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Disjunct eddy covariance measurements of monoterpene fluxes from a Norway spruce forest using PTR-MS

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Abstract

Interest in reliable quantification of organic trace compounds released from terrestrial ecosystems stems from their impact on oxidant levels such as ozone and hydroxyl radicals and on secondary organic aerosol formation. In an attempt to quantify these emissions, a disjunct sampler (DS) was coupled to a PTR-MS instrument. In the disjunct eddy covariance (DEC) technique, an instantaneous grab sample is taken at intervals of tens of seconds and vertical wind speed is recorded at the instant of sample collection. The intermittent periods are used for sample analysis by a moderately fast chemical sensor, in this case a PTR-MS instrument, which allows for fast and sensitive detection of biogenic volatile organic compounds. The vertical turbulent transport of a trace compound is then calculated from the covariance of the fluctuations in vertical wind speed and compound mixing ratio. Fluxes of monoterpenes from a Norway spruce forest were measured during the 2002 summer intensive field campaign of BEWA2000 and results compared well with data obtained using relaxed eddy accumulation (REA) and the enclosure approach. In addition to this field experiment, a laboratory test was carried out to validate the disjunct sampling procedure.

Keywords: Disjunct eddy covariance; Monoterpenes; Flux measurements; PTR-MS; BEWA2000

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1. Introduction

The eddy covariance (EC) technique is the most direct method of measuring vertical fluxes in the turbulently mixed planetary boundary layer. This method requires the use of fast sensors to record wind velocity, and the synchronised measurement of a scalar of interest. According to the sampling theorem, data must be taken at twice the rate of the highest flux-containing frequency. The smallest flux-carrying eddies are in the range of 5–10 Hz [1]. Sonic anemometers fulfill this requirement. However, for most of the volatile organic compounds (VOC) – except isoprene [2] – hitherto no established sensors measuring at rates of 5–10 Hz are available. Therefore, in most cases, alternative approaches are applied. These include the gradient method, and various methods derived from the EC method: true eddy accumulation [3], relaxed eddy accumulation (REA) [4], and disjunct eddy covariance (DEC) [5,6]. The gradient method and REA are both indirect methods, i.e., they rely on empirical parameterisation. The true eddy accumulation method has proven to be technically difficult to realise. The original technique requires the sampling flow to be proportional to vertical wind speed [7]. A simpler set-up uses a constant sampling flow, whereby sampling time is varied according to wind speed [8]. In DEC, rather than sampling continuously, samples are taken within a tenth of a second (disjunct or grab samples) and are separated by relatively long periods of time (tens of seconds) in order to enable analysis with moderately fast sensors. Although this procedure violates the sampling theorem, the subset of data

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obtained at well-defined conditions gives flux information with high precision. So far, DEC has been applied especially to grassland emissions [9,10], whereas for coniferous trees the disjunct true eddy accumulation technique has been used [6]. In this work, a disjunct sampler (DS) was coupled to a PTR-MS instrument to measure the flux of monoterpenes from a Norway spruce forest. In addition to the field experiment, a laboratory test was carried out to evaluate the quality of the disjunct sampling procedure.

2. Methods

2.1. The disjunct eddy covariance method

DEC is derived from the EC method. With the latter, fast sensors provide a quasi-continuous function of a scalar property s of the atmosphere (e.g., temperature or a trace gas concentration) and vertical wind speed w. Most of the vertical turbulent transport of scalars in the atmosphere occurs with frequencies below 5–10 Hz. The functions s and w are split up into an average term $\bar{s}$ and $\overline{w}$, respectively, and a fluctuation term s' and w', respectively:

$$s = \bar{s} + s' \quad \text{and} \quad w = \overline{w} + w' \tag{1}$$

Normally, $\bar{s}$ and $\overline{w}$ are calculated by taking a mean value or a linear trend in a time interval $[t_A, t_B]$. According to the continuity equation, $\overline{w}$ must be zero for horizontal terrain with uniform roughness. If there is a slope, usually the coordinate system of the wind vector is rotated to give $\overline{w} = 0$. The vertical turbulent flux of the scalar property s is then calculated as the following integral:

$$F_s = \overline{w's'} = \frac{1}{t_B - t_A}\int_{t_A}^{t_B} w'(t)s'(t)\mathrm{d}t \tag{2}$$

The integral is the covariance of the fluctuations of the scalar and the vertical wind speed within the time interval $[t_A, t_B]$. The required integration time for calculating a flux is determined by the number of samples and the size of the largest eddies. For most cases the interval size is in the range between 0.5 and 2 h.

Disjunct sampling methods were introduced to relax demands on time response of chemical sensors [6]. In these methods, a much lower number N of samples needs to be analysed for calculating a flux. Sampling occurs in constant time intervals τ so that s and w are then discrete functions of $t_i = i \times \tau$. Thus, the integral (2) is replaced by the sum:

$$F_s = \langle w' s' \rangle = \frac{1}{N}\sum_{i=1}^{N} w'(t_i)s'(t_i) \tag{3}$$

where $w'(t_i)_{1\le i\le N}$ and $s'(t_i)_{1\le i\le N}$ are exactly synchronised subsets of the values of the above mentioned functions $w'(t)$ and $s'(t)$ (Fig. 1).

2.2. Field experiment

During the 2002 summer intensive field campaign of BEWA2000, VOC measurements were conducted above a Norway spruce forest in a remote area of the German Fichtelgebirge (50°08′32″N, 11°52′04″O, 775 m a. s. l.), which is characterised by an alpine-like climate [11]. A disjunct sampler was mounted 31 m above ground at the front end of a horizontal boom on the uppermost platform of a scaffolding tower. The forest immediately surrounding the tower consisted of approximately 19 m tall, 57-year-old Norway spruce trees (*Picea abies* L. [Karst.]). The greater fetch area was densely covered by older trees of the same species.

The set-up of the DS unit is sketched in Fig. 2. Two passivated stainless steel canisters (Restek, Germany) equipped with fast-switching, high flow conductance inlet valves (Lucifer, E121K45) were used as intermediate storage reservoirs (ISRs). ISRs were kept at 30 °C and were operated in an al-

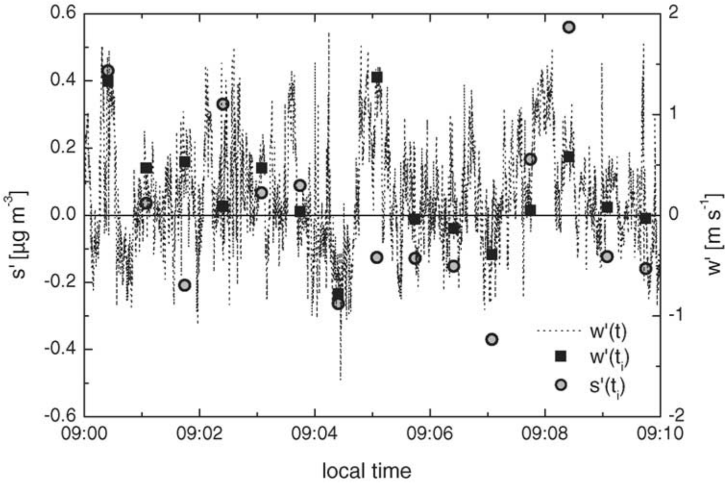

Fig. 1. Monoterpene fluctuations $s'(t_i)$ in disjunct samples and synchronous vertical wind speed data $w'(t_i)$ derived from a 10 Hz time series $w'(t)$.

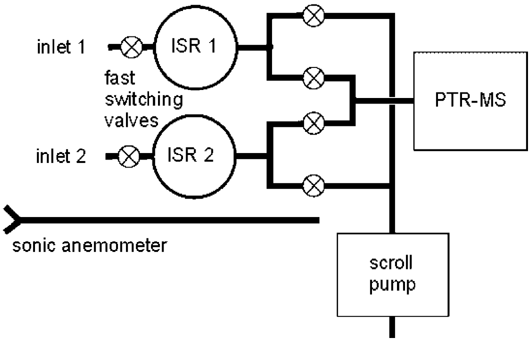

Fig. 2. Schematic diagram of the DS unit.

ternating cycle as follows:

1. ISR1 is evacuated below 1 mbar by a scroll pump (Varian SH-100). At the same time, ISR2 is analysed.
2. ISR1 is filled with an air sample within 0.1 s by opening the inlet valve.
3. ISR1 is then analysed while ISR2 is evacuated.
4. ISR2 is filled with an air sample in 0.1 s.

The time between stages 2 and 4 of the cycle is determined by two factors: (1) the time required for analysing the air of the ISR and (2) the time needed for evacuating the ISR. In this study, the time required for PTR-MS analysis was the limiting factor.

A sonic anemometer (Gill R350, United Kingdom) with an incorporated inclinometer was fixed at the same height as the DS. The Gill instrument has a precision of less than 1% for wind speed data. Care was taken that the DS did not disturb the wind pattern in the main horizontal wind direction. The inlets of the ISRs were placed about 0.4 m from the point of wind measurement. Additionally, the ISRs and the anemometer were oriented towards the main wind direction so that advection was not disturbed by the tower. Only data within the obstacle-free wind sector were processed further. Besides free advection, sufficient turbulence is required for calculating turbulent fluxes. A minimum of 0.1 m s^{-1} for friction velocity u* was set as a criterion for fluxes being turbulent.

Air samples collected by the DS were analysed using PTR-MS, a chemical ionisation technique that allows for fast detection of VOC present in the atmosphere [12–14]. A PTR-MS instrument was placed on the tower one platform below the DS. The DS unit was connected to the PTR-MS instrument by means of a 1/8″ Teflon PFA tube. The residence time in the tubing was less than 3 s. The analysis of a single VOC species required an integration time of 5–10 s, accounting for a total analysis time of approximately 35 s for the whole set of compounds measured. In the present study, methanol (33 atomic mass units (amu)), acetaldehyde (45 amu), ethanol (47 amu), acetone (59 amu), isoprene (69 amu), methyl vinyl ketone and methacrolein (both 71 amu) and the monoterpenes (137 amu) were monitored. PTR-MS cannot distinguish between isobaric species and therefore cannot separate various types of monoterpenes. Thus, mixing ratios as well as fluxes of monoterpenes reported in this paper represent the sum of all monoterpenes.

Synchronisation of the pulses at the ISR inlet valves with the anemometer is crucial for successful DEC measurements. Anemometer data were recorded on a separate computer and an identification label of the current wind vector was continuously handed over to a microcontroller unit, which activated the DS valves. When the ISR inlet valves were activated, the identification label was handed over to the PTR-MS computer. This procedure ensured that errors caused by different drifts of the computer system times were excluded. The activation delay was assessed to be less than 0.1 s.

2.3. Laboratory experiment

A laboratory experiment was performed to test the independence of two consecutive grab samples. In earlier experiments [6], a carry-over of 10% from the last sample did not affect flux results significantly. In the present experiment, the ISRs were evacuated below 1 mbar. However, memory effects caused by compounds sticking to the ISR inner surfaces could not be excluded a priori.

The DS was connected to a PTR-MS instrument (PTR-MS 1) and the inlet valves were attached to a Teflon bag (Fig. 3). The Teflon bag was flushed with humidified zero air, which was spiked with variable flows of VOC from a standard gas cylinder (Apel-Riemer, Environmental Inc., Denver, CO, USA; mixture of different VOC with volume mixing ratios (VMRs) in the range from 1 to 1.5 ppmV in nitrogen). Variations of VOC mixing ratios in the bag were continuously monitored with a second PTR-MS instrument (PTR-MS 2). As can be seen in Fig. 4, no measurable carry-over or memory effects were observed for monoterpenes and even for oxygenated species such as methanol. Note that the ISRs were run in an alternating cycle, so that successive data from PTR-MS 1 represent samples collected by different ISRs.

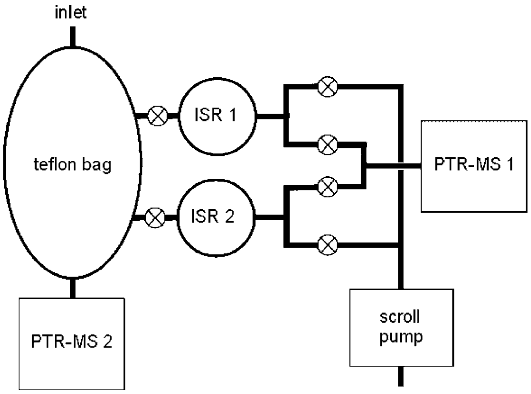

Fig. 3. Set-up of the laboratory experiment for studying memory effects in the DS unit. The DS was attached to a Teflon bag in which varying VOC mixing ratios were provided.

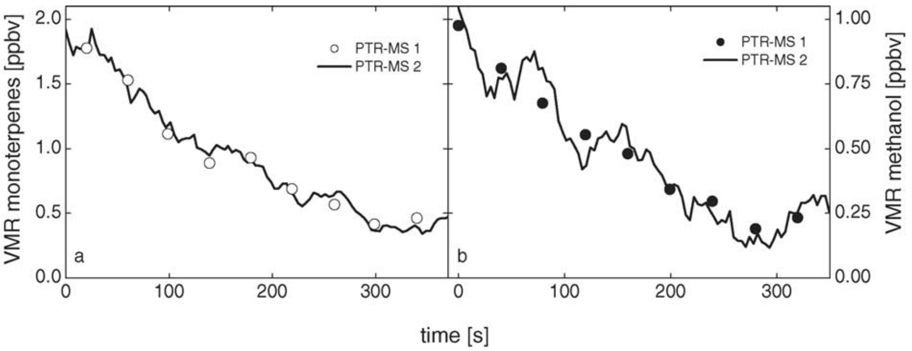

Fig. 4. Result of the laboratory experiment for (a) monoterpenes and (b) methanol. Circles indicate VOC VMRs alternately taken in ISR1 and ISR2 and determined by PTR-MS 1. Solid lines represent VOC VMRs in the Teflon bag measured continuously by PTR-MS 2.

3. Results and discussion

Due to initial instrumentation problems and the absence of stable high-pressure weather conditions, flux measurements were only possible for short periods of time. However, the applicability of the DS-PTR-MS method for measuring monoterpene fluxes from a conifereous forest could be demonstrated. Quality checked flux data reveal that during night monoterpene fluxes did not exceed 0.15 nmol m^{-2} s^{-1} (Fig. 5). After sunrise fluxes quickly rose to about 0.35 nmol m^{-2} s^{-1}. In the following hours monoterpene fluxes were variable with maximum values around 0.5 nmol m^{-2} s^{-1}. For the afternoon no data are reported as the wind direction changed and free advection was no longer guaranteed. Non-zero isoprene fluxes were detected during some half-hour intervals, but failed quality checks. No fluxes of oxygenated species were detected.

The distance between anemometer and ISR inlets, and the interval length between two grab samples are sources of systematic errors in flux measurements: The sonic anemometer had a horizontal displacement to the DS of about 0.4 m (Fig. 2) resulting in an underestimation of the flux of less than 7% [15]. The error caused by the duration of the time interval required for sample analysis can be determined using simulation results. Since DEC uses a subset of data from EC, a given EC dataset can be used to simulate a DEC measurement. Ruppert [16] used high frequency CO_2 and temperature data, obtained at the same tower in previous years, to carry out empirical calculations of the quality of DEC in comparison to EC results. According to these calculations, a sampling interval of 40 s yields an error of 32%.

In parallel to the DEC measurements an enclosure study was performed at trees surrounding the tower (Grabmer et al., in preparation). Air temperature in the canopy was a good approximation of leaf temperature for days with similar photosynthetic photon flux density (PPFD) values during the campaign. Thus, the emission of monoterpenes from trees in the fetch area around the tower was calculated using the common exponential algorithm (e.g., [17]) and air temperature data. At the tower site the leaf area index was 5.3 [11] and the specific leaf area was 5.7×10^{-3} m^2 g^{-1} d.wt. [18]. For 10th August 2002, this calculation yields a primary flux on the order of 0.5 nmol m^{-2} s^{-1}. This result is in good agreement with DEC flux data shown in Fig. 5. Furthermore, VOC fluxes were measured at the same location using the REA method. These measurements showed monoterpene fluxes

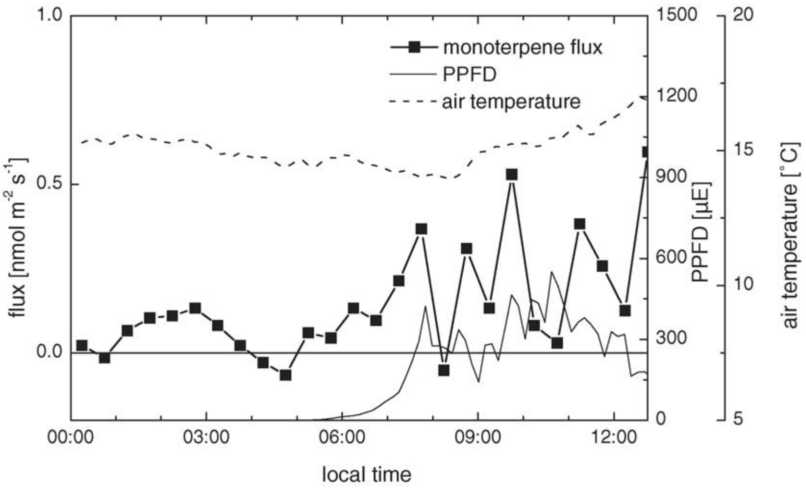

Fig. 5. Half-hour means of monoterpene flux rates as measured for 10th August, 2002 shown together with PPFD and air temperature.

up to 2.5 nmol m^{-2} s^{-1} on warm days and significantly lower flux values (in a range of a few tenths nmol m^{-2} s^{-1}) on days with moderate temperatures, as was the case on 10th August 2002 (Graus et al., in preparation).

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