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**Conditional CO$_2$ flux
analysis with the aid
of stable isotopes**

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Conditional CO$_2$ flux analysis of a managed grassland with the aid of stable isotopes

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Abstract

Short statured managed ecosystems, such as agricultural grasslands, exhibit high temporal changes in carbon dioxide assimilation and respiration fluxes for which measurements of the net CO_2 flux, e.g. by using the eddy covariance (EC) method, give only limited insight. We have therefore adopted a recently proposed concept for conditional EC flux analysis of forest to grasslands, in order to identify and quantify daytime sub-canopy respiration fluxes. To validate the concept, high frequency (≈ 5 Hz) stable carbon isotope analyis of CO_2 was used. We made eddy covariance measurements of CO_2 and its isotopologues during four days in August 2007, using a novel quantum cascade laser absorption spectrometer, capable of high time resolution stable isotope analysis. The effects of a grass cut during the measurement period could be detected and resulted in a sub-canopy source conditional flux classification, for which the isotope composition of the CO_2 could be confirmed to be of a respiration source. However, the conditional flux method did not work for an undisturbed grassland canopy. We attribute this to the flux measurement height that was chosen well above the roughness sublayer, where the natural isotopic tracer ($\delta_{13}C$) of respiration was too well mixed with background air.

1 Introduction

The investigation of the atmosphere-biosphere component of the global carbon cycle has developed rapidly in the last decade with the establishment of globally operating measurement networks for the determination of ecosystem exchange fluxes of CO_2. The method of choice for these flux measurements, the eddy covariance (EC) method, has been effectively applied for the analysis of temporal dynamics of the net ecosystem CO_2 exchange (NEE) but does not provide a direct measurement of the components of the NEE, assimilation and respiration (Baldocchi et al., 2001; Aubinet et al., 2000). NEE is the difference between photosynthesis driven assimilation flux and total ecosys-

tem respiration. On a diurnal scale, respiration flux can be determined from the net flux measured by eddy covariance during the night, while the assimilation flux occurs simultaneously with respiration fluxes during the day.

Several approaches have been studied to quantify daytime respiration and assimilation fluxes, namely by indirect measurements (e.g. chamber flux measurements with subsequent up-scaling), modelling (e.g. daytime respiration modelled from nighttime data) or isotope flux measurements (i.e., combining stable isotopes and flux measurements). Recently, a new method was proposed. In their work, Thomas et al. (2008) have presented a conceptual framework for investigation of daytime ecosystem respiration fluxes of sub-canopy origin using conventional eddy covariance (EC) measurements in combination with conditional quadrant flux analysis and successfully applied their approach to forest ecosystems. This approach could also be of great benefit to the research of short statured vegetation, such as managed grasslands, which show very high temporal dynamics in assimilation and respiration that is induced by management and consequent regrowth periods throughout the season, which is until now not well understood. Thus, we aim at adopting this new method to grassland ecosystems.

Adopting the conditional flux analysis concept to grasslands to separate subcanopy (soil) respiration fluxes requires validation, for instance using stable isotopes. Stable carbon isotopes of CO_2 can be used as tracer for biological processes underlying the dynamics in the atmosphere-biosphere exchange of CO_2. The slight mass differences between isotopes, e.g. ^{12}C and ^{13}C, cause a differentiation in abundance. The isotope ratio of an element is controlled by fractionation during reactions (e.g. biochemical pathways, diffusion, phase change of the substance) and therefore reflects an integration of the isotope effects during reactions, such as the discrimination in the metabolism pathways (Farquhar et al., 1982; Bowling et al., 2008). The reactions during plant photosynthesis therefore influence the stable isotope ratios of the remaining CO_2 in air during assimilation as well as the CO_2 released from respiration of previously metabolized organic compounds (e.g. respiration from the plant and from soil organic matter). As a result, the stable carbon isotope ratio ($\delta^{13}C$) of CO_2 in profiles

close to and within the canopy, where atmosphere-biosphere interaction is strong, can range between about −4 and −20‰ for C3 plants (see e.g., Buchmann et al., 2002). If we combine the conditional flux analysis concept with isotope composition of CO$_2$, a concept can be used in which updraft events that carry the flux signal of respiration should also exhibit the isotopic signature of CO$_2$ linked to the source of the respiration. Such updraft events should therefore isotopically differ from the second source of CO$_2$ in ecosystems, namely the CO$_2$ of atmospheric background origin.

To verify this assumption requires eddy covariance measurements that not only include the mixing ratios of CO$_2$, but also the isotopologues of CO$_2$ (^{12}C^{16}O$_2$, ^{13}C^{16}O$_2$ and ^{12}C^{18}O^{16}O). High time resolution observations of mixing ratios and isotopic composition of CO$_2$ in air are now made possible by recent developments of field deployable absorption spectrometers (Bowling et al., 2003; Zhang et al., 2006) and only very recently (Griffis et al., 2008; Tuzson et al., 2008) allow for a detailed analysis of isotope fluxes using the eddy covariance method.

Thus, we want to (a) investigate the applicability of the Thomas et al. (2008) approach to an intensively managed grassland with the aim to identify daytime release of respired CO$_2$, in particular from soil source, and to (b) identify the effects of management events, in particular grass cuts, on daytime respiration. Furthermore, we want to (c) validate the concept of quadrant flux analysis by using stable carbon isotopes as a tracer for respiration signatures in the CO$_2$ flux signal.

2 Theory

Thomas et al. (2008) state that their new method is not intended as a replacement of alternative and established approaches for partitioning daytime ecosystem respiration. Their conceptual model, revised from Scanlon and Albertson (2001), aims at separating of respiration flux in subcanopy and soil sources of respiration during daytime from the assimilation fluxes as measured by eddy covariance sensors. It is argued that episodic events of air movement from the understory to above the canopy could

be identified at eddy covariance sensor height from fluctuations in H_2O and CO_2 concentrations that deviate from the regression predicted by similarity theory. In such updraft events, the relation between water and carbon dioxide should bear a signature of respiration from subcanopy sources. Daytime respiration fluxes can be determined by using a conditional eddy covariance or a refined relaxed eddy accumulation (REA) approach. The concept has been tested in five forest ecosystems (vegetation dominated by *Quercus*, *Pinus*, *Picea* and *Pseudotsuga*, measurements conducted within the months May–August in 2003 or 2006) and the authors conclude that there are limitations for use on short vegetation. They specifically argue that the method is less suitable due to the close proximity of source and sinks of CO_2 and H_2O and strong turbulent mixing in such short statured ecosystems.

The framework for conditional flux analysis needs to be combined with stable carbon isotope fluxes and should encompass the changes due to management in the event of a grass cut. Following the concept for forests presented by Thomas et al. (2008), Fig. 1 shows the conceptual model of flux-gradient relations for a managed grassland before and after grass cut. Most notable is the difference in concentration height profile for CO_2 mixing ratios ($c(z)$, where z is height above ground level) and the stable isotope ratio $\delta^{13}C(z)$ of the CO_2 after the grass cut, when assimilation flux is reduced. The water vapor concentration profile, as expressed by specific humidity ($q(z)$), differs from the interpretation by Thomas et al. (2008). The maximum q in a height profile is not necessarily expected directly near the evaporating surface if temperatures (T) are also a function of z. The difference in air temperature of the shaded (Fig. 1a) versus the partly unshaded (Fig. 1b) leaves and soil can cause absolute amounts of water in the air to be higher just above the vegetation. Specifically at high relative humidity (low vapor pressure deficit) for a grassland with a dense canopy. After a grass cut, the profile is showing a (net) respiration signal for CO_2 and $\delta^{13}C$ until the canopy regains its assimilation capacity.

A comparison of CO_2 and H_2O fluxes is used to describe the origin of the measured CO_2 flux and separate the canopy-atmosphere exchange from sub-canopy/soil-

atmosphere exchange. Under ideal daytime conditions of plant assimilation and atmospheric turbulent mixing, the H_2O and CO_2 fluxes are predominantly exchanged between canopy and atmosphere and are directed in opposite directions due to their reverse source-sink relation. The ecosystem water use efficiency (WUE) can be used to express the relationship between ecosystem water and carbon dioxide fluxes, if defined as (Baldocchi et al., 2001)

$$WUE = -\frac{F_N}{F_{ET}} \tag{1}$$

where F_N is the net carbon flux (or net ecosystem CO_2 exchange) and F_{ET} denotes the net water vapor flux (or evapotranspiration). Using the eddy covariance method, the fluxes can be written in a Reynold's decomposition form as

$$WUE = -\frac{\overline{w'c'}}{\overline{w'q'}} \tag{2}$$

where the overbar denotes temporal averaging (typically 30 min), the primes denote perturbations from the average, and w, c and q denote the vertical wind speed, the CO_2 concentration and H_2O concentration, respectively. For daytime, well mixed turbulent conditions, we assume that a flux variance similarity and scalar similarity (Obukhov, 1959; Wyngaard et al., 1971; Kaimal et al., 1972) applies to the turbulent exchange. This implies that the regression between the turbulent exchange, represented in EC by the vertical wind vector, and different scalars (e.g. CO_2 and H_2O concentration) are the same, if these scalars are related to the same source and sink. The correlation coefficients for net carbon flux and net water vapor flux are defined as (Stull, 1988)

$$r_{c,w} = \frac{\overline{w'c'}}{\sigma_w \cdot \sigma_c} \tag{3}$$

$$r_{q,w} = \frac{\overline{w'q'}}{\sigma_w \cdot \sigma_q} \tag{4}$$

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where σ_c and σ_w denote the standard deviations of the CO_2 and H_2O concentration measurements, respectively. As postulated, we assume the regression between vertical wind vector and different scalars to be similar, therefore

$$|r_{c,w}| \approx |r_{q,w}| \tag{5}$$

and the ecosystem WUE (Eq. 2) can be approximated as

$$WUE \approx -\frac{\sigma_c}{\sigma_q} \tag{6}$$

For the purpose of statistical analysis, normalization can be used and we follow Thomas et al. (2008) in using normalized expressions for the variations in CO_2 and H_2O concentration, defined as $c' \cdot \sigma_c^{-1}$ and $q' \cdot \sigma_q^{-1}$, respectively. Combined with Eq. (6) and the relationships $\sigma_c^2 = \overline{c'^2}$ and $\sigma_q^2 = \overline{q'^2}$ in mind, it can therefore be shown that the two normalized variations relate as

$$\frac{c' \cdot \sigma_c^{-1}}{q' \cdot \sigma_q^{-1}} \approx -1 \tag{7}$$

if the requirements for the assumptions for flux variance and scalar similarity are met. If this is true, this further implies that in a plot of $c' \cdot \sigma_c^{-1}$ against $q' \cdot \sigma_q^{-1}$, the values will be on a -1 regression line (Fig. 2). Thomas et al. (2008) postulate that fluxes that distinctly deviate from the -1 regression line in a $c'-q'$ plane (Fig. 2) must have a different source-sink relationship in either c' or q'. Moreover, in case of a positive deviation from the average in both c' and q' during updraft eddy motions, the fluxes are related to sub-canopy/soil respiration.

The vertical movement is not directly expressed in the $c'-q'$ plane of normalized variations and can only be compared using additional conditional selection. An "updraft" and "downdraft" annotation is defined by $w' > 0$ and $w' < 0$, respectively, where w is the variation from mean of the vertical wind speed. Additionally, to clearly distinguish

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the specific updraft events of soil respiration Thomas et al. (2008) have defined a hyperbolic threshhold, $H = q' \cdot \sigma_q^{-1} \cdot c' \cdot \sigma_c^{-1}$, below which data are considered to be part of the normal variation within the canopy-atmosphere regression (Fig. 2). Application of the hyperbolic threshhold is necessary to prevent wrong classifications as a result of

5 small instationarities in the timeseries. For forests, Thomas et al. (2008) have found the reciprocal value of $H = 1/4$ to be the optimal choice for the hyperbola and we will continue to use this value here.

Thomas et al. (2008) use the different combinations of c', q' and w' to condition the eddy flux calculations. The net ecosystem exchange flux consists of flux components

10 for which we define

$$F_N = F_A + (F_{R,canopy} + F_{R,soil}),$$ (8)

where assimilation flux is denoted as F_A, and total ecosystem respiration consists of a above-ground vegetation respiration flux $F_{R,canopy}$ and sub-canopy/soil respiration flux $F_{R,soil}$. With eddy covariance flux calculations for net CO_2 fluxes being defined as

15 $$F_N = \overline{w'c'},$$ (9)

where the overbar denotes temporal averaging, Eq. (9) can be rewritten to fullfill the conditions for respiration excursions for which $q' > 0$, $c' > 0$ and $w' > 0$ represent daytime sub-canopy/soil respiration (Thomas et al. (2008) Eq. 1),

$$F_{R,soil} = \frac{1}{N} \sum_{i=0}^{N} w'(t_i) \cdot c'(t_i) \cdot I(t_i),$$ (10)

20 where $t(i)$ denotes the index within the measurement timeseries, and the indicator

function $I(t_i)$ is defined as (revised from Thomas et al., 2008, Eq. 10a).

$$
I(t_i) = \begin{cases}
1 \text{ if} \\
\quad w'(t_i) > 0, \\
\quad q'(t_i) > 0, \\
\quad c'(t_i) > 0, \\
\quad q'(t_i) \cdot \sigma_q^{-1} \cdot c'(t_i) \cdot \sigma_c^{-1} > H \\
0 \text{ otherwise}
\end{cases} \tag{11}
$$

Here we use the indicator function defined in Eq. (11) to analyze the coinciding stable isotope information. The stable carbon isotope information for carbon in CO_2 is expressed as a ratio versus an international standard, defined as

$$
\delta^{13}C = \left[\frac{R_{\text{Sample}}}{R_{\text{V-PDB}}} - 1 \right] \tag{12}
$$

where R is the ratio of abundance of the heavier versus lighter isotope ($R=[^{13}C]/[^{12}C]$) and V-PDB (Vienna PeeDee Belemnite) denotes the specific international reference standard. The quadrant analysis of stable isotopes has been conditioned using variations to Eq. (11) as indicator function (Table 1) for calculating the median $\delta^{13}C$ of CO_2 as

$$
\tilde{\delta}_{a,b} = \mu_{1/2} \left(\frac{1}{N} \sum_{i=0}^{N} \delta(t_i) \cdot I_{a,b}(t_i) \right) \tag{13}
$$

where $\delta(t_i)$ denotes the $\delta^{13}C$ time series and the indicator function $I(t_i)$ is defined (Table 1) for each combination of [a,b], indicating one of the four quadrants of the $c'-q'$ plane and the directions of the flux ("up" or "down" draft), respectively. In order to present a detailed distribution of the stable isotope information in the $c'-q'$ plane, the deviation to the mean $\delta^{13}C(t_i)$ is shown for data within an equally spaced raster grid on the $c'-q'$ plane. From here on we will continue to use the quadrant annotation of

the $c'-q'$ plane (quadrant Q1, Q2, Q3 and Q4) as shown in Fig. 2, but will refer to the indicator functions if a more specific portion of the data are discussed. For example, $I_{1,up}$ refers to updraft flux with a regression between c' and q' to above the hyperbola in quadrant Q1.

3 Methodology

3.1 Field experiment

From 15 to 30 August 2007, an intensive field study was conducted on an intensively managed grassland with >50% clover fraction located at the ETH Chamau research station in Central Switzerland, ($8°24'38''$ E, $47°12'36''$ N, 400 m a.s.l., Eugster and Zeeman, 2006). On the evening of 26 August, a part of the field within the EC footprint was cut, and the harvest was left on the field for drying until the morning of 27 August 2007. The change in canopy by cutting, expressed in canopy height (h_c), was from $h_c \approx 0.25$ m to $h_c \approx 0.07$ m. The reduction in leaf area index (LAI) was from 5.37 ± 0.28 m^2 m^{-2} (n=6) to 1.11 ± 0.25 m^2 m^{-2} (n=6), as measured with a plant canopy analyzer (LAI-2000, Li-Cor, Lincoln NB, USA).

In the days before and after the grass cut, an absorption spectrometer for measurements of CO_2 and CO_2 isotopologues was added to a continuously operating eddy covariance (EC) setup for CO_2 and H_2O flux monitoring. The EC measurement setup consisted of a three-dimensional sonic anemometer (model Solent R3, Gill Instruments, UK) and an open-path Infrared Gas Analyzers (IRGA; Li-7500, Li-Cor, Lincoln NB, USA), with the sensor centers at 2.51 m above the soil surface and operating at 20 Hz time resolution. The spectrometer, a closed-path Quantum Cascade Laser based Absorption Spectrometer (QCLAS, Aerodyne Inc., USA, Tuzson et al., 2008), was installed outside the footprint area in a container with air conditioning at 55 m distance from the EC setup, orthogonal to the main wind direction. The air inlet for the spectrometer was mounted 0.10 m below the EC sensors at 0.25 m from the center of

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the sonic anemometer's head and the QCLAS instrument was configured to output digital data for $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{12}C^{18}O^{16}O$ isotopologues at 5 Hz time resolution. The EC and isotope data streams were merged in situ on a field computer for post-calibration and later analysis. A detailed description of the performance of the QCLAS

5   system is given by Tuzson et al. (2008). Briefly summarized, the QCLAS instrument in field operation achieved an accuracy and precision of 0.2‰ on routine basis and over the whole measurement period, which must be considered as *state of the art*. This is the second so far reported application of high frequency measurements of stable isotopes for EC (Griffis et al., 2008). Conventional mass spectrometer based methods

10   deliver a slightly better accuracy and precision but at several orders of magnitude lower time resolution, as performed at the same site but different times (see e.g., Zeeman et al., 2008).

    A four-level profile (inlet heights at 2.21, 0.40, 0.13 and 0.06 m) was installed next to the eddy covariance setup for measurement of CO_2 concentrations by a closed-path

15   IRGA (Li-840, Li-Cor, Lincoln NB, USA) in 150 s time intervals per inlet, providing one full concentration profile every 10 min. The top most inlet was installed directly next to the QCLAS inlet at 0.35 m distance. The CO_2 concentration profile data were used for post-calibration of the QCLAS and determination of the storage of CO_2 below the EC sensor (ref). Soil CO_2 flux was measured every 30 min using a soil respiration cham-

20   ber system (Li-8100 with Long-term Chamber, Li-Cor, Lincoln NB, USA) on a 0.12 cm deep soil collar of 0.205 m diameter. To assure the chamber CO_2 flux measurements represented soil respiration, the vegetation inside the collar was cut to soil level on a bi-weekly base and before the measurement campaign was last cut on 15 August 2007. Although the soil in the collar received shading from the vegetation and the collar rim,

25   there was direct sunlight on the soil that could have influenced the temperature and consequently respiration, compared to the soil with full vegetation cover.

3.2 Calculations and corrections

The conditional variances of vertical wind speed (w'), water vapor (q'), carbon dioxide concentration (c') and δ^{13}C of CO_2 isotope ratio (δ') were calculated for 30-min periods using the *eth-flux* flux analysis tool (Eugster and Senn, 1995; Hiller et al., 2008;

5 Mauder et al., 2008) and R (R Development Core Team, 2008) for statistical analysis. A two-dimensional coordinate rotation was applied for the EC wind vector, for rotation into the mean stream line and aligning the vertical axis to yield $\overline{w}=0$ for each averaging period. The time lags between the closed-path QCLAS, the open-path IRGA and the sonic anemometer is calculated for each half hour (≈ 9.3 s for the QCLAS,

10 ≈ 0.15 s for the IRGA) and the time series is shifted accordingly before computing covariances. Calibrations of the QCLAS during the eddy covariance measurements period were conducted on an hourly base between 57–03 min in the hour with varying CO_2-in-air dilutions of a known δ^{13}C and once a day with standards in a range of δ^{13}C isotope ratios. The QCLAS and closed path IRGA did not share the same inlet and

15 the closed path IRGA was not calibrated against the same WMO referenced standard gasses or as frequent as the QCLAS. However, the instruments show good agreement ($c_{QCLAS}=0.983 \cdot c_{IRGA}+5.9$, $r^2=0.992$) for which the difference can in large part be explained by the use of different inlets and the less precise field calibration of the close path IRGA. Due to these differences in setup and due to the fact that the differences

20 in the concentration measurements are small, we have not applied post-calibrations based on the inter-comparison of the QCLAS and IRGA results. To ascertain coverage of the cut area within the EC footprint, the analysis of fluxes after the cut is limited to wind directions within a 300° to 20° range.

4 Results and discussion

25 Our first goal was to investigate the applicability of the Thomas et al. (2008) approach with measurements obtained over our intensively managed grassland, and to test,

whether daytime release of sub-canopy (or soil) respired CO_2 could be quantified using this method.

The diurnal patterns of the soil respiration flux and the nighttime data of the net ecosystem CO_2 flux show a soil respiration flux between 4 and 14 μmol m^{-1} s^{-2}, with

5 $>10\,\mu$mol m^{-1} s^{-2} during daytime before the grass was cut (Fig. 4). Two representative half hours of measurement data, at midday before and after the grass cut, were selected for a detailed comparison and conditional quadrant flux analysis. The undisturbed canopy before the cut showed a very strong regression between the two quadrants that represent assimilation and respiration, most pronounced in the downdraft

10 quadrant Q2 and updraft quadrant Q4, respectively (Fig. 5). Additionally, relatively small respiration signals (Q4, updraft) are counteracted by more variable assimilation fluxes (Q2, downdraft). However, the quadrant flux analysis leaves little room to investigate possible respiration in deviations from the −1 regression line into quadrant Q1, representing sub-canopy respiration fluxes, in either updraft or downdraft flux direction

15 before the grass cut (Fig. 5). There were offsets from the −1 regression line, with values deviating from the −1 regression line, which at close examination showed that these deviations occurred as a pattern of bandend −1 regressions. In other words, the short term regression slope appeared to be robust around −1, but the regression intercept was not constant. To increase legibility of Fig. 5 we plotted kernel probability densities

20 of the observations at full temporal resolution. When looking at the raw values more carefully, it becomes clear that the spread in kernel densities away from the theoretical regression line with a slope of −1 that passes through the origin of the quadrant analysis plots, was not a random process. For some time periods the individual pairs of c' and q' followed a line segment parallel to the theoretical regression line, but with

25 an offset perpendicular to that line. This means, that the underlying concept of water use efficiency, that should lead to movement of c'–q' data points along the regression line was indeed found, but even within the typical averaging time used for eddy covariance flux averaging these relationships were influenced by an additional process that either affected c', or q', or both, but with another ratio than what would be expected

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from the water use efficiency relationship alone. Most likely, this is caused by changes in the background concentrations during the averaging period and can be reduced by using an averaging time of less than 30 min, and would additionally require adaption of the indicator functions for the hyperbolic threshhold to a more narrow exclusion area. We have not changed the averaging period here to maintain comparability with the Thomas et al. (2008) study. The strong regression and the lack of data points in Q1 during daytime was found during our whole measurement period before the grass cut.

This reduces the method's quantitative power for our specific setup and vegetation type as we will explain in the following. Two postulated limits of the use of the conditional flux analysis for respiration of grassland vegetation are the potential for re-fixation of soil respired CO_2 and full mixing of air between vegetation and sensor. Re-fixation implies that subcanopy or soil-respired CO_2 does not reach the eddy flux height unchanged, thus cannot be clearly visible in the eddy flux signal. In dense canopies that are not limited in water and light availability, strong assimilation (CO_2 uptake) can induce re-fixation (or recycling) of subcanopy respired CO_2 (Sternberg et al., 1989). Re-fixation has been shown to be of relatively small importance, with a maximum of about 5% for forest (Lloyd et al., 1996; Buchmann et al., 1997), although some studies show calculated re-fixation of up to half of the respired CO_2 for a fast-growing agricultural crop Greaver et al. (2005). The effects of re-fixation should be visible in the stable carbon isotope composition of plant organic material and the CO_2 of respired plant organic material. Consequently, the assimilation products of the plant should show a more negative value than expected from the isotope discrimination during assimilation against the atmospheric background source. Here, the $\delta^{13}C$ of the bulk plant material (preliminary results, A. Gilgen, ETH Zurich, Switzerland, personal communication, 2008) as well as the respired CO_2 at night (Fig. 4) were well below −30‰ and therefore did not indicate a strong re-fixation influence.

Occurrences of periods with incomplete mixing could indicate that the eddy covariance measurements were made close to the roughness sublayer (Raupach, 1979; Arnfield, 2003). Our height (2.51 m) for measurements above a short statured vege-

tation (<0.30 m) is very likely to be high enough and thus outside the influence of the roughness sublayer. Consequently, turbulence at this height is well developed and the CO_2 fully mixed (cf. Tennekes, 1973; Raupach, 1979; Graefe, 2004). Thus, our inability to see respiration during the day is arguably more an effect of the difference in rela-
5 tive measurement height, compared to the forest locations discussed by Thomas et al. (2008). Using the eddy covariance flux method to analyze events of not fully mixed eddies requires caution. Measuring closer to the canopy and inside the roughness sublayer contradicts the requirements for the application of EC (Kaimal and Finnigan, 1994; Lee et al., 2004), although some studies have shown that the error to flux es-
10 timates is relatively small (<4%, Thomas and Foken, 2007). Thus, we suggest that there is a trade-off between (a) measuring high above the canopy to be well outside the roughness sublayer, which is best for EC flux measurements, but reduces the possibility to make use of the conditional quadrant flux approach; and (b) to measure close to the canopy, where CO_2 is not yet fully mixed in the atmosphere, which reduces the rep-
15 resentability of EC flux measurements but allows to explore the concurrent processes with conditional quadrant flux analysis.

Based on these findings, we directly address our second research question: whether we can identify the effects of management events, in particular grass cuts, on daytime respiration. The deviations from the -1 regression line in a $c'-q'$ plane were most
20 evident from data after the grass cut, where excursions into quadrant Q1 occur in updrafts as is expected from the Thomas et al. (2008) concept to represents sub-canopy-atmosphere exchange (Fig. 5). This shows that respiration after grass cut can potentially be detected, but this needs to be verified.

This leads us to our third question that we addressed: can concurrent stable carbon
25 isotope ratio measurements at high temporal resolution help to validate the concept of quadrant analysis in order to separate the daytime soil-respiration flux component?

Our conceptual model (Fig. 1) predicts the stable isotope ratios to vary between different quadrants of the $c'-q'$ plane. This is shown by the distribution of isotope ratio values on the $c'-q'$ plane (Fig. 6). For instance, the relative isotopic ratios of c' in

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quadrant Q2, representing assimilation, are more positive than those in quadrant Q4 or those in quadrant Q1 as found after the grass cut. If we examine each quadrant in more detail, this difference is shown clearly by the median $\delta^{13}C$ values per quadrant and vertical flux direction (Fig. 7). The median stable carbon isotope ratios were more positive in quadrant Q2 than in Q4. In the case of occurrences of values in quadrant Q1, the median stable carbon isotope ratios in quadrant Q1 were equal to or slightly more negative than those in quadrant Q4. The pattern can be summarized as following Eq. (13) $\tilde{\delta}_{2,\text{down}} > \tilde{\delta}_{4,\text{up}} \geq \tilde{\delta}_{1,\text{up}}$, and is valid before and after the grass cut. However, after the grass cut the differences in median stable carbon isotope ratios between the quadrants were more significant (Fig. 7, significance indicated by notches). A further comparison of quadrant Q2 and Q4 for updraft and downdraft flux directions over the course of the measurement period showed that the difference in c' and q' conditions was also generally reflected in the $\delta^{13}C$ values during day and night (Fig. 8). However, the quadrant Q1 updraft stable isotope ratios ($\tilde{\delta}_{1,\text{up}}$) were not indicating a $\delta^{13}C$ signal close to that of respired CO_2, as would be expected when updraft events carry only the soil respired CO_2 (Fig. 7). This is further highlighted when the quadrant comparison for $\tilde{\delta}_{2,\text{down}}$, $\tilde{\delta}_{4,\text{up}}$, $\tilde{\delta}_{1,\text{up}}$ is extended to several days prior to the grass cut (Fig. 9). The median $\delta^{13}C$ values for quadrant Q1 during the day, $\tilde{\delta}_{1,\text{up}}$, are not distinctly lower than in the other quadrants, in particular $\tilde{\delta}_{4,\text{up}}$ (Fig. 9), and analysis with higher thresholds for w' and selection of longer updraft durations, to focus on higher velocity eddies (more energy, larger size), did not change the results substantially. This supports the idea that the updraft air reached the measurement height, or height of the air inlet, in an already mixed form. The differences in carbon isotope signatures between the quadrants were however significant, even with the low share of quadrant Q1 taken into account. Differences in median $\delta^{13}C$ up to 3‰ are substantially large and well above the measurement accuracy of approximately 0.1‰ for the QCLAS instrument (Tuzson et al., 2008).

From the carbon isotope signatures we learn that different source signals can be detected, but typical $\delta^{13}C$ respiration values were not found if the fluxes were mea-

sured in a well-mixed atmospheric boundary layer in daytime. With a careful choice of measurement height, the isotope information adds the potential for validation of the conditional EC method. Moreover, the conditional EC flux method helps to indicate periods of interest for further (isotope) flux analysis and is thus useful for investiga-
5   tions on short statured vegetation, such as managed grasslands. Our present study, however, clearly revealed the trade-off between measurements made well above the canopy (best for EC fluxes) and those made close to the canopy, which appears to be essential to gain more insight with conditional EC analysis.

5   Conclusions

10 The high frequency stable isotope information of fluxes that can be obtained with fast optical spectrometers provide new possibilities for eddy covariance flux analysis. Here we aimed at using this information to validate the conditional flux concept as suggested by Thomas et al. (2008) in an application over short statured vegetation before and after a grass cut. This was only partly successful and provide evidence that the EC mea-
15 surement height is a critical factor that limits the potential for such an application. We found a trade-off between (a) the wish to perform EC measurements at large enough a height above the canopy to achieve large surface integration, and (b) the wish to resolve net flux components in the way Thomas et al. (2008) suggested. Our results strongly suggest that the methodology could be more successfull if EC measurements
20 were made closer to the canopy, inside the roughness sublayer where CO_2 molecules of different origin are not yet well mixed with ambient air.

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Table 1. Indicator functions for the classification of the time series data to each flux quadrant (Eq. 11). Quadrant index "0" indicates the omitted data by application of the indicator functions and related hyperbolic threshholds (see text).

quadrant, a	direction, b	$I_{a,b} = \begin{cases} 1 \text{ if}(\ldots) \\ 0 \text{ otherwise} \end{cases}$
0	up	$w'(t_i)>0, q'(t_i)>0, c'(t_i)>0, q'(t_i)\cdot\sigma_q^{-1} < \dfrac{H}{c'(t_i)\cdot\sigma_c^{-1}}$
		OR
		$w'(t_i)>0, q'(t_i)<0, c'(t_i)<0, q'(t_i)\cdot\sigma_q^{-1} > \dfrac{H}{c'(t_i)\cdot\sigma_c^{-1}}$
1		$w'(t_i)>0, q'(t_i)>0, c'(t_i)>0, q'(t_i)\cdot\sigma_q^{-1} > \dfrac{H}{c'(t_i)\cdot\sigma_c^{-1}},$
2		$w'(t_i)>0, q'(t_i)>0, c'(t_i)<0$
3		$w'(t_i)>0, q'(t_i)<0, c'(t_i)>0, q'(t_i)\cdot\sigma_q^{-1} < \dfrac{H}{c'(t_i)\cdot\sigma_c^{-1}},$
4		$w'(t_i)>0, q'(t_i)<0, c'(t_i)>0$
0	down	$w'(t_i)<0, q'(t_i)>0, c'(t_i)>0, q'(t_i)\cdot\sigma_q^{-1} < \dfrac{H}{c'(t_i)\cdot\sigma_c^{-1}}$
		OR
		$w'(t_i)<0, q'(t_i)<0, c'(t_i)<0, q'(t_i)\cdot\sigma_q^{-1} > \dfrac{H}{c'(t_i)\cdot\sigma_c^{-1}}$
1		$w'(t_i)>0, q'(t_i)>0, c'(t_i)>0, q'(t_i)\cdot\sigma_q^{-1} > \dfrac{H}{c'(t_i)\cdot\sigma_c^{-1}},$
2		$w'(t_i)<0, q'(t_i)>0, c'(t_i)<0$
3		$w'(t_i)<0, q'(t_i)<0, c'(t_i)>0, q'(t_i)\cdot\sigma_q^{-1} < \dfrac{H}{c'(t_i)\cdot\sigma_c^{-1}},$
4		$w'(t_i)<0, q'(t_i)<0, c'(t_i)>0$

Fig. 1. Idealized profiles of temperature (T), relative humidity (RH), water vapor (q), CO$_2$ mixing ratios (c) and δ^{13}C of the CO$_2$ (δ) for an intensively managed grassland, before (top panel) and after (bottom panel) grass cut. The areas Q1, Q2 and Q4 from which arrows are drawn, denote the flux components associated with the quadrants in a graph of $c' \cdot \sigma_c^{-1}$ versus $q' \cdot \sigma_q^{-1}$, as shown in Fig. 2, and the arrows indicate the vertical wind direction towards the eddy covariance measurement height (z_{EC}).
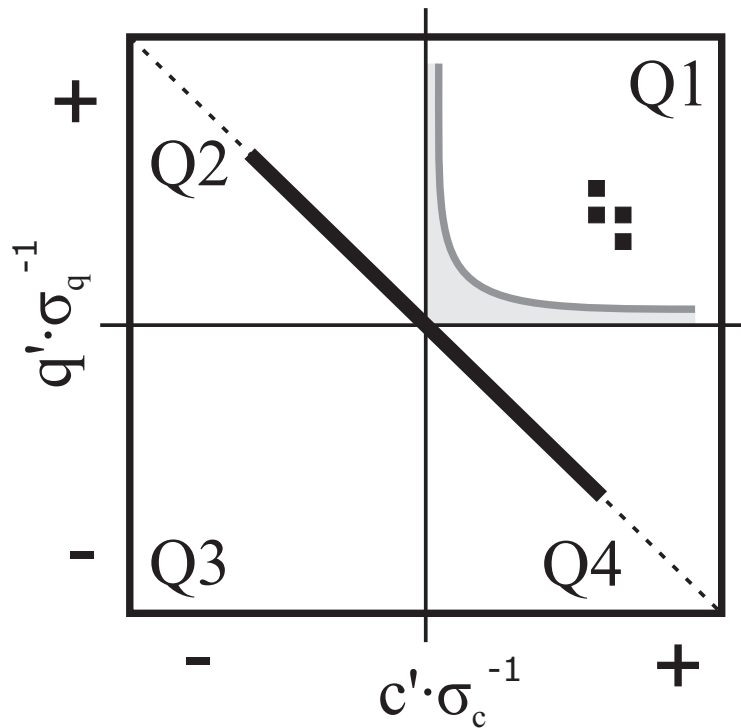
Fig. 2. Schematic representation of a plot of the normalized variation in concentrations of water vapor (q') and carbon dioxide (c') with numbered quadrants (Q1, Q2, Q3 and Q4) as used in the text. For quadrant Q1, only the values above the hyperbola (filled squares) are considered to clearly differ from values that follow the −1 regression line between $c' \cdot \sigma_c^{-1}$ and $q' \cdot \sigma_q^{-1}$. The same could be argued for Q3, but then the values below the hyperbola should be considered.

24–27 August, 2007

$y = 0.9827\,x + 5.957$

$r^2 = 0.992$

CO$_2$ mixing ratio, QCLAS [ppm]

CO$_2$ mixing ratio, Li–840 [ppm]
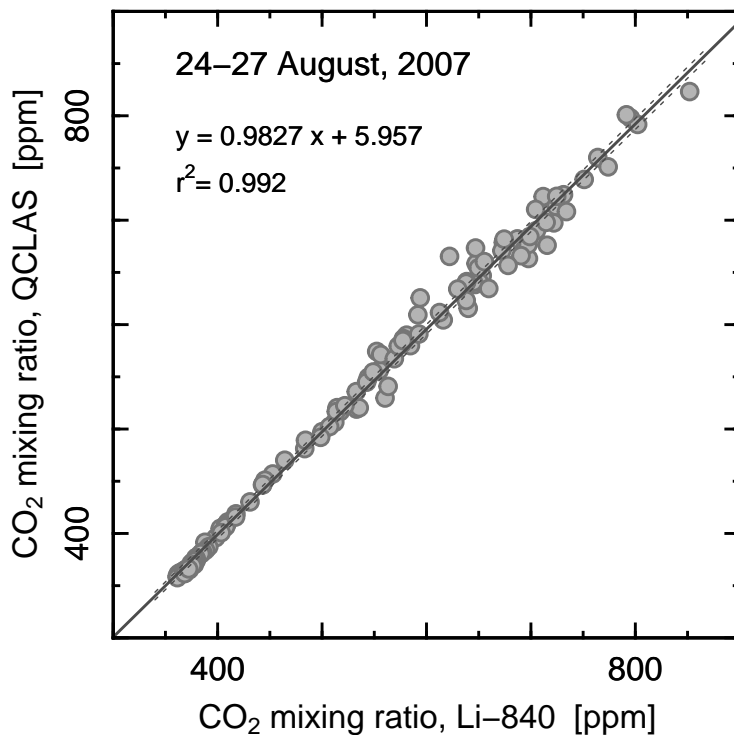
Fig. 3. Comparison of CO$_2$ concentration measured by the closed path IRGA and the QCLAS. The instruments were connected to two different air inlets that were installed next to each other. Regression (red line) and confidence intervals (95%, red dashed lines) show the good agreement and linearity between the CO$_2$ measurements.
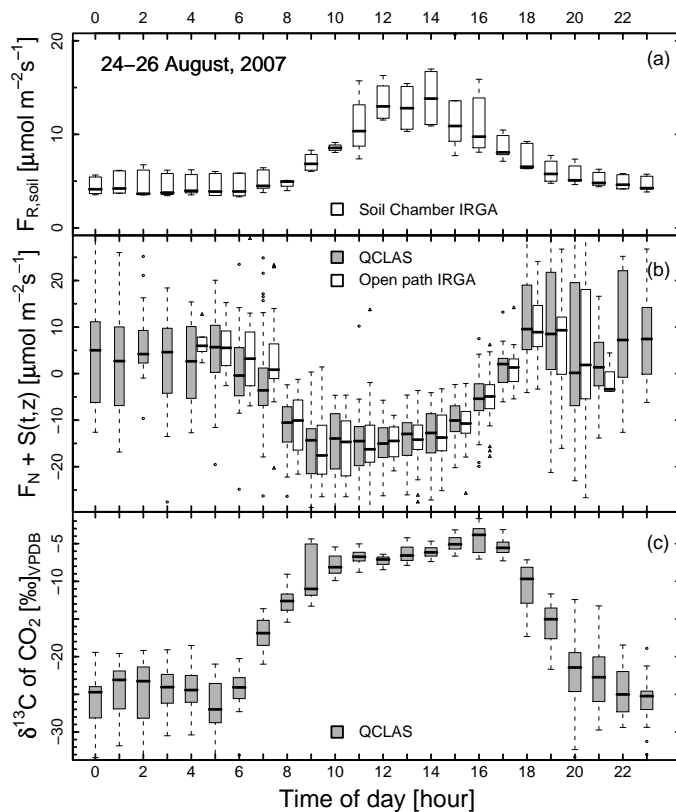
Fig. 4. Diurnal hourly averages of **(a)** soil respiration flux ($F_{R,soil}$) measured by a closed path IRGA connected to an automatic soil chamber, **(b)** the net ecosystem CO_2 flux (F_N) calculated using the EC method and corrected for CO_2 storage ($S(t,z)$) below the EC sensors based on measurements from two different instruments (open path IRGA and QCLAS) and **(c)** the $\delta^{13}C$ value of net ecosystem CO_2 flux, measured by the QCLAS.

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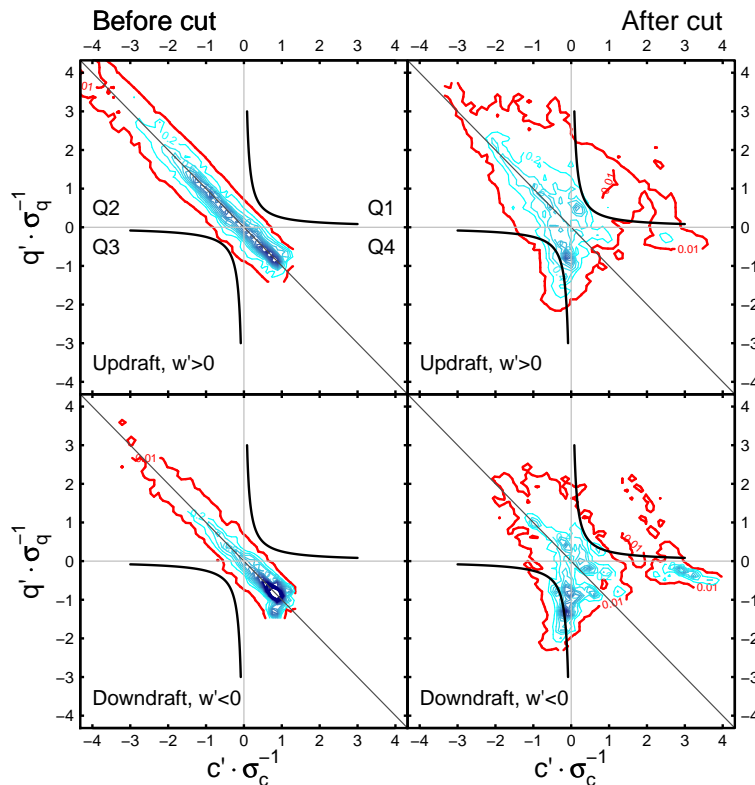
Fig. 5. Kernel probability density analysis for normalized $c' \cdot \sigma_c^{-1}$ versus $q' \cdot \sigma_q^{-1}$, separated into before and after the grass cut (left and right panels, respectively), and for updraft and downdraft flux directions (top and bottom panels, respectively). Data were collected at a managed grassland (Chamau) during 12:00 and 12:30 before (25 August 2007) and after grass cut (27 August 2007).
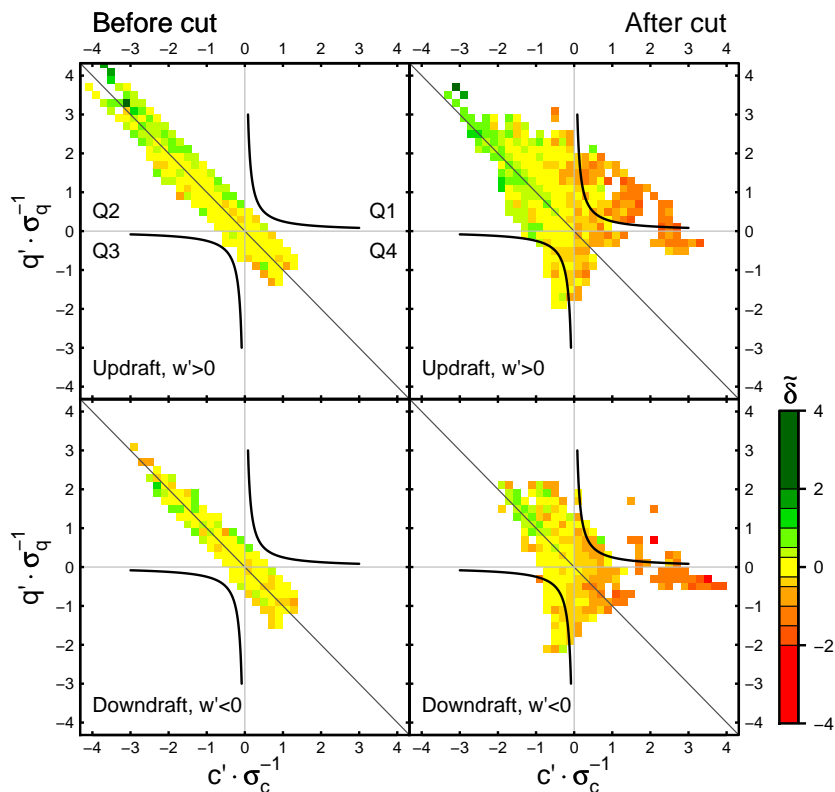
Fig. 6. Using carbon isotope signals in conditional quadrant flux analysis. The difference between the median $\delta^{13}C$ for $c' \cdot \sigma_c^{-1}$ and $q' \cdot \sigma_q^{-1}$ intervals of 0.2 and the average of all $\delta^{13}C$ values in the observed period are given ($\tilde{\delta}$). Data were collected at a managed grassland (Chamau) during 12:00 and 12:30 before (25 August 2007) and after grass cut (27 August 2007).

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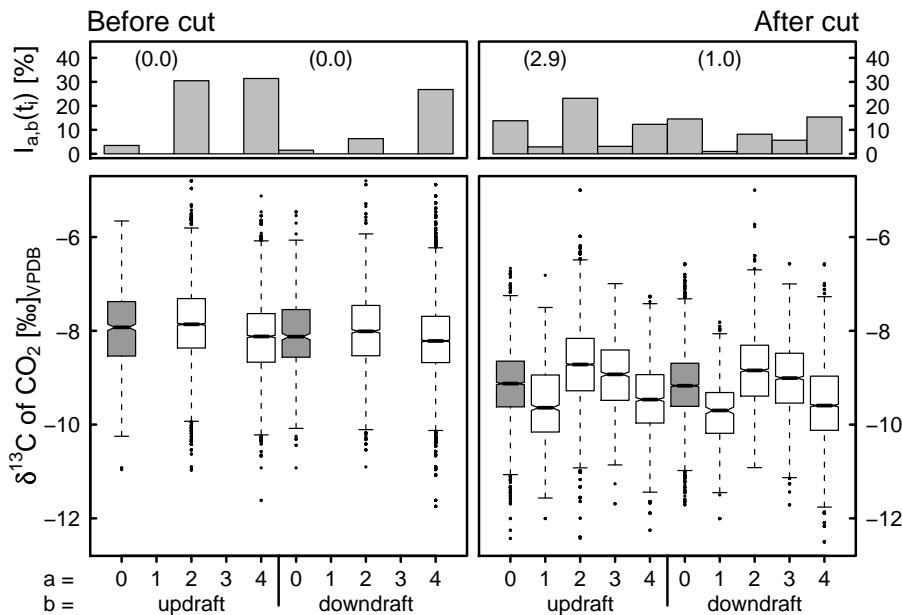
Fig. 7. Relative frequencies of the indicator function $I_{a,b}$ (Eq. 13) and the median stable isotope composition (bottom panel), for updraft and downdraft flux directions. In addition, the 95% confidence interval of the median (notches) and the 25–75% quartile (box) are shown. Quadrant index "a=0" represents the omitted data by applying the indicator function to Q1 and Q3 (see text). Data were collected at a managed grassland (Chamau) between 12:00 and 12:30 before (25 August 2007) and after grass cut (27 August 2007).
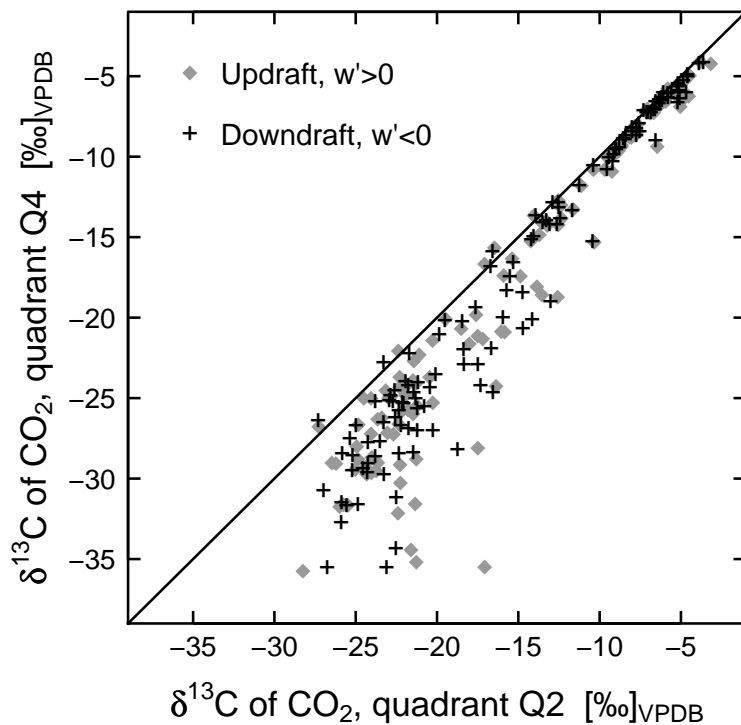
Fig. 8. Relationship between the $\delta^{13}C$ of CO_2 (30 min medians) classified to quadrant Q2 and quadrant Q4 for updraft and downdraft flux directions before and after grass cut (25–27 August 2007, day and night data).
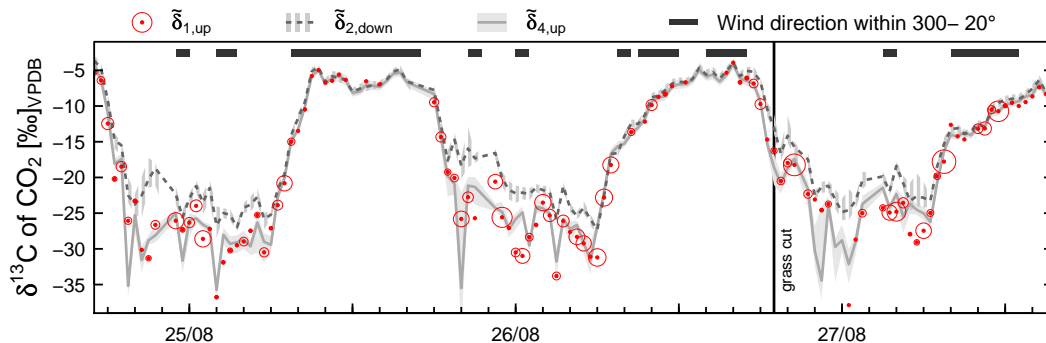
Fig. 9. Diurnal course of the δ^{13}C of CO$_2$ (30 min medians, $\tilde{\delta}$) for updraft Q1, downdraft Q2 and updraft Q4, before and after grass cut (25–27 August 2007). The 25 and 75% quartiles are shown as envelope areas°. The size of the outer circle in the notation for Q1 denotes the percentage of samples within the Q1 quadrant, i.e. the percentage of $I_{1,up}$, up to 15% for largest circle shown. Periods with wind directions from 300° to 20° N are shown as black bands.