



Application of REA  
on managed  
grassland

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# Application of relaxed eddy accumulation (REA) on managed grassland

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## Abstract

Relaxed eddy accumulation is applied for measuring fluxes of trace gases for which there is a lack of sensors fast enough in their resolution for eddy-covariance. 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 thereby 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,  $\text{CO}_2$  fluxes were continuously measured and  $^{13}\text{CO}_2$  isofluxes were determined with a high measurement precision on two representative days in summer 2010. This enabled the evaluation of the  $^{13}\text{CO}_2$  flux portion of the entire  $\text{CO}_2$  flux, in order to estimate potential influences on tracer experiments in ecosystem sciences and to compare a common method for the partitioning of the net ecosystem exchange into assimilation and respiration based on temperature and light response with an isotopic approach directly based on the isotope discrimination of the biosphere.

## 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 chamber (Goulden et al., 1996; Davidson et al., 2002; Dore et al., 2003; Subke and Tenhunen, 2004) and eddy-covariance (EC) measurements (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;

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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  $^{13}\text{CO}_2$  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 physical and biochemical processes such as stomatal uptake of  $\text{CO}_2$  and photosynthesis, which discriminate against the heavier isotope  $^{13}\text{C}$ , the air close to the biosphere is enriched in  $^{13}\text{CO}_2$  during the day. Consequently the biomass itself, and all following compartments within the dynamic C-cycle, are depleted in  $^{13}\text{C}$ , as is the respired  $\text{CO}_2$ . Both effects account for a distinct diurnal cycle of the  $^{13}\text{CO}_2$  concentration in ecosystem air (Flanagan et al., 1996; Lloyd et al., 1996). Resulting  $^{13}\text{CO}_2$  isofluxes can be determined with the flux-gradient method (Flanagan et al., 1996), by modeling approaches (Ogée et al., 2003; Lloyd et al., 1996), by hyperbolic relaxed eddy accumulation (HREA, Bowling et al., 2001; Bowling et al., 2003a; Wichura, 2009; Wichura et al., 2004) or laser supported measurements (Griffis et al., 2004; Bowling et al., 2003b).

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 strongly 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 potentially introduce certain restrictions for REA measurements. Previous studies indicated that errors in the REA flux often appeared when scalars of interest and proxy scalars behaved 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;

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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  $\text{CO}_2$  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 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), and 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.

A study of Wichura (2009) showed a 3%  $^{13}\text{C}$  flux as portion of the entire  $\text{CO}_2$  flux over a forest, while the proportion of  $^{13}\text{C}$  of the average terrestrial abundance concentration is just 1.11%, (Ehleringer and Osmond, 1989). It is assessed whether this result can be reproduced in general and especially over grassland, also with regard to potential effects on isotopic labeling or natural abundance experiments that in general do not consider atmospheric isotope fluxes (an overview is given by Kuzyakov and Domanski, 2000 and Yakir and Sternberg, 2000). Therefore a small number of the labour-intensive and sophisticated REA measurements is adequate. This also applies to another aim of this study: the evaluation of a commonly applied partitioning method for the net ecosystem exchange.

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  $R_{\text{ECO}}$  parameterization, nighttime NEE is used because it equals ecosystem respiration ( $R_{\text{ECO}}$ ) due to missing assimilation (Lloyd and Taylor, 1994;

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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).

## 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

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

derived from average up- and downward scalar concentration  $\overline{c_\uparrow}$  and  $\overline{c_\downarrow}$ , standard deviation of the mean vertical wind velocity  $\sigma_w$ , density of dry air  $\rho_a$  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 in fact widely unaffected by the atmospheric stability (Delany et al., 1991; Foken et al., 1995). For an ideal Gaussian joint frequency distribution (JFD) of the vertical wind speed and the scalar concentration,  $b$  is constant ( $b = 0.627$ ; Baker et al., 1992; Wyngaard and Moeng, 1992). But variations of  $b$  can be generated by just a small skewness of the JFD of  $w'$  and  $c'$  (Katul et al., 1996; 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

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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 by EC. The proportion of both proxy scalar fluxes,  $F_{\text{REA}}$  and the EC flux ( $F_{\text{EC}} = \overline{w'c'}$ ), provides  $b$ :

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

Above-mentioned  $b$  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) modified the method by discarding fluctuations around zero – that have only small influences on the entire flux anyhow – with a deadband, could the REA idea be implemented with regard to mechanical restrictions of the speed of valve switching.

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

The size of the linear 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 scalar concentration difference between up- and downdraft air samples, application of a hyperbolic deadband  $H$  is recommended (Bowling et al., 1999b). That

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is required for investigating, for example, differences in the order of the measurement precision. By application of  $H$  in hyperbolic REA (HREA),  $b(H)$  is reduced to lower values around  $0.22 \pm 0.05$  (Bowling et al., 1999b),  $0.15\text{--}0.27$  (Ruppert et al., 2006b), respectively.  $H$  is based on the fluctuation of the vertical wind velocity  $w'$  and the concentration  $c'$  of a proxy scalar, as well as their standard deviations  $\sigma_{w/c}$ :

$$H \geq \left| \frac{w'c'}{\sigma_w \sigma_c} \right| \quad (4)$$

Adequate scalar similarity is especially required for hyperbolic REA, because  $H$  depends on the proxy scalar concentration. 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 of canopy physiology (Williams et al., 2007).

Essential for successful REA application is the choice of the right proxy scalar. Often temperature, measured by 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; Ren et al., 2011) and sometimes both temperature and water vapor turn out to be adequate (Held et al., 2008). For  $^{13}\text{CO}_2$  isoflux measurements typically the proxy scalar  $\text{CO}_2$  is used (Bowling et al., 2003a; Wichura, 2009). Due to a lack of adequate high frequency measurements of  $^{13}\text{CO}_2$ , 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  $^{13}\text{C}$  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 northeast 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 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 CO<sub>2</sub> concentration were measured by 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 by 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 by 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

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combination with former studies as a reference (Ruppert, 2008), the hyperbolic dead-band 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  $\text{CO}_2$  concentration was used as 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  $\sigma_w$  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 ( $\text{H}_2\text{O}$ ). In order to evaluate their similarity to  $\text{CO}_2$  in the scalar time series, i.e. their suitability as a substitute for  $\text{CO}_2$ , scalar similarity had to be verified, and this was done by evaluating the consistency of the correlation coefficients  $r$ :

$$|r_{c_{\text{proxy}}}| = |r_c| \quad (5)$$

The correlation coefficients between the three scalars in this study:  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $T_S$ , were calculated by the following equation

$$r_{c, c_{\text{proxy}}} = \frac{\overline{c'c'_{\text{proxy}}}}{\sigma_c \sigma_{c_{\text{proxy}}}} \quad (6)$$

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).

### 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).

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REA measurements require high frequency vertical wind velocity and CO<sub>2</sub> concentration data, provided by an ultra-sonic anemometer and an infra-red 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 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 by the sonic anemometer (located 2.5 m above the ground). Before the REA measurements, time series of vertical wind velocity at the sonic anemometer and CO<sub>2</sub> concentration at the sample inlet and the sample segregating valves were generated. The time lag could then be detected by cross correlation analysis and finally provided in the controlling software.

All system components were either thoroughly cleaned with Acetone:Hexane 1 : 1 (nanograde) and heated (glass and steel parts), or possess non-reactive surface materials as Teflon<sup>®</sup> or Polyethylene to avoid fractionation processes and sample contamination. Mylar<sup>®</sup> 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<sup>®</sup> gas-dryer and finally dried by passing water traps with magnesium perchlorate granulate (Mg(ClO<sub>4</sub>)<sub>2</sub>). 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 up- and downdraft air were collected during each sampling process. Hence, the whole system, including sampling flasks for final storage for laboratory analysis, was

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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<sub>2</sub> mixing ratio analysis, were accomplished in the isotope and trace gas laboratory of the Max-Planck Institute in Jena, Germany. All <sup>13</sup>C isotopic signatures in this study were analyzed in relation to <sup>13</sup>C isotopic abundances in the international standards VPDB (Vienna Pee Dee Belemnite; Brand et al., 2009; Wendeborg et al., 2011; JRAS scale Ghosh et al., 2005; Wendeborg et al., 2011). The precision in the laboratory of 0.012‰ for δ<sup>13</sup>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 possible the resolution of up- and downdraft isotope ratio and concentration differences, and consequently the determination of δ<sup>13</sup>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 are 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 (19 samples, standard deviation: 0.014‰; Ruppert, 2008), the accuracy of the system for δ<sup>13</sup>C could be maintained (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<sub>2</sub> concentration and δ<sup>13</sup>C-isotope ratio differences in up- and downdrafts, δ<sup>13</sup>C isofluxes (F<sub>ISO</sub>) can be derived by introducing the δ-notation<sup>1</sup> to Eq. (1) (Bowling et al., 1999a; Ruppert, 2008; Wichura, 2009):

$$F_{\text{ISO}} = b(H_{\text{eff}})\sigma_w\rho_a \left( \overline{\delta^{13}\text{C}_{\uparrow}\text{C}_{\uparrow}} - \overline{\delta^{13}\text{C}_{\downarrow}\text{C}_{\downarrow}} \right) \quad (7)$$

$\overline{\text{C}_{\uparrow}}$  and  $\overline{\text{C}_{\downarrow}}$  represent the CO<sub>2</sub> mixing ratios, and  $\overline{\delta^{13}\text{C}_{\uparrow}}$  and  $\overline{\delta^{13}\text{C}_{\downarrow}}$  the isotope ratios of up- and downdrafts.  $b(H_{\text{eff}})$  was determined by applying  $H$  to Eq. (3) and by using effectively measured CO<sub>2</sub> REA and eddy fluxes.  $\sigma_w$  was derived from the time series of the vertical wind velocity, measured by the ultra sonic anemometer. Besides F<sub>ISO</sub>, information about the isotope ratios of assimilated and respired CO<sub>2</sub> is also necessary for CO<sub>2</sub> flux partitioning based on isotopic signatures.  $\delta_A$ , the isotope ratio of assimilated CO<sub>2</sub>, was derived by subtracting the ecosystem discrimination of <sup>13</sup>C (Δ<sub>e</sub>, Eq. 9) from the isotope ratio of the CO<sub>2</sub>, 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 (Farquhar et al., 1989; Buchmann et al., 1997, 1998; Wichura, 2009):

$$\delta_A = \overline{\delta^{13}\text{C}_{\uparrow}} - \Delta_e \quad (8)$$

$$\Delta_e = \frac{\overline{\delta^{13}\text{C}_{\downarrow}} - \overline{\delta^{13}\text{C}_{\uparrow}}}{1 + \overline{\delta^{13}\text{C}_{\uparrow}}} \quad (9)$$

δ<sub>R</sub>, the isotope ratio of respired CO<sub>2</sub>, was determined by the Keeling plot method (intercept of a plot of δ<sup>13</sup>C vs. inverse carbon concentration of respiration samples;

<sup>1</sup>The isotope ratios are expressed as isotopic signatures in δ-notation. All isotopic signatures are reported relative to <sup>13</sup>C isotopic abundances in the international standards VPDB (see Sect. 3.4).

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Keeling, 1958). Those samples were taken with the static alkali (NaOH) absorption method (Lundegardh, 1921; Kirita, 1971; Singh and Gupta, 1977). Dark chambers avoided assimilation and released  $\text{CO}_2$  was captured in the solution as sodium carbonate for laboratory analysis. This method allows determination of concentration as well as isotope 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  $\delta_{\text{R}}$  have a similar problem with different turbulence regimes, coming along with different atmospheric stratification, at night and daytime (Bowling et al., 2001).

Knowing  $F_{\text{ISO}}$ ,  $\delta_{\text{A}}$  and  $\delta_{\text{R}}$ ,  $F_{\text{EC}}$  could be partitioned into assimilation

$$F_{\text{A}} = \frac{F_{\text{ISO}} - \delta_{\text{R}}F_{\text{EC}}}{\delta_{\text{A}} - \delta_{\text{R}}} \quad (10)$$

and respiration flux

$$F_{\text{R}} = \frac{F_{\text{ISO}} - \delta_{\text{A}}F_{\text{EC}}}{\delta_{\text{R}} - \delta_{\text{A}}} \quad (11)$$

in accordance to Lloyd et al. (1996), Bowling et al. (2001, 2003a), Ruppert (2008) and Wichura (2009). Both equations were derived from the  $\text{CO}_2$  mass balance of a defined air column between ground surface and measurement height, considering  $\text{CO}_2$  entering and leaving the column,  $\text{CO}_2$  gain by respiration and loss by assimilation. By assuming adequate turbulent mixing and stationary conditions, after introduction of the corresponding  $\text{CO}_2$  isotope ratios to the mass balance elements and after mathematical conversion,  $F_{\text{A}}$  and  $F_{\text{R}}$  can be calculated. In order to finally evaluate the quality of the partitioning tool based on isotopic signatures, results were compared with a common flux partitioning model (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  $^{13}\text{CO}_2$ , the  $\text{CO}_2$  concentration 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 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 ten days before and twenty 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 concentration differences of up- and downdrafts used in Eq. (3) remain negative (C sink) in almost all cases, including after the management, the EC derived  $\text{CO}_2$  flux represented a higher NEE, which ranged up to positive and respiration dominated values. Because  $b(H)$  was reduced and large variations occurred, the proxy scalar  $\text{CO}_2$  was, in any case, significantly influenced by meadow cutting.

However, determination of  $b(H)$  with  $T_S$  and  $\text{H}_2\text{O}$  as proxy scalars seems to be less influenced by management events (not shown in this study), but those can lack required scalar similarity to  $^{13}\text{C}$  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  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and  $T_S$  was evaluated by calculating scalar correlation coefficients (Eq. 6). For both combinations

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(CO<sub>2</sub> and T<sub>S</sub>, CO<sub>2</sub> and H<sub>2</sub>O), Fig. 3 demonstrates an abrupt decrease of the correlation after the management. Thus, both, T<sub>S</sub> and H<sub>2</sub>O are no suitable alternatives to CO<sub>2</sub> shortly after management. Figure 3 also indicates faster recovery of scalar similarity after autumn rowen (dark symbols) than after mid summer mowing (bright symbols).

This can be linked to greater intervention in the ecosystem in mid summer, 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). Present diurnal variations of *b*(*H*) advise against application of constant *b* factors.

## 4.2 REA measurements

REA measurements in this study were conducted prior to, and five 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 m s<sup>-1</sup>, the wind velocity (*u*) on 22 June 2010 was half as large as on 25 August 2010 (on average 4 m s<sup>-1</sup> during the measurement period). On both days mean air temperature (*T*) and mean incoming shortwave radiation (*K*<sub>in</sub>) were comparable to some extent. *F*<sub>ISO</sub> as well as δ<sup>13</sup>C values partly follow fluctuations of *K*<sub>in</sub>, 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 <sup>13</sup>C in the atmosphere can be first observed in Fig. 4e. Sufficient water availability due to a high ground water level

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and moderate air temperature ( $\leq 17^\circ\text{C}$ ) excludes reduced stomatal conductance, i.e. noon depression. High enrichment of  $^{13}\text{C}$  at noon on 22 June relies on increased assimilation. This assumption is supported by the development of the NEE that shows the largest C uptake during that time (Fig. 7a). The pattern of  $F_{\text{ISO}}$  acts to a certain extent in accordance with the differences of the  $\delta^{13}\text{C}$  values of up- and downdrafts. On both days the ranges of  $F_{\text{ISO}}$  match results of other studies (Bowling et al., 2001; Wichura, 2009). This also applies to the evening break-down of  $F_{\text{ISO}}$  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  $\delta^{13}\text{C}$  differences between up- and downdraft samples were always achieved (on average  $0.15 \pm 0.04\text{‰}$ ; precision of IRMS Jena:  $0.012\text{‰}$ , Werner et al., 2001).

In addition to its dependence on wind velocity, i.e.  $\sigma_w$  in Eq. (7), factor  $b$  is decisive for  $F_{\text{ISO}}$ . Therefore  $b(H_{\text{eff}})$  was calculated from directly measured REA up- and downdraft samples and appropriate EC fluxes. In contrast to simulated  $b(H)$ , effective  $b$  factors  $b(H_{\text{eff}})$  do not overestimate the  $\text{CO}_2$  concentration differences (i.e. underestimate the necessary size of  $b$ ), due to a certain inevitable imprecision of the physical sample separation process of the measurement system compared to the simulation. Thus, effective  $b$  factors were slightly higher ( $0.28 \pm 0.05$ ) 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  $\delta_A$  and  $\delta_R$ , as well as  $F_{\text{ISO}}$  and  $F_{\text{EC}}$ , are required (Eqs. 10 and 11).  $\delta_A$  contains information about ecosystem discrimination against  $^{13}\text{C}$  ( $\Delta_e$ , Eq. 9), which is directly determined by REA up- and downdraft sampling and high precision isotope ratio measurements.  $\delta_A$  and  $\delta_R$  are sensitive factors in the model that have

to be discussed in detail (Ogée et al., 2004; Ruppert, 2008). Determination of  $\delta_R$  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  $\delta_R$  values to temporally varying photosynthetic activity due to time lag effects (Knohl and Buchmann, 2005), and unsolved problems applying night-time  $\delta_R$  measurements, suggest the application of integrative static chamber measurements. However, it is possible to improve resolution of the  $\delta_R$  data with modern laser  $\delta^{13}\text{C}$  measurements involving considerable expense (Griffis et al., 2004; Bowling et al., 2003b). Independent of the kind of data acquisition, the sensitivity of  $\delta_R$  related to  $\delta^{13}\text{C}$  measurements has to be evaluated (Zobitz et al., 2006; Pataki, 2003). In this study the Keeling plot intercept accounted for  $-24.9\text{‰}$  (Fig. 5) with a standard error of  $1.7\text{‰}$ , within a 95 % confidence interval of  $\pm 4.3\text{‰}$ .

Furthermore, a measure for  $\Delta_e$ , the  $F_{\text{ISO}}/F_{\text{EC}}$  ratio (Wichura, 2009), is shown in Fig. 6. The more negative this ratio, the more air is affected by assimilation. Maxima starting from 10 a.m. reflect reduced assimilation before noon on both measurement days, in accordance with the course of the NEE in Fig. 7. On the whole, ecosystem discrimination varies in a range from  $-28$  to  $-52\text{‰}$  during the day. Due to courses which are quite similar in size,  $F_{\text{ISO}}$  and  $F_{\text{EC}}$  balance to some extent except for the last value of 22 June, when the proportion of isoflux and  $\text{CO}_2$  flux was close to zero due to missing differences in up- and downdrafts. With an average of  $-40.5\text{‰}$ , the discrimination due to assimilation is comparable to other studies investigating C3 ecosystems ( $-20$  to  $-35\text{‰}$ ; Dawson et al., 2002;  $-37.4\text{‰}$ , Wichura, 2009). Furthermore, this adds up to an even smaller portion  $2.5\%$   $^{13}\text{CO}_2$  flux as part of the entire  $\text{CO}_2$  flux than found by Wichura (2009) over a forest.

On 22 June and 25 August 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. 7) based on two different approaches: the common flux partitioning model (FPM), based on Lloyd Taylor and Michaelis Menten functions, and the isotopic flux partitioning approach (Eqs. 10 and 11). On both days NEE (Fig. 7) shows variations

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according to incoming shortwave radiation (Fig. 4), with maximum CO<sub>2</sub> sink capacity of almost 0.02 mmol m<sup>-2</sup> s<sup>-1</sup> 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. 7a in the evening shows a special case. There is no longer any difference between up- and downdraft isotope ratios, so that isoflux, and consequently assimilation and respiration fluxes, become 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. 7) and low wind velocity and incoming shortwave radiation (Fig. 4). This pattern is not shown by the Lloyd Taylor and Michaelis Menten function based FPM. 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 <sup>13</sup>C is an input factor in the isotopic model. It is directly coupled to all assimilation-based processes. These become apparent in the assimilation flux closely connected to the incoming shortwave 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. 7) can be explained clearly by the diurnal cycles of incoming shortwave radiation and wind velocity (Fig. 4). Especially incoming shortwave radiation 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

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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 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 – even to negative values – because the concentration differences in the simulation did not follow the NEE determined by EC to have positive fluxes. Also, the scalar similarity assumption was not fulfilled for the evaluated proxy scalars  $\text{CO}_2$ ,  $T$  and  $\text{H}_2\text{O}$  after management. Consequently, 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. Thus, precursory EC-measurements in combination with REA simulations are suggested for assessing the influences of the management on the REA measurement. Apart from that, plant physiology monitoring would contribute to the consideration of the state of the ecosystem recovery. This study suggests waiting at least 22 days in summer and 12 days in autumn after management in like 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. Compared to the entire  $\text{CO}_2$  flux the isoflux was rather small (2.5%), so that noteworthy influences on isotopic tracer experiments can be excluded.

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The NEE was partitioned by an isotopic modeling approach based on information about isotope ratios of assimilation and respiration fluxes, EC- and isoflux, respectively. 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  $^{13}\text{C}$  and wind velocity into the model. The given uncertainties regarding determination of respiration characteristics have to be further investigated. E.g. chamber measurements require detailed consideration of atmospheric conditions (Riederer et al., 2013).

REA application in general is expensive and time consuming and is therefore only applicable for short term and special investigations. However, its versatility and the information about NEE component flux variability gained through its use still justify its application in ecosystem sciences.

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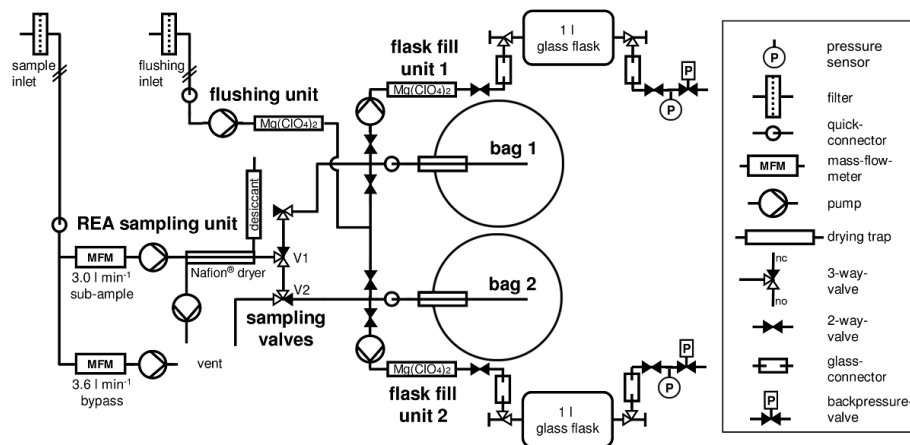
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**Figure 1.** Design of the whole-air REA system (Ruppert et al., 2012).

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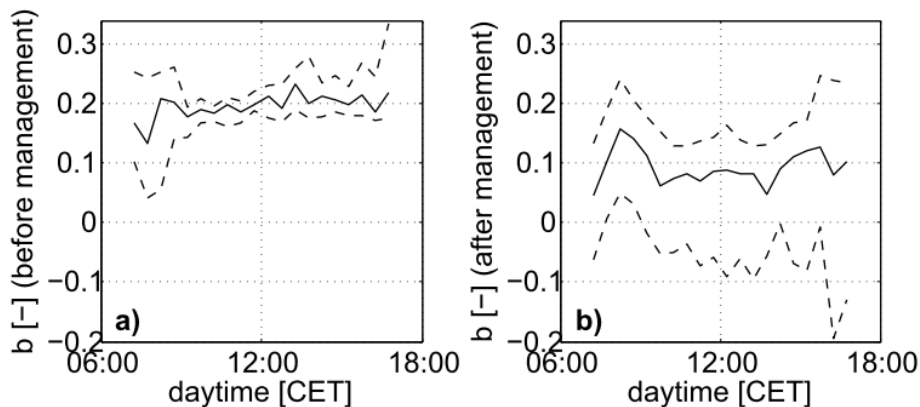
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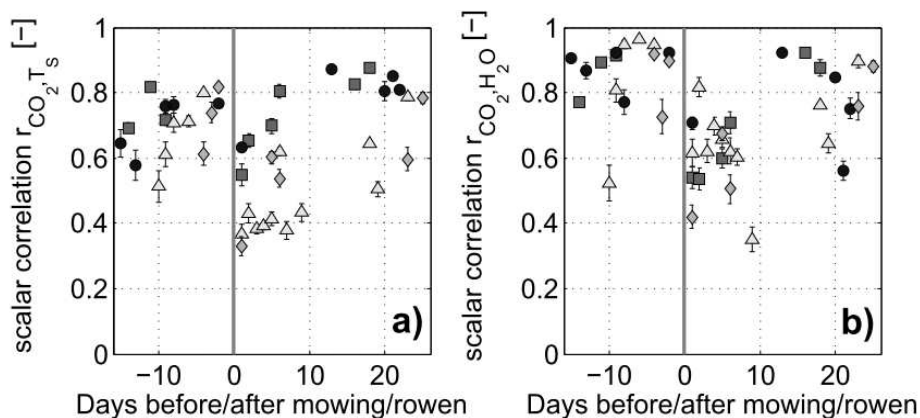


**Figure 2.** Daytime  $b(H)$  before **(a)** and after cutting events **(b)**; data from rowen in 2009, mowing and rowen in 2010 and mowing in 2011, median (solid line), 25% and 75% quantile (dashed line) of 16 days before and of 27 days after management are illustrated,  $H = 1.0$ , (proxy) scalar =  $\text{CO}_2$ .

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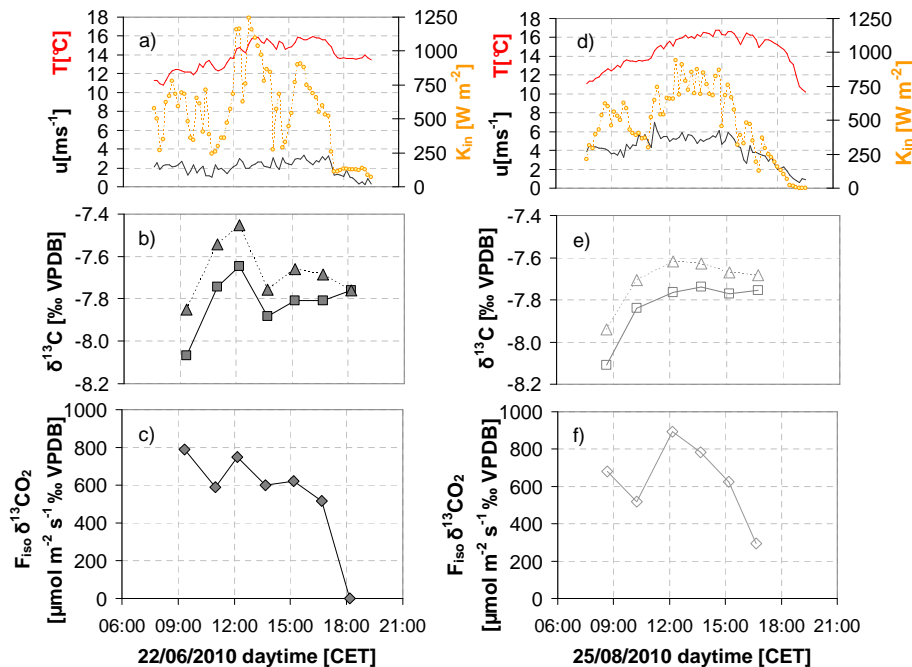
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**Figure 3.** Scalar correlation coefficients between  $CO_2$  and sonic temperature  $T_S$  (a) and  $CO_2$  and water vapor  $H_2O$  (b). Negative  $x$  axis values indicate days before, positive values days after mowing and rowen, respectively. Dark squares represent rowen data in September 2009, bright upward triangles mowing in July 2010, black circles rowen in September 2010 and grey diamonds 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.

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**Figure 4.** Environmental conditions (incoming shortwave radiation  $K_{in}$ , temperature  $T$  and wind velocity  $u$ ) are illustrated in (a) and (d); upward triangles in (b) and (e) represent isotopic composition of updraft, squares of downdraft  $\text{CO}_2$  measured with the REA system; (c) and (f) show the  $\delta^{13}\text{CO}_2$  isoflux ( $F_{iso}$ ); symbols are set in the middle of the 40 min measurement interval.

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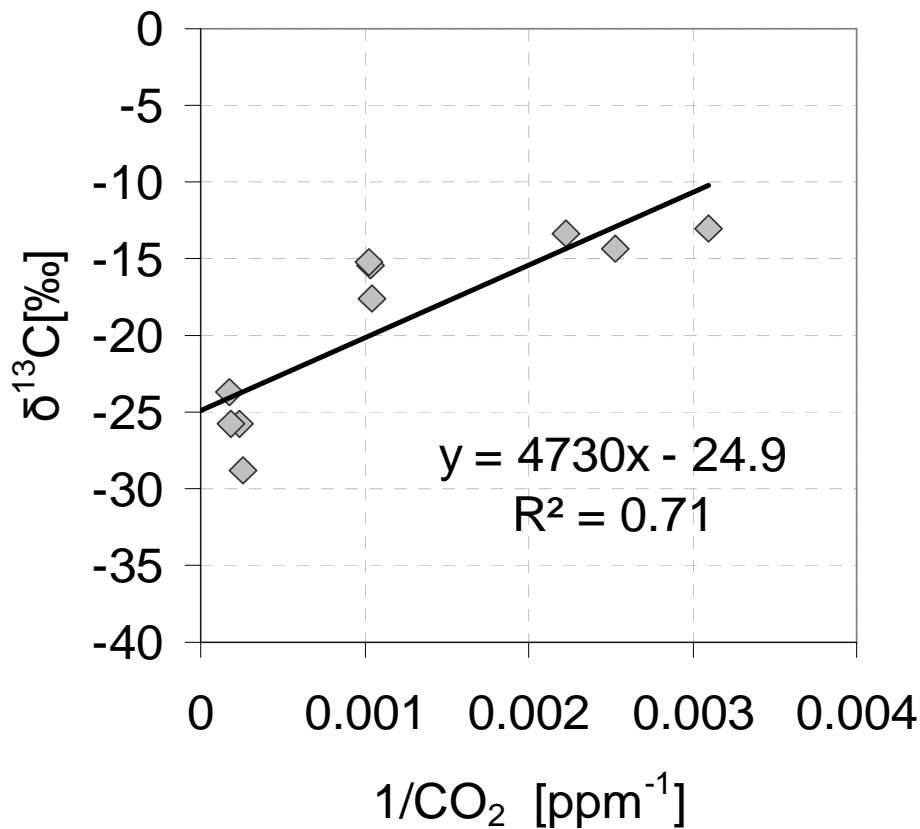
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**Figure 5.** Keeling plot of respiration samples for determination of isotope ratio of respiration;  $\delta_R$ ; Keeling plot intercept: 24.9 with a standard error of 1.7‰, within a 95 % confidence interval of  $\pm 4.3$ ‰. The solid line indicates the orthogonal regression line.  $R$  = correlation coefficient.

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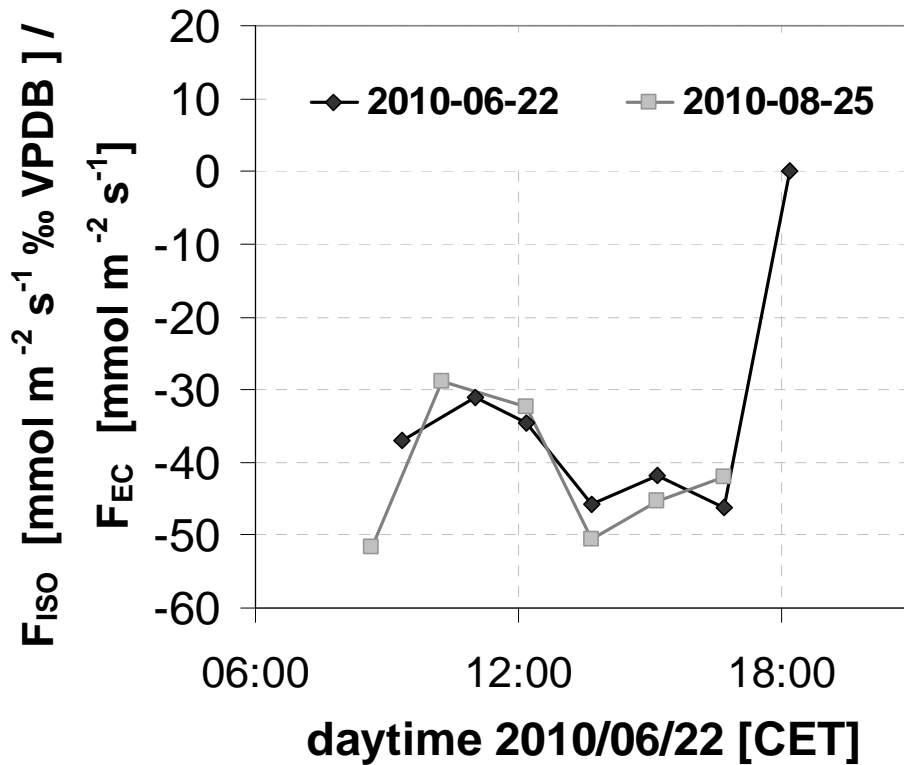
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**Figure 6.** Proportion of  $\delta^{13}\text{CO}_2$  isoflux ( $F_{\text{ISO}}$ ) and  $\text{CO}_2$  flux ( $F_{\text{EC}}$ ).

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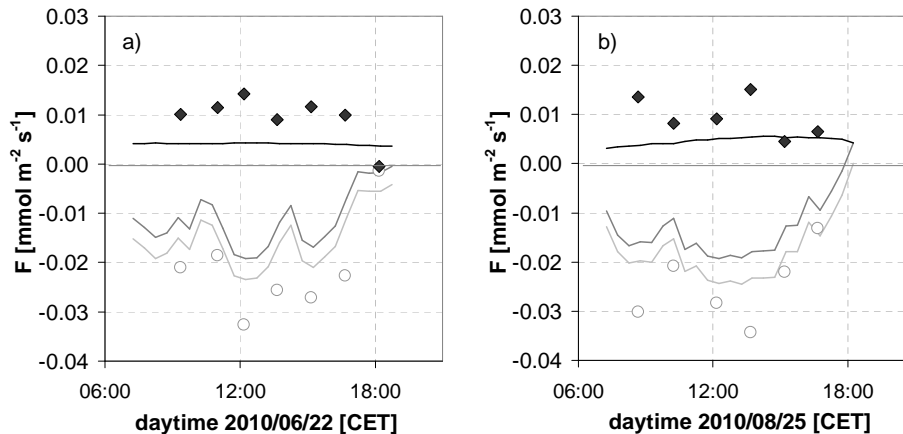
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**Figure 7.** Comparison of NEE flux partitioning with isotopic background (respiration flux  $F_R$ : black diamonds, assimilation flux  $F_A$ : light grey circles) and a common FPM (lines in same colors); the NEE measured by eddy-covariance is illustrated as dark grey solid line.

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