e.g. Guenther et al., 1995, 2006; Tarvainen et al., 2007; Millet et al., 2008, 2010; Karl et al., 2009; Keenan et al., 2009).

VOCs play a significant role in tropospheric chemistry (e.g. Koppmann, 2007). They affect concentrations of ozone, the hydroxyl radical, and the nitrate radical, and hence the oxidative capacity of the lower atmosphere (Atkinson and Arey, 2003). VOCs seem to have an influence on the atmospheric lifetime of methane as they compete

for hydroxyl radicals with this effective greenhouse gas (Kaplan et al., 2006). As once proposed by Went (1960), some VOCs are major contributors to aerosol particle formation and growth (e.g. Hoffmann et al., 1997; Claeys et al., 2004; Kulmala et al., 2004; Allan et al., 2006; Tunved et al., 2006; Kroll and Seinfeld, 2008; Hallquist et al., 2009). However, at least isoprene also has the potential to inhibit new particle formation (Kiendler-Scharr et al., 2009). In addition, VOCs may have an effect on the optical properties of aerosol particles (Nozière and Esteve, 2005). As aerosol particles absorb and scatter solar radiation and act as condensation nuclei for cloud droplets, they impact the Earth's radiation budget and therefore also the climate.

Given the intricate feedbacks between vegetation, biogenic VOC emissions, aerosol processes, and climate change, VOC measurements are an essential part of the current atmospheric research. They are often based on gas chromatographic analyses of air samples collected on adsorbents or in canisters. Such measurements are highly sensitive and give detailed information on the atmospheric VOC composition. However, these methods are usually too slow to follow fast concentration changes. Their response times are limited by the required sampling times, which can vary from a few seconds up to an hour. Also the acquisition and analysis of samples is often time-consuming and labour-intensive.

In this work, proton transfer reaction mass spectrometry (PTR-MS; Hansel et al., 1995; Lindinger et al., 1998a,b) was used in the VOC concentration measurements. It is an online technique based on chemical ionization of VOCs by proton transfer from hydronium ions (H_3O^+), followed by mass spectrometric analysis of the reagent and product ions. PTR-MS allows measurements of numerous VOCs with high sensitivity (10–100 parts per trillion by volume (pptv)) and fast response time (0.1–10 s). The technique does not require any sample treatment, such as drying or preseparation, and is thus suitable for oxygenated compounds, which are difficult to detect with other methods. The major disadvantage is that PTR-MS determines only the masses of the product ions. Instruments equipped with quadrupole mass analyzers, like the one used in this study, cannot distinguish between different VOCs with the same nominal mass. The better mass resolution of novel time-of-flight instruments enables separation of some isobaric compounds (e.g. Blake et al., 2004, 2009).

Since the introduction of the first commercial instruments (Ionicon Analytik GmbH) in the mid-nineties, PTR-MS has quickly become a popular tool in VOC measurements. Its historical development, different instrument configurations, and various

atmospheric applications have been reviewed by Lindinger et al. (1998a), de Gouw and Warneke (2007), and Blake et al. (2009). For example, PTR-MS has been utilized in ambient concentration measurements in urban, rural, and remote areas using aircraft-, ship-, vehicle-, or ground-based platforms (Crutzen et al., 2000; Holzinger et al., 2001; Wisthaler et al., 2002; Karl et al., 2003; de Gouw et al., 2004; Jiang et al., 2005; Rinne et al., 2005; Warneke et al., 2006; Jordan et al., 2009; Kim et al., 2010), in plant enclosure experiments to study shoot scale VOC emissions (Fall et al., 1999; Karl et al., 2002a; Hayward et al., 2004; Ruuskanen et al., 2005; Vickers et al., 2009), in micrometeorological flux measurements with eddy covariance techniques (Karl et al., 2001, 2002b; Rinne et al., 2001; Warneke et al., 2002; Spirig et al., 2005; Brunner et al., 2007; Langford et al., 2009; Müller et al., 2010), and in studies of VOC chemistry and aerosol particle formation, growth, and composition (Wisthaler et al., 2001; Paulsen et al., 2005; Lee et al., 2006a,b; Vartiainen et al., 2006; Hellén et al., 2008; Hao et al., 2009; Holzinger et al., 2010). Measurements of atmospheric sesquiterpene concentrations (Kim et al., 2009) and a comparative method for determining the total hydroxyl radical reactivity (Sinha et al., 2008, 2010) are examples of recent promising applications. Over the years, the performance, sensitivity, and specificity of PTR-MS have been well characterized (Hansel et al., 1997; Hayward et al., 2002; de Gouw et al., 2003a,b; Tani et al., 2003, 2004; Warneke et al., 2003; Ammann et al., 2004; Steinbacher et al., 2004; Inomata et al., 2008; Wisthaler et al., 2008; Ambrose et al., 2010; Jobson and McCoskey, 2010; Jobson et al., 2010).

Exchange rates of VOCs, i.e. VOC fluxes, between vegetation and the atmosphere can be measured with several methods which have been summarized by Dabberdt et al. (1993). Enclosure (i.e. cuvette or chamber) methods give fluxes at the shoot, leaf, or branch scale. Micrometeorological methods yield ecosystem scale fluxes by determining the vertical turbulent transfer of VOCs, caused by turbulent eddies, above vegetation in the atmospheric surface layer. Boundary layer mass balance and gradient methods provide fluxes at the regional scale. Apart from isoprene studies (e.g. Guenther and Hills, 1998; Pressley et al., 2005), micrometeorological VOC flux measurements with the eddy covariance method have relied mainly on PTR-MS. Like the present work, many of these measurements have been based on an approach called disjunct eddy covariance (DEC; Rinne et al., 2001; Karl et al., 2002b).

DEC and the conventional eddy covariance (EC) method have the same basic principle. The flux is calculated as the covariance of the vertical wind speed and the VOC

concentration. In the conventional approach, both variables are measured with fast response instruments at a high frequency (10–20 Hz). In the disjunct version, short VOC samples (0.1–0.5 s) are taken at intervals of several seconds, resulting in a disjunct time series. The wind velocity is measured at a high frequency also in DEC. Theoretical considerations and data simulations (Kaimal and Gaynor, 1983; Lenschow et al., 1994) as well as field studies (Rinne et al., 2008; Turnipseed et al., 2009; Hörtnagl et al., 2010) have shown that DEC is a reliable method for trace gas flux measurements. Since the first application by Rinne et al. (2001), DEC measurements with PTR-MS have provided fundamental information on VOC emissions from various ecosystems (Karl et al., 2002b; Warneke et al., 2002; Grabmer et al., 2004; Spirig et al., 2005; Holzinger et al., 2006; Brunner et al., 2007; Davison et al., 2009; Bamberger et al., 2010; Holst et al., 2010; Langford et al., 2010; Misztal et al., 2010).

In the research conducted for this thesis, the combination of DEC and PTR-MS was used for VOC flux measurements above a boreal Scots pine dominated forest in southern Finland. A substantial part of the work was related to quantitative measurement, calibration, and concentration and flux calculation methods. An important challenge in many DEC and some EC applications, the determination of the lag time between wind and concentration measurements was addressed with a view to systematizing and hastening DEC flux calculations. Fluxes of some oxygenated VOCs were measured to broaden the general picture of ecosystem scale emissions from coniferous forests. The division between the two origins of monoterpene emissions from Scots pine, specialized storage pools and de novo biosynthesis, was estimated in order to provide new information for emission algorithm development and evaluation. In summary, the main objectives of this thesis included

1) developing measurement, calibration, and calculation procedures for long-term VOC concentration and flux measurements with PTR-MS (**Papers I–III**),

2) assessing the performance of different methods for lag time determination in DEC measurements with PTR-MS (**Paper III**),

3) comparing ecosystem scale emissions of three oxygenated VOCs (methanol, acetaldehyde, and acetone) with monoterpene emissions from a boreal Scots pine dominated forest (**Paper II**),

4) and estimating the role of de novo biosynthesis in monoterpene emissions from Scots pine (**Papers IV–V**).

2 Background

2.1 Disjunct eddy covariance (DEC)

DEC is based on the same principles as all micrometeorological flux measurement methods (for a review, see Dabberdt et al., 1993). Measurements are performed above the surface in the atmospheric surface layer. The vertical turbulent flux, defined as the covariance of the vertical wind speed and the VOC concentration, represents the VOC flux between the surface and the atmosphere:

$$F = \overline{w'c'} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} w'(t)c'(t)dt \qquad (1)$$

(e.g. Kaimal and Finnigan, 1994). Here $w' = w - \bar{w}$ is the momentary deviation of the vertical wind speed from its average and $c' = c - \bar{c}$ is that of the VOC concentration. The beginning and end of the flux averaging time are denoted by t_1 and t_2. The micrometeorological convention is that upward (emission) fluxes are positive and downward (deposition) fluxes are negative.

The assumption of the equality between the vertical turbulent flux at the measurement height and the flux at the atmosphere–surface interface stipulates some requirements for the measurement site, atmospheric conditions, and measured compounds. The surface around the site has to be fairly flat and horizontally homogeneous in roughness and source strength. Turbulence should be strong enough with quasi-stationary conditions, i.e. the turbulence statistics should approach a stable value when the averaging time is increased. In addition, the chemical degradation or production of the measured compound should be much slower than the time scale of turbulent mixing (e.g. **Paper II**). All these prerequisites result from the general scalar conservation equation (e.g. Kaimal and Finnigan, 1994). In practice, their realization can be estimated with various flux quality assessment methods (e.g. Foken and Wichura, 1996; Göckede et al., 2004; Spirig et al., 2005).

The estimation of the flux source area (i.e. flux footprint) is part of the interpretation of measurements. The footprint is located mostly upwind from the measurement point. Its size increases when the measurement height increases, the surface roughness decreases, or when the atmospheric stability changes from unstable to stable. Also chemical reactions affect the footprints of reactive trace gases (Strong et al., 2004).

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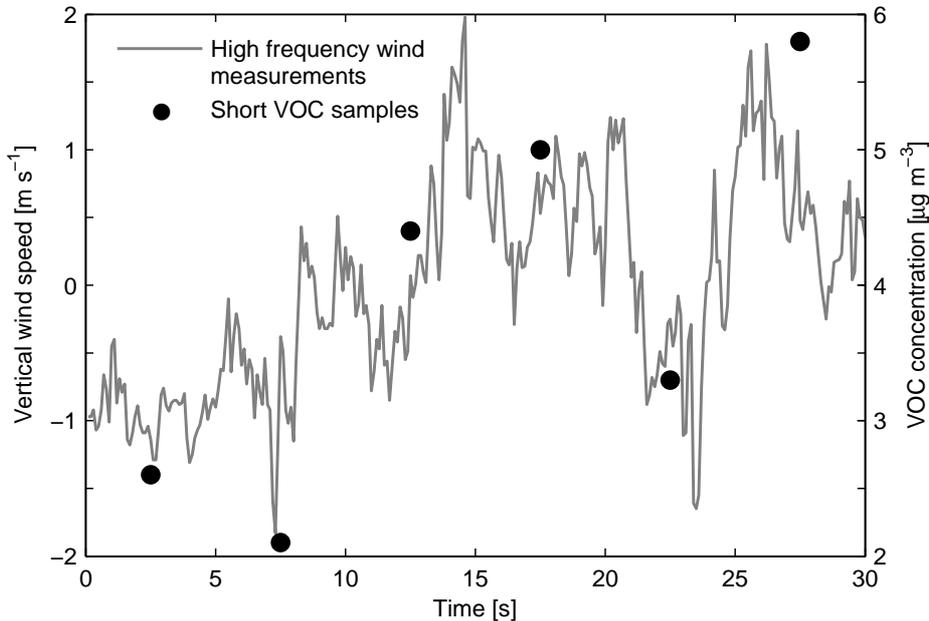
Fig. 1. Schematic figure of the sampling procedure in DEC. The wind velocity is measured at a high frequency and short VOC samples are taken at intervals of several seconds, resulting in a disjunct concentration time series.

Footprints can be calculated with analytic and stochastic models (e.g. Kormann and Meixner, 2001; Markkanen et al., 2003; Strong et al., 2004).

Both DEC and the conventional EC method are direct methods. The measured flux is derived from the covariance of the vertical wind speed and the VOC concentration without any empirical coefficients, only the time integral in Eq. (1) is replaced with a discrete sum:

$$F = \frac{1}{n} \sum_{i=1}^{n} w'(i)c'(i). \tag{2}$$

Here n is the number of measurements during the flux averaging time. However, DEC and EC differ in the sampling procedure. In the conventional approach, both variables are measured with fast response instruments at a high frequency, normally 10–20 Hz. In the disjunct version, short VOC samples of 0.1–0.5 s are taken at intervals of 1–30 s (Fig. 1). The wind velocity is measured at a high frequency also in DEC.

DEC has the great advantage of enabling the use of slow response instruments, which probably was the reason for its introduction into VOC flux measurements (Rinne et al.,
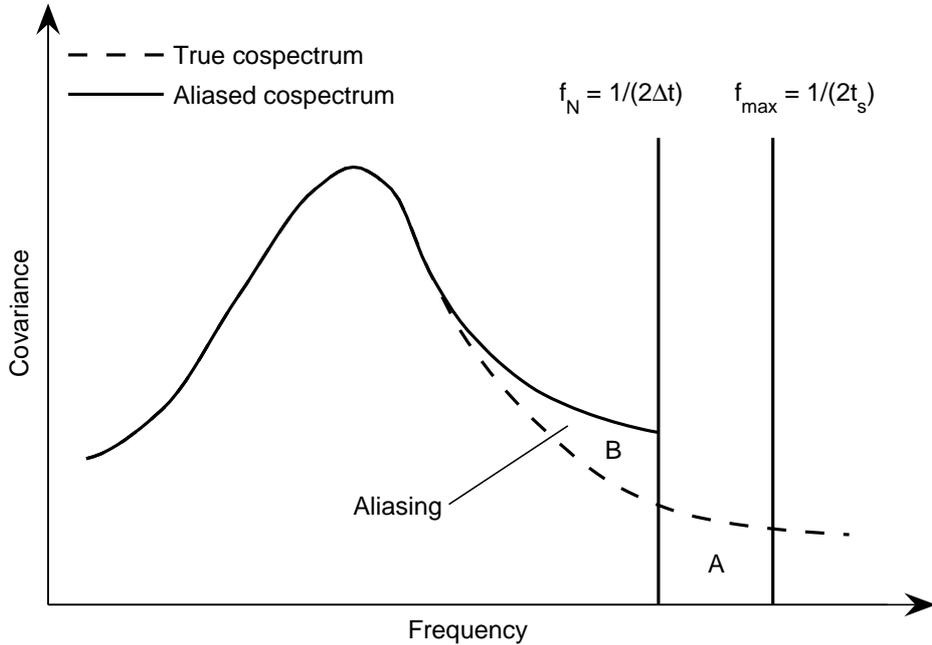
Fig. 2. Schematic figure of the cospectrum of the vertical wind speed and the VOC concentration. The sampling interval, Δt, determines the highest resolvable frequency f_N. The highest frequency contributing to a flux value measured with DEC, f_{max}, is determined by the sampling time t_s. Due to aliasing, the contribution of the frequencies between f_N and f_{max} (Area A) transfers to the resolvable frequencies (Area B).

2001). Slow response instruments can be used also in the gradient and eddy accumulation methods. However, they are often more difficult to implement and, apart from the true eddy accumulation method, rely on empirical coefficients (Dabberdt et al., 1993). In DEC each short VOC sample can be first collected in an intermediate sample container and then analyzed during the long sampling interval (Rinne et al., 2001). Due to the typical response times of less than 0.5 s, the present PTR-MS instruments are adequate for multi-compound DEC measurements with a continuous sampling flow, sometimes referred as virtual DEC (Karl et al., 2002b). In this case, several compounds are measured successively, which results in a disjunct concentration time series for all of them.

Figure 2 illustrates the principle of DEC with a schematic example of the cospectrum of the vertical wind speed and the VOC concentration. The cospectrum gives the contribution of each eddy frequency to the turbulent flux and hence the area under

the curve represents the total VOC flux (Kaimal and Finnigan, 1994). The sampling interval, Δt, determines the highest resolvable frequency, $f_N = 1/(2\Delta t)$, known as the Nyquist frequency. The highest frequency contributing to the measured flux, $f_{max} = 1/(2t_s)$, is determined by the sampling time t_s. The contribution of the frequencies between f_N and f_{max} (Area A) transfers to the resolvable frequencies (Area B) due to aliasing (Kaimal and Finnigan, 1994). Thus the total area under the aliased cospectrum is equal to the total area outlined by the true cospectrum and the maximum frequency f_{max}.

Due to the short sampling time, DEC does not introduce a systematic error when compared with EC. A flux measurement with DEC captures the same frequency range as a conventional EC measurement, provided that the sampling time and the flux averaging time do not differ between the methods. However, the random error is higher in DEC. It increases when the sampling interval becomes longer, i.e. when the number of measurements during the flux averaging time decreases (Lenschow et al., 1994; Rinne et al., 2008; Turnipseed et al., 2009). Additional random errors caused by DEC have typically been smaller than 15% (Lenschow et al., 1994; Karl et al., 2002b; Turnipseed et al., 2009; Holst et al., 2010; Hörtnagl et al., 2010).

Although DEC and EC are direct methods, corrections to measured fluxes are advisable to reduce systematic errors caused by instrument response times, instrument separation, signal processing, flux averaging times, and air density fluctuations (Dabberdt et al., 1993; Lenschow et al., 1994; Aubinet et al., 2000; Massman, 2000; Ammann et al., 2006). However, there is no established procedure for applying these corrections to DEC measurements. The flux underestimation due to a PTR-MS response time of 1 s can be even 20–30% (Davison et al., 2009). Also the calibration of PTR-MS and the determination of the lag time between wind and concentration measurements seem crucial to the accuracy of DEC measurements with PTR-MS (**Papers I, III**).

2.2 Proton transfer reaction mass spectrometry (PTR-MS)

PTR-MS is an online technique for measuring VOC concentrations. Various instrument configurations are currently available, including alternative ion sources and mass analyzers (Blake et al., 2009). The VOC concentration measurements included in this thesis were conducted with a commercial PTR-MS instrument featuring a quadrupole
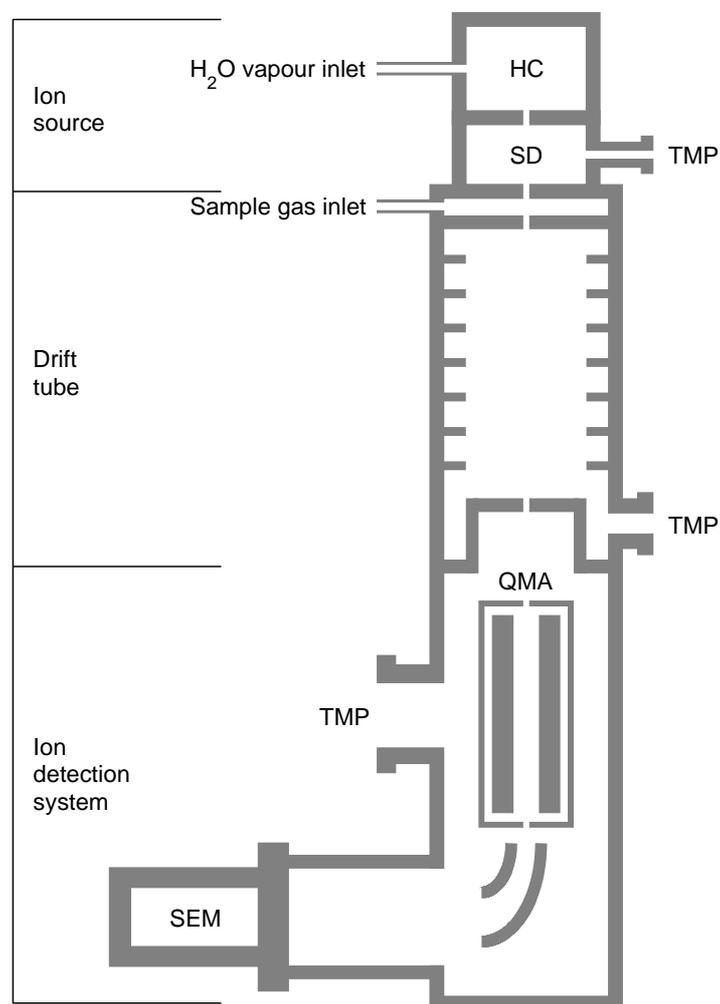
Fig. 3. Schematic illustration of the PTR-MS instrument used in this work (adapted from Lindinger et al., 1998a). HC: hollow cathode, SD: source drift region, TMP: turbomolecular pump, QMA: quadrupole mass analyzer, SEM: secondary electron multiplier.

mass analyzer (Ionicon Analytik GmbH). Several papers have discussed its development and technical properties in detail (Hansel et al., 1995; Lindinger et al., 1998a,b; de Gouw and Warneke, 2007; Blake et al., 2009).

In short, the instrument consists of four main components: an ion source, a drift tube, a quadrupole mass analyzer, and an ion detector (Fig. 3). Primary ions (H_3O^+) are produced from water vapour within the hollow cathode discharge ion source. Proton transfer reactions between the primary ions and VOCs take place in the drift tube,

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which is maintained at a pressure of about 2 hPa. An electric field is applied in the axial direction of the drift tube and ambient air is pumped through continuously at a flow rate of about 10 ml min^{-1}. The primary and product ions are selected according to their mass-to-charge ratios using the quadrupole mass analyzer and detected as count rates by a secondary electron multiplier. As only a single mass can be selected at a time, different masses must be measured successively. An integration (or dwell) time can be chosen for each mass, enabling longer measurement times for VOCs at low concentrations. The molecular ion, detected at the VOC mass plus one, is often the dominant product ion as proton transfer is a soft ionization method, which typically leads to low fragmentation of VOCs.

Due to their low proton affinities, the major components of air do not react with the primary ions in the drift tube. However, VOCs having a proton affinity higher than that of water (691 kJ mol^{-1}) are ionized in proton transfer reactions:

$$H_3O^+ + R \rightarrow RH^+ + H_2O. \tag{3}$$

The number concentration of RH$^+$ ions produced in this reaction is given by

$$[RH^+] = [H_3O^+]_0 \left(1 - e^{-k[R]t_{\text{react}}}\right) \approx [H_3O^+]k[R]t_{\text{react}} \tag{4}$$

(e.g. Lindinger et al., 1998a; de Gouw et al., 2003a; de Gouw and Warneke, 2007). Here $[H_3O^+]_0$ is the number concentration of the primary ions injected from the ion source, k is the proton transfer reaction rate coefficient, $[R]$ is the number concentration of the compound R in the drift tube, and t_{react} is the reaction time.

Equation (4) is the basis for VOC concentration calculations. It shows that $[RH^+]$ is linearly proportional to $[R]$ and $[H_3O^+]$, the number concentration of the primary ions at the end of the drift tube. The approximation is valid if only a small proportion of the primary ions reacts in the drift tube, i.e. if $[R]$ is not too high compared with $[H_3O^+]$ (e.g. de Gouw et al., 2003a). A number of recommendations on how to derive VOC concentrations starting from Eq. (4) has been given in previous studies (Lindinger et al., 1998a; de Gouw et al., 2003a; Ammann et al., 2004; Steinbacher et al., 2004). These guidelines, complemented with some minor modifications, were followed in the concentration calculation procedure described in Sect. 3.4.

2.3 Origins of monoterpene emissions from Scots pine

Scots pine is one of the dominant evergreen tree species in Eurasian boreal forests. Its monoterpene emissions have traditionally been assumed to originate as evaporation from large pools in specialized storage structures such as resin ducts (e.g. Guenther et al., 1991, 1993; Grote and Niinemets, 2008). Thus monoterpene emissions would depend mainly on temperature. However, there is increasing evidence that a substantial part of them originates directly from de novo biosynthesis in a light and temperature dependent manner (Steinbrecher et al., 1999; Shao et al., 2001; **Paper IV**). Here de novo emissions refer to emissions directly after monoterpene production (within minutes to hours) without intermediate storage in specialized storage pools. Since monoterpene production is closely linked to photosynthesis, the ratio of de novo emissions to total emissions can be determined by applying $^{13}CO_2$ fumigation and analyzing the monoterpene isotope fractions in the subsequent emissions with PTR-MS (see **Paper IV**).

In monoterpene emission modelling, semi-empirical algorithms have often been used to describe emissions from specialized storage pools (e.g. Tingey et al., 1980; Guenther et al., 1991, 1993). Process-based algorithms have been developed to take account of various physiological, phenological, and biochemical details of monoterpene biosynthesis (e.g. Niinemets et al., 2002; Bäck et al., 2005; Grote et al., 2006). The two origins of monoterpene emissions have been combined in hybrid algorithms which describe both pool and de novo emissions (e.g. Schuh et al., 1997; Shao et al., 2001; Spanke et al., 2001; Haapanala et al., 2009; Schurgers et al., 2009; **Paper IV**).

The traditional pool algorithm developed by Guenther et al. (1991, 1993) has been the established choice for Scots pine, especially when interpreting measurements (e.g. Janson, 1993; Rinne et al., 2000; Ruuskanen et al., 2005; Tarvainen et al., 2005; Hakola et al., 2006; **Paper II**; Räisänen et al., 2009). Hybrid algorithms, which now seem to be biologically more realistic, have been used rather rarely (Steinbrecher et al., 1999; Shao et al., 2001; Spanke et al., 2001; **Papers IV−V**). A description of the traditional pool algorithm and the hybrid algorithm applied in this work is given in Sect. 3.6.

3 Methods

3.1 Measurement site

The SMEAR II (Station for Measuring Ecosystem–Atmosphere Relations II) station of the University of Helsinki served as the flux measurement site. It is located in the south boreal vegetation zone at Hyytiälä, southern Finland (61°51′ N, 24°17′ E, 180 m a.s.l.), about 200 km north-west of Helsinki. Detailed descriptions of the station have been given by Vesala et al. (1998), Kulmala et al. (2001), and Hari and Kulmala (2005). The measurement periods related to this thesis were 14–17 July 2005 (**Paper II**), 3–8 July 2006 (**Paper IV**), 27 March–26 April 2007 (**Paper I**), 9–14 August 2007 (**Paper III**), and May–August 2007 (**Paper V**).

The station is situated at a rather homogeneous Scots pine (*Pinus sylvestris*) dominated forest which was sown in 1962 after controlled burning and light soil preparation. The forest had a relatively open canopy with a dry needle biomass density of 540 $\mathrm{g\,m^{-2}}$ (in 2005; **Paper II**) and an average tree height of 15–16 m. The stand also contained some Norway spruce (*Picea abies*), silver and downy birch (*Betula pendula* and *pubescens*), common aspen (*Populus tremula*), and grey alder (*Alnus incana*). The undergrowth consisted mainly of cowberry (*Vaccinium vitis-idaea*), bilberry (*Vaccinium myrtillus*), and mosses (*Pleurozium schreberi, Dicranum polysetum*). Of the area of 40×40 km^2 around the station, spruce dominated forests covered 26%, pine dominated forests 23%, mixed forests 21%, water bodies 13%, and agricultural land 10% (see e.g. Haapanala et al., 2007). In addition to the ambient concentration and shoot and ecosystem scale flux measurements with PTR-MS (Rinne et al., 2005; Ruuskanen et al., 2005; **Papers I–II**; Eerdekens et al., 2009; Lappalainen et al., 2009; **Papers III–V**), several VOC measurements have been conducted at the station using gas chromatographic methods (e.g. Rinne et al., 2000; Janson and de Serves, 2001; Hakola et al., 2003, 2006; Tarvainen et al., 2005; Hellén et al., 2006).

3.2 Measurement setup and procedure

The measurement setup consisted of a sonic anemometer (Gill Instruments Ltd., Solent HS1199), a proton transfer reaction quadrupole mass spectrometer (Ionicon Analytik GmbH), a sampling system, and a calibration system (Fig. 4; **Papers I–II**). The

sampling system had three sampling heights: the lowest (4 m) in the trunk space of the canopy, the middle one (14 m) in the crown space of the canopy, and the highest (22 m) above the top of the canopy. The highest sampling line was used in the DEC measurements. The horizontal displacement between its inlet and the sonic anemometer was about 30 cm and the vertical about 5 cm. All sampling lines were 30 m long, 8 mm in inner diameter, holding a continuous flow of $17.5 \, \mathrm{l \, min^{-1}}$, and made of Teflon (PTFE). They were heated a few degrees warmer than ambient air with Teflon-coated heating cables. Until November 2006 (**Papers II, IV**), the setup featured five sampling lines (also at 7 and 10 m), all non-heated, 32 m long, and operating at a flow of $15 \, \mathrm{l \, min^{-1}}$.

A side flow of 80–$100 \, \mathrm{ml \, min^{-1}}$ was taken from the sampling lines into the PTR-MS through PTFE tubing, which was 1.3 m in length (1 m until November 2006) and 1.6 mm in inner diameter. The operating parameters of the PTR-MS were held constant during the measurement periods, except for the detector voltage which was optimized before every calibration (**Paper I**). The drift tube pressure, temperature, and voltage were 2.0 hPa, 50 °C, and 450 V, respectively. The parameter E/N was about 106 Td ($1 \, \mathrm{Td} = 10^{-17} \, \mathrm{V \, cm^2}$) and the reaction time was about 120 μs.

The PTR-MS measurement procedure contained three hour-long sequences. Every third hour was allocated for the DEC measurements. The other two sequences were allocated for ambient concentration measurements at the different sampling heights and for shoot scale flux measurements with a dynamic enclosure method. Before the start of the shoot scale measurements in March 2007, the DEC measurements were performed every second hour. The PTR-MS measurement cycle included 11–14 masses which were measured successively (Table 1). This cycle was repeated for 48–49 min at a time. The cycle length was 5.6–6.6 s and the integration time was 0.5 s for each VOC-related mass. Zero air measurements, where VOC-free air was fed into the PTR-MS, were conducted every second or third hour for 8–9 min within the DEC measurement sequence to determine VOC background signals of the instrument.

The wind velocity was measured continuously at 10 Hz and the data were saved on a different computer than the PTR-MS data. To synchronize the clocks of the computers, the vertical wind speed was recorded also in the PTR-MS data (except in **Paper II**). The time difference was determined from the sharp maximum of the autocorrelation function of the vertical wind speed (**Paper III**).
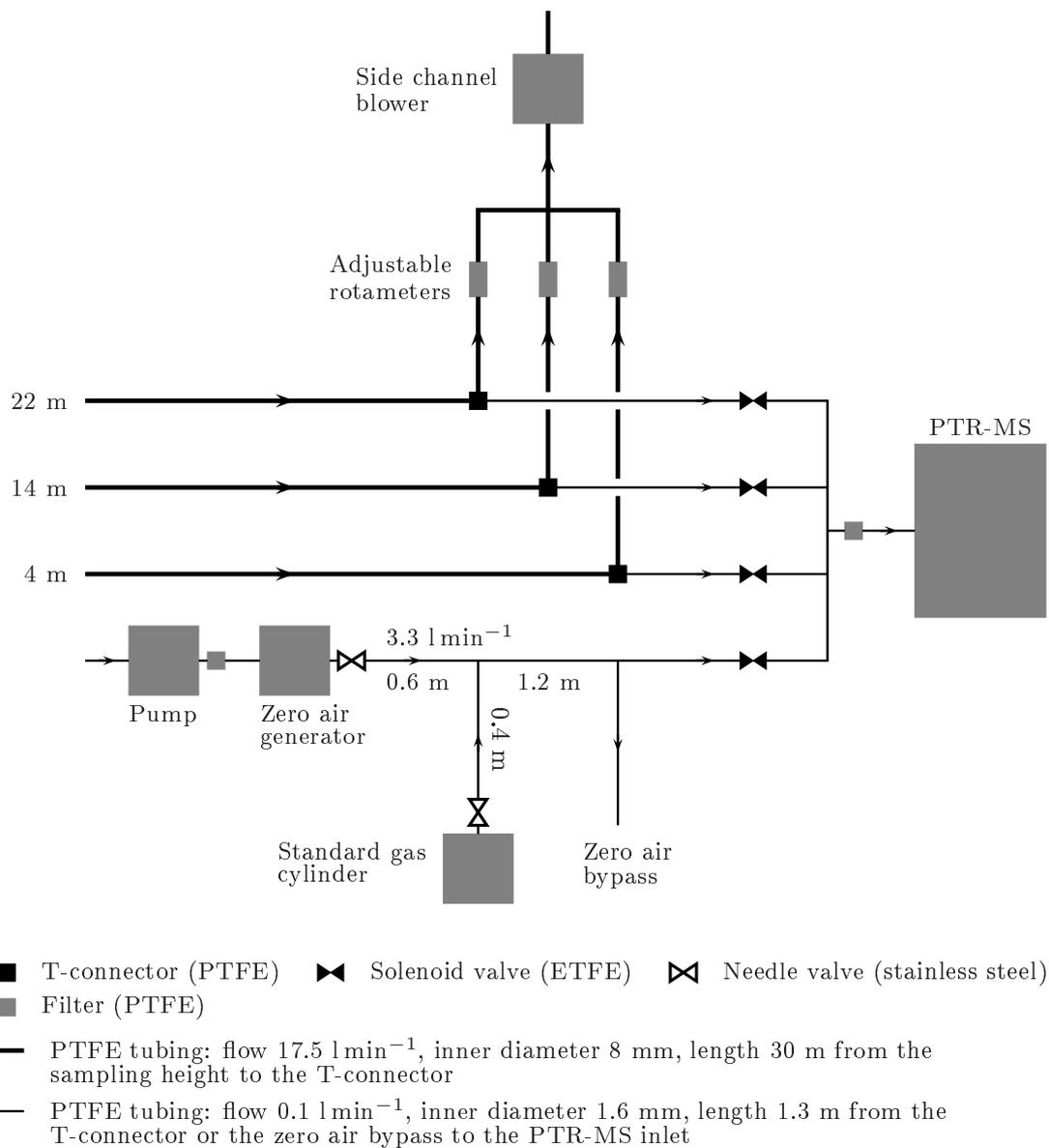
Fig. 4. Measurement and calibration setup for long-term VOC concentration and flux measurements. The sampling line at 22 m was used in the DEC measurements and its inlet was installed close to the sonic anemometer. The shown setup was in use from November 2006 (**Papers I, III, V**). Until then, the setup featured five sampling lines (also at 7 and 10 m), all 32 m long and operating at a flow of $15\,\mathrm{l\,min^{-1}}$ (**Papers II, IV**). The tubing length from the T-connector or the zero air bypass to the PTR-MS inlet was 1 m and the zero air flow was $1\,\mathrm{l\,min^{-1}}$.

Table 1. PTR-MS measurement cycles in the DEC measurements, the compounds contributing to the measured masses, and the PTR-MS integration (or dwell) times. The cycle length was 5.9 s (**Paper II**), 6.6 s (**Papers III, V**), or 5.6 s (**Paper IV**).

Protonated mass [amu] and contributing compound(s)	Formula	Dwell time [s]		
		II	**III** and **V**	**IV**
21 water	$H_2{}^{18}O$	0.2	0.1	0.1
25 (control mass)		0.2	–	–
31 formaldehyde	CH_2O	–	0.5	0.5
32 oxygen•	O_2	0.2	–	–
33 methanol	CH_4O	0.5	0.5	0.5
37 water cluster	$(H_2O)_2$	0.2	0.05	0.05
39 water cluster	$H_2OH_2{}^{18}O$	0.2	–	–
45 acetaldehyde	C_2H_4O	0.5	0.5	0.5
55 water cluster	$(H_2O)_3$	0.2	–	–
57 water cluster	$(H_2O)_2H_2{}^{18}O$	0.2	–	–
59 acetone	C_3H_6O	0.5	0.5	0.5
69 isoprene methylbutenol fragment	C_5H_8	–	0.5	–
81 monoterpene fragments hexenal fragment		0.5	0.5	0.5
87 methylbutenol	$C_5H_{10}O$	–	0.5	0.5
99 hexenal	$C_6H_{10}O$	0.5	0.5	0.5
101 *cis*-3-hexenol hexanal	$C_6H_{12}O$ $C_6H_{12}O$	0.5	0.5	0.5
113		–	0.5	–
137 monoterpenes	$C_{10}H_{16}$	0.5	0.5	0.5

• molecular mass

The lag time method comparison presented in **Paper III** was partly based on simulated DEC data derived from high frequency H_2O concentration measurements with an infrared gas analyzer (IRGA, LI-COR Inc., LI-6262). The H_2O data were recorded at 10 Hz on the same computer as the wind data of the DEC measurements (for details, see Keronen et al., 2003). This enabled conventional EC measurements of H_2O fluxes which served as a reference in the comparison.

Table 2. Compositions of the PTR-MS calibration gas standards (**Paper I**). The standard A was in use until 12 July 2007 and the standard B thereafter. The maximum uncertainty of the volume mixing ratio (VMR) was 6% (Apel–Riemer Environmental, Inc.). The last column contains the proton transfer reaction rate coefficients (k) reported by Zhao and Zhang (2004).

VOC and its protonated mass [amu]	Formula		VMR in A [ppmv]	VMR in B [ppmv]	k [10^{-9} cm^3 s^{-1}]
33 methanol	CH_4O	●	1.03	1.05	2.33
42 acetonitrile	C_2H_3N	●	1.08	1.01	4.74
45 acetaldehyde	C_2H_4O	●	1.06	0.99	3.36
47 ethanol	C_2H_6O		1.06	–	
59 acetone	C_3H_6O		1.09	1.05	
69 isoprene	C_5H_8		1.09	1.02	
71 methacrolein	C_4H_6O	●	1.08	–	3.55
71 methyl vinyl ketone	C_4H_6O	●	0.92	0.92	3.83
73 methyl ethyl ketone	C_4H_8O	●	1.08	1.06	3.48
79 benzene	C_6H_6	●	1.07	1.03	1.97
93 toluene	C_7H_8	●	1.07	1.04	2.12
101 *cis*-3-hexenol	$C_6H_{12}O$		0.96	–	
101 hexanal	$C_6H_{12}O$		0.97	0.90	
107 m-xylene	C_8H_{10}	●	1.07	1.03	2.26
107 o-xylene	C_8H_{10}	●	1.07	1.05	2.32
121 1,2,4-trimethylbenzene	C_9H_{12}	●	–	0.98	2.40
129 naphthalene	$C_{10}H_8$	●	–	1.00	2.59
137 α-pinene	$C_{10}H_{16}$		1.05	0.93	
182 1,2,4-trichlorobenzene	$C_6H_3Cl_3$		–	1.01	

● These non-fragmenting compounds were taken into account in the determination of a relative transmission curve.

3.3 PTR-MS calibrations

The PTR-MS calibration setup (Fig. 4; **Paper I**) consisted of a calibration gas standard (Apel–Riemer Environmental, Inc.) and a zero air generator (catalytic converter, Parker Hannifin Corp., ChromGas Zero Air Generator 3501 (1001 until November 2006)). The calibration gas standard was replaced with a new one in July 2007. Both standards contained 16 VOCs in nitrogen (Table 2).

The PTR-MS was calibrated every or every other week. The optimal detector voltage was checked before each calibration. The VOC concentrations in the standard gas were diluted from about 1 ppmv (part per million by volume) to a concentration range of 15–50 ppbv (parts per billion by volume) using VOC-free air produced from ambient air with the zero air generator. The standard gas flow and the zero air flow were measured with a primary flow meter (Bios International Corp., DryCal DC-2M). The flows were not changed during the calibration, so each calibration was performed at a single VOC concentration. PTFE tubing (1.6 mm inner diameter) was used in the calibration lines and the calibration system was connected to the PTR-MS in the same way as the main sampling lines. The system was utilized also in the regular zero air measurements.

3.4   Concentration measurements with PTR-MS

3.4.1   Concentration calculation steps

A concentration calculation procedure for long-term VOC measurements, based on Eq. (4) and guidelines given in previous studies (e.g. Lindinger et al., 1998a; de Gouw et al., 2003a; Ammann et al., 2004; Steinbacher et al., 2004), was presented in **Paper I**. The procedure took into account the following factors:

- *Transmission* (Eq. (3) in **Paper I**). The transmission coefficients for RH^+ and H_3O^+ ions, $T(RH^+)$ and $T(H_3O^+)$, describe how effectively these ions are extracted from the drift tube into the mass spectrometer, guided through the quadrupole mass analyzer, and detected by the secondary electron multiplier. Their values range between zero and one. The transmission coefficients are mainly mass dependent but vary also over time (de Gouw et al., 2003a; Ammann et al., 2004; Steinbacher et al., 2004).

- *Fragmentation* (Eq. (4) in **Paper I**). Although PTR-MS uses a soft chemical ionization method, several VOCs are known to fragment in the drift tube (e.g. Tani et al., 2003; Warneke et al., 2003; de Gouw and Warneke, 2007). The fragmentation coefficient, $F(RH^+)$, gives the proportion of RH^+ ions to all product ions (i.e. RH^+ and fragment ions). For non-fragmenting compounds $F(RH^+) = 1$.

- *Water cluster ion formation* (Eq. (4) in **Paper I**). The primary ions can cluster with water molecules in the sampled air and the formed water cluster ions

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($H_3O^+H_2O$, $H_3O^+(H_2O)_2$, etc.) can ionize most VOCs via proton transfer and ligand switching reactions (e.g. Warneke et al., 2001; Tani et al., 2004). Both fragmentation and cluster ion formation depend strongly on the parameter E/N, the ratio of the electric field to the number density of the gas in the drift tube. Fragmentation increases and cluster ion formation decreases when E/N is increased. Cluster ion formation depends also on the humidity of the sampled air (Warneke et al., 2001; Ammann et al., 2006). A new approach to taking account of the abundance of the water cluster ions was introduced in **Paper I**. The approach relied on the ratio of the transmission coefficient for $H_3O^+H_2O$ ions to that for H_3O^+ ions. The value of this ratio (α) was determined in every calibration.

– *Subtraction of VOC background signals* (Eq. (5) in **Paper I**). Significant background counts are usually observed for many VOC-related masses. They are most likely caused by desorption of impurities inside the instrument and the sampling system (Steinbacher et al., 2004). To take account of these VOC background signals, the average of the ion count rates observed in the zero air measurements was subtracted from the count rate observed in the actual measurements.

– *Normalized ion count rate* (Eq. (6) in **Paper I**). The normalized count rate of RH^+ ions, $I(RH^+)_{norm}$, enables the comparison of signals observed in different measurements (de Gouw et al., 2003b; Tani et al., 2004). It is expressed in normalized counts per second (ncps). The definition of the normalized count rate, given in **Paper I**, takes into account changes in the primary and water cluster ion signal and in the drift tube pressure.

After these steps, the number concentration of the compound R in Eq. (4) could be converted into a volume mixing ratio, VMR, given in ppbv (10^{-9}; Eq. (8) in **Paper I**):

$$\text{VMR} = 10^9 \frac{[\text{R}]}{N} = 10^9 \frac{p_{\text{drift}}}{I_{\text{norm}} p_{\text{norm}}} \frac{\mu_0 N_0}{kL} \frac{E}{N^2} \frac{T(\text{H}_3\text{O}^+)}{F(\text{RH}^+) T(\text{RH}^+)} I(\text{RH}^+)_{\text{norm}}. \tag{5}$$

In this equation, p_{drift} is the drift tube pressure, μ_0 is the normalized ion mobility of the primary ions, N_0 is the number density of air at the standard pressure (1013.25 hPa) and temperature (273.15 K), and L is the drift tube length. The normalization constants are $I_{\text{norm}} = 10^6$ cps and $p_{\text{norm}} = 2$ hPa.

3.4.2 Normalized sensitivities and relative transmission curves

The parameters and coefficients in Eq. (5) can be subsumed into a calibration coefficient called the normalized sensitivity,

$$S_{\mathrm{norm}} = \frac{I(\mathrm{RH}^+)_{\mathrm{norm}}}{\mathrm{VMR}}, \tag{6}$$

given in $\mathrm{ncps\,ppbv}^{-1}$ (e.g. de Gouw et al., 2003a). In **Papers I**, **III**, and **V**, the concentrations for the compounds in the calibration gas standards were calculated using this equation by first determining the normalized sensitivities from the calibrations and then solving the equation for VMR. A similar equation (Eq. (2) in **Paper II**), although based on a slightly different definition of the normalized ion count rate, was used in **Papers II** and **IV**.

The concentrations for the compounds not present in the calibration gas standards were calculated using relative transmission coefficients. For this purpose, a method for determining a relative transmission curve for the mass range 19–170 amu was developed (**Paper I**). The method relied on direct calibrations and compounds that do not fragment significantly. For these compounds $F(\mathrm{RH}^+) = 1$ and, according to Eqs. (5) and (6), the relative transmission coefficient is

$$T(\mathrm{RH}^+)_{\mathrm{rel}} = \frac{T(\mathrm{RH}^+)}{T(\mathrm{H_3O}^+)} = 10^9 \frac{p_{\mathrm{drift}}}{I_{\mathrm{norm}} p_{\mathrm{norm}}} \frac{\mu_0 N_0}{kL} \frac{E}{N^2} S_{\mathrm{norm}}. \tag{7}$$

Using the normalized sensitivities observed in the calibrations, these coefficients were calculated for the masses related to the non-fragmenting VOCs in the gas standards (Table 2). After each calibration, the relative transmission curve was determined by fitting an interpolation function to six parameters derived from the calculated coefficients (see Sect. 2.4.3 in **Paper I**).

Finally, to calculate the concentrations for the non-calibrated compounds, the values of $T(\mathrm{RH}^+)_{\mathrm{rel}}$ obtained from the relative transmission curves were substituted to Eq. (5). The fragmentation coefficient was set to one as the non-calibrated compounds considered in this work did not fragment substantially. In general, the method can also be applied to fragmenting compounds (Eq. (12) in **Paper I**).

3.5 Flux measurements using DEC combined with PTR-MS

3.5.1 Covariance functions

The determination of the lag time between wind and concentration measurements is a major challenge in DEC when measuring VOC fluxes near the detection limit. The lag time, resulting from the sample transit time through the sampling line, has to be determined before the wind and concentration time series can be synchronized. The flux value is then given by the covariance derived from the matched time series. Different methods for the lag time determination in DEC measurements with PTR-MS were compared in **Paper III**.

In all DEC measurements, the lag time determination relied on covariance functions. They were calculated for all VOC-related masses (Table 1) and the water cluster ions detected at 37 amu (M37) and in **Paper III** also for H_2O measured with the IRGA. A covariance function gives the covariance of the vertical wind speed and the gas concentration as a function of lag time (Fig. 5; e.g. Kaimal and Finnigan, 1994):

$$F(t_{\text{lag}}) = \frac{1}{n} \sum_{i=1}^{n} w'(i - t_{\text{lag}}/\Delta t_w) c'(i). \tag{8}$$

Here t_{lag} is the lag time, w' is the momentary deviation of the vertical wind speed from its average, and c' is that of the VOC mass concentration, the normalized M37 count rate, or the H_2O mass concentration. The sampling interval in the wind measurements, Δt_w, was 0.1 s and the number of measurements during the 45-min flux averaging time, n, was 410–480 in DEC and 27000 in EC (**Paper III**). The lag time window was ± 180 s with a time resolution of 0.1 s.

Before the covariance function calculations, three-dimensional coordinate rotation and linear detrending were applied to the data using established methods (Kaimal and Finnigan, 1994). As the PTR-MS integration time was 0.5 s for each VOC-related mass, five-point running averages of the vertical wind speed were used for them. To make the covariance functions temporally concordant, the actual measurement time of each mass within the PTR-MS measurement cycle was taken into account. Also the flux error estimation was based on the covariance functions. The uncertainty of a flux value was determined by calculating standard deviations from the lag time ranges -180 to -140 s and 140 to 180 s (-180 to -160 s and 160 to 180 s in **Paper II**; Wienhold
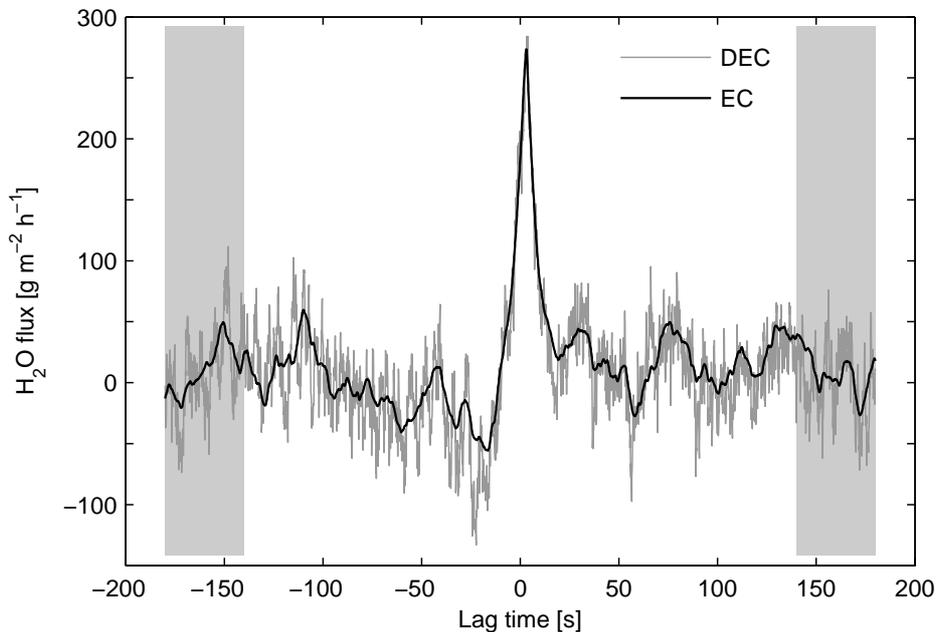
Fig. 5. Covariance function of H_2O calculated in the EC and DEC manner (9 August 2007 12:00–12:45). The sampling interval was 0.1 s in EC and 6.6 s in DEC. The comparison illustrates how DEC increases the noise and thus the flux uncertainty. The shaded areas show the lag time ranges used in the uncertainty estimation, which was based on the standard deviations of the covariance function. EC fluxes of H_2O were used as a reference in **Paper III**.

et al., 1994; Spirig et al., 2005). The average of the standard deviations was multiplied by 1.96 to get the 95% confidence interval for each flux measurement (**Paper II**).

3.5.2 Lag time methods

The theme of **Paper III** was the comparison of five lag time methods. One of them relied on a theoretical constant value, while in the other methods lag times were determined directly from the covariance functions. As the motivation was stand-alone DEC measurements with PTR-MS, this straightforward procedure was deemed viable. Also more complex and perhaps better alternatives have been proposed (e.g. Shaw et al., 1998; Massman, 2000), but usually they require spectral analysis and hence high frequency measurements, which makes them unsuitable for DEC.
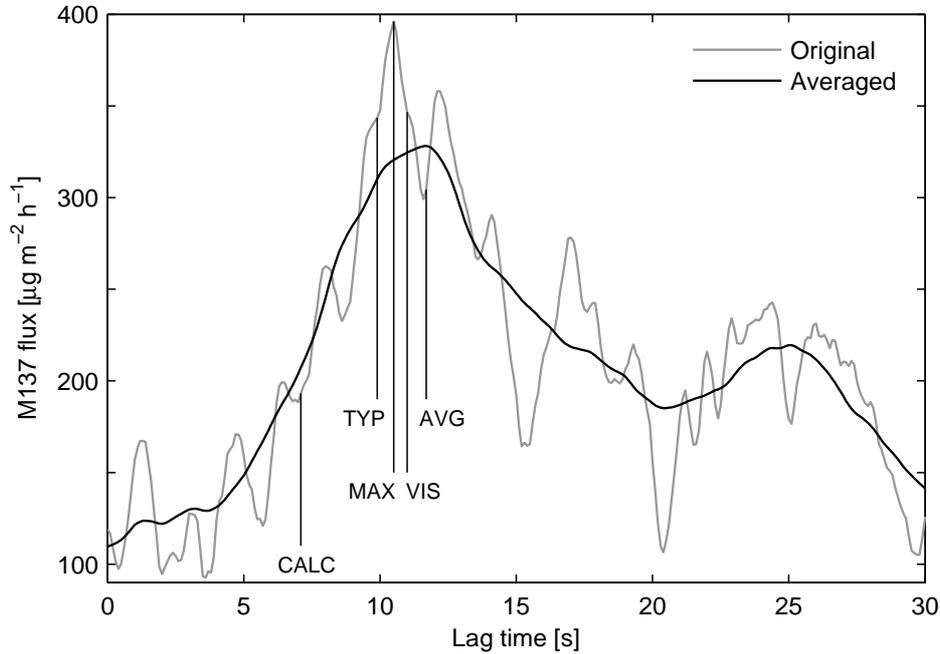
Fig. 6. Principles of the lag time methods illustrated with a covariance function of monoterpenes (M137, 11 August 2007 12:00–12:45; **Paper III**). The calculated (CALC) and typical (TYP) constant lag times were 7.1 and 9.9 s. In the maximum covariance method (MAX), the lag time was 10.5 s. The averaging approach (AVG) yielded a lag time of 11.7 s, which was determined from the maximum of the averaged covariance function. However, the final flux value was derived from the original covariance function. The visual assessment method (VIS) gave a lag time of 11.0 s.

The lag time methods were based on the following principles (Fig. 6):

- CALC: The lag time was calculated from the sampling flow and the sampling line dimensions and was kept constant throughout the measurement period.

- TYP: The lag time represented a typical daytime value deduced from measurements with distinct covariance function maxima. It was kept constant over the measurement period. The objective was to illustrate consequences of considering a limited number of measurements representative of the whole period.

- MAX: The lag time was determined from the maximum absolute value of the covariance function within a given lag time window. This is the prevalent method in EC (e.g. Aubinet et al., 2000).

– AVG: In the new averaging approach, the covariance function was first averaged using a five-second running average to make patterns more distinguishable (Fig. 6). The lag time was derived from this averaged covariance function using the MAX method. Although averaging was practised to aid the lag time identification, the final flux value was always determined from the original covariance function at the indicated lag time. This ensured that no part of the real flux signal was eliminated due to the averaging. The width of the averaging window was deemed wide enough to allow a sufficient noise reduction but also narrow enough to prevent a considerable shift in the covariance function maximum.

– VIS: The lag time was determined visually from a figure showing a covariance function for the lag time range -180 to 180 s. This first view gave a general idea of the function patterns and noise. It was zoomed in on the lag time window used in MAX to look for a positive or negative peak with a minimum height of about two times the noise and a minimum base width of about 2–3 s. The lag time was derived from around the middle of the peak, i.e. not necessarily from the maximum. If an unambiguous resolution was impossible, only the flux uncertainty was calculated.

In **Paper II**, the lag time determination was based on the MAX method complemented with visual verification. The VIS method was used in **Paper IV** and the AVG method in **Paper V**.

3.6   Monoterpene emission algorithms

Two emission algorithms were applied to interpreting the DEC measurements of monoterpene emissions. The basis for the analysis in **Paper V** was the hybrid algorithm formulated in **Paper IV** starting from the traditional pool and synthesis algorithms developed by Guenther et al. (1991, 1993). The traditional pool algorithm was in use in **Paper II**. It also served as a point of comparison for the hybrid algorithm in **Papers IV** and **V**.

The hybrid algorithm assumes that the monoterpene emission, M, has two independent origins, de novo biosynthesis and evaporation from specialized storage pools:

$$M = M_{\mathrm{synth}} + M_{\mathrm{pool}} = M_{0,\mathrm{synth}}C_T C_L + M_{0,\mathrm{pool}}\gamma. \tag{9}$$

Here $M_{0,\text{synth}}$ and $M_{0,\text{pool}}$ are the emission potentials for de novo and pool emissions. The synthesis activity factors for temperature and light, C_T and C_L, are the same as in the traditional synthesis algorithm (Guenther et al., 1991, 1993). They describe the dependence of enzyme activity on temperature and the dependence of electron transport rate on light. The temperature activity factor, γ, has the same form as in the traditional pool algorithm (Guenther et al., 1991, 1993). It describes the dependence of monoterpene saturation vapour pressure on temperature.

Equation (9) can be converted into the final hybrid formulation given in **Paper IV**:

$$M = M_0[f_{\text{synth}}C_T C_L + (1 - f_{\text{synth}})\gamma]. \tag{10}$$

Here $M_0 = M_{0,\text{synth}} + M_{0,\text{pool}}$ is the total emission potential and $f_{\text{synth}} = M_{0,\text{synth}}/M_0$ is the ratio of the de novo emission potential to the total emission potential. This hybrid algorithm and the traditional pool algorithm, $M_{\text{pool}} = M_{0,\text{pool}}\gamma$, were fitted to the measured emissions using non-linear regression in the least squares sense. The fitting procedure gave the values of M_0, f_{synth}, and $M_{0,\text{pool}}$. The values of the other parameters, including the standard temperature and light (30 °C and 1000 μmol m^{-2} s^{-1}) and the temperature dependence coefficient in γ (0.09 °C^{-1}), were taken from Guenther (1997). Half-hour averages of air temperature and photosynthetically active radiation were used as the input variables in the algorithms. They were acquired from a set of SMEAR II routine measurements (Junninen et al., 2009).

4 Results and discussion

4.1 Long-term VOC measurements with PTR-MS

PTR-MS was first advertised as a calibration-free technique (Ionicon Analytik GmbH), meaning that VOC concentrations could be derived directly from the observed ion signals, the proton transfer reaction rate coefficients (e.g. Zhao and Zhang, 2004), the reaction times, and the instrument parameters. It soon turned out that regular calibrations were essential to achieve the accuracy needed in atmospheric VOC measurements (de Gouw and Warneke, 2007). However, normalized sensitivities cannot always be determined for all measured compounds due to lack of calibration standards. Hence relative transmission coefficients and proton transfer reaction rate coefficients are still often necessary in concentration calculations.

These facts led to the development of the measurement, calibration, and calculation methods reported in **Paper I**. The goal was to design systematic and practical procedures suitable for long-term, stand-alone field measurements with PTR-MS. A salient point was the introduction of a novel method for determining both normalized sensitivities and a relative transmission curve using information obtained from a calibration with a gas standard. This curve enabled consistent concentration calculations for non-calibrated VOCs.

As discussed in **Paper I**, the normalized sensitivity varied substantially between compounds, increasing from less than 5 ncps ppbv^{-1} to around 40 ncps ppbv^{-1}. It also varied over time. Figure 7 shows an example of the considerable temporal variation observed in 16 calibrations during May–August 2007. The interquartile range (from the 25th to 75th percentile) was 26% of the median value for methanol, 27% for acetaldehyde, 28% for acetone, and 27% for α-pinene. The actual sensitivity, which is based on non-normalized count rates and hence strongly dependent on the primary ion signal, naturally exhibited even larger variation (not shown). The proportions of the interquartile ranges to the medians were 75, 77, 70, and 82%. Over the whole period, the minimum value, 28 cps ppbv^{-1}, was measured for α-pinene and the maximum value, 600 cps ppbv^{-1}, for acetone.

The conclusion is that regular calibrations and the use of the normalized sensitivity and the normalized ion count rate are necessary to ensure a reasonable accuracy in
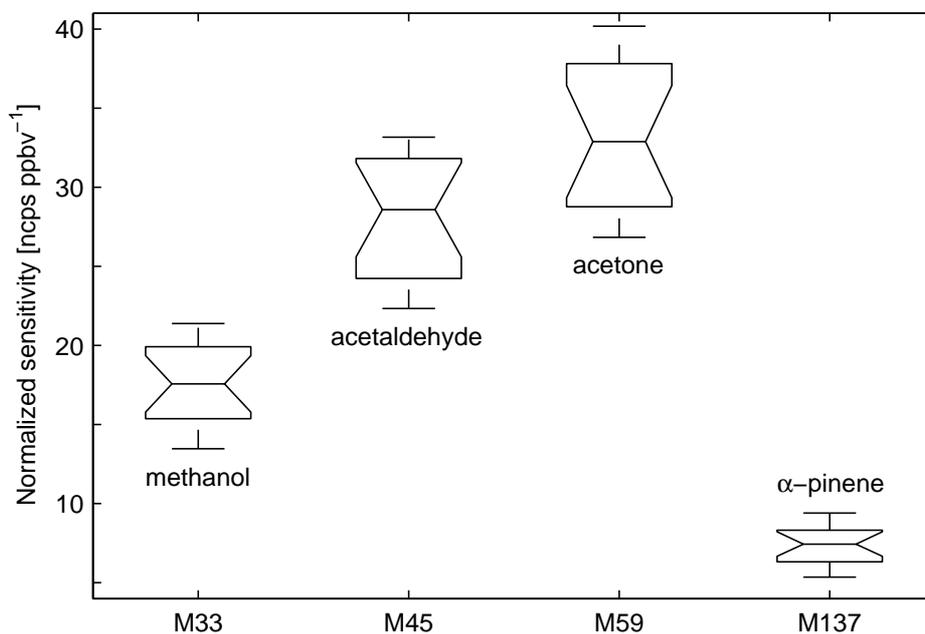
Fig. 7. Normalized sensitivities determined from 16 calibrations during May–August 2007. The shown values for α-pinene, which in this work proved to be a representative compound for monoterpene calibrations (**Paper I**), were derived from the molecular ion signal at 137 amu. For an explanation of the box plot, see the legend of Fig. 9.

long-term PTR-MS measurements. Normalization has been long recognized as an important step in PTR-MS data analysis (e.g. Warneke et al., 2001; de Gouw et al., 2003b). The definition of the normalized ion count rate in **Paper I** took account of the abundance of the water cluster ions, which is related to the humidity of the sampled air (Ammann et al., 2006). However, normalization procedures hardly remove the effects of ambient humidity on the detection of several compounds, including monoterpenes (Hansel et al., 1997; Warneke et al., 2001; Tani et al., 2004; Inomata et al., 2008; Sinha et al., 2009; Jobson and McCoskey, 2010; Vlasenko et al., 2010). Hence humidity dependent calibrations would be a good addition to the methods presented in **Paper I**. The drawback is that humidity measurements should be carried out simultaneously with PTR-MS measurements, not only during the calibrations. Another advisable improvement would be a multi-step calibration procedure using several VOC concentrations to verify the linearity of the PTR-MS instrument.

The method for determining a relative transmission curve proved to be sensitive enough to capture both mass and time dependent changes in the transmission (Fig. 8; **Paper**
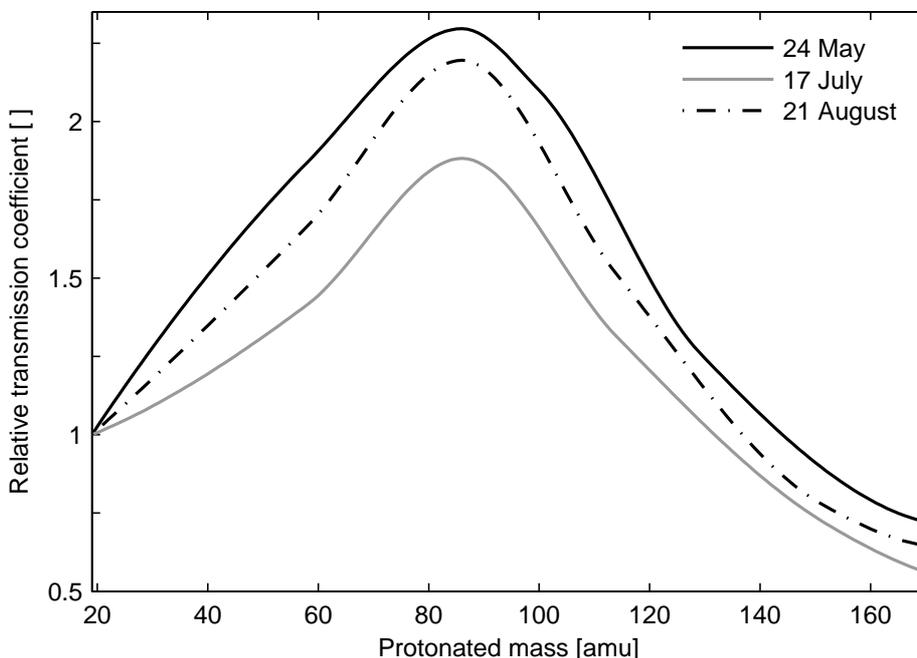
Fig. 8. Relative transmission curves for the mass range 19–170 amu derived from three calibrations in 2007 using the method described in **Paper I**. The relative transmission coefficient for H_3O^+ ions (19 amu) is one by definition (Eq. (7)).

I). The general level of the curve varied depending on the measured normalized sensitivities, but the shape of the curve remained rather constant. The maximum was around 85 amu, and the descending part of the curve above 100 amu was normally slightly steeper than the ascending part. The maximum values were typically 60–130% higher and the minimum values 25–50% lower than the relative transmission coefficient for the primary ions. Similar results have been observed also for other quadrupole instruments (Ammann et al., 2004; Steinbacher et al., 2004; Kim et al., 2009).

In general, concentration calculations using relative transmission coefficients and proton transfer reaction rate coefficients often result in lower accuracies than calculations with normalized sensitivities. This is due to the larger uncertainties in relative transmission curves and proton transfer reaction rate coefficients (e.g. de Gouw and Warneke, 2007). However, provided the relative transmission curve is carefully determined, the accuracy can be reasonable, even for such reactive, heavy, and easily fragmenting compounds as sesquiterpenes (204 amu; Kim et al., 2009). A better determination for masses beyond 130 amu should be the next step to improve the relative

transmission curve fitting procedure described in **Paper I**. Still, the low transmission inevitably reduces the sensitivity for heavy compounds, a limitation which is probably overcome only by the better transmission characteristics of time-of-flight instruments (e.g. Blake et al., 2009).

4.2   DEC measurements with PTR-MS

The results reported in **Paper II** demonstrated that the sensitivity of the flux measurement setup was adequate for DEC measurements above a boreal forest. Although the flux uncertainties were relatively large, significant emissions of methanol, acetaldehyde, acetone, and monoterpenes could be detected (see Sect. 4.3). The analysis with a stochastic Lagrangian transport model showed that the effect of chemical degradation on the measured fluxes of these compounds was negligible.

After the first measurements, the motivation in the DEC method development focused on the determination of the lag time between wind and concentration measurements. The lag time method comparison in **Paper III** was based on the DEC measurements with the PTR-MS and simulated DEC data derived from the high frequency H_2O measurements with the IRGA. To increase noise, and thus improve the resemblance of the IRGA and PTR-MS measurements, normally distributed random numbers were added to the original H_2O time series. This manipulated H_2O signal (H_2O_{noise}) was then converted into a disjunct time series using the sampling interval of the actual DEC measurements. The simulated DEC fluxes were evaluated against the EC fluxes of H_2O.

The DEC simulation results in Fig. 9 illustrate that each lag time method produced a median flux for the six-day measurement period that was in agreement with the median of the reference EC fluxes. In contrast, the error analysis exposed systematic differences between the methods. The median errors of the new averaging method (AVG) and the visual assessment method (VIS) did not differ statistically from zero at the 95% confidence level. The constant lag time methods (CALC and TYP) underestimated the absolute values of the fluxes and the maximum covariance method (MAX) was prone to overestimation.

The MAX method is the conventional choice in EC (e.g. McMillen, 1988; Aubinet et al., 2000). However, noisy covariance functions, common in DEC measurements, inflict
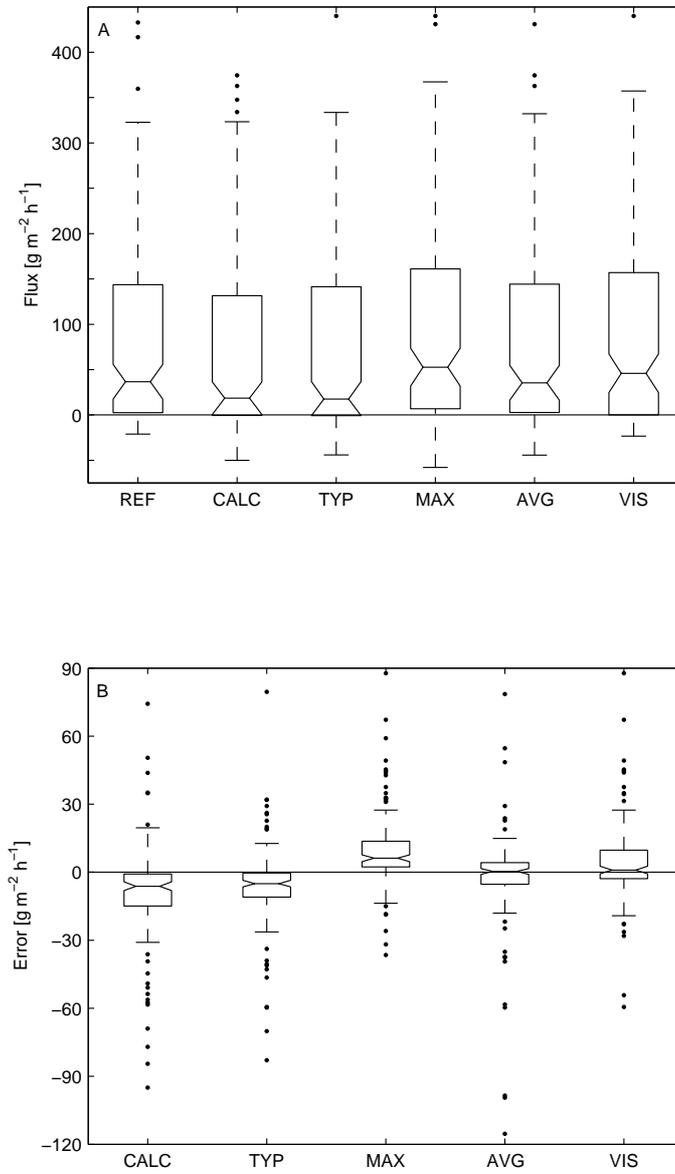
Fig. 9. Lag time method comparison (**Paper III**). Panel (**A**) gives the statistics of the DEC fluxes of H_2O_{noise} and the EC fluxes of H_2O. Panel (**B**) shows the error analysis. The DEC fluxes were calculated using the five lag time methods (Sect. 3.5.2) and evaluated against the reference EC fluxes (REF). The line in the middle of each box is the median with the 95% confidence interval indicated by the notches. The lower and upper line are the 25th and 75th percentile, the distance between them is the interquartile range. The error bars extend from the 25th or 75th percentile to the furthest data value within 1.5 times the interquartile range.

difficulties on its application. As demonstrated by the DEC simulation, a systematic overestimation of the absolute flux is possible when the lag time is derived from the maximum absolute covariance. Of course, this flaw can also afflict EC measurements, but its impact is more harmful in DEC where the signal-to-noise ratio tends to be much lower.

The feasibility of CALC and TYP was questionable due to the tendency to underestimate the absolute fluxes and the observed lag time variation during the measurement period (**Paper III**). This was somewhat expected as constant lag time methods are often considered inadvisable (Massman, 2000; Shimizu, 2007), especially in long-term measurements. In addition, the differences between the lag times of methanol, monoterpenes, and the water cluster ions suggested that the lag time should be determined individually for each compound. Such compound-specific behaviour has been observed also in CO_2 and H_2O studies (e.g. Su et al., 2004; Ibrom et al., 2007), which probably reflects the difference in the polarity between these compounds.

Based on the DEC simulation and the sensitivity analysis of the actual DEC fluxes (**Paper III**), the new AVG approach appears a promising alternative for the lag time determination in DEC measurements. Due to the averaging, it is less sensitive to the maximum absolute covariance and thus less prone to a positive bias in the absolute flux than the MAX method. Further, by making flux calculations more systematic and less labour-intensive, AVG is a convenient alternative to VIS, which is rather ill-defined and dependent on interpretation.

Despite the increasing number of DEC measurements in the past decade, the lag time determination is still often a critical point in the automation of flux calculations. As noisy covariance functions hinder the use of the MAX method, novel regimes are needed to advance the DEC methodology (Hörtnagl et al., 2010; **Paper III**). The AVG approach is one such candidate, practically suitable for any EC application when measuring fluxes near the detection limit. It should be scrutinized in further studies to better assess its performance in different micrometeorological conditions.

4.3 Ecosystem scale VOC emissions from a boreal Scots pine forest

Besides the DEC and PTR-MS method development, this work aimed at broadening understanding of ecosystem scale VOC emissions from a boreal Scots pine dominated forest. One of the objectives of **Paper II** was to measure emissions of oxygenated VOCs and to compare them with monoterpene emissions. The idea of **Paper IV** was to determine the contribution of de novo biosynthesis to monoterpene emissions from common boreal and alpine tree species using $^{13}CO_2$ labelling. Considering this thesis, the main results were the observed split between de novo and pool emissions for Scots pine and the demonstrated ability of a hybrid emission algorithm to improve ecosystem scale emission modelling. **Paper V** pursued the same matter and estimated the role of de novo biosynthesis directly from the DEC measurements.

4.3.1 Oxygenated VOC and monoterpene emissions

One current challenge in the research on VOC emissions from Eurasian boreal ecosystems is to quantify emissions of non-terpenoid compounds (Rinne et al., 2009). These compounds include, inter alia, the oxygenated VOCs studied in this work: methanol, acetaldehyde, and acetone. Their measurement has been greatly facilitated by the advent of PTR-MS, which enabled also the first ecosystem scale emission measurements in the Eurasian boreal zone (**Paper II**).

Figure 10 offers a general idea of the VOC emissions, photosynthetically active radiation (PAR, at 74 m), and air temperature (at 8.4 m) during the summer 2007. For instance, the sudden rise in the emissions, PAR, and temperature in early June indicates the correlation between these variables. As demonstrated in **Paper V**, the continuous DEC measurements provided an indirect means of studying the biological mechanisms controlling monoterpene emissions when combined with the hybrid emission algorithm (Sect. 3.6). The interpretation is more challenging for oxygenated VOCs since the use of emission algorithms can be complicated by deposition fluxes (e.g. Karl et al., 2005). In fact, a significant number of negative fluxes, observed mainly at night, were excluded from Fig. 10. Thus the possibility of intermittent deposition of both oxygenated VOCs and monoterpenes seems to deserve more attention in VOC flux measurements and modelling.
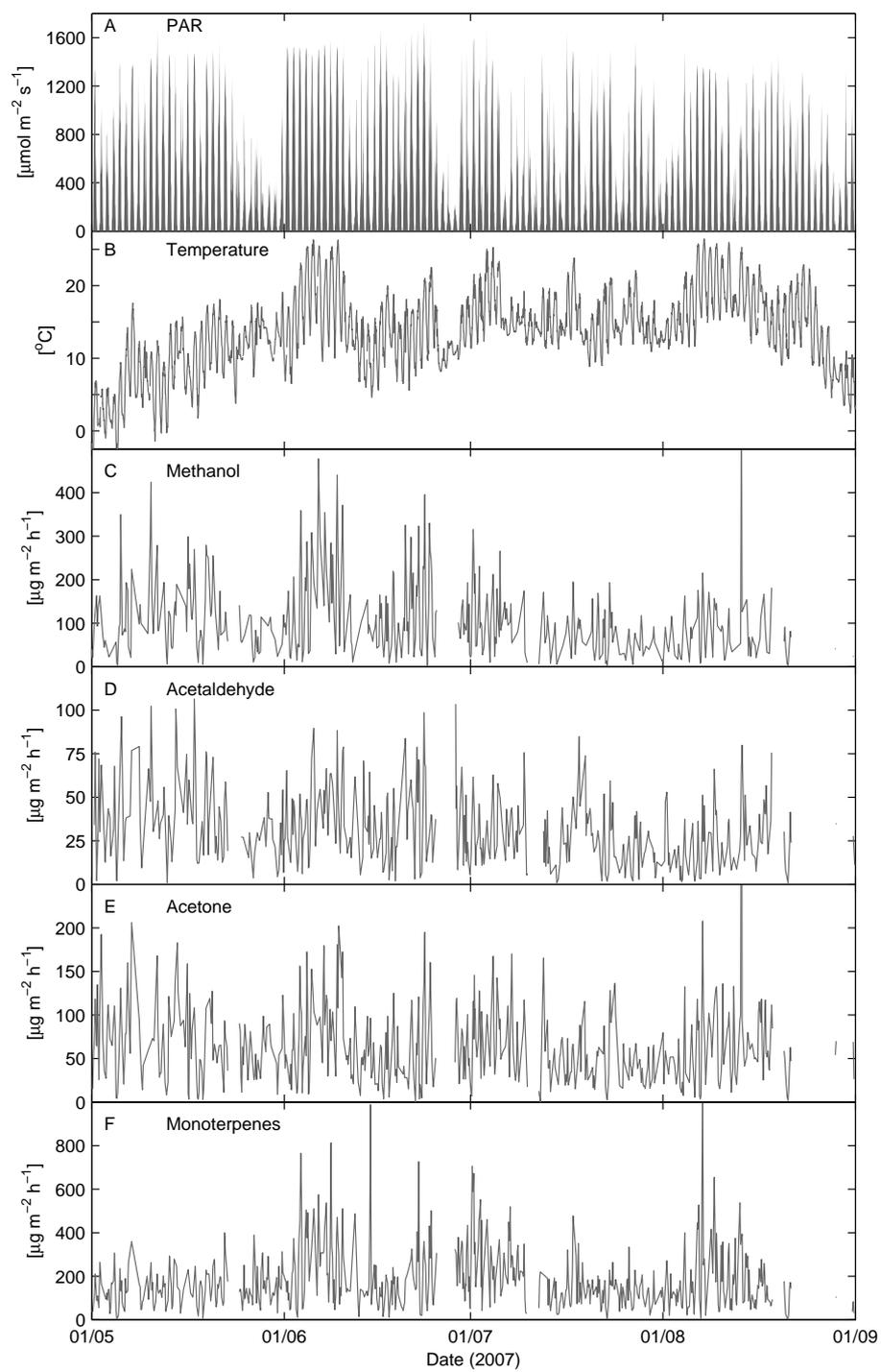
Fig. 10. Photosynthetically active radiation (PAR), air temperature, and VOC emissions during May–August 2007.
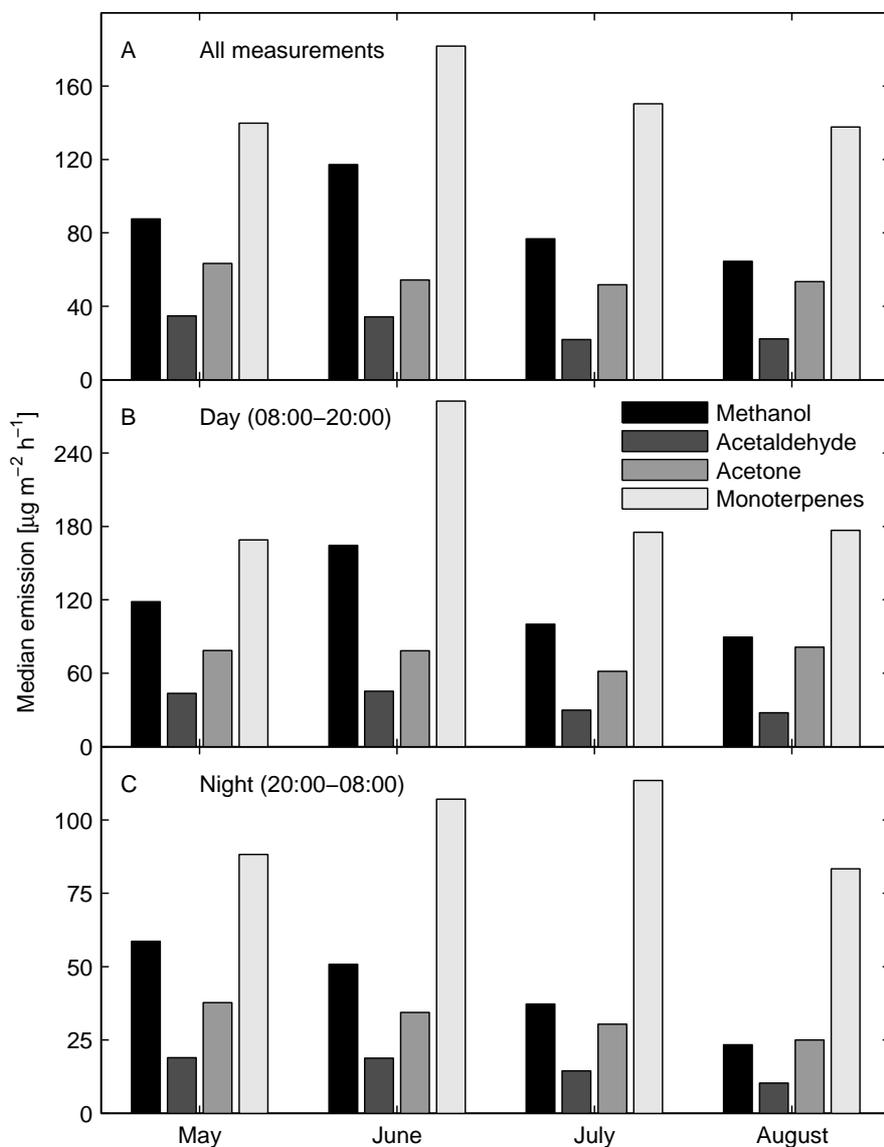
Fig. 11. Monthly medians of VOC emissions during the summer 2007.

Figure 11 illustrates that the contribution of oxygenated VOCs to the total emissions was substantial throughout the summer, ranging from 50 to 57% when calculated on a mass basis from the monthly medians of all measurements. The proportion derived from the measurements in July 2005 was 43% (**Paper II**). The highest oxygenated VOC emissions were those of methanol, comprising 23–30% of the total, followed by acetone with the shares of 14–19%. The acetaldehyde emissions were 7–11% of the total.

As discussed in **Paper II**, the oxygenated VOC and monoterpene emissions were roughly comparable with the results of previous measurements at SMEAR II or in other pine forest ecosystems. Although the emissions were deemed to have originated mainly from the forest canopy, simultaneous DEC and enclosure measurements are needed to better estimate the source distribution between the canopy, undergrowth, and soil. The chemical production of oxygenated VOCs, for example in sesquiterpene reactions, may cause positive biases to their fluxes, which further complicates the interpretation of DEC measurements.

4.3.2   Role of de novo biosynthesis in monoterpene emissions

Monoterpene emissions from Scots pine are often assumed to originate as evaporation from specialized storage pools and thus modelled with temperature dependent algorithms (e.g. Tingey et al., 1980; Guenther et al., 1991, 1993). In the alternative view, a significant part of these emissions is thought to originate directly from de novo biosynthesis in a light and temperature dependent manner (e.g. Steinbrecher et al., 1999; Shao et al., 2001). To elucidate this ambiguity, the proportion of de novo emissions to total emissions was determined in the $^{13}CO_2$ labelling study in **Paper IV**. It demonstrated that this proportion can be over 50% for Scots pine saplings.

In **Paper V**, the simple hybrid algorithm describing both pool and de novo emissions (Sect. 3.6) was used to interpret the DEC measurements. This method revealed two interesting features of the monoterpene emissions (Fig. 12). First, the total emission potential given by the hybrid algorithm had a decreasing summertime trend. A similar decrease was observed in the pool emission potential determined with the traditional pool algorithm. Second, the contribution of de novo biosynthesis to the ecosystem scale emissions differed from zero throughout the summer.

The trend in the emission potential was statistically significant in both algorithms, indicating that the potential of the forest to emit monoterpenes diminished over the summer. This possibly reflected seasonal changes both in the monoterpene biosynthesis and in the monoterpene diffusion rate from the pools into the atmosphere. A similar decline in the pool emission potential has been observed also in shoot scale measurements at the same site (Tarvainen et al., 2005; Hakola et al., 2006). For instance, the results of Hakola et al. (2006) correspond rather well with the ecosystem scale pool emission potential (Fig. 12a), which suggests that the ecosystem scale emissions
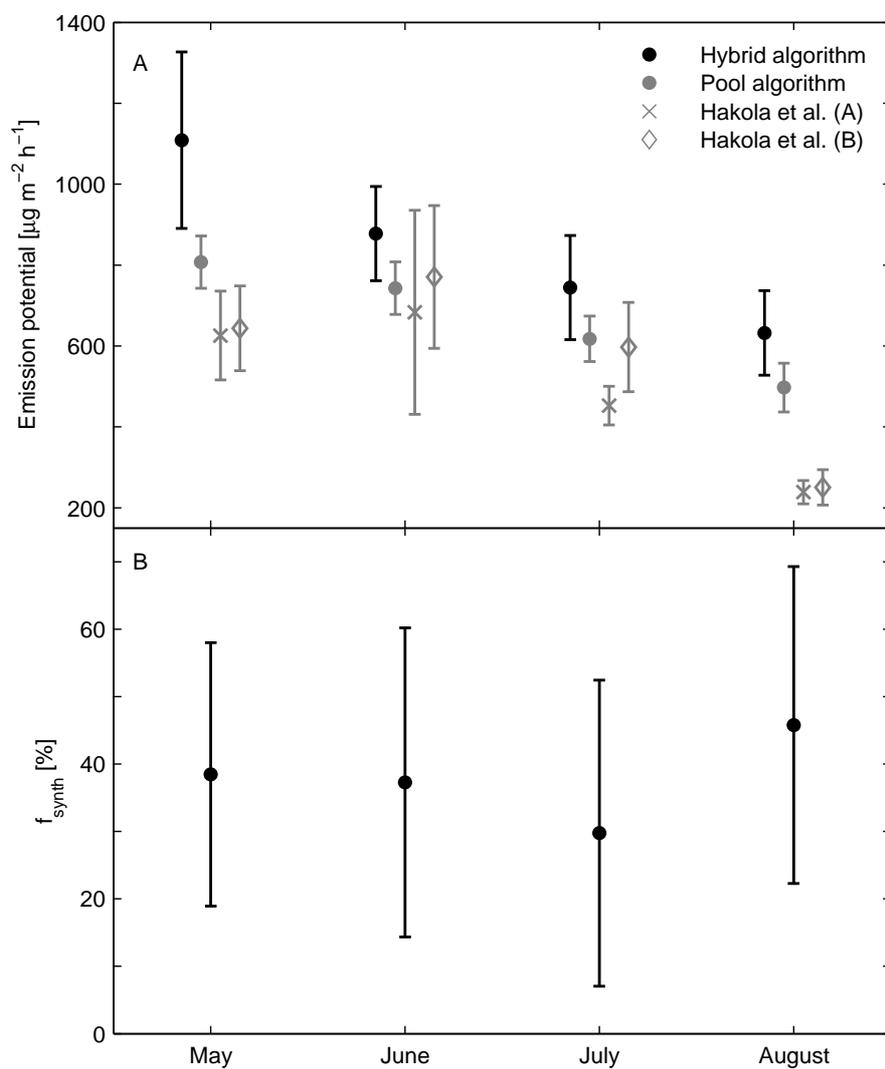
Fig. 12. Interpretation of the monoterpene emissions measured during the summer 2007 (**Paper V**). (**A**) Monthly variation in the total emission potential and the pool emission potential. The pool emission potentials based on measurements with two Scots pine branches were derived from the results of Hakola et al. (2006) using a needle biomass density of 540 $\mathrm{g\,m^{-2}}$. (**B**) The ratio of the de novo emission potential to the total emission potential (f_{synth}). The error bars represent the 95% confidence intervals.

originated mainly from the canopy.

The ratio of the de novo emission potential to the total emission potential varied between 30 and 46% (Fig. 12b). The monthly changes were not significant at the 95%
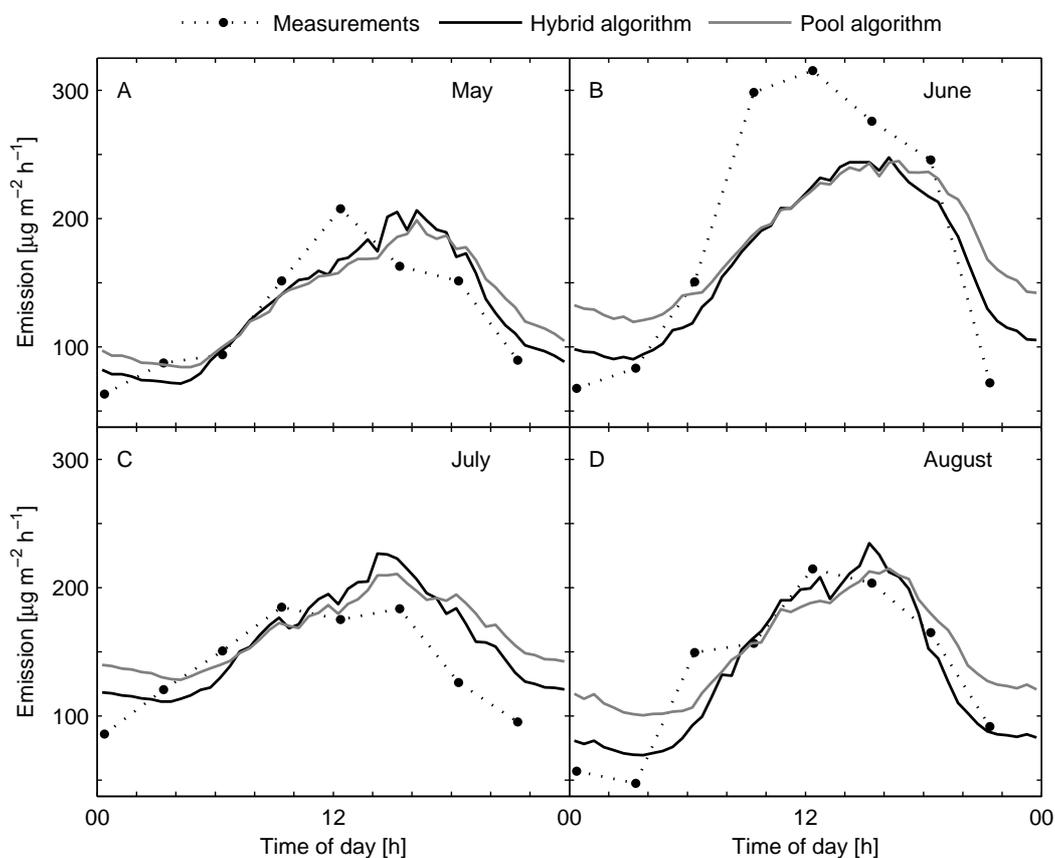
Fig. 13. Median daily cycles of the monoterpene emissions during the summer 2007 as given by the DEC measurements and the two emission algorithms (**Paper V**).

confidence level and hence the seasonal variation in biosynthesis (Fischbach, 2001) could not be determined. However, the ratio always differed statistically from zero, indicating that de novo biosynthesis had a significant role in the ecosystem scale monoterpene emissions. The percentages in Fig. 12b agree with the percentage of 58% found in **Paper IV** when the uncertainties in both studies are taken into account.

The results of **Paper V** probably gave the first direct suggestion of the significance of biosynthesis in ecosystem scale monoterpene emissions. Together with the findings of **Paper IV**, they offered a guideline to follow when modelling emissions from Scots pine dominated forests: the algorithm should describe emissions from both storage pools and de novo biosynthesis. Figure 13 illustrates one consequence of the incorporation of biosynthesis into the monoterpene emission algorithm (**Paper V**). It shows the median daily cycle as given by the DEC measurements and the two algorithms. As noticed

also in **Paper IV**, the hybrid algorithm reproduced the daily variation somewhat better than the pool algorithm. Due to the light dependence of de novo emissions, it reduced especially the night-time overestimation. However, the hybrid algorithm should be contrasted with independent measurements to get more reliable estimates of its performance. Also the partition between pool and de novo emissions is still poorly known, even though **Papers IV** and **V** enhanced the knowledge considerably. Seasonal changes in the partition as well as the detailed structure of a sound and practical hybrid algorithm remain as important research objectives.

5 Review of papers and the author's contribution

Paper I presents the PTR-MS measurement, calibration, and concentration calculation methods used in the VOC flux measurements. It demonstrates the importance of regular calibrations and introduces a new method for determining a relative transmission curve, which enables consistent concentration calculations also for compounds that are not calibrated directly.

Paper II describes the DEC measurement setup and reports the first DEC measurements of methanol, acetaldehyde, acetone, and monoterpene emissions from a boreal Scots pine dominated forest. The results show that the role of oxygenated VOCs in the ecosystem scale emissions is significant. An analysis with a stochastic Lagrangian transport model surveys the effects of chemical degradation on the measured fluxes.

Paper III addresses a major pragmatic challenge in DEC applications: the determination of the lag time between wind and concentration measurements. A comparison of five lag time methods supports the use of a new averaging approach which is less prone to overestimation of the absolute values of fluxes than the traditional choice, the maximum covariance method.

Paper IV investigates the origin of monoterpene emissions from boreal and alpine tree species using $^{13}CO_2$ labelling. Contrary to the common assumption that monoterpene emissions from Scots pine originate mainly as evaporation from specialized storage pools, the results demonstrate the substantial contribution from de novo biosynthesis. The inclusion of the observed division between pool and de novo emissions in a hybrid emission algorithm suggests a better description of ecosystem scale monoterpene emissions.

Paper V proposes a novel approach to interpreting ecosystem scale emissions. The analysis with the hybrid algorithm of **Paper IV** illustrates the evident role of de novo biosynthesis in monoterpene emissions from a boreal Scots pine forest. Concordant with previous shoot scale observations, the monoterpene emission potential exhibits a decreasing summertime trend also on the ecosystem scale.

The author of this thesis contributed to the design, installation, and conduct of the VOC concentration and flux measurements. He was responsible for the PTR-MS data acquisition programs and the concentration and flux calculation procedures used

throughout this work. He did a major part of the data analysis and writing in **Papers I**, **III**, and **V**. In **Paper II**, he was responsible for the data analysis and figures related to the VOC flux measurements and commented on the manuscript. In **Paper IV**, the author did the data analysis related to the ecosystem scale emission measurements and modelling. He also participated in the formulation of the hybrid emission algorithm and commented on the manuscript.

6   Conclusions

During the past decade, the combination of DEC and PTR-MS has emerged as a popular technique for micrometeorological flux measurements of VOCs. Like the conventional EC method, DEC is free from empirical parameterizations and thus, at least in this sense, readily implementable. However, long-term DEC measurements with PTR-MS still involve challenging issues related to the measurement, calibration, and calculation methods. The first part of this thesis discussed some of these issues, in particular the advancements in the calibration and lag time determination procedures. The second part focused on the ecosystem scale emissions of oxygenated VOCs and monoterpenes from a boreal coniferous forest in southern Finland. The specific interest was the role of de novo biosynthesis in monoterpene emissions from Scots pine.

The main conclusions of this thesis are the following:

1) The combination of DEC and PTR-MS was well suited to the long-term VOC flux measurements. The regular PTR-MS calibrations with the gas standards were necessary to ensure a reasonable and invariable accuracy during the measurement periods. The novel method for determining a relative transmission curve provided a systematic means of calculating concentrations for the non-calibrated compounds.

2) Due to noisy covariance functions, the lag time determination is often a critical point in the automation of DEC flux calculations. The new averaging approach based on running averaged covariance functions was less prone to overestimation of the absolute values of fluxes than the maximum covariance method, which is the traditional choice in conventional EC measurements. Thus the averaging method seems an advisable option for DEC and EC applications when measuring fluxes near the detection limit. More information on its performance in different micrometeorological conditions is still needed.

3) The ecosystem scale emissions of methanol, acetaldehyde, and acetone were substantial. The contribution of these three oxygenated VOCs to the total emissions was around 40–60%, with the rest comprised of monoterpenes. DEC measurements of oxygenated VOCs may help to determine the relevance of these compounds to plant physiology and tropospheric chemistry in more detail.

4) As indicated by the $^{13}CO_2$ labelling experiment and the DEC measurements, the role of de novo biosynthesis in the monoterpene emissions was evident. This implies that hybrid algorithms, describing both pool and de novo emissions, are the appropriate choice when modelling monoterpene emissions from Scots pine dominated forests. Seasonal variation in the monoterpene biosynthesis should be determined in further studies.

In the most modernistic view, DEC measurements with PTR-MS may already be considered obsolete as the novel PTR-MS instrument featuring a time-of-flight mass analyzer has proven sensitive enough for conventional EC measurements. This fusion of modern and classical admittedly has an overwhelming benefit. It enables simultaneous high frequency EC measurements of virtually all VOCs detected within the mass range of the time-of-flight instrument. However, by virtue of being an established and, thereby, cheaper option, DEC measurements with quadrupole instruments may still remain indispensable for many years, hopefully profiting from the work conducted for this thesis.

References

Allan, J. D., Alfarra, M. R., Bower, K. N., Coe, H., Jayne, J. T., Worsnop, D. R., Aalto, P. P., Kulmala, M., Hyötyläinen, T., Cavalli, F., and Laaksonen, A.: Size and composition measurements of background aerosol and new particle growth in a Finnish forest during QUEST 2 using an Aerodyne Aerosol Mass Spectrometer, Atmos. Chem. Phys., 6, 315–327, 2006.

Ambrose, J. L., Haase, K., Russo, R. S., Zhou, Y., White, M. L., Frinak, E. K., Jordan, C., Mayne, H. R., Talbot, R., and Sive, B. C.: A comparison of GC-FID and PTR-MS toluene measurements in ambient air under conditions of enhanced monoterpene loading, Atmos. Meas. Tech., 3, 959–980, 2010.

Ammann, C., Spirig, C., Neftel, A., Steinbacher, M., Komenda, M., and Schaub, A.: Application of PTR-MS for measurements of biogenic VOC in a deciduous forest, Int. J. Mass Spectrom., 239, 87–101, 2004.

Ammann, C., Brunner, A., Spirig, C., and Neftel, A.: Technical note: Water vapour concentration and flux measurements with PTR-MS, Atmos. Chem. Phys., 6, 4643–4651, 2006.

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

Aubinet, M., Grelle, A., Ibrom, A., Rannik, Ü., Moncrieff, J., Foken, T., Kowalski, A. S., Martin, P. H., Berbigier, P., Bernhofer, Ch., Clement, R., Elbers, J., Granier, A., Grünwald, T., Morgenstern, K., Pilegaard, K., Rebmann, C., Snijders, W., Valentini, R., and Vesala, T.: Estimates of the annual net carbon and water exchange of forests: The EUROFLUX methodology, Adv. Ecol. Res., 30, 113–175, 2000.

Bäck, J., Hari, P., Hakola, H., Juurola, E., and Kulmala, M.: Dynamics of monoterpene emissions in *Pinus sylvestris* during early spring, Boreal Environ. Res., 10, 409–424, 2005.

Bamberger, I., Hörtnagl, L., Schnitzhofer, R., Graus, M., Ruuskanen, T. M., Müller, M., Dunkl, J., Wohlfahrt, G., and Hansel, A.: BVOC fluxes above mountain grassland, Biogeosciences, 7, 1413–1424, 2010.

Blake, R. S., Whyte, C., Hughes, C. O., Ellis, A. M., and Monks, P. S.: Demonstration of proton-transfer reaction time-of-flight mass spectrometry for real-time analysis of trace volatile organic compounds, Anal. Chem., 76, 3841–3845, 2004.

Blake, R. S., Monks, P. S., and Ellis, A. M.: Proton-transfer reaction mass spectrometry, Chem. Rev., 109, 861–896, 2009.

Brunner, A., Ammann, C., Neftel, A., and Spirig, C.: Methanol exchange between grassland and the atmosphere, Biogeosciences, 4, 395–410, 2007.

Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P., and Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, Science, 303, 1173–1176, 2004.

Crutzen, P. J., Williams, J., Pöschl, U., Hoor, P., Fischer, H., Warneke, C., Holzinger, R., Hansel, A., Lindinger, W., Scheeren, B., and Lelieveld, J.: High spatial and temporal resolution measurements of primary organics and their oxidation products over the tropical forests of Surinam, Atmos. Environ., 34, 1161–1165, 2000.

Dabberdt, W. F., Lenschow, D. H., Horst, T. W., Zimmerman, P. R., Oncley, S. P., and Delany, A. C.: Atmosphere–surface exchange measurements, Science, 260, 1472–1481, 1993.

Davison, B., Taipale, R., Langford, B., Misztal, P., Fares, S., Matteucci, G., Loreto, F., Cape, J. N., Rinne, J., and Hewitt, C. N.: Concentrations and fluxes of biogenic volatile organic compounds above a Mediterranean macchia ecosystem in western Italy, Biogeosciences, 6, 1655–1670, 2009.

de Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrom. Rev., 26, 223–257, 2007.

de Gouw, J., Warneke, C., Karl, T., Eerdekens, G., van der Veen, C., and Fall, R.: Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry, Int. J. Mass Spectrom., 223–224, 365–382, 2003a.

de Gouw, J., Warneke, C., Holzinger, R., Klüpfel, T., and Williams, J.: Inter-comparison between airborne measurements of methanol, acetonitrile and acetone

using two differently configured PTR-MS instruments, Int. J. Mass Spectrom., 239, 129–137, 2004.

de Gouw, J. A., Goldan, P. D., Warneke, C., Kuster, W. C., Roberts, J. M., Marchewka, M., Bertman, S. B., Pszenny, A. A. P., and Keene, W. C.: Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002, J. Geophys. Res., 108(D21), 4682, doi:10.1029/2003JD003863, 2003b.

Eerdekens, G., Yassaa, N., Sinha, V., Aalto, P. P., Aufmhoff, H., Arnold, F., Fiedler, V., Kulmala, M., and Williams, J.: VOC measurements within a boreal forest during spring 2005: on the occurrence of elevated monoterpene concentrations during night time intense particle concentration events, Atmos. Chem. Phys., 9, 8331–8350, 2009.

Fall, R., Karl, T., Hansel, A., Jordan, A., and Lindinger, W.: Volatile organic compounds emitted after leaf wounding: On-line analysis by proton-transfer-reaction mass spectrometry, J. Geophys. Res., 104(D13), 15 963–15 974, 1999.

Fischbach, R.: Monoterpensynthasen in Blättern der Fichte (*Picea abies* (L.) Karst.) und der Steineiche (*Quercus ilex* L.), Ph.D. thesis, University of Freiburg, Germany, 188 pp., 2001.

Foken, Th. and Wichura, B.: Tools for quality assessment of surface-based flux measurements, Agr. Forest Meteorol., 78, 83–105, 1996.

Göckede, M., Rebmann, C., and Foken, T.: A combination of quality assessment tools for eddy covariance measurements with footprint modelling for the characterisation of complex sites, Agr. Forest Meteorol., 127, 175–188, 2004.

Grabmer, W., Graus, M., Lindinger, C., Wisthaler, A., Rappenglück, B., Steinbrecher, R., and Hansel, A.: Disjunct eddy covariance measurements of monoterpene fluxes from a Norway spruce forest using PTR-MS, Int. J. Mass Spectrom., 239, 111–115, 2004.

Grote, R. and Niinemets, Ü.: Modeling volatile isoprenoid emissions – a story with split ends, Plant Biol., 10, 8–28, 2008.

Grote, R., Mayrhofer, S., Fischbach, R. J., Steinbrecher, R., Staudt, M., and Schnitzler, J.-P.: Process-based modelling of isoprenoid emissions from evergreen leaves of *Quercus ilex* (L.), Atmos. Environ., 40, S152–S165, 2006.

Guenther, A.: Seasonal and spatial variations in natural volatile organic compound emissions, Ecol. Appl., 7(1), 34–45, 1997.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100(D5), 8873–8892, 1995.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181–3210, 2006.

Guenther, A. B. and Hills, A. J.: Eddy covariance measurement of isoprene fluxes, J. Geophys. Res., 103(D11), 13 145–13 152, 1998.

Guenther, A. B., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: Observations with eucalyptus and emission rate algorithm development, J. Geophys. Res., 96(D6), 10 799–10 808, 1991.

Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses, J. Geophys. Res., 98(D7), 12 609–12 617, 1993.

Haapanala, S., Rinne, J., Hakola, H., Hellén, H., Laakso, L., Lihavainen, H., Janson, R., O'Dowd, C., and Kulmala, M.: Boundary layer concentrations and landscape scale emissions of volatile organic compounds in early spring, Atmos. Chem. Phys., 7, 1869–1878, 2007.

Haapanala, S., Ekberg, A., Hakola, H., Tarvainen, V., Rinne, J., Hellén, H., and Arneth, A.: Mountain birch – potentially large source of sesquiterpenes into high latitude atmosphere, Biogeosciences, 6, 2709–2718, 2009.

Hakola, H., Tarvainen, V., Laurila, T., Hiltunen, V., Hellén, H., and Keronen, P.: Seasonal variation of VOC concentrations above a boreal coniferous forest, Atmos. Environ., 37, 1623–1634, 2003.

Hakola, H., Tarvainen, V., Bäck, J., Ranta, H., Bonn, B., Rinne, J., and Kulmala, M.: Seasonal variation of mono- and sesquiterpene emission rates of Scots pine, Biogeosciences, 3, 93–101, 2006.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, 2009.

Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., and Lindinger, W.: Proton transfer reaction mass spectrometry: on-line trace gas analysis at the ppb level, Int. J. Mass Spectrom., 149/150, 609–619, 1995.

Hansel, A., Singer, W., Wisthaler, A., Schwarzmann, M., and Lindinger, W.: Energy dependencies of the proton transfer reactions $H_3O^+ + CH_2O \Leftrightarrow CH_2OH^+ + H_2O$, Int. J. Mass Spectrom., 167/168, 697–703, 1997.

Hao, L. Q., Yli-Pirilä, P., Tiitta, P., Romakkaniemi, S., Vaattovaara, P., Kajos, M. K., Rinne, J., Heijari, J., Kortelainen, A., Miettinen, P., Kroll, J. H., Holopainen, J. K., Smith, J. N., Joutsensaari, J., Kulmala, M., Worsnop, D. R., and Laaksonen, A.: New particle formation from the oxidation of direct emissions of pine seedlings, Atmos. Chem. Phys., 9, 8121–8137, 2009.

Hari, P. and Kulmala, M.: Station for Measuring Ecosystem–Atmosphere Relations (SMEAR II), Boreal Environ. Res., 10, 315–322, 2005.

Hayward, S., Hewitt, C. N., Sartin, J. H., and Owen, S. M.: Performance characteristics and applications of a proton transfer reaction-mass spectrometer for measuring volatile organic compounds in ambient air, Environ. Sci. Technol., 36, 1554–1560, 2002.

Hayward, S., Tani, A., Owen, S. M., and Hewitt, C. N.: Online analysis of volatile organic compound emissions from Sitka spruce (*Picea sitchensis*), Tree Physiol., 24, 721–728, 2004.

Hellén, H., Hakola, H., Pystynen, K.-H., Rinne, J., and Haapanala, S.: C_2–C_{10} hydrocarbon emissions from a boreal wetland and forest floor, Biogeosciences, 3, 167–174, 2006.

Hellén, H., Dommen, J., Metzger, A., Gascho, A., Duplissy, J., Tritscher, T., Prevot, A. S. H., and Baltensperger, U.: Using proton transfer reaction mass spectrometry for online analysis of secondary organic aerosols, Environ. Sci. Technol., 42, 7347–7353, 2008.

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

Holst, T., Arneth, A., Hayward, S., Ekberg, A., Mastepanov, M., Jackowicz-Korczynski, M., Friborg, T., Crill, P. M., and Bäckstrand, K.: BVOC ecosystem flux measurements at a high latitude wetland site, Atmos. Chem. Phys., 10, 1617–1634, 2010.

Holzinger, R., Kleiss, B., Donoso, L., and Sanhueza, E.: Aromatic hydrocarbons at urban, sub-urban, rural (8°52′N; 67°19′W) and remote sites in Venezuela, Atmos. Environ., 35, 4917–4927, 2001.

Holzinger, R., Lee, A., McKay, M., and Goldstein, A. H.: Seasonal variability of monoterpene emission factors for a Ponderosa pine plantation in California, Atmos. Chem. Phys., 6, 1267–1274, 2006.

Holzinger, R., Williams, J., Herrmann, F., Lelieveld, J., Donahue, N. M., and Röckmann, T.: Aerosol analysis using a Thermal-Desorption Proton-Transfer-Reaction Mass Spectrometer (TD-PTR-MS): a new approach to study processing of organic aerosols, Atmos. Chem. Phys., 10, 2257–2267, 2010.

Hörtnagl, L., Clement, R., Graus, M., Hammerle, A., Hansel, A., and Wohlfahrt, G.: Dealing with disjunct concentration measurements in eddy covariance applications: A comparison of available approaches, Atmos. Environ., 44, 2024–2032, 2010.

Ibrom, A., Dellwik, E., Larsen, S. E., and Pilegaard, K.: On the use of the Webb–Pearman–Leuning theory for closed-path eddy correlation measurements, Tellus, 59B, 937–946, 2007.

Inomata, S., Tanimoto, H., Kameyama, S., Tsunogai, U., Irie, H., Kanaya, Y., and Wang, Z.: Technical Note: Determination of formaldehyde mixing ratios in air with PTR-MS: laboratory experiments and field measurements, Atmos. Chem. Phys., 8, 273–284, 2008.

Isidorov, V. A., Zenkevich, I. G., and Ioffe, B. V.: Volatile organic compounds in the atmosphere of forests, Atmos. Environ., 19, 1–8, 1985.

Janson, R. and de Serves, C.: Acetone and monoterpene emissions from the boreal forest in northern Europe, Atmos. Environ., 35, 4629–4637, 2001.

Janson, R. W.: Monoterpene emissions from Scots pine and Norwegian spruce, J. Geophys. Res., 98(D2), 2839–2850, 1993.

Jiang, M., Marr, L. C., Dunlea, E. J., Herndon, S. C., Jayne, J. T., Kolb, C. E., Knighton, W. B., Rogers, T. M., Zavala, M., Molina, L. T., and Molina, M. J.: Vehicle fleet emissions of black carbon, polycyclic aromatic hydrocarbons, and other pollutants measured by a mobile laboratory in Mexico City, Atmos. Chem. Phys., 5, 3377–3387, 2005.

Jobson, B. T. and McCoskey, J. K.: Sample drying to improve HCHO measurements by PTR-MS instruments: laboratory and field measurements, Atmos. Chem. Phys., 10, 1821–1835, 2010.

Jobson, B. T., Volkamer, R. A., Velasco, E., Allwine, G., Westberg, H., Lamb, B. K., Alexander, M. L., Berkowitz, C. M., and Molina, L. T.: Comparison of aromatic hydrocarbon measurements made by PTR-MS, DOAS and GC-FID during the MCMA 2003 Field Experiment, Atmos. Chem. Phys., 10, 1989–2005, 2010.

Jordan, C., Fitz, E., Hagan, T., Sive, B., Frinak, E., Haase, K., Cottrell, L., Buckley, S., and Talbot, R.: Long-term study of VOCs measured with PTR-MS at a rural site in New Hampshire with urban influences, Atmos. Chem. Phys., 9, 4677–4697, 2009.

Junninen, H., Lauri, A., Keronen, P., Aalto, P., Hiltunen, V., Hari, P., and Kulmala, M.: Smart-SMEAR: on-line data exploration and visualization tool for SMEAR stations, Boreal Environ. Res., 14, 447–457, 2009.

Kaimal, J. C. and Finnigan, J. J.: Atmospheric Boundary Layer Flows, Oxford University Press, Inc., New York, United States, 1994.

Kaimal, J. C. and Gaynor, J. E.: The Boulder Atmospheric Observatory, J. Clim. Appl. Meteorol., 22, 863–880, 1983.

Kaplan, J. O., Folberth, G., and Hauglustaine, D. A.: Role of methane and biogenic volatile organic compound sources in late glacial and Holocene fluctuations of atmospheric methane concentrations, Global Biogeochem. Cy., 20, GB2016, doi: 10.1029/2005GB002590, 2006.

Karl, M., Guenther, A., Köble, R., Leip, A., and Seufert, G.: A new European plant-specific emission inventory of biogenic volatile organic compounds for use in atmospheric transport models, Biogeosciences, 6, 1059–1087, 2009.

Karl, T., Guenther, A., Jordan, A., Fall, R., and Lindinger, W.: Eddy covariance measurement of biogenic oxygenated VOC emissions from hay harvesting, Atmos. Environ., 35, 491–495, 2001.

Karl, T., Curtis, A. J., Rosenstiel, T. N., Monson, R. K., and Fall, R.: Transient releases of acetaldehyde from tree leaves – products of a pyruvate overflow mechanism?, Plant Cell Environ., 25, 1121–1131, 2002a.

Karl, T., Hansel, A., Märk, T., Lindinger, W., and Hoffmann, D.: Trace gas monitoring at the Mauna Loa Baseline Observatory using Proton-Transfer Reaction Mass Spectrometry, Int. J. Mass Spectrom., 223–224, 527–538, 2003.

Karl, T., Harley, P., Guenther, A., Rasmussen, R., Baker, B., Jardine, K., and Nemitz, E.: The bi-directional exchange of oxygenated VOCs between a loblolly pine (*Pinus taeda*) plantation and the atmosphere, Atmos. Chem. Phys., 5, 3015–3031, 2005.

Karl, T. G., Spirig, C., Rinne, J., Stroud, C., Prevost, P., Greenberg, J., Fall, R., and Guenther, A.: Virtual disjunct eddy covariance measurements of organic compound fluxes from a subalpine forest using proton transfer reaction mass spectrometry, Atmos. Chem. Phys., 2, 279–291, 2002b.

Keenan, T., Niinemets, Ü., Sabate, S., Gracia, C., and Peñuelas, J.: Process based inventory of isoprenoid emissions from European forests: model comparisons, current knowledge and uncertainties, Atmos. Chem. Phys., 9, 4053–4076, 2009.

Keronen, P., Reissell, A., Rannik, Ü., Pohja, T., Siivola, E., Hiltunen, V., Hari, P., Kulmala, M., and Vesala, T.: Ozone flux measurements over a Scots pine forest using eddy covariance method: performance evaluation and comparison with flux-profile method, Boreal Environ. Res., 8, 425–443, 2003.

Kiendler-Scharr, A., Wildt, J., Dal Maso, M., Hohaus, T., Kleist, E., Mentel, Th. F., Tillmann, R., Uerlings, R., Schurr, U., and Wahner, A.: New particle formation in forests inhibited by isoprene emissions, Nature, 461, 381–384, doi: 10.1038/nature08292, 2009.

Kim, S., Karl, T., Helmig, D., Daly, R., Rasmussen, R., and Guenther, A.: Measurement of atmospheric sesquiterpenes by proton transfer reaction-mass spectrometry (PTR-MS), Atmos. Meas. Tech., 2, 99–112, 2009.

Kim, S., Karl, T., Guenther, A., Tyndall, G., Orlando, J., Harley, P., Rasmussen, R., and Apel, E.: Emissions and ambient distributions of Biogenic Volatile Organic Compounds (BVOC) in a ponderosa pine ecosystem: interpretation of PTR-MS mass spectra, Atmos. Chem. Phys., 10, 1759–1771, 2010.

Koppmann, R., ed.: Volatile Organic Compounds in the Atmosphere, Blackwell Publishing Ltd, Oxford, United Kingdom, 2007.

Kormann, R. and Meixner, F. X.: An analytical footprint model for non-neutral stratification, Bound.-Lay. Meteorol., 99, 207–224, 2001.

Kroll, J. H. and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, Atmos. Environ., 42, 3593–3624, 2008.

Kulmala, M., Hämeri, K., Aalto, P. P., Mäkelä, J. M., Pirjola, L., Nilsson, E. D., Buzorius, G., Rannik, Ü., Dal Maso, M., Seidl, W., Hoffman, T., Janson, R., Hansson, H.-C., Viisanen, Y., Laaksonen, A., and O'Dowd, C. D.: Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR), Tellus, 53B, 324–343, 2001.

Kulmala, M., Suni, T., Lehtinen, K. E. J., Dal Maso, M., Boy, M., Reissell, A., Rannik, Ü., Aalto, P., Keronen, P., Hakola, H., Bäck, J., Hoffmann, T., Vesala, T., and Hari, P.: A new feedback mechanism linking forests, aerosols, and climate, Atmos. Chem. Phys., 4, 557–562, 2004.

Langford, B., Davison, B., Nemitz, E., and Hewitt, C. N.: Mixing ratios and eddy covariance flux measurements of volatile organic compounds from an urban canopy (Manchester, UK), Atmos. Chem. Phys., 9, 1971–1987, 2009.

Langford, B., Misztal, P. K., Nemitz, E., Davison, B., Helfter, C., Pugh, T. A. M., MacKenzie, A. R., Lim, S. F., and Hewitt, C. N.: Fluxes and concentrations of volatile organic compounds from a South-East Asian tropical rainforest, Atmos. Chem. Phys., 10, 8391–8412, 2010.

Lappalainen, H. K., Sevanto, S., Bäck, J., Ruuskanen, T. M., Kolari, P., Taipale, R., Rinne, J., Kulmala, M., and Hari, P.: Day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors, Atmos. Chem. Phys., 9, 5447–5459, 2009.

Lee, A., Goldstein, A. H., Keywood, M. D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N. L., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes, J. Geophys. Res., 111, D07 302, doi:10.1029/2005JD006437, 2006a.

Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, J. Geophys. Res., 111, D17 305, doi: 10.1029/2006JD007050, 2006b.

Lenschow, D. H., Mann, J., and Kristensen, L.: How long is long enough when measuring fluxes and other turbulence statistics?, J. Atmos. Ocean. Tech., 11, 661–673, 1994.

Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) – Medical applications, food control and environmental research, Int. J. Mass Spectrom., 173, 191–241, 1998a.

Lindinger, W., Hansel, A., and Jordan, A.: Proton-transfer-reaction mass spectrometry (PTR-MS): on-line monitoring of volatile organic compounds at pptv levels, Chem. Soc. Rev., 27, 347–354, 1998b.

Loreto, F. and Schnitzler, J.-P.: Abiotic stresses and induced BVOCs, Trends Plant Sci., 15, 154–166, 2010.

Markkanen, T., Rannik, Ü., Marcolla, B., Cescatti, A., and Vesala, T.: Footprints and fetches for fluxes over forest canopies with varying structure and density, Bound.-Lay. Meteorol., 106, 437–459, 2003.

57

Massman, W. J.: A simple method for estimating frequency response corrections for eddy covariance systems, Agr. Forest Meteorol., 104, 185–198, 2000.

McMillen, R. T.: An eddy correlation technique with extended applicability to non-simple terrain, Bound.-Lay. Meteorol., 43, 231–245, 1988.

Millet, D. B., Jacob, D. J., Custer, T. G., de Gouw, J. A., Goldstein, A. H., Karl, T., Singh, H. B., Sive, B. C., Talbot, R. W., Warneke, C., and Williams, J.: New constraints on terrestrial and oceanic sources of atmospheric methanol, Atmos. Chem. Phys., 8, 6887–6905, 2008.

Millet, D. B., Guenther, A., Siegel, D. A., Nelson, N. B., Singh, H. B., de Gouw, J. A., Warneke, C., Williams, J., Eerdekens, G., Sinha, V., Karl, T., Flocke, F., Apel, E., Riemer, D. D., Palmer, P. I., and Barkley, M.: Global atmospheric budget of acetaldehyde: 3-D model analysis and constraints from in-situ and satellite observations, Atmos. Chem. Phys., 10, 3405–3425, 2010.

Misztal, P. K., Owen, S. M., Guenther, A. B., Rasmussen, R., Geron, C., Harley, P., Phillips, G. J., Ryan, A., Edwards, D. P., Hewitt, C. N., Nemitz, E., Siong, J., Heal, M. R., and Cape, J. N.: Large estragole fluxes from oil palms in Borneo, Atmos. Chem. Phys., 10, 4343–4358, 2010.

Müller, M., Graus, M., Ruuskanen, T. M., Schnitzhofer, R., Bamberger, I., Kaser, L., Titzmann, T., Hörtnagl, L., Wohlfahrt, G., Karl, T., and Hansel, A.: First eddy covariance flux measurements by PTR-TOF, Atmos. Meas. Tech., 3, 387–395, 2010.

Niinemets, Ü., Seufert, G., Steinbrecher, R., and Tenhunen, J. D.: A model coupling foliar monoterpene emissions to leaf photosynthetic characteristics in Mediterranean evergreen *Quercus* species, New Phytol., 153, 257–275, 2002.

Niinemets, Ü., Arneth, A., Kuhn, U., Monson, R. K., Peñuelas, J., and Staudt, M.: The emission factor of volatile isoprenoids: stress, acclimation, and developmental responses, Biogeosciences, 7, 2203–2223, 2010a.

Niinemets, Ü., Monson, R. K., Arneth, A., Ciccioli, P., Kesselmeier, J., Kuhn, U., Noe, S. M., Peñuelas, J., and Staudt, M.: The leaf-level emission factor of volatile isoprenoids: caveats, model algorithms, response shapes and scaling, Biogeosciences, 7, 1809–1832, 2010b.

Nozière, B. and Esteve, W.: Organic reactions increasing the absorption index of atmospheric sulfuric acid aerosols, Geophys. Res. Lett., 32, L03 812, doi: 10.1029/2004GL021942, 2005.

Owen, S. M. and Pẽnuelas, J.: Opportunistic emissions of volatile isoprenoids, Trends Plant Sci., 10, 420–426, 2005.

Pẽnuelas, J. and Llusià, J.: Plant VOC emissions: making use of the unavoidable, Trends Ecol. Evol., 19, 402–404, 2004.

Paulsen, D., Dommen, J., Kalberer, M., Prévôt, A. S. H., Richter, R., Sax, M., Steinbacher, M., Weingartner, E., and Baltensperger, U.: Secondary organic aerosol formation by irradiation of 1,3,5-trimethylbenzene–NO_x–H_2O in a new reaction chamber for atmospheric chemistry and physics, Environ. Sci. Technol., 39, 2668–2678, 2005.

Piccot, S. D., Watson, J. J., and Jones, J. W.: A global inventory of volatile organic compound emissions from anthropogenic sources, J. Geophys. Res., 97(D9), 9897–9912, 1992.

Pressley, S., Lamb, B., Westberg, H., Flaherty, J., Chen, J., and Vogel, C.: Long-term isoprene flux measurements above a northern hardwood forest, J. Geophys. Res., 110, D07 301, doi:10.1029/2004JD005523, 2005.

Räisänen, T., Ryyppö, A., and Kellomäki, S.: Monoterpene emission of a boreal Scots pine (*Pinus sylvestris* L.) forest, Agr. Forest Meteorol., 149, 808–819, 2009.

Rinne, H. J. I., Guenther, A. B., Warneke, C., de Gouw, J. A., and Luxembourg, S. L.: Disjunct eddy covariance technique for trace gas flux measurements, Geophys. Res. Lett., 28(16), 3139–3142, 2001.

Rinne, J., Hakola, H., Laurila, T., and Rannik, Ü.: Canopy scale monoterpene emissions of *Pinus sylvestris* dominated forests, Atmos. Environ., 34, 1099–1107, 2000.

Rinne, J., Ruuskanen, T. M., Reissell, A., Taipale, R., Hakola, H., and Kulmala, M.: On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem, Boreal Environ. Res., 10, 425–436, 2005.

Rinne, J., Douffet, T., Prigent, Y., and Durand, P.: Field comparison of disjunct and conventional eddy covariance techniques for trace gas flux measurements, Environ. Pollut., 152, 630–635, 2008.

Rinne, J., Bäck, J., and Hakola, H.: Biogenic volatile organic compound emissions from the Eurasian taiga: current knowledge and future directions, Boreal Environ. Res., 14, 807–826, 2009.

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

Schuh, G., Heiden, A. C., Hoffmann, Th., Kahl, J., Rockel, P., Rudolph, J., and Wildt, J.: Emissions of volatile organic compounds from sunflower and beech: Dependence on temperature and light intensity, J. Atmos. Chem., 27, 291–318, 1997.

Schurgers, G., Arneth, A., Holzinger, R., and Goldstein, A. H.: Process-based modelling of biogenic monoterpene emissions combining production and release from storage, Atmos. Chem. Phys., 9, 3409–3423, 2009.

Shao, M., Czapiewski, K. V., Heiden, A. C., Kobel, K., Komenda, M., Koppmann, R., and Wildt, J.: Volatile organic compound emissions from Scots pine: Mechanisms and description by algorithms, J. Geophys. Res., 106(D17), 20 483–20 491, 2001.

Sharkey, T. D. and Singsaas, E. L.: Why plants emit isoprene, Nature, 374, 769, 1995.

Shaw, W. J., Spicer, C. W., and Kenny, D. V.: Eddy correlation fluxes of trace gases using a tandem mass spectrometer, Atmos. Environ., 32, 2887–2898, 1998.

Shimizu, T.: Practical applicability of high frequency correction theories to CO_2 flux measured by a closed-path system, Bound.-Lay. Meteorol., 122, 417–438, doi: 10.1007/s10546-006-9115-z, 2007.

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

Sinha, V., Custer, T. G., Kluepfel, T., and Williams, J.: The effect of relative humidity on the detection of pyrrole by PTR-MS for OH reactivity measurements, Int. J. Mass Spectrom., 282, 108–111, 2009.

Sinha, V., Williams, J., Lelieveld, J., Ruuskanen, T. M., Kajos, M. K., Patokoski, J., Hellen, H., Hakola, H., Mogensen, D., Boy, M., Rinne, J., and Kulmala, M.: OH reactivity measurements within a boreal forest: evidence for unknown reactive emissions, Environ. Sci. Technol., 44, 6614–6620, 2010.

Spanke, J., Rannik, Ü., Forkel, R., Nigge, W., and Hoffmann, T.: Emission fluxes and atmospheric degradation of monoterpenes above a boreal forest: field measurements and modelling, Tellus, 53B, 406–422, 2001.

Spirig, C., Neftel, A., Ammann, C., Dommen, J., Grabmer, W., Thielmann, A., Schaub, A., Beauchamp, J., Wisthaler, A., and Hansel, A.: Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry, Atmos. Chem. Phys., 5, 465–481, 2005.

Steinbacher, M., Dommen, J., Ammann, C., Spirig, C., Neftel, A., and Prevot, A. S. H.: Performance characteristics of a proton-transfer-reaction mass spectrometer (PTR-MS) derived from laboratory and field measurements, Int. J. Mass Spectrom., 239, 117–128, 2004.

Steinbrecher, R., Hauff, K., Hakola, H., and Rössler, J.: A revised parameterisation for emission modelling of isoprenoids for boreal plants, in: Biogenic VOC emissions and photochemistry in the boreal regions of Europe, edited by: Laurila, T. and Lindfors, V., Air Pollution Research Report, 70, Commission of the European Communities, Luxembourg, 29–43, 1999.

Strong, C., Fuentes, J. D., and Baldocchi, D.: Reactive hydrocarbon flux footprints during canopy senescence, Agr. Forest Meteorol., 127, 159–173, 2004.

Su, H.-B., Schmid, H. P., Grimmond, C. S. B., Vogel, C. S., and Oliphant, A. J.: Spectral characteristics and correction of long-term eddy-covariance measurements over two mixed hardwood forests in non-flat terrain, Bound.-Lay. Meteorol., 110, 213–253, 2004.

Tani, A., Hayward, S., and Hewitt, C. N.: Measurement of monoterpenes and related compounds by proton transfer reaction-mass spectrometry (PTR-MS), Int. J. Mass Spectrom., 223–224, 561–578, 2003.

Tani, A., Hayward, S., Hansel, A., and Hewitt, C. N.: Effect of water vapour pressure on monoterpene measurements using proton transfer reaction-mass spectrometry (PTR-MS), Int. J. Mass Spectrom., 239, 161–169, 2004.

Tarvainen, V., Hakola, H., Hellén, H., Bäck, J., Hari, P., and Kulmala, M.: Temperature and light dependence of the VOC emissions of Scots pine, Atmos. Chem. Phys., 5, 989–998, 2005.

Tarvainen, V., Hakola, H., Rinne, J., Hellén, H., and Haapanala, S.: Towards a comprehensive emission inventory of terpenoids from boreal ecosystems, Tellus, 59B, 526–534, 2007.

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

Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P. P., Komppula, M., and Kulmala, M.: High natural aerosol loading over boreal forests, Science, 312, 261–263, 2006.

Turnipseed, A. A., Pressley, S. N., Karl, T., Lamb, B., Nemitz, E., Allwine, E., Cooper, W. A., Shertz, S., and Guenther, A. B.: The use of disjunct eddy sampling methods for the determination of ecosystem level fluxes of trace gases, Atmos. Chem. Phys., 9, 981–994, 2009.

Vartiainen, E., Kulmala, M., Ruuskanen, T. M., Taipale, R., Rinne, J., and Vehkamäki, H.: Formation and growth of indoor air aerosol particles as a result of D-limonene oxidation, Atmos. Environ., 40, 7882–7892, 2006.

Vesala, T., Haataja, J., Aalto, P., Altimir, N., Buzorius, G., Garam, E., Hämeri, K., Ilvesniemi, H., Jokinen, V., Keronen, P., Lahti, T., Markkanen, T., Mäkelä, J. M., Nikinmaa, E., Palmroth, S., Palva, L., Pohja, T., Pumpanen, J., Rannik, Ü., Siivola, E., Ylitalo, H., Hari, P., and Kulmala, M.: Long-term field measurements of atmosphere–surface interactions in boreal forest combining forest ecology, micrometeorology, aerosol physics and atmospheric chemistry, Trends in Heat, Mass and Momentum Transfer, 4, 17–35, 1998.

Vickers, C. E., Possell, M., Cojocariu, C. I., Velikova, V. B., Laothawornkitkul, J., Ryan, A., Mullineaux, P. M., and Hewitt, C. N.: Isoprene synthesis protects transgenic tobacco plants from oxidative stress, Plant Cell Environ., 32, 520–531, 2009.

Vlasenko, A., Macdonald, A. M., Sjostedt, S. J., and Abbatt, J. P. D.: Formaldehyde measurements by Proton transfer reaction – Mass Spectrometry (PTR-MS): correction for humidity effects, Atmos. Meas. Tech., 3, 1055–1062, 2010.

Warneke, C., van der Veen, C., Luxembourg, S., de Gouw, J. A., and Kok, A.: Measurements of benzene and toluene in ambient air using proton-transfer-reaction mass spectrometry: calibration, humidity dependence, and field intercomparison, Int. J. Mass Spectrom., 207, 167–182, 2001.

Warneke, C., Luxembourg, S. L., de Gouw, J. A., Rinne, H. J. I., Guenther, A. B., and Fall, R.: Disjunct eddy covariance measurements of oxygenated volatile organic compounds fluxes from an alfalfa field before and after cutting, J. Geophys. Res., 107(D8), 4067, doi:10.1029/2001JD000594, 2002.

Warneke, C., de Gouw, J. A., Kuster, W. C., Goldan, P. D., and Fall, R.: Validation of atmospheric VOC measurements by proton-transfer-reaction mass spectrometry using a gas-chromatographic preseparation method, Environ. Sci. Technol., 37, 2494–2501, 2003.

Warneke, C., de Gouw, J. A., Stohl, A., Cooper, O. R., Goldan, P. D., Kuster, W. C., Holloway, J. S., Williams, E. J., Lerner, B. M., McKeen, S. A., Trainer, M., Fehsenfeld, F. C., Atlas, E. L., Donnelly, S. G., Stroud, V., Lueb, A., and Kato, S.: Biomass burning and anthropogenic sources of CO over New England in the summer 2004, J. Geophys. Res., 111, D23S15, doi:10.1029/2005JD006878, 2006.

Went, F. W.: Blue hazes in the atmosphere, Nature, 187, 641–643, 1960.

Wienhold, F. G., Frahm, H., and Harris, G. W.: Measurements of N_2O fluxes from fertilized grassland using a fast response tunable diode laser spectrometer, J. Geophys. Res., 99(D8), 16 557–16 567, 1994.

Wisthaler, A., Jensen, N. R., Winterhalter, R., Lindinger, W., and Hjorth, J.: Measurements of acetone and other gas phase product yields from the OH-initiated oxidation of terpenes by proton-transfer-reaction mass spectrometry (PTR-MS), Atmos. Environ., 35, 6181–6191, 2001.

Wisthaler, A., Hansel, A., Dickerson, R. R., and Crutzen, P. J.: Organic trace gas measurements by PTR-MS during INDOEX 1999, J. Geophys. Res., 107(D19), 8024, doi:10.1029/2001JD000576, 2002.

Wisthaler, A., Apel, E. C., Bossmeyer, J., Hansel, A., Junkermann, W., Koppmann, R., Meier, R., Müller, K., Solomon, S. J., Steinbrecher, R., Tillmann, R., and Brauers, T.: Technical Note: Intercomparison of formaldehyde measurements at the atmosphere simulation chamber SAPHIR, Atmos. Chem. Phys., 8, 2189–2200, 2008.

Yuan, J. S., Himanen, S. J., Holopainen, J. K., Chen, F., and Stewart, C. N. Jr.: Smelling global climate change: mitigation of function for plant volatile organic compounds, Trends Ecol. Evol., 24, 323–331, 2009.

Zhao, J. and Zhang, R.: Proton transfer reaction rate constants between hydronium ion (H_3O^+) and volatile organic compounds, Atmos. Environ., 38, 2177–2185, 2004.