Atmospheric
Measurement
Techniques

Prerequisites for application of hyperbolic relaxed eddy accumulation on managed grasslands and alternative net ecosystem exchange flux partitioning

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Abstract. Relaxed eddy accumulation is still applied in ecosystem sciences for measuring trace gas fluxes. On managed grasslands, the length of time between management events and the application of relaxed eddy accumulation has an essential influence on the determination of the proportionality factor b and thus on the resulting flux. In this study this effect is discussed for the first time. Also, scalar similarity between proxy scalars and scalars of interest is affected until the ecosystem has completely recovered. Against this background, CO_2 fluxes were continuously measured and $^{13}CO_2$ isofluxes were determined with a high measurement precision on two representative days in summer 2010.

Moreover, a common method for the partitioning of the net ecosystem exchange into assimilation and respiration based on temperature and light response was compared with an isotopic approach directly based on the isotope discrimination of the biosphere. This approach worked well on the grassland site and could enhance flux partitioning results by better reproducing the environmental conditions.

1 Introduction

In ecosystem sciences the interface of atmosphere, biosphere and soil is of particular importance and affords insight into the carbon (C) cycle from various angles of view with various methods that, in turn, have to be adapted and evaluated. Insight from an atmospheric perspective is mostly achieved by means of chamber (Goulden et al., 1996; Davidson et al., 2002; Dore et al., 2003; Subke and Tenhunen, 2004) and micrometeorological techniques such as eddy covariance (EC; Moncrieff et al., 1997; Aubinet et al., 2000, 2012; Baldocchi et al., 2001; Baldocchi, 2003). While chambers are able to directly measure ecosystem carbon source and sink fluxes on small spatial scales, EC provides net ecosystem carbon exchange (NEE) on larger spatial scales. More detailed information about underlying fluxes can be achieved by applying flux partitioning models (FPMs; Stoy et al., 2006; Desai et al., 2008; Lasslop et al., 2010; Reichstein et al., 2012). Those are also used to gap-fill missing or excluded flux data (Falge et al., 2001; Stoy et al., 2006; Ruppert et al., 2006a; Desai et al., 2008; Papale, 2012). Those models may provide fluxes with unrealistic temporal variation or magnitude (Stoy et al., 2006). However, an alternative is partitioning based on additional determination of the $^{13}CO_2$ isoflux (Yakir and Wang, 1996; Bowling et al., 2001; Knohl and Buchmann, 2005; Ogée et al., 2004; Wichura, 2009; Wichura et al., 2004;

Ruppert, 2008; Lloyd et al., 1996). Due to C3 vegetation discriminates against the heavier isotope ^{13}C during stomatal uptake of CO_2 and photosynthesis, the biomass and all following compartments within the dynamic C cycle are ^{13}C depleted with respect to the atmosphere. Therefore the ^{13}C isotopic ratio increases in the air during the assimilation period. Both effects account for a distinct diurnal cycle of the $^{13}CO_2$ mixing ratio in ecosystem air (Flanagan et al., 1996; Lloyd et al., 1996). Resulting $^{13}CO_2$ isofluxes can be determined by means of the flux-gradient method (Flanagan et al., 1996), modeling approaches (Ogée et al., 2003; Lloyd et al., 1996), hyperbolic relaxed eddy accumulation (HREA; Bowling et al., 2001, 2003a; Wichura, 2009; Wichura et al., 2004), the hybrid eddy covariance–flask gradient method (Bowling et al., 1999a; Griffis et al., 2004) and direct isotopic eddy covariance (Griffis et al., 2008; Sturm et al., 2012; Wehr et al., 2013).

This study examines the application of the REA method on managed grasslands. European grassland ecosystems are still to be defined as a net carbon sink or source. For this reason, detailed investigation is greatly required (Ciais et al., 2010; Soussana and Lüscher, 2007). In addition to the general uncertainty regarding the sink/source behavior of grasslands, management of grassland ecosystems causes anomalies in the seasonal carbon cycle (Flechard et al., 2005). Such events have to be observed carefully but can potentially introduce certain restrictions for REA measurements. Previous studies have indicated that errors in the REA flux often appear when scalars of interest and proxy scalars behave differently in their turbulent transportation efficiency (Ruppert et al., 2006b). This so-called scalar similarity is especially required for hyperbolic REA, because two important factors – the hyperbolic deadband H and the proportionality factor b, and consequently the REA flux – will be flawed without it (Oncley et al., 1993; Ruppert et al., 2006b). Even if b factors are often treated as constant (Meyers et al., 2006; Haapanala et al., 2006), they show a certain diurnal variation. Other studies on managed ecosystems apply CO_2 and water vapor (Baum and Ham, 2009) and mostly temperature (Myles et al., 2007; Hensen et al., 2009) as proxy scalars, sometimes shortly after the management (Nemitz et al., 2001). Whether this practice can be problematic was thoroughly investigated in this study by means of numerous simulations with data from mown and unmown grassland. The real REA measurements of this study were conducted – in correspondence with the results of the simulation – before (22 June), as well as a sufficient period of time after the mowing (25 August) in the main growth period of 2010. The reasons for this procedure will be explained in the following, especially in Sect. 4.1. Another aim of this study is to evaluate a commonly applied partitioning method for the net ecosystem exchange with a small number of the labor-intensive and sophisticated REA measurements. Ruppert (2008) and Wichura (2009) investigated an isotopic approach by Lloyd et al. (1996) for partitioning the net ecosystem exchange (NEE) above forest ecosystems, and

found some restrictions due to complicated coupling conditions (Thomas and Foken, 2007). In the current study, this approach is tested above grassland and finally evaluated by comparison with a common flux partitioning model (FPM) based on the temperature dependence of respiration after the Lloyd–Taylor function (Lloyd and Taylor, 1994). For R_{ECO} parameterization, nighttime NEE is used because it equals ecosystem respiration (R_{ECO}) due to missing assimilation (Lloyd and Taylor, 1994; Falge et al., 2001; Ruppert et al., 2006a; Ammann et al., 2007; Reichstein et al., 2005). To parameterize daytime solar-radiation-dependant gross primary production (GPP; Falge et al., 2001; Ruppert et al., 2006a), light response regression based on Michaelis–Menten function (Michaelis and Menten, 1913) was applied. Instead of a temperature binning approach, a time window scheme was applied, which is preferred for sites with distinct seasonal variation or treatments generating abrupt changes in ecosystem behavior (Ammann et al., 2007).

In summary, this paper comprises the examination of REA application on managed grasslands by comparing scalar similarity and the b factor before and after management events. Then two real REA measurements were conducted in correspondence to the results of the simulation. The results of those were used to test an isotopic flux partitioning approach above grassland and to evaluate it by comparison with common flux partitioning.

2 REA theory and framework

The basic idea of Desjardins in 1972 (Desjardins, 1977) of separating the vertical wind into an up- and downward component was applied by Businger and Oncley (1990). They combined this eddy accumulation method (EA) with the flux-variance similarity and created an indirect method: the relaxed eddy accumulation (REA), with the REA flux

$$F_{REA} = b\sigma_w \rho_a \left(\overline{c_\uparrow} - \overline{c_\downarrow} \right) \quad (1)$$

derived from average up- and downward mixing ratio of the scalar $\overline{c_\uparrow}$ and $\overline{c_\downarrow}$, standard deviation of the mean vertical wind velocity σ_w, density of dry air ρ_a, and an empirical and dimensionless proportionality factor b that compensates for the loss of information due to the mentioned "relaxation" (Ruppert et al., 2006b). Air samples are thereby taken with a constant flow rate and are not weighted according to the vertical wind speed (Businger and Oncley, 1990). b is often suggested to be unaffected by the atmospheric stability (Businger and Oncley, 1990; Delany et al., 1991; Foken et al., 1995), but it can also depend on it (Andreas et al., 1998b). For an ideal Gaussian joint frequency distribution (JFD) of the vertical wind speed and the mixing ratio of the scalar, b is constant ($b = 0.627$; Baker et al., 1992; Wyngaard and Moeng, 1992). But variations in b can be generated by just a small skewness of the JFD of w' and c' (Katul et al., 1996; Fotiadi et al., 2005; Ruppert et al., 2006b), the application

to different trace gases (Businger and Oncley, 1990; Baker et al., 1992; Oncley et al., 1993; Pattey et al., 1993) or the use in different ecosystem compartments (Gao, 1995). b may also vary significantly during individual 30 min integration intervals (Businger and Oncley, 1990; Baker et al., 1992; Oncley et al., 1993; Pattey et al., 1993; Beverland et al., 1996; Katul et al., 1996; Bowling et al., 1999a; Ammann and Meixner, 2002; Ruppert et al., 2006b). Variations from 0.54 to 0.60 were found for several experimental data. Consequently, to reduce relative errors in flux determination, individually simulated b values for every measurement location and period are to be favored over application of a constant b (Ruppert et al., 2006b; Foken, 2008). Thus, b is determined individually by REA simulation of a proxy scalar, which can be additionally measured via EC. The proportion of both proxy scalar fluxes – F_{REA} and the EC flux ($F_{EC} = \overline{w'c'}$) – provides b:

$$b = \frac{\overline{w'c'}}{\rho_a \sigma_w \left(\overline{c_\uparrow} - \overline{c_\downarrow} \right)}. \tag{2}$$

The abovementioned b values were determined in theoretical simulations, where it is possible to separate up- and downdrafts exactly by sign, down to the smallest values. Not until Businger and Oncley (1990) had modified the method by discarding fluctuations around zero – which, in any case, only have small influences on the entire flux – with a deadband could the REA idea be implemented with regard to mechanical restrictions of the speed of valve switching.

$$b(w_0) = \frac{\overline{w'c'}}{\rho_a \sigma_w \left(\overline{c_\uparrow} (w > w_0) - \overline{c_\downarrow} (w < -w_0) \right)}. \tag{3}$$

The size of the deadband w_0 around zero is determined individually according to experimental conditions and the particular scalar of interest. The same applies to $b(w_0)$, which has to be determined individually by conducting simulations with proxy scalars.

To maximize mixing ratio difference between up- and downdraft air samples, application of a hyperbolic deadband H is recommended (Bowling et al., 1999b). This is required for investigating, for example, differences on the order of the measurement precision. By application of H in hyperbolic REA (HREA), $b(H)$ is reduced to lower values around 0.22 ± 0.05 (Bowling et al., 1999b) and 0.15–0.27 (Ruppert et al., 2006b). H is based on the fluctuation of the vertical wind velocity w' and the mixing ratio c' of a proxy scalar, as well as their standard deviations σ_w and σ_c:

$$\left| \frac{w'c'}{\sigma_w \sigma_c} \right| \geq H. \tag{4}$$

Real-time knowledge of σ_w and σ_c was achieved via continuous online recalculation from the most recent 6 min of data. The standard deviations σ_w and σ_c were weighted by applying a linear function by which the newest data were rated three times more important than the oldest data (Ruppert et

al., 2012). Adequate scalar similarity is especially required for hyperbolic REA, because H depends on the mixing ratio of the proxy scalar. Generally, $b(H)$ and the REA flux as the final product will be flawed without scalar similarity between the scalar of interest and the proxy scalar (Oncley et al., 1993; Ruppert et al., 2006b). Scalar similarity was defined by Kaimal et al. (1972) and Pearson et al. (1998) as similarity in the scalar time series over all the scalar spectra. This means that scalar quantities are transported with similar efficiency by turbulence elements of diverse characteristics (Ruppert et al., 2006b). Differences in distribution (Andreas et al., 1998a; Ruppert et al., 2006b; Held et al., 2008), amount and strength (Katul et al., 1999; Katul and Hsieh, 1999) of scalar sources and sinks are reasons for differences in turbulent exchange of the scalars and for lacking scalar similarity. Furthermore, scalar similarity is influenced by the seasonal variation in canopy physiology (Williams et al., 2007).

Essential for successful REA application is the choice of the right proxy scalar. Often temperature, measured with a sonic anemometer, is used (Graus et al., 2006; Lee et al., 2005; Grönholm et al., 2007; Bash and Miller, 2008; Bowling et al., 1998; Gaman et al., 2004; Ren et al., 2011), and sometimes both temperature and water vapor turn out to be adequate (Held et al., 2008). For $^{13}CO_2$ isoflux measurements, typically the proxy scalar CO_2 is used (Bowling et al., 2003a; Wichura, 2009). Due to a lack of adequate high-frequency measurements of $^{13}CO_2$, scalar similarity between both cannot be evaluated, but it is assumed that both scalars behave similarly. However, sources and sinks are quite different in strength and distribution with respect to discrimination against ^{13}C during assimilation (Bowling et al., 2003a).

3 Material and methods

3.1 Study area

All experiments relevant for this study were conducted on the extensively managed submontane grassland site "Voitsumra" at the edge of the low mountain range "Fichtelgebirge" in northeastern Bavaria, Germany, located 624 m a.s.l. ($50°05'25''$ N, $11°51'25''$ E). For the last 10 years the site has been used as extensively managed grassland without fertilization or grazing, but with sporadic mowing once or twice a year. The plant community is described as *Molinio-Arrhenatheretea* R. Tx. 1937 – economic grassland (Oberdorfer, 2001), and the most dominant of the 48 species are *Alchemilla monticola*, *Juncus filiformis*, *Polygonum bistorta*, *Ranunculus acris* and *Trifolium repens*.

3.2 EC measurements

High-frequency data for both EC and REA were collected 2.5 m above ground at 20 Hz. Water vapor and the CO_2 mixing ratio were measured with an open-path gas analyzer (LI-7500, LI-COR Biosciences, Lincoln, Nebraska, USA),

and wind vector and sonic temperature (T_S) by a 3-D sonic anemometer (CSAT3, Campbell Scientific Inc., Logan, Utah, USA). All turbulence data were stored on a data logger (CR3000, Campbell Scientific Inc., Logan, Utah, USA) and collected daily using a micro-computer system (MICRO-ITX, CarTFT.com) as a backup. To avoid inconsistencies in the wind vector time series, the inclination of the CSAT3 was monitored by an inclinometer on the top of the measurement mast. The computation of the EC flux was accomplished with the software package TK2 developed at the University of Bayreuth (Mauder and Foken, 2004); TK3 has become available in the meantime (Mauder and Foken, 2011). This software contains all necessary data correction and data quality assessment tools (Foken et al., 2012b) and was approved in comparison with six other commonly used software packages (Mauder et al., 2008) and successfully applied in considerable field campaigns (Mauder et al., 2006, 2007; Eigenmann et al., 2009).

Data processing for determining turbulent EC fluxes begins with spike and outlier filtering (Rebmann et al., 2012). Data can then already be used for REA simulation. All following steps in TK2 relating to determination, quality testing and validation of the EC flux are explained in detail by Mauder and Foken (2004), Foken (2008) and Foken et al. (2012a). This also includes planar fit correction (Wilczak et al., 2001), which was also applied in the REA controlling software (Ruppert, 2005). Wind velocity data sets of the 4 weeks before each REA field measurement were analyzed and planar fit corrections were implemented in the REA controlling software (Ruppert, 2005). Due to very small rotation angles, only minor corrections were necessary. To assure that the signal measured via EC originated exclusively from the target land use type "grassland", footprint analysis was performed (Göckede et al., 2004, 2006; Rannik et al., 2012). It has been proven that more than 95 % of the data originated from grassland and were not influenced by surrounding land use types such as tracks and creeks.

3.3 Simulation for $b(H)$ and H

Due to the great importance of the b factor for proper REA flux determination, and especially due to the lack of information about possible effects of management events on grasslands, the variation in $b(H)$ was investigated via simulation. Therefore, a 2-year eddy covariance data set (2010, 2011) and accompanying low-frequency measurements of meteorological parameters were available. Hence, an adequate number of days with similar atmospheric conditions could be chosen within pre- and post-mowing periods to secure better comparability and to focus exclusively on the effects induced by management. Also, the variation in $b(H)$ within the diurnal cycle was evaluated.

However, the first step was to determine the hyperbolic deadband H. The size of H was defined in advance and adapted according to the outcome of b. Finally, in combina-

tion with former studies as a reference (Ruppert, 2008), the hyperbolic deadband was defined constant as $H = 1$. During the simulation, the sign of the fluctuation of the vertical wind component w' determines partitioning of the scalar of interest in up- and downdraft, just as during real REA sampling. In this case, the CO_2 mixing ratio was used as a proxy scalar. The difference of the separately summed proxy scalar values $(\overline{c_\uparrow} - \overline{c_\downarrow})$ and the standard deviation of the vertical wind speed σ_w were calculated. By comparison of the product $\sigma_w (\overline{c_\uparrow} - \overline{c_\downarrow})$ to the corresponding EC flux $\overline{w'c'}$ – determined by high-frequency measurements and TK2 software – individual factors $b(H)$ could be derived (Eq. 3). That evaluation was also applied to other commonly used proxy scalars such as T_S and water vapor (H_2O). In order to evaluate their similarity to CO_2 in the scalar time series, i.e., their suitability as a substitute for CO_2, scalar similarity had to be verified, and this was done by evaluating the consistency of the correlation coefficients r. Those coefficients were calculated for the combinations of the scalars $CO_2 - H_2O$ and $CO_2 - T_S$ by the following equation:

$$r_{c_{\text{proxy1}}, c_{\text{proxy2}}} = \frac{\overline{c'_{\text{proxy1}} c'_{\text{proxy2}}}}{\sigma_{c_{\text{proxy1}}} \sigma_{c_{\text{proxy2}}}}, \tag{5}$$

as already applied in other studies with the correlation coefficient ranging from zero (no correlation) to one (full correlation; Gao, 1995; Katul and Hsieh, 1999; Ruppert et al., 2006b; Held et al., 2008). To figure out possible differences before and after the management, daily average correlation coefficients (between 09:00 and 17:00 CET, for 16 days before and 27 days after the management) were calculated.

3.4 REA preparation and measurements

The REA device used in this study (Fig. 1) was constructed and tested by Ruppert et al. (2012) and has already been applied in other field experiments (Ruppert, 2008). REA measurements require a high-frequency vertical wind velocity and CO_2 mixing ratio, provided by an ultrasonic anemometer and an infrared gas analyzer. According to the hyperbolic deadband (Eq. 4), these data control the mechanical valve system for taking up- and downdraft air samples. The filter-protected intake line of the system, tested and optimized for time lag and turbulent flow (Reynolds number = 2433; Ruppert et al., 2012), was installed close to the measurement path of the sonic anemometer. The time lag between the air sample in the tube and the signal of the sonic anemometer was determined beforehand via cross-correlation analysis and provided in the REA controlling software for online correction (Ruppert, 2005). Valve switching for the separation of up- and downdrafts (located in the REA device) was thereby synchronized with the vertical wind velocity fluctuation, measured with the sonic anemometer (located 2.5 m above the ground).

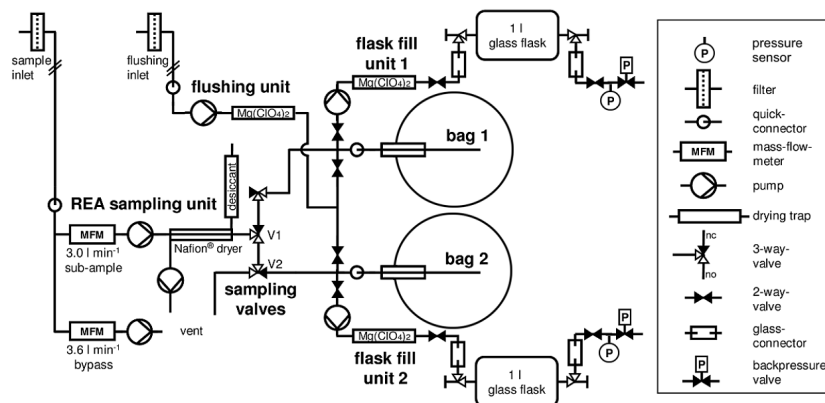All system components were either thoroughly cleaned with acetone : hexane 1 : 1 (nanograde) and heated (glass and

Figure 1. Design of the whole-air REA system (Ruppert et al., 2012).

steel parts) or they possessed non-reactive surface materials such as Teflon® or polyethylene to avoid fractionation processes and sample contamination. Mylar® balloons, also with polyethylene as the inner surface, were used as intermediate sample reservoirs at ambient pressure. Isotopic integrity for up to a residence time of 60 min in the balloons could be achieved by repeated flushing and heating before application (cf. Bowling et al., 2003a; Ruppert et al., 2012). After a final leakage test the REA system was applied in the field. There was no need for density corrections, because the sample air was pre-dried with a Nafion® gas dryer and finally dried by passing water traps with magnesium perchlorate granulate ($Mg(ClO_4)_2$). Between two sampling processes the system was flushed extensively with dry air from the measurement height to avoid any leftover sample air from previous sampling. More than 10 L of up- and downdraft air was collected during each sampling process. Hence, the whole system, including sampling flasks for final storage for laboratory analysis, was repeatedly flushed and conditioned with dried air to achieve high sampling accuracy for subsequent high-precision isotope ratio mass spectrometry (IRMS) analysis (Brand, 2005; Rothe et al., 2005; Sturm et al., 2004). This, as well as the CO_2 mixing ratio analysis, were accomplished in the isotope and trace gas laboratory of the Max Planck Institute in Jena, Germany. All ^{13}C isotopic signatures in this study were analyzed in relation to ^{13}C isotopic abundances in the international standards VPDB (Vienna Pee Dee Belemnite; Brand et al., 2009; Wendeberg et al., 2011; JRAS scale; Ghosh et al., 2005; Wendeberg et al., 2011). The precision in the laboratory of 0.012 ‰ for $\delta^{13}C$ (for more detailed information about the laboratory analysis see Werner et al., 2001), the application of a hyperbolic deadband (hyperbolic relaxed eddy accumulation, HREA; Bowling et al., 1999b) and comprehensive REA system and component laboratory tests made the resolution of up- and downdraft isotope ratio and mixing ratio differences possible, and consequently the determination of $\delta^{13}C$ isofluxes (Wichura, 2009; Ruppert et al., 2012).

Besides the already-mentioned leakage test, the balloon bag intermediate reservoirs were tested for sample contamination resulting from fractionation processes and chemical compounds degassing from the inner balloon surface. The results proved the suitability of the balloons for a sample storage time of up to 2 h, although 30–40 min is enough for REA sampling (Ruppert et al., 2012). During the system test, the REA device operated as in a real field experiment but sampled standardized air from a compressed air tank. According to a previous system test in 2003 (19 samples, standard deviation: 0.014 ‰; Ruppert, 2008), the accuracy of the system for $\delta^{13}C$ could be maintained after the restart in 2012 (10 samples 0.011 ‰; Ruppert et al., 2012). Hence, the precision of the applied sampling operations was close to that of the mass spectrometer. The mean up- and downdraft isotope ratio difference accounted for 0.15 ± 0.04 ‰ and was larger than the instrument precision by a factor of 13. Consequently, the measurement precision accounted for only 8 % and the up- and downdraft difference could be resolved very well.

3.5 Isoflux and partitioning

With adequate resolution of CO_2 and $\delta^{13}C$ isotope mixing ratio differences in up- and downdrafts, $\delta^{13}C$ isofluxes (F_{ISO}) can be derived by introducing the δ notation[1] to Eq. (1) (Bowling et al., 1999a; Ruppert, 2008; Wichura, 2009) and rewriting as

$$F_{ISO} = b\,(H_{eff})\,\sigma_w\,\rho_a\,\left(\overline{\delta^{13}C_\uparrow}\,\overline{C_\uparrow} - \overline{\delta^{13}C_\downarrow}\,\overline{C_\downarrow}\right). \qquad (6)$$

$\overline{C_\uparrow}$ and $\overline{C_\downarrow}$ represent the CO_2 mixing ratios, and $\overline{\delta^{13}C_\uparrow}$ and $\overline{\delta^{13}C_\downarrow}$ the isotope mixing ratios of up- and downdrafts. $b\,(H_{eff})$ was determined by applying H to Eq. (3) and by using effectively measured CO_2 REA and eddy fluxes. σ_w

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[1]The isotope ratios are expressed as isotopic signatures in δ notation. All isotopic signatures are reported relative to ^{13}C isotopic abundances in the international standards VPDB (see Sect. 3.4).

was derived from the time series of the vertical wind velocity, measured with the ultrasonic anemometer. Besides F_{ISO}, information about the isotopic ratios of assimilated and respired CO_2 is also necessary for CO_2 flux partitioning based on isotopic signatures. δ_A, the isotopic ratio of assimilated CO_2, was derived by subtracting the ecosystem discrimination of ^{13}C (Δ_e) from the isotopic ratio of the CO_2, leaving the respective air column (i.e., the signature of the air between ground surface and REA sample inlet) that is affected by the assimilating biosphere (Wichura, 2009). Equation (7) is based on the mass balance equations of Lloyd et al. (1996; see also Bowling et al., 2001, 2003a) and represents the tool to determine δ_A that cannot be measured directly:

$$\delta_A = \overline{\delta^{13}C_\uparrow} - \Delta_e. \tag{7}$$

Equation (8) is based on the general definition of isotopic discrimination Δ by Farquhar et al. (1989). In Buchmann et al. (1997; see also Buchmann et al., 1998), this definition was utilized to derive the ecosystem discrimination Δ_e. Ruppert (2008) found that, on small timescales, Δ_e can be defined as the ecosystem discrimination of the atmospheric exchange at measurement height against isotopes in the lower boundary layer air:

$$\Delta_e = \frac{\overline{\delta^{13}C_\downarrow} - \delta_c}{1 + \delta_c}. \tag{8}$$

$\overline{\delta^{13}C_\downarrow}$ thereby represents the source air from above the measurement height. δ_c is the signature of the turbulent exchange which can be measured directly (Ruppert, 2008):

$$\delta_c = \frac{\overline{\delta^{13}C_\uparrow}\,\overline{C_\uparrow} - \overline{\delta^{13}C_\downarrow}\,\overline{C_\downarrow}}{(\overline{C_\uparrow} - \overline{C_\downarrow})}. \tag{9}$$

δ_R, the isotopic ratio of respired CO_2, was determined by the Keeling plot method (intercept of a plot of δ^{13}C vs. inverse carbon concentration of respiration samples; Keeling, 1958). Those samples were taken by means of the static alkali (NaOH) absorption method (Lundegardh, 1921; Kirita, 1971; Singh and Gupta, 1977). Dark chambers avoided assimilation, and released CO_2 was captured in the solution as sodium carbonate for laboratory analysis. This method allows for determination of concentration as well as isotopic ratio during night- and daytime. It is well known and often discussed that chamber methods cannot completely reproduce influences of atmospheric turbulence on the flux (Kimball and Lemon, 1971; Pumpanen et al., 2004; Rochette and Hutchinson, 2005), but alternative nighttime isotopic measurements with atmospheric methods (REA, laser techniques) for determining δ_R have a similar problem with different turbulence regimes due to different atmospheric stratification, during night- and daytime (Bowling et al., 2001).

Knowing F_{ISO}, δ_A and δ_R, F_{EC} could be partitioned into assimilation flux,

$$F_A = \frac{F_{ISO} - \delta_R F_{EC}}{\delta_A - \delta_R}, \tag{10}$$

and respiration flux,

$$F_R = \frac{F_{ISO} - \delta_A F_{EC}}{\delta_R - \delta_A}, \tag{11}$$

in accordance to Lloyd et al. (1996), Bowling et al. (2001, 2003a), Ruppert (2008) and Wichura (2009). Both equations were derived from the CO_2 mass balance of a defined air column between ground surface and measurement height, considering CO_2 entering and leaving the column, CO_2 gain by respiration and loss by assimilation. By assuming adequate turbulent mixing and stationary conditions, after introduction of the corresponding CO_2 isotope ratios to the mass balance elements and after mathematical conversion, F_A and F_R can be calculated. In order to finally evaluate the quality of the partitioning tool based on isotopic signatures, results were compared with a common FPM based on Lloyd–Taylor (Lloyd and Taylor, 1994) and Michaelis–Menten functions (Michaelis and Menten, 1913).

4 Results and discussion

4.1 Simulation of REA on managed grassland

To measure isofluxes of $^{13}CO_2$, the CO_2 mixing ratio is naturally the preferred proxy scalar used to control the sampling process and to determine hyperbolic deadband (H) and proportionality factor b. Because there is a consistent distribution of relevant values in the different quadrants, and in order that the hyperbolic thresholds do not lead to the exclusion of too much data, $H = 1$ was chosen in accordance to Eq. (4) after simulation (cf. Ruppert et al., 2006b). Correct REA fluxes require correct b factors. By investigating managed grassland, influences of mowing and rowen on the seasonal cycle have to be considered. Ongoing EC measurements provided data for REA simulation before and after cutting events. Days with similar weather conditions up to 10 days before and 20 days after the management were used to compute $b(H)$ – on the basis of a hyperbolic deadband – by day. Those periods showed completely different results (Fig. 2). Before the management, mean $b(H)$ was 0.2, with an interquartile variation of about 20 % (with exception of the early morning and evening hours). After the management, $b(H)$ was found to have been reduced by half, but the variation had increased by more than 80 % (Fig. 2b). While the mixing ratio differences of up- and downdrafts used in Eq. (3) remain negative (C sink) in almost all cases, including after the management, the EC-derived CO_2 flux represented a higher NEE, which ranged up to positive and respiration-dominated values. Both the reduction and the larger varia-
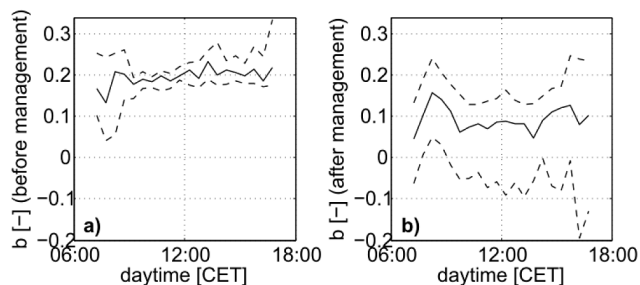
Figure 2. Daytime $b(H)$ before **(a)** and after cutting events **(b)**. Data from rowen in 2009, mowing and rowen in 2010, and mowing in 2011; the median (solid line) and the 25 and 75 % quantile (dashed line) of 16 days before and of 27 days after management are illustrated. $H = 1.0$; (proxy) scalar: CO_2.

Figure 3. Absolute scalar correlation coefficients between CO_2 and sonic temperature T_S **(a)** and CO_2 and water vapor H_2O **(b)**. Negative x-axis values indicate days before and positive values days after mowing and rowen, respectively. Dark squares represent rowen data in September 2009, bright upward triangles represent mowing in July 2010, black circles represent rowen in September 2010, and grey diamonds represent the late mowing in August 2011. The error bars show standard errors of the daily mean of r between 09:00 and 17:00 CET.

tions in $b(H)$ can be attributed to the management-induced source/sink changes of the proxy scalar CO_2.

However, determination of $b(H)$ with T_S and H_2O as proxy scalars seems to be less influenced by management events (not shown in this study), but those can lack required scalar similarity to ^{13}C as scalars of interest. This is an essential precondition for high-quality REA measurements and must be controlled with adequate effort. In this study, on all days of simulation, scalar similarity between CO_2 and H_2O and T_S was evaluated by calculating scalar correlation coefficients (Eq. 5). For both combinations (CO_2 and T_S, CO_2 and H_2O), Fig. 3 demonstrates an abrupt decrease in the correlation after the management. Thus, neither T_S nor H_2O are suitable alternatives to CO_2 shortly after management. Figure 3 also indicates faster recovery of scalar similarity after autumn rowen (dark symbols) than after midsummer mowing (bright symbols). This can be linked to greater intervention in the ecosystem in midsummer, i.e., removing more productive biomass than in autumn. In both cases scalar similarity increased with ecosystem recovery up to pre-cutting values. The lack of scalar similarity after the management confirms dependence on plant physiology (Williams et al., 2007) and source/sink influences (Andreas et al., 1998a; Katul et al., 1999; Katul and Hsieh, 1999; Ruppert et al., 2006b; Held et al., 2008; Ruppert, 2008). In general, it is suggested that REA not be applied shortly after management events due to the fact that b can only be properly determined before management events and after an adequate period of ecosystem recovery. Under the environmental conditions present in this study, it is suggested that REA not be applied for 22 days after the summer mowing and for 12 days after the rowen in autumn (Fig. 3). As a result of present diurnal variations in $b(H)$, constant b factors should not be applied.

4.2 REA measurements

REA measurements in this study were conducted prior to, and 5 weeks after, summer mowing to fulfill the precondition of an undisturbed ecosystem. Apart from the selection
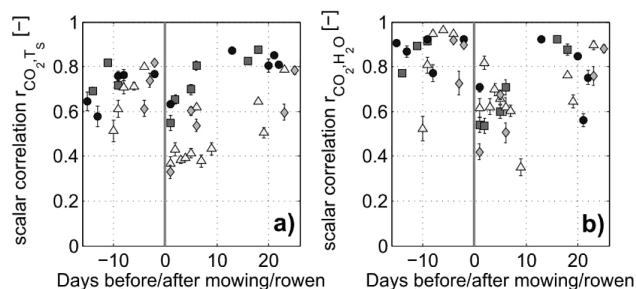
according to the meadow management, two REA measurement days with different wind conditions were chosen. With an average of $2\,\mathrm{m\,s^{-1}}$, the wind velocity (u) on 22 June 2010 was half as large as on 25 August 2010 (on average $4\,\mathrm{m\,s^{-1}}$ during the measurement period). On both days mean air temperature (T) and mean incoming shortwave radiation (K_{in}) were comparable to some extent. F_{ISO} and δ^{13}C values partly follow fluctuations of K_{in}, although REA sampling processes lasted 40 min to generate adequate amounts of sample air, and unfortunately integrated over very different radiation conditions (Fig. 4). First, the enrichment of ^{13}C in the atmosphere can be observed in Fig. 4e. Sufficient water availability due to a high ground water level and moderate air temperature ($\leq 17\,°$C) excludes reduced stomatal conductance, i.e., noon depression. High enrichment of ^{13}C at noon on 22 June relies on increased assimilation. This assumption is supported by the development of the NEE which shows the largest C uptake during that time (Fig. 5a). The pattern of F_{ISO} acts to a certain extent in accordance with the differences of the δ^{13}C values of up- and downdrafts. On both days the ranges of F_{ISO} match results of other studies (Bowling et al., 2001; Wichura, 2009). This also applies to the evening breakdown of F_{ISO} due to missing up- and downdraft isotope ratio differences, coming along with absent shortwave radiation and consequently biosphere activity (last sampling on 22 June). With the exception of this last measurement, adequate δ^{13}C differences between up- and downdraft samples were always achieved (on average $0.15 \pm 0.04\,‰$; precision of IRMS Jena: $0.012\,‰$; Werner et al., 2001). In addition to its dependence on wind velocity, i.e., σ_w in Eq. (6), factor b is decisive for F_{ISO}. Therefore $b(H_{\mathrm{eff}})$ was calculated from directly measured REA up- and downdraft samples and appropriate EC fluxes. In contrast to simulated $b(H)$, effective b factors $b(H_{\mathrm{eff}})$ do not overestimate the CO_2 mixing ratio differences (i.e., underestimate the necessary size of b), due
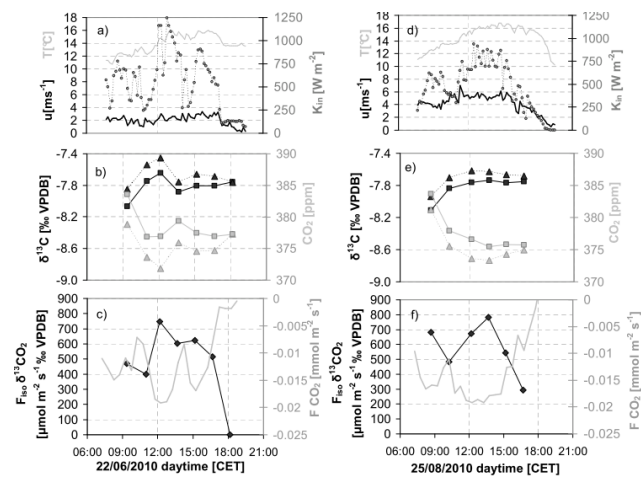
Figure 4. Incoming shortwave radiation K_{in} (grey dashed line with circles), temperature T and wind velocity u (bold black line) are illustrated in **(a)** and **(d)**. Dark upward triangles in **(b)** and **(e)** represent isotopic composition of updraft, dark squares represent that of downdraft CO_2, and bright symbols represent CO_2 mixing ratios. **(c)** and **(f)** show the $\delta^{13}CO_2$ isoflux (F_{ISO}), dark diamonds, set in the middle of the 40 min measurement interval; bright lines show the CO_2 flux.

Figure 5. Comparison of NEE flux partitioning with isotopic background (respiration flux F_R: black diamonds, assimilation flux F_A: light-grey circles) and a common FPM (dashed lines in same colors); the NEE measured via eddy covariance is illustrated as a dark-grey solid line.

-24.9 ‰ (Fig. 6), with a standard error of 1.7 ‰, within a 95 % confidence interval of ± 4.3 ‰.

On 22 June and 25 August in 2010, before and long after meadow mowing, all parameters were determined in order to partition NEE into assimilation (F_A) and respiration (F_R; Fig. 5) based on two different approaches: the common FPM, based on Lloyd–Taylor and Michaelis–Menten functions, and the isotopic flux partitioning approach (Eqs. 10 and 11). On both days NEE (Fig. 5) shows variations according to incoming shortwave radiation (Fig. 4), with maximum CO_2 sink capacity of almost $0.02\,\mathrm{mmol\,m^{-2}\,s^{-1}}$ during the day. While the morning rise of photosynthetic activity was not sampled, evening breakdown to a respiration-dominated system was captured. The last value in Fig. 5a in the evening shows a special case. There is no longer any difference between up- and downdraft isotope ratios, and so isoflux, and consequently assimilation and respiration fluxes, becomes zero. This comes along with a lack of photosynthesis and discrimination, but above all with turbulent fluxes that come to a standstill, as confirmed by a very small NEE (Fig. 5) and low wind velocity and incoming shortwave radiation (Fig. 4). This pattern is not shown by the Lloyd–Taylor- and Michaelis–Menten-function-based FPMs. Apart from that, the isotopic flux partitioning shows a much greater variability, whereas the FPM insufficiently reproduces natural respiration changes, causing assimilation fluxes to exactly follow the NEE. Sometimes both approaches provide partially similar fluxes, but the isotopic model is able to describe various underlying fluxes of the NEE; that is, more intense reactions to environmental conditions are attributed to the ecosystem (Ruppert, 2008). The quite constant respiration provided by the temperature-based FPM results from relatively small temperature variations during both periods around the measurement days. Temperature is only one of the driving mechanisms of respiration; for example, photosynthetic activity supplies root exudates to soil life and accounts for a large portion of root-derived respiration (Kuzyakov and Gavrichkova, 2010). Discrimination of ^{13}C is an input

to a certain inevitable imprecision of the physical sample separation process of the measurement system compared to the simulation. Sample carryover during the real REA measurement can also be a reason for that. Thus, effective b factors were slightly higher (0.28 ± 0.05) than the simulated values shown in Fig. 2. This has already been observed in previous studies (Baker et al., 1992; Beverland et al., 1996; Moncrieff et al., 1998; Ruppert et al., 2012).

4.3 Flux partitioning

To partition NEE into assimilation and respiration fluxes based on the isotopic method, their isotopic signatures δ_A and δ_R, as well as F_{ISO} and F_{EC}, are required (Eqs. 10 and 11). δ_A and δ_R are sensitive factors in the model that have to be discussed in detail (Ogée et al., 2004; Ruppert, 2008). Determination of δ_R is based on the Keeling plot method (Keeling, 1958). Therefore, samples were taken with the static alkali absorption method in dark soil chambers. The complex assignment of δ_R values to temporally varying photosynthetic activity due to time lag effects (Knohl and Buchmann, 2005), as well as unsolved problems applying nighttime δ_R measurements, suggests the application of integrative static chamber measurements. However, it is possible to improve the resolution of the δ_R data with modern laser $\delta^{13}C$ measurements, although causing considerable expense (Griffis et al., 2004; Bowling et al., 2003b). Independent of the kind of data acquisition, the sensitivity of δ_R related to $\delta^{13}C$ measurements has to be evaluated (Zobitz et al., 2006; Pataki, 2003). In this study the Keeling plot intercept accounted for
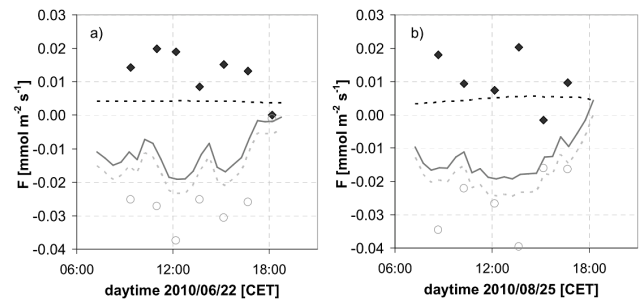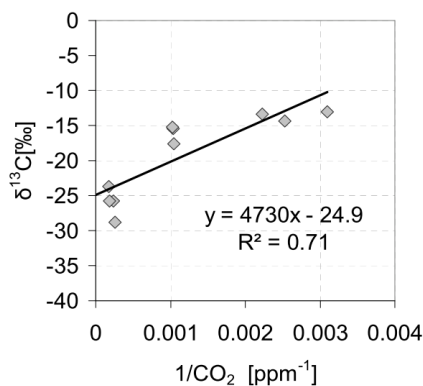
Figure 6. Keeling plot of respiration samples for determination of isotopic ratio of respiration, δ_R; Keeling plot intercept: -24.9, with a standard error of 1.7 ‰, within a 95 % confidence interval of ± 4.3 ‰. The solid line indicates the orthogonal regression line. R is the correlation coefficient.

factor in the isotopic model. It is directly coupled to all assimilation-based processes, which become apparent in the assimilation flux closely connected to the incoming short-wave radiation. The same applies to wind velocity, essential for atmospheric fluxes and considered only in the isotopic model as an input parameter of F_{ISO}. The diurnal cycle of the assimilation flux – determined from F_{ISO} – (Fig. 5) can be explained clearly by the diurnal cycles of incoming short-wave radiation and wind velocity (Fig. 4). Incoming short-wave radiation in particular drives surface temperature and assimilation-dependent, soil-organic-matter-derived respiration (Kuzyakov and Gavrichkova, 2010). Almost all values of the isotopic model show these dependences to some extent. This representation of environmental influences in combination with the accordance to the established common flux partitioning model suggests good performance of the isotopic model, and there is no evidence for comparable restrictions found for complicated coupling regimes in high vegetation ecosystems (Ruppert, 2008; Wichura, 2009).

5 Conclusions

Detailed investigation of pre- and post-mowing conditions by means of REA simulations on managed grassland demonstrated serious constraints for REA application directly after management. At this time, simulated b factors showed larger uncertainty and decreased strongly because the mixing ratio differences in the simulation did not follow the NEE determined via EC to have positive fluxes. Also, the scalar similarity assumption was not fulfilled for the evaluated proxy scalars CO_2, T and H_2O after management. Consequently, the REA technique cannot be applied shortly after meadow management without the risk of huge REA-flux errors. This restriction should be carefully considered in future REA studies. A distinct decision of when to use REA again

depends on environmental conditions and plant community structure. Both factors are decisive for plant community recovery and hence the development of scalar concentration and flux behavior. For several scalar quantities, plant physiology monitoring and consideration of the state of the ecosystem recovery could be helpful. This study suggests waiting at least 22 days in summer and 12 days in autumn after management in similar circumstances. With carefully evaluated b factors, application of a hyperbolic deadband and high-precision laboratory analysis, up- and downdraft differences can be resolved and isofluxes can be derived.

The NEE was partitioned via an isotopic modeling approach based on information about isotopic ratios of assimilation and respiration fluxes, i.e., EC flux and isoflux. It turned out that the isotopic approach works well on the grassland experiment site compared to former studies where it was applied over forest ecosystems with special coupling regimes. Moreover, it can enhance results of a common flux partitioning tool based on Lloyd–Taylor and Michaelis–Menten functions. An advantage is a better reproduction of environmental conditions, due to directly including ecosystem discrimination of ^{13}C and wind velocity in the model. However, the method is very sensitive and requires exact determination of the isotopic signatures (Ruppert, 2008). Also, given uncertainties regarding determination of respiration, characteristics need to be further investigated. Chamber measurements require detailed consideration of atmospheric conditions (Riederer et al., 2014).

The application of REA in general is expensive and time consuming and is therefore only applicable for short-term and special investigations. Its versatility and the information about NEE component flux variability gained through its use justify its application in ecosystem sciences. However, in the future it will be more and more replaced by, for example, direct isotopic eddy covariance measurements that are also adapted for long-term experiments (Wehr et al., 2013).

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