Dealing with disjunct concentration measurements in eddy covariance applications: A comparison of available approaches

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ABSTRACT

Using proton transfer reaction mass spectrometry equipped with a quadrupol mass analyser to quantify the biosphere-atmosphere exchange of volatile organic compounds (VOC), concentrations of different VOC are measured sequentially. Depending on how many VOC species are targeted and their respective integration times, each VOC is measured at repeat rates on the order of a few seconds. This represents an order of magnitude longer sample interval compared to the standard eddy covariance (EC) method (5−20 Hz sampling rates). Here we simulate the effect of disjunct sampling on EC flux estimates by decreasing the time resolution of CO_2 and H_2O concentrations measured at 20 Hz above a temperate mountain grassland in the Austrian Alps. Fluxes for one month are calculated with the standard EC method and compared to fluxes calculated based on the disjunct data (1, 3 and 5 s sampling rates) using the following approaches: i) imputation of missing concentrations based on the nearest neighbouring samples ($iDEC_{nn}$), ii) imputation by linear interpolation ($iDEC_{li}$), and iii) virtual disjunct EC (vDEC), i.e. flux calculation based solely on the disjunct concentrations. It is shown that the two imputation methods result in additional low-pass filtering, longer lag times (as determined with the maximum cross-correlation method) and a flux loss of 3−30% as compared to the standard EC method. A novel procedure, based on a transfer function approach, which specifically corrects for the effect of data treatment, was developed, resulting in improved correspondence (to within 2%). The vDEC method yields fluxes which approximate the true (20 Hz) fluxes to within 3−7% and it is this approach we recommend because it involves no additional empirical corrections. The only drawback of the vDEC method is the noisy nature of the cross-correlations, which poses problems with lag determination − practical approaches to overcome this limitation are discussed.

1. Introduction

The biosphere and the atmosphere are linked by the exchange of mass and energy occurring at their interface − changes in the properties and composition of the atmosphere affect the biosphere, and likewise changes in the structure and function of the biosphere feed back to the atmosphere (Pielke et al., 1998). In order to predict how likely climate change will affect the biosphere in the future and how changes in the biosphere will feed back on the atmosphere

it is necessary to understand how the biosphere responds to atmospheric forcing and the role the biosphere is playing in modulating climate (Kulmala et al., 2004; Arneth et al., 2009; Goldstein et al., 2009).

The most direct approach for quantifying the biosphere-atmosphere exchange of mass and energy is the eddy covariance (EC) method (Swinbank, 1951). In the absence of advection (Aubinet, 2008), the net exchange of some non-reactive scalar χ is given as

$$F = \int_0^h \overline{\frac{\delta \chi}{\delta t}} dz + \overline{w'\chi'}(h) \tag{1}$$

where the first term on the right-hand side (RHS) represents the storage change flux, i.e. the time-rate-of-change in scalar concentration below the height (h) at which measurements are made

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(z referring to the vertical direction). The second term on the RHS of Eq. (1) is the vertical turbulent exchange (the eddy term) given as the covariance between the vertical wind speed and the scalar χ. The primes denote deviations from the temporal mean calculated by Reynolds decomposition as

$$w' = w - \overline{w}, \ \chi' = \chi - \overline{\chi} \tag{2}$$

with w and χ representing instantaneous values.

The EC method is usually applied in the surface layer, with wind speed and scalar concentration measurements made with fast sensors (response time ~ 0.1 s) at high temporal resolution (5–20 Hz) in order to capture as much as possible of the (small and fast) turbulent fluctuations which carry a significant proportion of the flux (Kaimal and Finnigan, 1994).

As shown by Rinne et al. (2001), the requirement of a fast sampling rate can be relaxed, as long as the response time is appropriate, resulting in a variant of the standard EC method termed disjunct eddy covariance (DEC) method. With the DEC method, air samples are taken (grabbed) during a short time interval (~ 0.1 s) and then analysed over a longer period ($\Delta T < 30$ s) by a relatively slow sensor, resulting in a time series with relatively long time intervals between the (fast-response) concentration and wind speed measurements. The DEC has been used for example over coniferous forest (monoterpenes – Grabmer et al., 2004), crops (methanol – Rinne et al., 2001; various oxygenated VOCs – Warneke et al., 2002) or grassland (water vapour – Rinne et al., 2008).

Another variant of this method was introduced by Karl et al. (2002), coined virtual disjunct EC (vDEC). With the vDEC method disjunct concentration samples thus do not result from the slow analysis of the grab-samples as with the DEC approach, but rather from the sequential, fast-response measurement of several atmospheric compounds. The vDEC method is tailored to the characteristics of the proton transfer reaction mass spectrometer (PTR-MS), a fast sensor capable of quantifying a wide range of different volatile organic compounds (VOCs; Lindinger et al., 1998). A PTR-MS, equipped with a quadrupol mass filter, analyses different VOCs one by one in a sequential fashion. The response time for individual VOCs is on the order of 0.1 s (Karl et al., 2001). Since the introduction of the PTR-MS (Hansel et al., 1995), it has been used on several occasions with the vDEC method, for example over coniferous forest (several VOC – Karl et al., 2002; Rinne et al., 2007) or an urban canopy (Langford et al., 2009).

Recently, Spirig et al. (2005) proposed another method for dealing with disjunct time series data delivered by the PTR-MS, which consists of imputation, i.e. filling up, of the gaps between the disjunct samples to the time resolution of the wind vector time series (usually 5–20 Hz) based on the nearest neighbouring concentration value (Fig. 1). This method, which will be referred to as iDEC method (i.e. imputed disjunct EC) in the following, has been used for quantifying the fluxes of various VOCs over a forest (Spirig et al., 2005) and over grassland (Brunner et al., 2007; Davison et al., 2008) and for water vapour over grassland (Ammann et al., 2006).

Previous theoretical and experimental evaluations of the DEC and vDEC method have shown negligible systematic errors and little random uncertainty as long as the disjunct sampling interval does not exceed the integral turbulence time scale (Lenschow et al., 1994; Bosveld and Beljaars, 2001; Rinne et al., 2008; Turnipseed et al., 2009). Ammann et al. (2006) found good correspondence between iDEC and EC water vapour flux measurements as long as the low-pass filtering associated with the iDEC method was accounted for. While the DEC, vDEC and iDEC methods have been compared against fluxes measured independently by means of the EC method (Ammann et al., 2006; Rinne et al., 2008; Turnipseed et al., 2009), such comparisons are often hampered by systematic
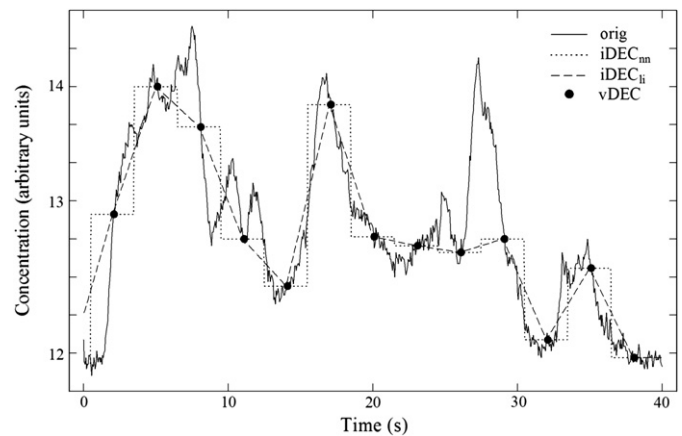

Fig. 1. Example concentration time series illustrating disjunct sampling (vDEC, using a 3 s sampling interval) of the original 20 Hz data and the imputation of missing samples by the iDEC$_{nn}$ and iDEC$_{li}$ methods.

and random uncertainties associated with the EC method (Moncrieff et al., 1996; Hollinger and Richardson, 2005), which serves as the reference. Alternatively, the disjunct sampling process may be simulated by reducing the time resolution of high-frequency EC measurements, which offers the advantage of knowing the true flux. To this end, the sensible heat flux measured by means of a sonic anemometer (Bosveld and Beljaars, 2001; Spirig et al., 2005; Turnipseed et al., 2009) or the latent heat flux measured by a co-located water vapour sensor (Rinne et al., 2008) have been used. These exercises, however, may not very well represent the effects of disjunct sampling on scalars measured in a closed instrument dislocated from the sonic anemometer by sampling air through a tube, which causes concentration signals to be dampened and phase-shifted (Massman, 2000).

The objective of the present paper is thus a systematic comparison of the ability of the vDEC and the iDEC methods for quantifying the true biosphere-atmosphere mass exchange of scalars measured in a closed setup by sampling through a tube. To this end we simulate disjunct sampling by degrading the sampling interval of carbon dioxide (CO_2) and water vapour (H_2O) fluxes measured with a closed-path EC system at a sampling rate of 20 Hz above a mountain grassland in Austria (Hammerle et al., 2008; Wohlfahrt et al., 2008). CO_2 and H_2O, respectively, have been chosen as examples for scalars with negligible and non-negligible interactions with the walls of the inlet tubing required for transporting the air to the sensor (Ibrom et al., 2007; Massman and Ibrom, 2008).

2. Material and methods

2.1. Site description

The study site is located at a meadow in the vicinity of the village Neustift ($47°07'$N, $11°19'$E) in the Stubai Valley (Austria) at an elevation of 970 m a.s.l. in the middle of the flat valley bottom. The fetch is homogenous up to 300 m to the east and 900 m to the west of the instrument tower, the dominant day and night time wind directions, respectively. A detailed description of the study site in terms of soil, vegetation and climate may be found in Hammerle et al. (2008) and Wohlfahrt et al. (2008).

2.2. Eddy covariance (EC)

The net ecosystem CO_2 and H_2O exchanges were measured according to the EUROFLUX project using the EC method and

instrumentation described by Baldocchi et al. (1988) and Aubinet et al. (2000). For the purpose of this analysis we used flux data taken in July 2007.

The three wind components and the speed of sound were measured by a three-dimensional sonic anemometer (R3IA, Gill Instruments, UK), CO_2 and H_2O mole fractions by a closed-path infrared gas analyser (Li-6262, Li-Cor, USA). Air was pulled from the intake point at a distance of 0.1 m from the centre of the sensor volume of the sonic anemometer mounted at 3 m above ground, through a 4 m Teflon tube of 0.004 m inner diameter through a filter (Acro 50, Gelman, USA) to the infrared gas analyser (IRGA) at a flow rate of 9 standard l min^{-1} (N035ANE, KNF Neuberger, Germany). The IRGA was operated in the absolute mode, flushing the reference cell with dry N_2 from a gas cylinder at 0.1 l min^{-1}. The 10 Hz signals of the IRGA were synchronised with the 20 Hz sonic signals. All unprocessed data were saved on a harddisk using the *EdiSol* software (University of Edinburgh).

The calculation of half-hourly mean eddy flux values was done using the post-processing software *EdiRe* (University of Edinburgh) and involved the following five steps:

(1) Conversion of raw signals to appropriate units;
(2) Three-axis co-ordinate rotation aligning the co-ordinate system's vector basis with the mean wind streamlines (Kaimal and Finnigan, 1994);
(3) Cross-correlation analysis for determining and removing time delays of the CO_2 and H_2O signals with respect to the vertical wind velocity (McMillen, 1988);
(4) Calculation of the covariance between vertical wind speed and CO_2 and H_2O concentrations respectively after Reynolds (block) averaging;
(5) Application of frequency response corrections accounting for low-pass (sensor separation, dynamic frequency response, scalar and vector path averaging, frequency response mismatch and the attenuation of concentration fluctuations down the sampling tube) and high-pass filtering following Moore (1986) and Aubinet et al. (2000).

Note that no corrections for density effects (Webb et al., 1980) were necessary with this setup as water vapour (dilution) effects were corrected internally by the IRGA and air temperature fluctuations may be assumed negligible by the time the air arrives in the IRGA (Ibrom et al., 2007).

2.3. Quality control

Half-hourly eddy fluxes were screened for validity by removal of time periods with (i) the CO_2 and H_2O signals outside a physically plausible range (CO_2: 340–900 μmol mol^{-1}, H_2O: 4–22 mmol mol^{-1}), (ii) the coefficient of variation for CO_2 and H_2O concentration and pressure within the IRGA outside an experiential plausible range (CO_2, H_2O: 0.001–0.1, P: 0.0001–0.001), (iii) the third rotation angle exceeding ± 10° (McMillen, 1988), (iv) the stationarity test for the CO_2 and H_2O flux exceeding 60% (Foken and Wichura, 1996), (v) deviation of the integral similarity characteristics larger than 60% (Foken and Wichura, 1996) and (vi) the maximum of the footprint function (Hsieh et al., 2000) outside the boundaries of the meadow. In total 617 out of the 1488 half-hourly flux records (58/42% unstable/stable conditions) met these criteria and were used in the subsequent analysis.

2.4. Cospectral analysis

Cospectra of the vertical wind speed and CO_2 and H_2O, respectively, were calculated with the *EdiRe* software package: To obtain the high-frequency component of the cospectra, each run of 36 000 points was divided into nine segments ($2^{12} = 4096$ points each), the last segment being zero-padded to bring it up to 4096 points. Before employing the Fast Fourier Transformation, data were conditioned by removing the mean, linear detrending, and by tapering the time series with a Hamming window (Kaimal and Finnigan, 1994). To obtain the low frequency component, the same procedure as described above was followed except for data being averaged into 4096 blocks each consisting of nine values. The low and high frequency cospectra were then merged and averaged into 50 logarithmically spaced bins.

2.5. Simulation of disjunct sampling and flux calculation approaches

While disjunct flux methods have been successfully used with sampling intervals up to 30 s (Turnipseed et al., 2009), we aimed at simulating the lower end, typical, and upper end sampling rates with a PTR-MS (Spirig et al., 2005; Brunner et al., 2007) and generated disjunct concentration time series by resampling the original 20 Hz CO_2 and H_2O concentrations at 1, 3 and 5 s sampling intervals (ΔT). Depending on the magnitude of the flux and ambient concentrations, it is usually necessary that the PTR-MS integrates longer than 50 ms per VOC mass in order to improve the limit of detection of the respective VOC. Aiming to represent typical integration times used in VOC flux measurements with a PTR-MS we have simulated 50, 250 and 500 ms integration times (Spirig et al., 2005; Brunner et al., 2007; Custer and Schade, 2007). Together with the three simulated sampling intervals this yielded a total of 9 variations of the disjunct time series. For comparison with earlier work we include results for simulated sampling intervals of 10 and 20 s on a few occasions, but do not show the corresponding data.

The various approaches for calculating fluxes from these disjunct time series are illustrated in Fig. 1. In the approach first proposed by Spirig et al. (2005), the disjunct concentration measurements were filled up to the time resolution of the wind components (20 Hz) by repeating each disjunct concentration in time half of the sampling interval before and after the disjunct measurement, which will be referred to as iDEC$_{nn}$, where the subscript stands for nearest neighbour. Because it is not *a priori* apparent why ambient concentrations are assumed to be constant between the disjunct measurements in the iDEC$_{nn}$ method, we additionally tested a new variant which assumes concentrations to change linearly between the disjunct measurements (Fig. 1), referred to as iDEC$_{li}$ (subscript stands for linear interpolation) method in the following. In the vDEC method, fluxes were calculated without filling the gaps between the disjunct concentration measurements (Fig. 1).

3. Results

3.1. Cross-correlation (lag) analysis

Lag times calculated with the maximum cross-correlation method using the original 20 Hz data clustered around ∼0.7 s and ∼1 s for CO_2 and H_2O data, respectively, with somewhat more variation for the H_2O lag times (Fig. 2). The lag time calculated from tube dimensions and flow rates, not accounting for instrument and filter volumes, amounted to ∼0.4 s. The frequency distributions of lag times of the three disjunct methods were much broader and peaks shifted to longer lag times as compared to the original 20 Hz data, in particular for the iDEC methods (Fig. 2). Both the shift in the peak and the broadening of the frequency distribution (Fig. 2) became more prominent with longer sampling intervals. At 10 and 20 s simulated sampling intervals, the frequency distribution of the
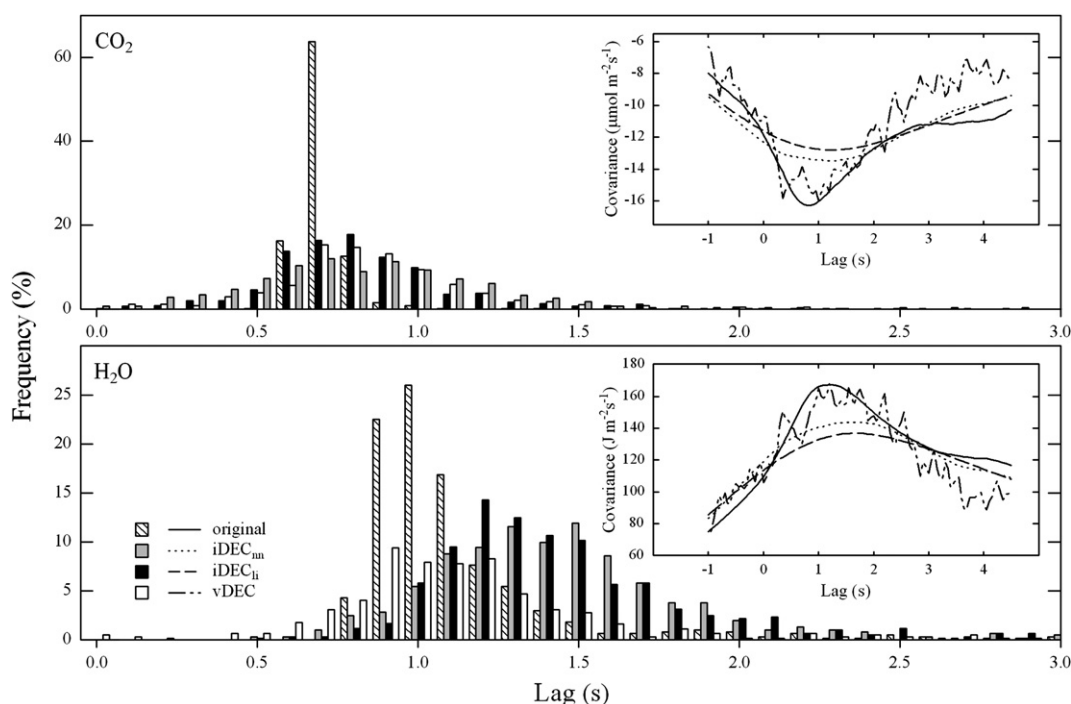
Fig. 2. Frequency distribution of lag times calculated with the maximum cross-correlation method for the original 20 Hz data and the vDEC, $iDEC_{nn}$ and $iDEC_{li}$ methods using a 3 s sampling interval (250 ms integration time). Insets show results of the cross-correlation analysis for one typical half-hourly period around noon.

iDEC methods became almost flat, while lag times of the vDEC method still exhibited a peak around the true value (data not shown). Varying the integration time had no discernable effect on lag times (data not shown).

Representative examples of half-hourly cross-correlation analyses are shown as insets in Fig. 2. The cross-correlation curves based on the vDEC data generally followed the one based on the original 20 Hz data and reached similar maximum covariances at similar lag times, but were much noisier due to the reduced number of samples (600 vs. 1800 samples in the example given in the insets of Fig. 2). With the iDEC methods cross-correlation curves were smooth, but exhibited both a shift to longer lag times and lower peak covariances as compared to the original 20 Hz data (insets in Fig. 2).

3.2. Flux comparison

Flux loss due to disjunct sampling was least for the vDEC method, where an average flux loss of around 5%, largely independent of the disjunct sampling rate (up to $\Delta T = 20$ s − data not shown), was observed (Table 1). For the iDEC methods flux loss increased with decreasing sampling rate up to 30% at a sampling rate of 5 s (at $\Delta T = 20$ s less than 50% of the flux are measured − data not shown), with a clearly larger flux loss for the $iDEC_{li}$ method (average flux loss of 19 vs. 15% $iDEC_{nn}$) and somewhat larger flux loss for CO_2 as compared to H_2O (Table 1). The integration time had little influence on flux loss (Table 1). Decreasing the sampling rate led to an increase in the variability (i.e. decreased the r^2) for all methods (Table 1), which became more prominent at 10 and 20 s sampling intervals (data not shown). The effect of disjunct sampling and imputation of missing samples on bin-averaged diurnal courses of CO_2 and H_2O fluxes is exemplified in Fig. 3.

A cospectral analysis (Fig. 4) revealed that the observed flux loss with the iDEC methods was due to additional low-pass filtering due to the imputation of the missing samples (as the data basis and all

other processing steps are identical), while vDEC cospectra were characterised by larger noise. As this additional source of flux loss with the iDEC methods is not presently taken into account by our flux calculation procedure we aimed at parameterising this effect for inclusion into the transfer function approach after Moore (1986). To this end we followed the approach by Aubinet et al. (2000) for calculating experimental low-pass filtering transfer functions for EC systems. Co-spectral ratios of the $iDEC_{nn}$ and $iDEC_{li}$ to the original 20 Hz (CO_2 and H_2O) data were calculated and, after appropriate normalisation (cf. Aubinet et al., 2000), fitted to the following empirical transfer function:

$$TF(f) = \exp\left(-\left(\frac{f}{f_o}\right)^2\right) \tag{3}$$

where f refers to the frequency and f_o to the frequency where $TF(f) = 1/e$ (~ 0.37; e being the Euler's number), referred to as the cut-off frequency in the following. Assuming that other low-pass filtering effects (e.g. the attenuation of concentration fluctuations down the sampling tube) affect the original and disjunct time series in the same manner, Eq. (3) describes additional low-pass filtering due to the imputation of gaps in the disjunct concentration time series. As shown in Fig. 5, the cut-off frequency was lower for the $iDEC_{li}$ method (implying a larger flux loss) and decreased for both methods as the sampling interval increased (with little differences between CO_2 and H_2O). Using the cut-off frequencies shown in Fig. 5 and implementing Eq. (3) as an additional transfer function in our post-processing scheme, allowed us to correct iDEC fluxes for this effect. As shown in Table 1, this procedure efficiently removed the error for these two methods to within 2%.

4. Discussion

The exchange of biogenic VOCs between terrestrial ecosystems and the atmosphere has emerged as a crucial influence on the

Table 1
Results of a linear regression analysis (forced through the origin) of fluxes (CO_2: μmol m^{-2} s^{-1}, H_2O: J m^{-2} s^{-1}) calculated with the original 20 Hz data against the three disjunct methods (vDEC, iDEC$_{nn}$, iDEC$_{li}$). *iDEC$_{nn}$ and *iDEC$_{li}$ refers to results where an additional empirical transfer-function based correction (Eq. (3)) has been applied to the data, as described in the text.

CO_2	ΔT	Integration period					
		50 ms		250 ms		500 ms	
		k	r^2	k	r^2	k	r^2
vDEC	1 s	0.95	0.99	0.95	0.99	0.95	1.00
iDEC$_{nn}$		0.95	1.00	0.95	1.00	0.95	1.00
*iDEC$_{nn}$		1.01	1.00	1.02	1.00	1.02	1.00
iDEC$_{li}$		0.93	1.00	0.93	1.00	0.92	1.00
*iDEC$_{li}$		1.00	1.00	1.01	1.00	1.01	1.00
vDEC	3 s	0.96	0.99	0.96	0.99	0.95	0.99
iDEC$_{nn}$		0.83	0.99	0.83	0.99	0.83	0.99
*iDEC$_{nn}$		1.00	1.00	1.01	1.00	1.02	1.00
iDEC$_{li}$		0.79	0.98	0.79	0.98	0.79	0.98
*iDEC$_{li}$		1.00	1.00	1.01	1.00	1.02	1.00
vDEC	5 s	0.95	0.98	0.95	0.98	0.95	0.99
iDEC$_{nn}$		0.75	0.97	0.75	0.97	0.75	0.97
*iDEC$_{nn}$		1.00	0.99	1.01	0.99	1.00	0.99
iDEC$_{li}$		0.70	0.97	0.70	0.97	0.70	0.97
*iDEC$_{li}$		0.99	0.99	1.01	0.99	1.00	0.99
H_2O							
vDEC	1 s	0.96	1.00	0.96	1.00	0.96	1.00
iDEC$_{nn}$		0.97	1.00	0.96	1.00	0.96	1.00
*iDEC$_{nn}$		1.01	1.00	1.02	1.00	1.01	1.00
iDEC$_{li}$		0.94	1.00	0.94	1.00	0.94	1.00
*iDEC$_{li}$		1.01	1.00	1.01	1.00	1.00	1.00
vDEC	3 s	0.97	0.99	0.93	0.98	0.96	0.98
iDEC$_{nn}$		0.85	0.99	0.85	0.99	0.85	0.99
*iDEC$_{nn}$		1.01	1.00	1.01	1.00	1.01	1.00
iDEC$_{li}$		0.80	0.99	0.80	0.99	0.80	0.99
*iDEC$_{li}$		1.00	1.00	1.00	1.00	1.01	1.00
vDEC	5 s	0.97	0.98	0.96	0.99	0.95	0.99
iDEC$_{nn}$		0.75	0.98	0.75	0.98	0.75	0.98
*iDEC$_{nn}$		0.99	0.99	0.99	1.00	0.98	1.00
iDEC$_{li}$		0.70	0.98	0.70	0.98	0.70	0.98
*iDEC$_{li}$		0.99	0.99	1.00	0.99	0.99	0.99

k, slope of linear regression (dimensionless); r^2, coefficient of determination, ΔT, disjunct sampling interval (s).

climate of the earth system (Kulmala et al., 2004; Arneth et al., 2009; Goldstein et al., 2009). While the time-of-flight (TOF) PTR-MS technology (Blake et al., 2004), which allows concurrent quantification of a wide number of VOCs, has recently gained sufficient sensitivity to be applied in EC flux measurements (Jordan et al., 2009), sequential measurement of VOCs using a conventional PTR-MS (Lindinger et al., 1998) will remain state-of-the-art for long-term sensitive fast-response concentration measurements for at least the near future, because of the difficulties involved in dealing with the vast amount of data generated by a TOF-PTR-MS (Müller et al., 2009).

At present two approaches are commonly used for calculating VOC fluxes from disjunct concentration data measured with a PTR-MS: (i) the vDEC method (Karl et al., 2002) and (ii) the nearest neighbour imputation method (iDEC$_{nn}$) put forward by Spirig et al. (2005). While earlier (semi-)theoretical studies have investigated the effect of disjunct sampling and the imputation of missing samples on systematic and random uncertainties of calculated fluxes (Lenschow et al., 1994; Bosveld and Beljaars, 2001; Spirig et al., 2005; Ammann et al., 2006; Turnipseed et al., 2009), no systematic inter-comparison between the vDEC and iDEC methods has been done, in particular for the situation where scalar concentrations are measured in a closed setup by sampling through a tube.

Our study confirms earlier comparisons of this kind which showed little systematic differences (3–7% in our study) between
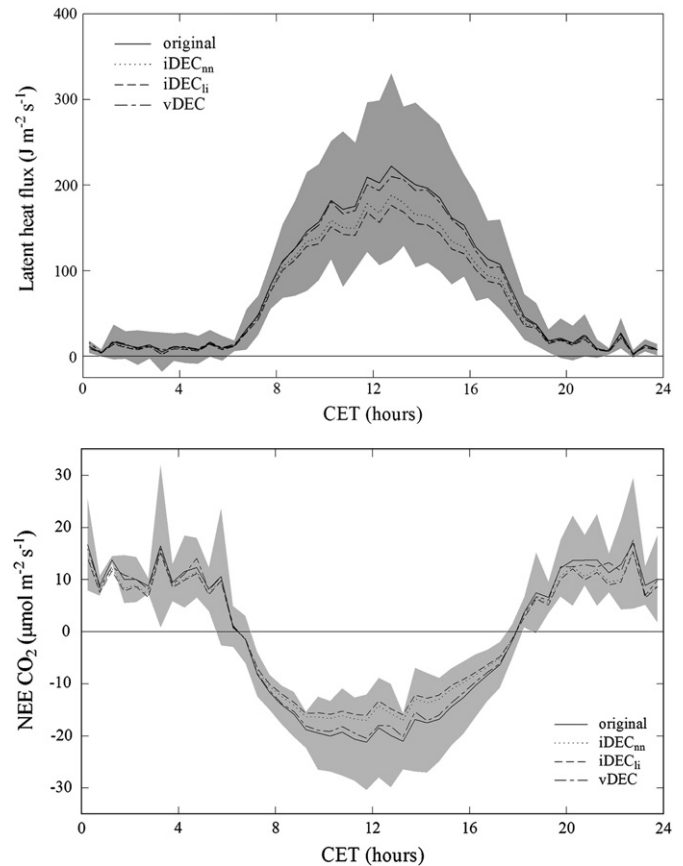

Fig. 3. Bin-averaged diurnal courses of the net ecosystem CO_2 and latent heat fluxes. The grey envelope refers to ± 1 standard deviation around the fluxes based on the original 20 Hz data. A 3 s sampling interval (250 ms integration time) was used for the vDEC, iDEC$_{nn}$ and iDEC$_{li}$ methods.

fluxes calculated from vDEC and "standard" EC data (Lenschow et al., 1994; Rinne et al., 2007; Turnipseed et al., 2009). The reduced number of (disjunct) samples, however, goes along with an increase in the statistical uncertainty of the flux measurement
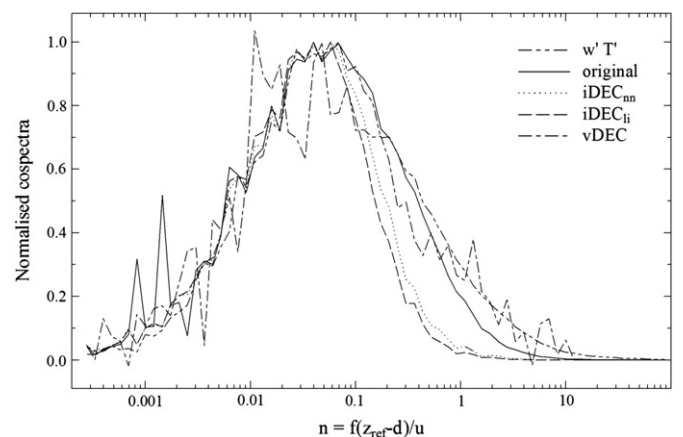

Fig. 4. Average normalised cospectra for unstable conditions of the vertical wind component (w′) and concentrations of CO_2 for the vDEC, iDEC$_{nn}$ and iDEC$_{li}$ methods (using a 3 s sampling interval and 250 ms integration time) in comparison with the original 20Hz data. Sensible heat (w′T′) cospectra are shown as a reference. Note that frequency on the x-axis has been normalised with $(z_{ref}-d)/u$, where z_{ref} and d refer to the reference and zero-plane displacement height (m) and u to the mean horizontal wind speed (m s^{-1}).
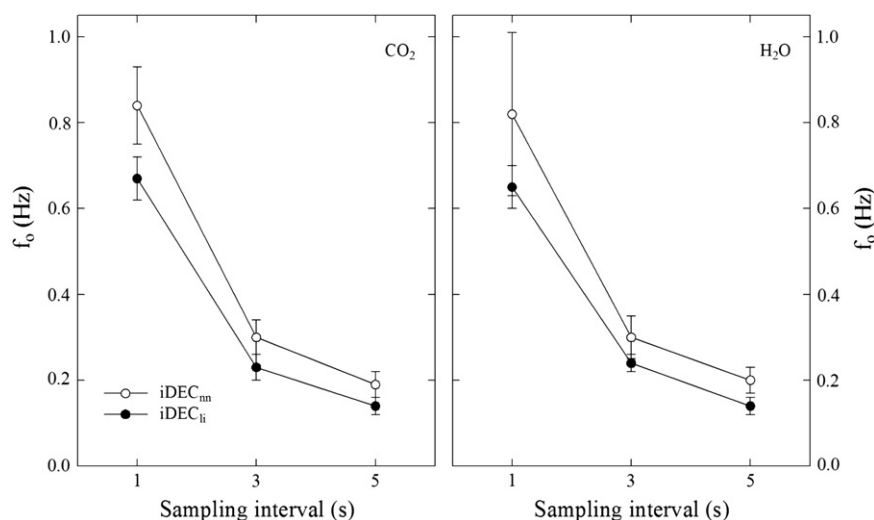
Fig. 5. Parameter f_o from Eq. (3) describing the additional low-pass filtering effect induced by the iDEC$_{nn}$ and iDEC$_{li}$ methods. Error bars refer to $\pm$ 1 standard deviation. Lines represent best fits to the data using the following equations, where ΔT (s) refers to the sampling interval: iDEC$_{nn}$: f_o (CO$_2$) = 0.8897 $\Delta T^{-0.9625}$, f_o (H$_2$O) = 0.899 $\Delta T^{-0.9434}$; iDEC$_{li}$: f_o (CO$_2$) = 0.6834 $\Delta T^{-0.9346}$, f_o (H$_2$O) = 0.6645 $\Delta T^{-0.9278}$.

(Bosveld and Beljaars, 2001), noted as a decrease in r^2 with increasing ΔT (Table 1) and noisier cross-correlation curves (Fig. 2) and cospectra (Fig. 4). Turnipseed et al. (2009) recently proposed an empirical equation for estimating the random error imposed by disjunct sampling, which for our setup (averaging period of 30 min, ΔT 1–5 s) yields standard deviations between 5 and 18% for the slope of the linear regression between EC and vDEC fluxes, which compares nicely with the range of 4–23% (data not shown) found in our study.

In contrast to the vDEC method, a significant underestimation of fluxes (up to 30% with ΔT = 5s; Table 1) was found for both iDEC methods and was shown (Fig. 4) to be due to additional low-pass filtering associated with the imputation of missing samples with these two methods. The same conclusion was already reached by Spirig et al. (2005), who found 11% flux loss when the sampling rate of sensible heat flux measurements was degraded from 200 ms to 3 s and the missing samples imputated based on the iDEC$_{nn}$ method. Spirig et al. (2005), and later Ammann et al. (2006), corrected for low-pass filtering with the iDEC$_{nn}$ method by dividing the raw flux by the ratio between the cospectra of sensible heat to the scalar of interest, assuming negligible low-pass filtering of the sensible heat flux. In contrast to this bulk correction, which does not distinguish between the various sources of low-pass filtering, we have presented (Eq. (3)) and parameterised (Fig. 5) an approach by which the low-pass filtering of the imputation process may be accounted for in isolation. The corresponding cut-off frequencies for CO$_2$ and H$_2$O were very similar, further underlining the impact of the data treatment, i.e. the imputation of missing samples. Our proposed method of correction is compatible with the approach described by Moore (1986), which corrects for various (low-and high-pass) filtering effects separately. The major advantage with this approach, as opposed to the bulk correction employed by Spirig et al. (2005) and Ammann et al. (2006), is that changes in the setup of the EC system which affect low-pass filtering, e.g. length of tubes or flow rates, may be readily accommodated by replacing the appropriate parameter, while the bulk correction has to be re-parameterised (see also Massman and Lee, 2002). In contrast to Ammann et al. (2006), who found that the transfer function approach by Moore (1986) was underestimating correction factors, our study shows that this approach may be successfully used for correcting iDEC flux measurements provided that the additional

low-pass filtering associated with the imputation of missing samples is accounted for (e.g. via Eq. (3) and Fig. 5). Further independent support for our approach derives from Bamberger et al. (2010), who were able to show that iDEC$_{nn}$ methanol fluxes (ΔT = 2.82 s, 200 ms integration time) corrected based on Eq. (3) and the parameterisation of the cut-off frequency shown in Fig. 5 differed by only 6% from the corresponding fluxes calculated with the vDEC method despite a different setup (lower measurement height, longer tubes).

Interpolation between disjunct samples, the iDEC$_{li}$ method, lead to even more damping (Figs. 2, 4 and 5) and higher flux losses (Table 1, Fig. 3) as compared to the iDEC$_{nn}$ method. We thus conclude that linear interpolation may not be a good approximation to the actual concentration fluctuations, which is visible in Fig. 1.

As varying integration times showed no significant differences in our calculations (but see Henjes et al., 1999; Horst and Oncley, 2006) and because the flux loss and noise increased with increasing the sampling rate (Table 1), it is recommended to keep the sampling interval as short as possible with the iDEC methods. For VOC flux measurements with a PTR-MS this requires making a compromise between the number of sequentially sampled masses and their dwell times. For the present setup and meteorological conditions, our analysis suggests that in order to keep flux corrections below 20%, the sampling rate should not exceed 3 s for the iDEC methods. This recommendation can be relaxed when flux measurements are performed at taller towers and/or above aerodynamically rougher canopies, where the flux carried by higher frequencies is lower as compared to our comparably smooth, low-statured grassland canopy (Spirig et al., 2005; Ammann et al., 2006).

Effects of disjunct sampling and imputation of missing samples on the determination/removal of any phase shift between measurements of the vertical wind speed and the scalar concentration have received little attention up to now, because previous work explicitly used or was tailored to co-located instruments (Bosveld and Beljaars, 2001; Spirig et al., 2005; Rinne et al., 2008; Turnipseed et al., 2009), where phase shifts are much smaller as compared to dislocated instruments which sample air through a tube.

Lag times calculated with the maximum cross-correlation method (McMillen, 1988) were generally longer for the disjunct

methods as compared to the 20 Hz data (Fig. 2). Lengthening of lag times with the iDEC methods can be explained by the additional low-pass filtering associated with the imputation of missing samples: The convolution of a time series with a filter is equivalent to the product of the cross spectrum with the filter transfer function in frequency space. The cross spectrum, in turn, is related to the cross covariance function (p. 60, Kaimal and Finnigan, 1994) and therefore any filtering will be seen in the cross-correlation. This is pictured in Fig. 6, which shows the cross-correlation between an exemplary half-hourly sonic temperature time series and that same time series to which a recursive filter has been applied in order to mimic the effect of tube attenuation. Fig. 6 shows that filtering causes the peak of the cross-correlation curve to shift from short lags at very small time constants, and an exponential decay similar to the auto-correlation function (Fig. 2.2 in Kaimal and Finnigan, 1994), to longer lag times as the time constant of the recursive filter is increased. Imputation of missing samples represents additional low-pass filtering and causes the peak of the cross-correlation to shift to longer lag times and a reduced correlation at the peak lag time (Figs. 2 and 6). Lag times based on the maximum cross-correlation method thus do not only represent the physical setup of the EC system (i.e. length and diameter of tubes, tube flow), but any filtering of the concentration data and thus whether or not and how gaps in the time series are filled. This finding echoes the results of Massman (2000) who studied the total phase shift associated with closed-path EC systems and showed that in addition to any lag time associated with sensor separation (dependent on wind speed and direction) and the length of the tube (dependent on tube flow), there is an influence of the intrinsic (i.e. overall) time constant of the scalar concentration measurements. If we interpret the additional low-pass filtering associated with the iDEC methods (Fig. 4) as an increase in the intrinsic time constant, this explains the observed lengthening of the time lags calculated with the maximum cross-correlation method. As a consequence, using the generally shorter original 20 Hz lag times (i.e. our reference) for the disjunct flux calculations would result in an additional flux loss due to an unaccounted phase shift. Beyond 5 s simulated

sampling intervals, the frequency distribution of lag times became almost flat with the iDEC methods, indicating a practical limit of ≤5 s for this method in conjunction with the system described in this paper. If lag times are poorly identified at longer sampling intervals, this will cause the total flux error being increasingly dominated by the unaccounted phase shift. In this situation, Eq. (3), which accounts only for dampening of high-frequency flux contributions, will likely not be able to properly correct fluxes.

Lag determination with vDEC data resulted in noisy cross-correlation curves and, similar to the iDEC methods, longer lag times as compared to the original 20 Hz data (Fig. 2). In contrast to the iDEC methods, we believe these longer lag times to result from the asymmetric character of the cross-correlation curve (p. 60 in Kaimal and Finnigan, 1994) compounded with the noise of the vDEC approach (Figs. 2 and 6) causing localized peaks at longer than average lag times to be over-represented compared to localized peaks at shorter than average lag times. Therefore, unsupervised, direct use of run-determined lag times for the vDEC method is discouraged unless an appropriate smoothing function is applied to the cross-correlation curve before peak determination. We also discourage from using iDEC lag times in vDEC flux calculations as done by some researchers (pers. comm. Thomas Karl/ NCAR), because these may not necessarily overlap with the peaks of the vDEC cross-correlation even if their frequency distribution of lag times was similar (Fig. 2). Provided proper account is taken of external controls on lag times (e.g. pump speed: Shimizu, 2007; tube age: Su et al., 2004; relative humidity: Ibrom et al., 2007), vDEC lag times averaged over multiple runs (in order to reduce the effect of the noise) may represent a practical option for the vDEC method. Alternatively, instead of using the maximum cross-correlation method (McMillen, 1988) to determine time lags, it may be more appropriate to correct for the total phase shift in spectral space (Massman, 2000; Wohlfahrt et al., 2009). We note however that quantitatively the shift to longer lag times with the vDEC method is not very important (i.e. little flux loss as compared to the original EC data; Table 1), because distant multiple peaks usually exhibit relatively similar levels of covariance (Fig. 2).
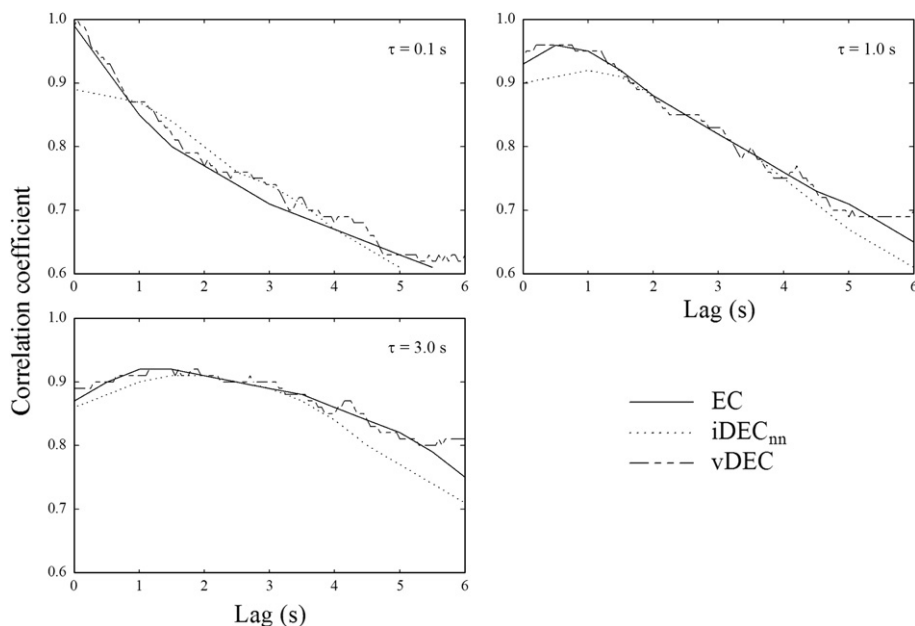

Fig. 6. Cross-correlation of an exemplary half-hourly sonic temperature time series with the same time series subject to a recursive filter (EC) which has been sub-sampled with a 3 s sampling interval (vDEC) and imputated (iDEC$_{nn}$). A recursive filter of the form $y_i = x_i + \exp(-\Delta/\tau)\,(y_{i-1} - x_i)$ was used to create a filtered time series (y), where x represents the original (unfiltered) time series, Δ the sampling rate (0.05 s) and τ the filter time constant (0.1, 1 and 3 s).

In conclusion, all approaches investigated in this study yielded reasonable results (as compared to the original 20 Hz data), provided that the appropriate corrections for flux loss were applied. Confirming the findings of Spirig et al. (2005) and Ammann et al. (2006), the imputation of missing samples with the iDEC methods was shown to amount to applying an additional low-pass filter to the (already filtered) concentration time series. As a major contribution to this field, an empirical method which corrects exclusively for this effect, was devised. This correction is compatible with the transfer function approach by Moore (1986) and has the advantage of being independent of the remaining sources of low-pass filtering associated with any EC system. In order to avoid overly large empirical corrections of iDEC fluxes our analysis suggests the sampling interval not to exceed 3 s with the present setup. The vDEC method involves no additional empirical corrections and was applicable with small flux losses ($\sim 5\%$) up to sampling intervals of 20 s. We therefore favour this method over the iDEC methods, which in our view offer only the practical advantage of the equidistant data being easier to manage and process. The sole drawback of the vDEC method is the noisy nature of the cross-correlations, which poses problems with lag determination using the maximum cross-correlation method.

Acknowledgments

References

Ammann, C., Brunner, A., Spirig, C., Neftel, A., 2006. Technical note: water vapour concentration and flux measurements with PTR-MS. Atmospheric Chemistry and Physics 6, 4643–4651.

Arneth, A., Sitch, S., Bondeau, A., Butterbach-Bahl, K., Foster, P., Gedney, N., de Noblet-Ducoudre, N., Prentice, I.C., Sanderson, M., Thonicke, K., Wania, R., Zaehle, S., 2009. From biota to chemistry and climate: towards a comprehensive description of trace gas exchange between the biosphere and atmosphere. Biogeosciences Discussions 6, 7717–7788.

Aubinet, M., 2008. Eddy covariance CO_2 flux measurements in nocturnal conditions: an analysis of the problem. Ecological Applications 18 (6), 1386–1387.

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., Vesala, T., 2000. Estimates of the annual net carbon and water exchange of forest: the EUROFLUX methodology. Advances in Ecological Research 30, 113–175.

Baldocchi, D.D., Hicks, B.B., Meyers, T.P., 1988. Measuring biosphere-atmosphere exchanges of biologically related gases with micrometeorological methods. Ecology 69, 1331–1340.

Bamberger, I., Hörtnagl, L., Schnitzhofer, R., Graus, M., Ruuskanen, T.M., Müller, M., Dunkl, J., Wohlfahrt, G., Hansel, A., 2010. Long term BVOC fluxes above mountain grassland. Biogeosciences Discussions 7, 83–110.

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

Bosveld, F.C., Beljaars, A.C.M., 2001. The impact of sampling rate on eddy-covariance flux estimates. Agricultural and Forest Meteorology 109, 39–45.

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

Custer, T., Schade, G., 2007. Methanol and acetaldehyde fluxes over ryegrass. Tellus 59, 673–684.

Davison, B., Brunner, A., Ammann, C., Spirig, C., Jocher, M., Neftel, A., 2008. Cut-induced VOC emissions from agricultural grasslands. Plant Biology 10, 76–85.

Foken, T., Wichura, B., 1996. Tools for quality assessment of surface-based flux measurements. Agricultural and Forest Meteorology 78, 83–105.

Goldstein, A.H., Koven, Ch.D., Heald, C.L., Fung, I.Y., 2009. Biogenic and anthropogenic pollutants combine to form a cooling haze over the southeastern United States. Proceedings of the National Academy of Sciences 106, 8835–8840.

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

Hammerle, A., Haslwanter, A., Tappeiner, U., Cernusca, A., Wohlfahrt, G., 2008. Leaf area controls on energy partitioning of a temperate mountain grassland. Biogeosciences 5, 421–431.

Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., Lindinger, W., 1995. Proton transfer reaction mass spectrometry: on-line trace gas analysis at ppb level. International Journal of Mass Spectrometry and Ion Processes 149/150, 609–619.

Henjes, K., Taylor, P.K., Yelland, M.J., 1999. Effect of pulse averaging on sonic anemometer spectra. Journal of Atmospheric and Oceanic Technology 16 (1), 181–184.

Hollinger, D.Y., Richardson, A.D., 2005. Uncertainty in eddy covariance measurements and its application to physiological models. Tree Physiology 25, 873–885.

Horst, T.W., Oncley, S.P., 2006. Corrections to inertial-range power spectra measured by CSAT3 and solent sonic anemometers, 1. Path-averaging errors. Boundary-Layer Meteorology 119, 375–395.

Hsieh, C.I., Katul, G., Chi, T.W., 2000. An approximate analytical model for footprint estimation of scalar fluxes in thermally stratified atmospheric flows. Advances in Water Resources 23, 765–772.

Ibrom, A., Dellwik, E., Flyvbjerg, H., Jensen, N.O., Pilegaard, K., 2007. Strong low-pass filtering effects on water vapour flux measurements with closed-path eddy correlation systems. Agricultural and Forest Meteorology 147, 140–156.

Jordan, A., Haidacher, S., Hanel, G., Hartungen, E., Märk, L., Seehauser, H., Schottkowsky, R., Sulzer, P., Märk, T.D., 2009. A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS). International Journal of Mass Spectrometry 286, 122–128.

Kaimal, J.C., Finnigan, J.J., 1994. Atmospheric Boundary Layer Flows. Oxford University Press, Oxford, 289 pp.

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

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

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., Hari, P., 2004. A new feedback mechanism linking forests, aerosols, and climate. Atmospheric Chemistry and Physics 4, 557–562.

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

Lenschow, D.H., Mann, J., Kristensen, L., 1994. How long is long enough when measuring fluxes and other turbulence statistics? Journal of Atmospheric and Oceanic Technology 11, 661–673.

Lindinger, W., Hansel, A., Jordan, A., 1998. 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. International Journal of Mass Spectrometry and Ion Processes 173, 191–241.

Massman, W.J., 2000. A simple method for estimating frequency response correction for eddy covariance systems. Agricultural and Forest Meteorology 104, 185–198.

Massman, W.J., Ibrom, A., 2008. Attenuation of concentration fluctuations in water vapor and other trace gases in turbulent tube flow. Atmospheric Chemistry and Physics 8, 6245–6259.

Massman, W.J., Lee, X., 2002. Eddy covariance flux corrections and uncertainties in long-term studies of carbon and energy exchange. Agricultural and Forest Meteorology 113, 121–144.

McMillen, R.T., 1988. An eddy correlation system with extended applicability to non-simple terrain. Boundary-Layer Meteorology 43, 231–245.

Moncrieff, J.B., Malhi, Y., Leuning, R., 1996. The propagation of errors in long-term measurements of land-atmosphere fluxes of carbon and water. Global Change Biology 2, 231–240.

Moore, C.J., 1986. Frequency response corrections for eddy correlation systems. Boundary-Layer Meteorology 37, 17–35.

Müller, M., Graus, M., Ruuskanen, T., Schnitzhofer, R., Bamberger, I., Kaser, L., Titzmann, T., Hörtnagl, L., Wohlfahrt, G., Karl, T., Hansel, A., 2009. First eddy covariance measurements by PTR-TOF. Atmospheric Measurement Techniques Discussions 2, 3265–3290.

Pielke, R.A., Avissar, R., Raupach, M., Dolman, A.J., Zeng, X., Denning, A.S., 1998. Interactions between the atmosphere and terrestrial ecosystems: influence on weather and climate. Global Change Biology 4, 461–475.

Rinne, H.J.I., Guenther, A.B., Warneke, C., de Gouw, J.A., Luxembourg, S.L., 2001. Disjunct eddy covariance technique for trace gas flux measurements. Geophysical Research Letters vol. 28 (No. 16), 3139–3142.

Rinne, J., Taipale, R., Markkanen, T., Ruuskanen, T., Hellen, H., Kajos, M.K., Vesala, T., Kulmala, M., 2007. Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modelling. Atmospheric Chemistry and Physics 7, 3361–3372.

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

Shimizu, T., 2007. Practical applicability of high frequency correction theories to CO_2 flux measured by a closed-path system. Boundary-Layer Meteorology 122, 417–438.

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

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

Swinbank, W.C., 1951. The measurement of vertical transfer of heat and water vapor by eddies in the lower atmosphere. Journal of Atmospheric Science 8, 135–145.

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

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

Webb, E.K., Pearman, G.I., Leuning, R., 1980. Correction of flux measurements for density effects due to heat and water vapour transfer. Quarterly Journal of the Royal Meteorological Society 106, 85–100.

Wohlfahrt, G., Hammerle, A., Haslwanter, A., Bahn, M., Tappeiner, U., Cernusca, A., 2008. Seasonal and inter-annual variability of the net ecosystem CO_2 exchange of a temperate mountain grassland: effects of weather and management. Journal of Geophysical Research 113, D08110. doi:10.1029/2007JD009286.

Wohlfahrt, G., Hörtnagl, L., Hammerle, A., Graus, M., Hansel, A., 2009. Measuring eddy covariance fluxes of ozone with a slow-response analyser. Atmospheric Environment 43, 4570–4576.