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Disjunct eddy covariance technique for trace gas flux measurements

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Abstract. A new approach for eddy covariance flux measurements is developed and applied for trace gas fluxes in the atmospheric surface layer. In disjunct eddy covariance technique, quick samples with a relatively long time interval between them are taken instead of continuously sampling air. This subset of the time series together with vertical wind velocity data at corresponding sampling times can be correlated to give a flux. The disjunct eddy sampling gives more time to analyze the trace gas concentrations and thus makes eddy covariance measurements possible using slower sensors. In this study a proton-transfer-reaction mass spectrometer with response time of about 1 second was used with a disjunct eddy sampler to measure fluxes of volatile organic compounds from an alfalfa field. The measured daytime maximum methanol fluxes ranged from 1 mg m^{-2} h^{-1} from uncut alfalfa to 8 mg m^{-2} h^{-1} from freshly cut alfalfa. Night-time fluxes were around zero.

Introduction

The eddy covariance method is the most direct method for surface layer flux measurements. Its use has been restricted to relatively few atmospheric compounds due to the requirement of fast response sensors. Other micrometeorological methods for obtaining data on the trace gas exchange between atmosphere and surfaces include gradient and eddy accumulation techniques [*Fuentes et al.*, 1996; *Desjardins*, 1977; *Businger and Oncley*, 1990]. These are however more indirect, i.e., they are based on empirical parameterizations, except the true eddy accumulation method. They are also often more labor intensive than the eddy covariance method. The true eddy accumulation method, which is a direct flux measurement technique, has proved to be technically very difficult to realize [e.g., *Speer et al.*, 1985]. The relaxed eddy accumulation method, which is technically easier, relies on empirical parameterizations [e.g., *Kramm et al.*, 1999].

The traditional approach for the eddy covariance technique is to sample air continuously. As it is possible to calculate fluxes using only a subset of the whole time-series, one can also take short grab-samples with a relatively long time

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interval between them [*Haugen*, 1978; *Kaimal and Gaynor*, 1983; *Lenschow et al.*, 1994; *Rinne et al.*, 2000]. This disjunct eddy sampling approach relaxes the requirement for fast concentration measurement and makes eddy covariance flux measurements possible using relatively slow sensors.

In this paper a new measurement system for trace gas fluxes applying the disjunct eddy covariance method (DEC) is described. The analysis of grab-samples was done using proton-transfer-reaction mass spectrometry (PTR-MS) [*Lindinger et al.*, 1998]. The method is demonstrated by field measurement of methanol fluxes above an alfalfa field before and immediately after the harvest.

Methods

The vertical flux of an atmospheric property F_s is most directly determined by measuring the covariance of the property $s = \bar{s} + s'$ and the vertical wind velocity $w = \bar{w} + w'$

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

using an instrument with fast enough response time. The typical sampling frequencies of sensors used for such continuously sampling eddy covariance measurements are 5-10 Hz. It is, however, possible to calculate the flux using a subset of the whole time series used in equation (1). In this case the flux is determined by

$$F_s = \langle w's' \rangle = \frac{1}{N} \sum_{i=1}^{N} w_i' s_i'. \qquad (2)$$

The samples w_i' and s_i' can be taken in a periodic or a-periodic manner, but the sampling must be conducted randomly relative to the values of w' and s'. Figure 1 shows an example of vertical wind velocity and methanol concentration sampled in periodic disjunct manner. When the samples have a relatively long time interval between them, a slower sensor can be used for eddy covariance flux measurements. This disjunct eddy sampling has previously been applied with true eddy accumulation measurements [*Rinne et al.*, 2000].

The disjunct eddy sampler (DES), similar to the one used for the true eddy accumulation measurements by *Rinne et al.* [2000], was used to take grab samples from ambient air. These samples were subsequently analyzed by PTR-MS [*Lindinger et al.*, 1998]. In the PTR-MS instrument positive ions are formed from trace compounds by proton transfer reactions with H_3O^+ primary ions. The primary and product
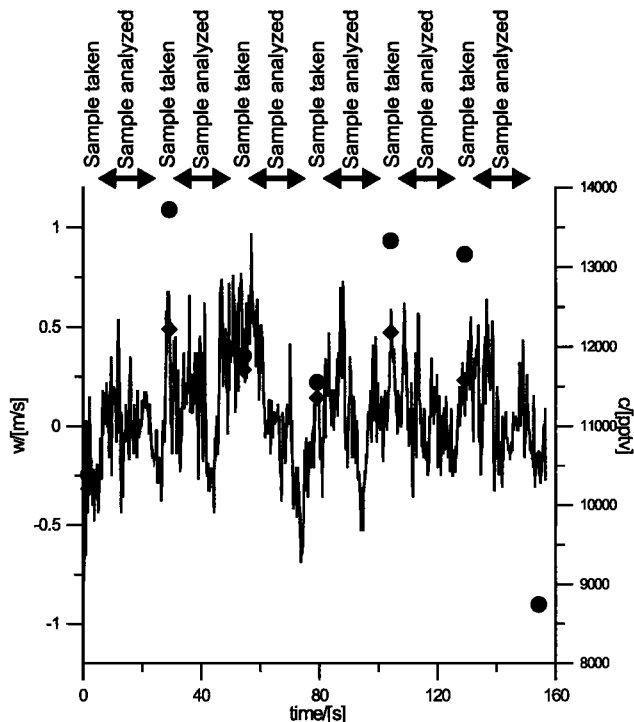
Figure 1. A continuous 10 Hz time series of vertical wind velocity (solid line), disjunct 0.2 second samples of the vertical wind velocity (diagonal squares), and disjunct 0.2 s samples of methanol concentration (circles).

ions are mass-selected with a quadrupole mass spectrometer and detected with an electron multiplier [*Lindinger et al.*, 1998; *de Gouw et al.*, 2000].

The DES consisted of two 1000 ml intermediate storage reservoirs (ISR) made of PTFE (Figure 2). Ambient air was sampled into an evacuated ISR by opening a valve with high flow conductance (α-valve, Skinner 7121SSN33N00N0L111P3). Part of this sample was then pulled into the PTR-MS from the ISR through Teflon bodied valves (Fluoroware 203-1414-415) and Teflon tubing, and analyzed for several hydrocarbons. Simultaneously the other ISR is evacuated. When the first sample has been analyzed, the next sample is taken into the other ISR and subsequently analyzed and the first ISR is evacuated in preparation for the next cycle.

The sampling time is 0.2 s, in which the ISRs are filled to about 90 % of the ambient pressure. The ISRs are evacuated to 8 % of the full pressure. As discussed by *Rinne et al.* [2000], 10 % carryover from one sample to another causes about a 4 % underestimation of the flux estimate. The interval between two samples is 25 s. In this time the PTR-MS scans through 9 masses, measuring each mass for 2 seconds.

The DES/PTR-MS system was deployed to measure hydrocarbon fluxes from an alfalfa field before, during and after cutting. The experiment was conducted in Morgan County, Colorado, USA, in August 3-17, 2000. The DES was installed at a 2.6 m height which was 0.6 m below an acoustic anemometer (Applied Technologies Inc., SATI 3K). According to *Kristensen et al.* [1997] this setup causes less than 5 % underestimation to the flux values due to loss of correlation in small scale eddies. The PTR-MS used to

analyze the samples was situated below the tower and the sample was conducted into it via 2 m 2.1 mm i.d. Teflon tubing.

The alfalfa field around the instrument was very flat and extended 300 m from the instrument in all directions. Alfalfa (*Medicago sativa*) is the third most common crop plant in the US. It is usually harvested four times a year in Colorado. The sonic anemometer pointed towards 80°. In sector 210-240° air-flow was obstructed by the measurement trailer and the alfalfa irrigation system (0° points to north and degrees increase clockwise). The height of the alfalfa was about 0.5 m before the third cutting of the year, which started in the morning of August 13th. By noon a 120 m circle around the measurement mast was cut and in the evening most of the field was cut.

Results

Figure 3 shows two scatter-plots of measured methanol concentrations and vertical wind velocities during two half-hour periods, and two diurnal cycles of the methanol flux determined from the measurements. The weather during these measurements was sunny and daytime maximum temperatures were 29-34°C. Figure 3a shows a half-hour period in the afternoon of August 12th, the day before cutting the alfalfa. As can be seen the correlation between w and c was weak ($r^2 = 0.060$) and the flux is only 0.29 ± 0.09 mg $m^{-2}h^{-1}$. Figure 3b shows a half-hour period on August 13th, after the alfalfa around the measurement mast had been cut. In this case the w and c show better correlation ($r^2 = 0.29$) and the flux is 2.1 ± 0.7 mg $m^{-2}h^{-1}$. The diurnal cycles of fluxes on August 12th and 13th (Figure 3c) show a significant flux on the day before cutting and high fluxes during and after cutting. The uncertainty of a half-hourly flux value due to the natural geophysical variability can be estimated to be around 15 % for this set-up [*Wesely and Hart*, 1985]. Simulation of disjunct eddy sampling by using temperature and w time series showed good correlation between sensible heat fluxes calculated using disjunct and continuous time series, with $H_{disj.} = 1.03 \times H_{cont.} + 0.13$ W m^{-2} and $r^2 = 0.94$. With heat fluxes above 50 W m^{-2} and friction velocity above 0.1 m s^{-1} the mean deviation between heat fluxes was 15 %. For all the data with $|H| > 20$ W m^{-2} the mean deviation was 20 %. The random uncertainty due
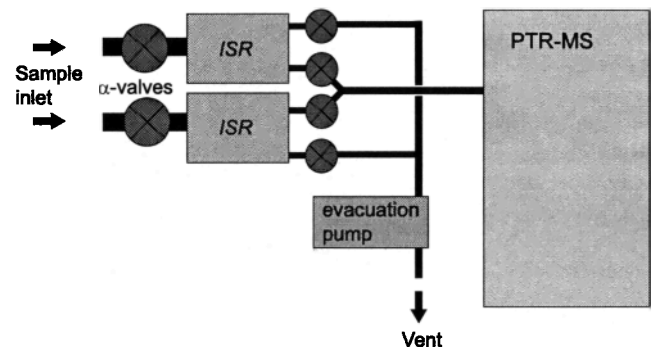

Figure 2. A schematic of the disjunct eddy sampler with proton-transfer-reaction mass spectrometer (PTR-MS). Circles with diagonal crosses are valves and black lines are Teflon tubing. α-Valves are fast, high flow conductance solenoid valves, and ISRs are intermediate storage reservoirs.
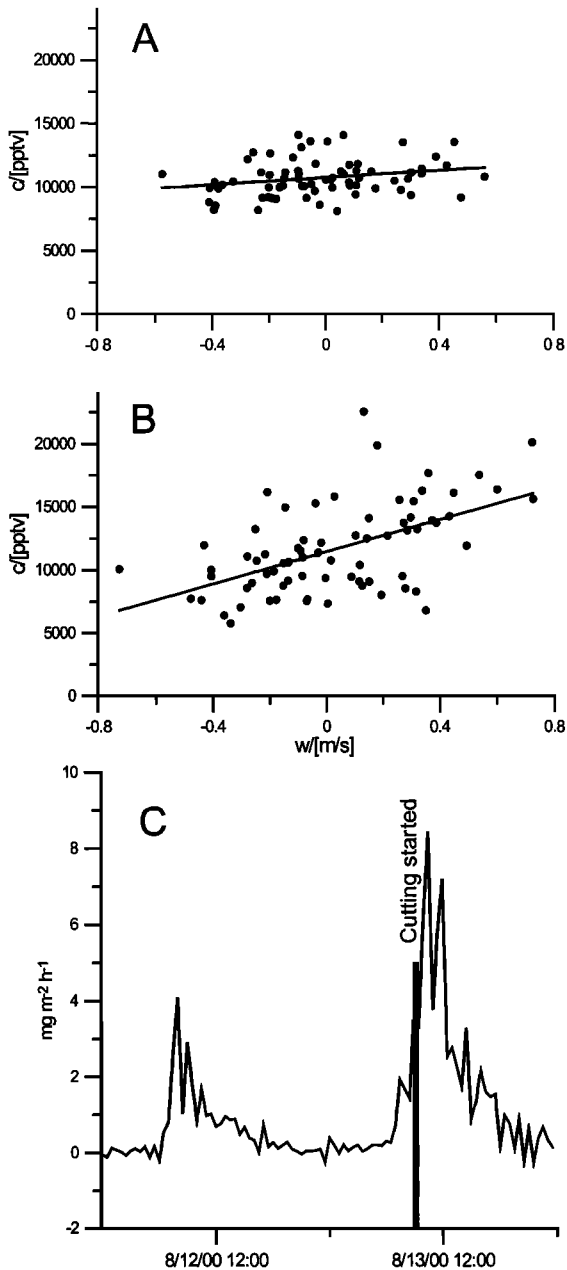
Figure 3. Correlation between methanol concentration and vertical wind velocity 3.30-4.00 p.m. on August 12th (A) and 13th (B), and measured methanol fluxes during August 12th and 13th (C). The estimated uncertainty of each half-hourly flux value is less than 20 %

to the instrument noise in the concentration measurement is estimated to be negligible. Together these make up a random uncertainty of less than 25 % for each half-hour value. The uncertainty of the calibration of the PTR-MS is 20 %, which causes systematic uncertainty to the measured fluxes. The sampling time of 0.2 seconds causes underestimation of measured fluxes which ranges from below 5 % under unstable daytime conditions to over 20 % during stable nighttime [*Moore*, 1986].

For methanol fluxes accumulated over the two days the effect of the random uncertainties diminishes to less than 5 %. The methanol flux accumulated over the two days,

together with their uncertainty, is 49.7 mg m^{-2} ± 10.2 mg m^{-2} with calibration uncertainty of the PTR-MS dominating the estimated uncertainty of the cumulative flux. This uncertainty estimate does not take into account the effects of footprint extending beyond the alfalfa field under stable night time conditions.

We also measured fluxes of acetaldehyde and acetone but these were lower than methanol fluxes. These results are qualitatively similar to enclosure measurements [*de Gouw et al.*, 2000] and other eddy flux measurements [*Karl et al.*, 2001]. A more detailed analysis of the results will be given by *Warneke et al.* [2001].

Conclusions

The results show that by using the disjunct eddy sampling (DES) with proton-transfer-reaction mass spectrometer (PTR-MS) it is possible to measure fluxes of biogenic and by inference other VOCs using direct eddy covariance method. As this method does not rely on empirical parameterizations, they do not introduce systematic errors into the measured fluxes. As the DES approach will often require a rather bulky sampler and high sampling rates, the sampler needs to be displaced from the acoustic anemometer. This sets limitations to lower measurement heights.

Future applications of disjunct eddy sampling can be classified into three categories depending on the response time of the analyzer used:

1) Instruments with response time too slow for continuous eddy covariance measurements (3 seconds to 3 minutes). Within the slower end of this range, averaging times longer than one hour are needed to obtain reasonably reliable flux estimates [*Haugen*, 1978]. This, however, can lead to non-stationarity of the time series. Instruments in this category includes analyzers for mercury (cold vapor atomic fluorescence spectrophotometry), nitrous oxide (fourier transform infrared spectroscopy), ozone (UV absorption analyzers) and carbon monoxide (reducing gas detector).

2) Instruments with relatively fast response time (0.3-3 seconds). These can be used for continuously sampling eddy covariance measurements under suitable conditions but disjunct sampling can extend their applicability. Instruments in this category include e.g. condensational particle counters, tunable diode laser absorption spectrometers, fast isoprene analyzers and most PTR-MS and similar chemical ionization mass spectrometer instruments.

3) Instruments, which are fast enough for continuous eddy covariance and are able to measure multiple compounds but not simultaneously. The disjunct eddy sampling approach could be used by scanning through the compounds of interest, resulting in a disjunct time series of each compound concentration. Faster PTR-MS instruments could be applied to this method.

Even though there are instruments capable of measuring many of the compounds mentioned above fast enough for continuously sampling eddy covariance measurements, the disjunct eddy sampling enables eddy covariance measurements with instruments that are often more stable, easy to operate and inexpensive than the fast instruments. The disjunct eddy sampling also extends the field of eddy covariance measurements to many new compounds.

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