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Measuring and modelling the isotopic composition of soil respiration: insights from a grassland tracer experiment

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Abstract

The carbon isotopic composition (δ^{13} C) of CO₂ efflux (δ_{efflux}) in ecosystems is generally interpreted to represent the actual isotopic composition of respiration (δ_{resp}). However, soils contain a large CO₂ pool in air-filled pores. This pool receives CO₂

- ⁵ from belowground respiration and exchanges CO₂ with the atmosphere (via diffusion and advection) and the soil liquid phase (via dissolution). Natural or artificial modification of δ^{13} C of atmospheric CO₂ (δ_{atm}) or δ_{resp} causes isotopic disequilibria in the soil-atmosphere system. Such disequilibria generate divergence of δ_{efflux} from δ_{resp} (termed disequilibrium effect).
- ¹⁰ Here, we use a soil CO₂ transport model and data from a 13 CO₂/ 12 CO₂ tracer experiment to quantify the disequilibrium between δ_{efflux} and δ_{resp} . The model accounted for diffusion of CO₂ in soil air, advection of soil air, dissolution of CO₂ in soil water, belowground and aboveground respiration of both 12 CO₂ and 13 CO₂ isotopologues. The tracer data were obtained in a grassland ecosystem exposed to a δ_{atm} of -46.9% during daytime for 2 weeks. Nighttime δ_{efflux} from the ecosystem was estimated with
- three independent methods: a laboratory-based cuvette system, in-situ steady-state open chambers, and in-situ closed chambers.

The δ_{efflux} measurements of the laboratory-based and steady-state systems were consistent, and likely reflected δ_{resp} (see Gamnitzer et al., 2009). Conversely, the δ_{efflux} measured using the closed chamber technique differed from these by -11.2%. Most of this disequilibrium effect (9.5‰) was predicted by the CO₂ transport model. Isotopic disequilibria in the soil-chamber system were introduced by changing δ_{atm} in the chamber headspace at the onset of the measurements. When dissolution was excluded, the simulated disequilibrium effect was only 3.6‰. Dissolution delayed the isotopic equilibration between soil CO₂ and the atmosphere, as the storage capacity for labelled CO₂ in water-filled soil pores was 18 times that of soil air.

These mechanisms are potentially relevant for many studies of δ_{resp} in soils and ecosystems, including FACE experiments and chamber studies in natural conditions.



Isotopic disequilibria in the soil-atmosphere system may result from temporal variation in δ_{resp} or diurnal changes in the mole fraction and δ^{13} C of atmospheric CO₂. Dissolution effects are most important under alkaline conditions.

1 Introduction

- ⁵ The carbon isotopic composition (δ^{13} C) of respiration (δ_{resp}) in ecosystems is often interpreted in terms of environmental and metabolic effects on ecosystem carbon dynamics (e.g., Bowling et al., 2002; Pataki et al., 2003; Knohl et al., 2005; Lai et al., 2005; Schaeffer et al., 2008). In general, δ_{resp} is not measured directly, but is equated with δ^{13} C of CO₂ efflux (δ_{efflux}). However, ecosystem CO₂ efflux can differ isotopically from concurrent respiratory CO₂ production due to transient conditions within the soil CO₂ pool. This divergence (termed "disequilibrium effect" in the following) complicates the interpretation of δ_{resp} . Here we investigate mechanisms affecting this disequilibrium effect.
- Transient conditions in the soil diffusive system can occur naturally (Nickerson and ¹⁵ Risk, 2009a; Moyes et al., 2010), but may be greatly amplified by tracer application. For instance, Staddon et al. (2003) and Leake et al. (2006) noted a diffusion of CO_2 tracer into the soil during pulse-labelling experiments and mentioned this as a potential source of error for estimates of δ_{resp} . Indeed, Subke et al. (2009) used a diffusion model to show that ¹³CO₂ pulse-labelling of atmospheric CO₂ led to a change in the ²⁰ δ^{13} C of CO₂ in soil pores, due to transfer of the tracer into the soil pore space. Backdiffusion of the tracer into the atmosphere after labelling was thought to cause abiotic tracer flux (non-biological tracer flux from the soil into the overlying atmosphere, due to physical processes rather than to respiration of previously assimilated labelled carbon) for up to 2 d after tracer application. As yet, to our knowledge, such effects of tracer application on δ_{efflux} have not been quantitatively explained.

In addition to the soil air pores, Högberg et al. (2008) suggested that isotopically labelled CO_2 would also dissolve in soil water. The amount of CO_2 dissolved in water



(more precisely the sum of dissolved CO_2 , carbonic acid, bicarbonate and carbonate) can be several times higher than the amount of CO_2 in the same volume of air. Thus, transients in dissolved CO_2 will likely lead to an enhancement of the abiotic tracer flux. The extent of the contribution from the dissolved CO_2 storage pool depends on the

- ⁵ equilibration time between CO₂ in the gaseous and dissolved phase: when this equilibration occurs quickly compared to the residence time of CO₂ in soil air pores, then the total soil CO₂ pool (gaseous+dissolved CO₂) is expected to influence δ_{efflux} and, hence, the magnitude of the disequilibrium effect. Despite the potential of dissolution to affect δ_{efflux} , a quantitative investigation of this effect is still lacking.
- ¹⁰ Another mechanism influencing soil CO₂ efflux is advective transport by bulk fluid flow (rather than diffusion). Bowling et al. (2009) illustrated that the δ^{13} C within the soil CO₂ depends on the physical nature of the transport mechanism. Advection is also expected to transfer an atmospheric tracer signal into soil air. Phillips et al. (2010) found indications that advection introduced by sampling affected estimations of δ_{resp} .
- Advective transport has been described to occur due to fluctuations in wind speed (termed wind pumping or pressure pumping, e.g., Kimball and Lemon, 1971; Baldocchi and Meyers, 1991; Takle et al., 2004; Massman, 2006) or due to chamber artefacts (e.g., Kanemasu et al., 1974; Fang and Moncrieff, 1998; Lund et al., 1999; Davidson et al., 2002; Pumpanen et al., 2004). Even small pressure differences between the inside and outside of chambers, in the order of 1 Pa, have been shown to considerably influence the soil CO₂ efflux (Fang and Moncrieff, 1998; Lund et al., 1999).

The disequilibrium effect can occur in all systems where the diffusive flux profile varies over time. For example, isotopic disequilibrium can be caused by introduction of an isotopic tracer via ¹³CO₂ (Ostle et al., 2000; Carbone and Trumbore, 2007; Högberg et al., 2008; Subke et al., 2009) or ¹⁴CO₂ (Horwath et al., 1994; Carbone et al., 2007) pulse labelling, or in Free-Air CO₂ Enrichment (FACE and webFACE) experiments (e.g., Nitschelm et al., 1997; Matamala et al., 2003; Asshoff et al., 2006; Keel et al., 2006; Pregitzer et al., 2006; Taneva et al., 2006). Similarly, changes in chamber headspace CO₂ due to flushing with CO₂-free air can affect the measurement of δ_{efflux} (Ohlsson



et al., 2005). Transients in diffusive flux profiles in the soil of natural (unlabelled) systems can be caused by time-varying respiratory CO_2 production (Moyes et al., 2010), advection induced by pressure pumping (Massman and Frank, 2006), and geologic contributions along faults, caves, or fumaroles (Lewicki et al., 2003; Camarda et al.,

- ⁵ 2007; Benavente et al., 2010). Numerical approaches considering diffusion of CO₂ in soil air have been applied to simulate the impact of transient changes in environmental variables (Nickerson and Risk, 2009a; Moyes et al., 2010) or the deployment of respiration chambers (Nickerson and Risk, 2009b,c; Ohlsson, 2010) on δ_{efflux} and, again, the disequilibrium effect. For example, CO₂ accumulating in the headspace of closed
- chambers and associated chamber-soil feedbacks can cause deviation of Keeling plots (Keeling, 1958) from linearity (Nickerson and Risk, 2009b; Kammer et al., 2011). For various soil respiration chambers, they predicted disequilibrium effects mostly ranging around several permil, with a maximum of 15‰ (Nickerson and Risk, 2009c). These effects are expected to be even larger when additionally CO₂ dissolved in soil water is involved in soil-atmosphere CO₂ transport.

The aim of the present work is to quantify the disequilibrium effect between δ_{resp} and δ_{efflux} which is related to diffusion of CO₂ in soil gas, dissolution of CO₂ in soil water and advection of soil gas. For this purpose, we present a new soil CO₂ transport model which accounts for respiratory CO₂ production, diffusion, dissolution, and advection for both ¹²CO₂ and ¹³CO₂. We investigate data from a 2-week labelling experiment with continuous day-time exposure of a grassland ecosystem to CO₂ with a δ^{13} C of -46.9‰ (Gamnitzer et al., 2009). In this experiment we measured nocturnal δ_{efflux} of the ecosystem with three independent methods: steady-state open chambers, closed chambers (both in-situ in the field), and laboratory-based cuvettes with excised

²⁵ soil+vegetation blocks. The open chamber measurements agreed with the cuvette measurements and most-likely did not exhibit a disequilibrium effect (Gamnitzer et al., 2009). Conversely, the closed chamber measurements, which employed a Keeling plot approach, deviated by ~10‰, indicating a disequilibrium effect. Since the closed chamber δ_{efflux} indicated increased tracer content compared to δ_{resp} , we applied the



soil CO_2 transport model to elucidate the mechanism(s) underlying abiotically-driven flux of tracer. We simulated the labelling experiment and predicted Keeling plot intercepts for nocturnal CO_2 accumulation in the closed chambers with the model. Simulation results were compared to observations to assess the quantitative importance of the different mechanisms underlying the disequilibrium effect. Lastly, we discuss the consequences of these mechanisms for commonly used isotopic approaches for the study of soil and ecosystem respiration.

2 Materials and methods

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2.1 Soil CO₂ transport model

The transport of CO₂ in soil pore spaces and exchange with the overlying atmosphere was simulated using a vertical (one-dimensional) soil CO₂ transport model, which also included an aboveground (shoot) respiration component. Isotopologues of CO₂ were treated as separate gases using a separate set of equations for each. The total CO₂ concentration (¹²CO₂+¹³CO₂) and the δ¹³C of CO₂ (δ¹³C=R_{sample}/R_{standard}-1, where
 R_{sample} and R_{standard} are the ¹³C/¹²C ratios in the sample and in the international VPDB standard) were calculated from modelled ¹²CO₂ and ¹³CO₂. The model was based on the following mass balance equation (Šimůnek and Suarez, 1993; Fang and Moncrieff, 1999):

$$\frac{\partial c_{\rm T}}{\partial t} = -\frac{\partial}{\partial z} (J_{\rm diff} + J_{\rm adv}) + P.$$
⁽¹⁾

 $_{20}$ J_{diff} and J_{adv} describe the CO₂ fluxes (µmol m⁻² s⁻¹) caused by diffusion in the gas phase and by advection of soil air, respectively. *P* represents the respiratory CO₂ production (µmol m⁻³ s⁻¹). *t* denotes the time (s) and *z* the depth (m) below the soil surface. c_{T} is the total CO₂ concentration (molar concentration; µmol m⁻³) in both the



gas and liquid phases and is given by

 $c_{\mathsf{T}} = c_{\mathsf{a}} \varepsilon_{\mathsf{a}} + c_{\mathsf{w}} \varepsilon_{\mathsf{w}},$

where c_a and c_w are the CO₂ concentrations (µmol m⁻³) in the gas and dissolved phase, and ε_a and ε_w the volumetric fractions (m³ m⁻³) of air and water in the soil. The total (air-filled+water-filled) porosity of the soil, ε_{tot} (m³ m⁻³), is given by

 $\varepsilon_{\rm tot} = \varepsilon_{\rm a} + \varepsilon_{\rm w}$.

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The total amount of carbon in the dissolved phase was calculated according to Wood et al. (1993) as the sum of $H_2CO_3(aq)$ (which summarises $CO_2(aq)$ and H_2CO_3 , as is commonly used) and HCO_3^- (bicarbonate). Thus,

10 $C_{\rm w} = [H_2 CO_3(aq)] + [HCO_3^-],$

where the square brackets indicate concentrations. $H_2CO_3(aq)$ and HCO_3^- represent 99.9% of the dissolved carbon species in the pH range at our study site (pH ~7.5, see Table 1). Thus, CO_3^{2-} was neglected. The chemical equilibrium reactions and constants can be expressed as (e.g., Stumm and Morgan, 1996)

¹⁵
$$\operatorname{CO}_2(g) + \operatorname{H}_2 O \rightleftharpoons \operatorname{H}_2 \operatorname{CO}_3(\operatorname{aq}), \quad K_{\mathrm{H}} = \frac{[\operatorname{H}_2 \operatorname{CO}_3(\operatorname{aq})]}{\rho_{\mathrm{CO}_2}},$$
 (5)

$$H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^-, \quad K_1 = \frac{[H^+] \cdot [HCO_3^-]}{[H_2CO_3(aq)]}.$$
 (6)

These allow the calculation of the concentrations $[H_2CO_3(aq)]$ and $[HCO_3^-]$ (mol L⁻¹) when p_{CO_2} , the CO₂ partial pressure (kPa), and the pH are known. p_{CO_2} was derived from $p_{CO_2} = RTc_a$, where *R* is the universal gas constant (8.314 kg m² s⁻² K⁻¹ mol⁻¹) and *T* the temperature (K). Numerical values for K_H , the Henry's law constant, and the equilibrium constant K_1 were taken from Stumm and Morgan (1996). Fractionation for



(2)

(3)

(4)

the dissolution of CO_2 in water was included according to Mook et al. (1974) and Vogel et al. (1970), see Mook (2000). This description of dissolution of CO_2 in soil water implies instantaneous equilibration between the gaseous and the dissolved phase.

The CO₂ fluxes were defined by

$$_{5} \quad J_{\text{diff}} = -D_{\text{soil}} \frac{\partial c_{\text{a}}}{\partial z}, \tag{7}$$

$$J_{\rm adv} = q_{\rm a} c_{\rm a}$$

 D_{soil} is the diffusion coefficient for CO₂ in soil air (m² s⁻¹), and q_{a} is the volume flux of air per unit soil area (m s⁻¹). Equation (7) corresponds to Fick's First Law. D_{soil} was derived from D_0 , the diffusion coefficient (m² s⁻¹) for CO₂ in air, according to Millington (1959),

$$D_{\rm soil} = D_0 \frac{\varepsilon_{\rm a}^{10/3}}{\varepsilon_{\rm tot}^2}.$$

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 D_0 was derived for the average soil temperature during the field experiment following Fuller et al. (1966) (see also Campbell and Norman, 1998). Fractionation during diffusion was taken into account by applying different diffusivities for the isotopologues (Cerling et al., 1991): $D_{\text{soil}}({}^{12}\text{CO}_2)/D_{\text{soil}}({}^{13}\text{CO}_2)=1.0044$. The volume flux q_a was derived from Darcy's law,

$$q_{a} = \frac{k_{a}}{\eta_{a}} \cdot \frac{\Delta p}{\Delta z},$$
(10)

where k_a is the air permeability of the soil, η_a the dynamic viscosity of air, and Δp the pressure difference occuring over the distance Δz .

For numerical solution of Eq. (1), the soil was divided into *n* horizontal layers of thickness $\Delta z = L/n$, where *L* is the total soil depth. An additional top layer (depth 0) represented the atmosphere above the soil. Respiratory CO₂ production *P* corresponded to belowground (soil) respiration in the soil layers, and to above ground (shoot) respiration



(8)

(9)

in the top (atmospheric) layer. Gravel below the soil was assumed to exhibit no respiratory CO₂ production. Porosity (ε_a and ε_w), temperature and pH were set constant with time and soil depth. The balance equation (Eq. 1) was combined with Eqs. (2–8) and discretised as

$$= D_{\text{soil}} \frac{\left(\varepsilon_{a} + \varepsilon_{w} K_{H} RT\left(1 + \frac{K_{1}}{[H^{+}]}\right)\right) \frac{c_{a}(z, t + \Delta t) - c_{a}(z, t)}{\Delta t}}{\Delta z^{2}} - q_{a} \frac{c_{a}(z, t) - c_{a}(z - \Delta z, t)}{\Delta z} + P.$$
 (11)

Solving Eq. (11) for $c_a(z,t+\Delta t)$ allows one to derive the CO₂ concentration $c_a(z,t+\Delta t)$ in each layer after a time step Δt from the concentrations before the time step Δt in that layer ($c_a(z,t)$) and in the adjacent layers below ($c_a(z+\Delta z,t)$) and above ($c_a(z-\Delta z,t)$). In the bottom layer (depth *L*), the diffusive exchange occurred only with the layer above. Diffusive exchange with the air pores in the gravel below the soil was neglected, since CO₂ concentration in the soil at depth *L* and in the gravel were identical in the steady-state. Treatment of the top layer depended on the simulated situation, see Sect. 2.3 below.

15 2.2 Field labelling experiment

10

In a 13 C/ 12 C labelling experiment, described in detail by Gamnitzer et al. (2009), a temperate grassland ecosystem at Grünschwaige Grassland Research Station (Schnyder et al., 2006) was continuously labelled for 2 weeks, using an open-top chamber system. The label was applied during daytime hours by altering the δ^{13} C of CO₂ in the cham-²⁰ ber headspace air, while CO₂ mole fraction was kept similar to ambient. The δ^{13} C of the CO₂ inside the chamber, to which the plants were exposed during photosynthesis, was -46.9%. Each night during the labelling experiment, ecosystem respiration was measured in the field using two different approaches: first, closed chamber measure



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of the two respiration measurement approaches in the field see below. In both approaches, CO_2 mole fraction and $\delta^{13}C$ were analysed in the field with an infrared gas analyser (LI 7000; Li-Cor, Lincoln, NE, USA) and a continuous-flow isotope-ratio mass spectrometer (Delta Plus Advantage; Thermo Electron, Bremen, Germany) interfaced ⁵ with a Gasbench II (providing sample gas separation via a built-in gas chromatograph, and sample and reference gas injection to the mass spectrometer; Thermo Electron, Bremen, Germany) (Schnyder et al., 2004).

2.2.1 Open chamber approach to measure ecosystem respiration

For the open chamber (more exactly termed steady-state flow-through system, Livingston and Hutchinson, 1995) respiration measurements, the chambers were flushed with air, and CO₂ mole fraction and δ^{13} C were analysed in air entering and leaving the chamber. Differences between inlet and outlet were attributed to respiratory CO₂ production of the ecosystem enclosed in the chamber according to mass balance equations. The total CO₂ flux from the ecosystem into the chamber headspace, F_{efflux} , was calculated as

$$F_{\text{efflux}} = \frac{F_{\text{air}}}{V_{\text{mol}}A_{\text{chamber}}} \cdot (C_{\text{out}} - C_{\text{in}}),$$

and the δ^{13} C of ecosystem CO₂ efflux, δ_{efflux} , as

$$\delta_{\text{efflux}} = \frac{\delta_{\text{out}} C_{\text{out}} - \delta_{\text{in}} C_{\text{in}}}{C_{\text{out}} - C_{\text{in}}}.$$
(13)

 $F_{\rm air}$ is the air flow through the chamber (corresponding to 100 L min⁻¹ at standard conditions), $A_{\rm chamber}$ the chamber base area (0.83 m²) and $V_{\rm mol}$ the molar volume of an ideal gas (22.4 L mol⁻¹ at standard conditions; adapted to site conditions for temperature and pressure). $C_{\rm in}$ and $C_{\rm out}$ are the CO₂ mole fractions (µmol mol⁻¹) at the chamber inlet and outlet, and $\delta_{\rm in}$ and $\delta_{\rm out}$ are the respective δ^{13} C values.

(12)

2.2.2 Closed chamber approach to measure ecosystem respiration

For the closed chamber (more exactly termed non-steady-state non-flow-through system, Livingston and Hutchinson, 1995) respiration measurements, the chamber air supply was disconnected. The chamber was lifted and then placed back in its origi-

- ⁵ nal position immediately before the beginning of closed chamber measurements. The lifting flushed the labelled air from the chamber headspace and replaced it with ambient air. Thus, the mole fraction and δ^{13} C of chamber headspace CO₂ at chamber closure in the labelled plots were the same as those in the unlabelled control measurements. The chamber top was then closed with a lid. Subsequently, the CO₂ mole fraction
- and δ^{13} C were monitored by analysing 6 consecutive samples (1 sample every 120 s) within a measurement cycle. Sample air was pumped continuously from the chamber headspace to the analysers at ~1.5 L min⁻¹ at standard conditions. The chamber was not sealed tightly to allow for replacement of the air removed for sampling by ambient air. The replacement air had the same mole fraction and δ^{13} C of CO₂ as the chamber
- headspace air at chamber closure. It accounted for ~3% of the total headspace volume of the chamber by the end of a measurement cycle. Thus, replacement air slightly diluted the efflux signal in the chamber headspace.

From the time course of the CO_2 increase, F_{efflux} was calculated as

$$F_{\text{efflux}} = \frac{\Delta C}{\Delta t} \cdot \frac{V_{\text{chamber}}}{V_{\text{mol}}A_{\text{chamber}}},\tag{14}$$

²⁰ where ΔC is the observed increase in CO₂ mole fraction in the chamber headspace during a time interval Δt , and V_{chamber} the chamber volume (663 L, corrected for dilution with ambient air during the measurement cycle). The δ_{efflux} was determined following the approach of Keeling (1958). The 6 samples analysed in the measurement cycle following chamber closure were pooled in one Keeling plot, resulting in an intercept reflecting ecosystem δ_{efflux} . The Keeling plot intercepts are invariant to the dilution of the efflux signal with background air.



2.3 Simulation runs

Model input parameters characterising conditions for CO₂ transport in the soil were determined for the Grünschwaige field site (Table 1). The soil of depth L=25 cm was divided into 125 layers of thickness $\Delta z=2$ mm. This high depth resolution along with short time steps Δt , ranging between 1 s and 12 s, ensured sufficient accuracy of the discrete mass balance approximation (Eq. 11). Advection was implemented as vertical (downwards) movement of soil air during daytime labelling, in accordance with an observed chamber pressurisation of 5 Pa above ambient due to high air flow during daytime (Gamnitzer et al., 2009). The impact of the dissolution of labelling CO₂ in soil water and the advection of soil air on the disequilibrium effect was investigated. For this purpose, model runs were performed including or excluding the individual mechanisms.

2.3.1 Step changes in δ^{13} C of atmospheric CO₂

This simulation investigated the disequilibrium effect that would result from changes in δ^{13} C of chamber headspace CO₂. In the labelling experiment, such changes occurred at the beginning of the closed chamber measurements, when the labelled air in the chamber headspace was substituted with ambient air. Thus, step changes of δ^{13} C of CO_2 in the atmospheric layer (δ_{atm}) from -8.5% (ambient conditions, see Fig. 1) to -46.9‰ (labelling conditions, see Fig. 1), and vice versa, were simulated. To exclude disequilibrium effects not related to changes in δ_{atm} , all other parameters (including 20 δ_{resp}) were kept constant and advection was excluded. Soil CO₂ efflux was derived from the simulated CO₂ concentration according to Fick's First Law:

$$efflux(t) = D_{soil} \cdot \frac{\Delta c_{a}(t)}{\Delta z}, \qquad (15)$$

where Δc_a is the concentration difference at the soil surface (between the air pores of the uppermost soil layer and the overlying atmosphere). The δ_{efflux} was derived from 25 the ratio of the simulated ${}^{12}CO_2$ and ${}^{13}CO_2$ effluxes.

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2.3.2 Labelling experiment and chamber-based respiration measurements

To simulate CO_2 mole fraction and $\delta^{13}C$ during the labelling experiment (Fig. 1), boundary conditions for the atmospheric layer were chosen according to the respective chamber mode. First, the model was run under ambient conditions, keeping CO_2 mole frac-

- ⁵ tion and δ^{13} C in the atmospheric layer at fixed values (371 µmol mol⁻¹ and -8.5‰, see Fig. 1), until soil profiles of CO₂ and δ^{13} C reached steady-state. Then closed chamber measurements of δ_{efflux} of the unlabelled ecosystem (control) were simulated by replacing the atmospheric layer with the chamber headspace volume, in which soil CO₂ efflux and shoot-respired CO₂ accumulated. Analogous to Keeling plot sampling
- ¹⁰ during the field measurements, 6 consecutive values of simulated atmospheric layer CO_2 mole fraction and $\delta^{13}C$ in 2 min intervals were pooled to generate a Keeling plot. Subsequently, conditions during open chamber measurements were simulated by forcing CO_2 mole fraction and $\delta^{13}C$ in the atmospheric layer to be constant for 7 h (fraction of the dark period not covered by closed chamber simulations). Then, a daytime la-
- ¹⁵ belling period of 16 h followed: the CO₂ in the atmospheric layer was kept constant at labelling conditions (367 µmol mol⁻¹ and -46.9‰, see Fig. 1), and δ_{resp} was adapted to include a fractional contribution of labelled carbon. The cycle of modelling nighttime measurements in closed and open chambers and daytime labelling was repeated, with increasing amount of label in CO₂ produced by respiration from day to day, to simulate ²⁰ the 2-week-long continuous labelling experiment.

The fraction of labelled carbon in respiratory CO₂ production was derived from open chamber measurements (Gamnitzer et al., 2009). To partition belowground (soil) and aboveground (shoot) respiratory CO₂ production (which are required as model input), three respiratory sources were distinguished. The first, decomposition of soil organic ²⁵ matter, was located in the soil, did not respire any tracer and contributed approximately half of ecosystem respiration (Gamnitzer et al., 2009). The other two sources reflected aboveground and belowground autotrophic respiration. Both supplied recently-assimilated carbon from a pool turned over with a half-life of 2.6 d (Gamnitzer et al.,



2009), and each was assumed to contribute between 20% and 80% of this recently-assimilated carbon pool.

To investigate model sensitivity, simulation runs were performed with individual input parameters varying within the ranges given in Table 1. These ranges represent the uncertainty in determination of the input parameters. Lateral diffusion was negligible in the present chamber investigation according to the requirements provided by Nickerson and Risk (2009b,c) on soil diffusivity, air-filled porosity and chamber deployment time. This was further supported by the fact that the chamber used here was about 10 times larger in diameter than the one studied by Nickerson and Risk.

10 3 Results

3.1 Experimental tracer time series of nocturnal ecosystem CO₂ efflux

The δ_{efflux} time series measured in the open chambers during the 14-day labelling period (Fig. 2, open circles) was taken to reflect that of δ_{resp} (see Introduction). Therefore, the fit to this time series (Fig. 2, solid line) was used as model input parameter for δ_{resp} . Prior to the start of labelling, measurements of δ_{efflux} with the closed chamber method (Fig. 2, black squares) did not differ significantly from that with open chambers. But during labelling, closed chamber δ_{efflux} was depleted by 11.2‰ on average compared to that of open chamber measurements. Notably, the rate of nocturnal CO₂ efflux was the same with both methods: F_{efflux} averaged 6.8±0.4 µmol m⁻² s⁻¹ (±SE, *n*=72) in the closed chamber, and 6.7±0.3 µmol m⁻² s⁻¹ in the open chamber (±SE, *n*=68; Gamnitzer et al., 2009).

3.2 Simulation of CO₂ in soil air in ambient conditions

The modelled depth profiles for CO_2 mole fraction and $\delta^{13}C$, in ambient atmospheric conditions, are shown in Fig. 3. The CO_2 mole fraction increased with depth from



371 μmol mol⁻¹ in the overlying atmosphere to 6500–18600 μmol mol⁻¹ at the bottom of the soil (Fig. 3a,c). The δ^{13} C of CO₂ changed continuously from –8.5‰ in the atmospheric layer to values between –21.6‰ and –22.1‰ at the bottom of the soil (Fig. 3b,d). The δ^{13} C profile corresponded to the theoretical mixing line (Bowling et al., 2009) between atmospheric air (–8.5‰) and soil air (–22.3‰), with the latter 4.4‰ enriched (Cerling et al., 1991) relative to δ_{resp} (–26.7‰). The gradients of both profiles were large in the top few centimeters of the soil and decreased with depth. Accordingly,

the main changes occurred above the soil collar depth of 12 cm.

Sensitivity of modelled profiles to uncertainties in input parameters was smallest for temperature, with changes of soil air CO_2 mole fraction within 170 µmol mol⁻¹ and

- changes in δ^{13} C within 0.1‰. Sensitivity was largest for the depth distribution of CO₂ production in the soil: up to a doubling of CO₂ mole fraction was predicted if production occurred deeper in the soil. In contrast, δ^{13} C varied little (within 0.3‰). All selected input parameter values provided realistic depth profiles of CO₂ mole fraction and δ^{13} C.
- ¹⁵ The amount of CO₂ in the dissolved phase was 9.5 to 34 times that in soil air. Conversely, CO₂ mole fraction and δ^{13} C in soil air were independent of dissolution (data not shown).

3.3 Simulation of step changes in δ_{atm}

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First, a step change of δ_{atm} from -8.5% (ambient conditions) to -46.9% (labelling conditions) was studied, with δ_{resp} kept constant at -26.7% (Fig. 4a). Immediately following the change of δ_{atm} , the modelled δ_{efflux} became 26.2% enriched relative to δ_{resp} (Fig. 4c). Thereafter, δ_{efflux} decreased asymptotically towards δ_{resp} . Eventually (within hours to days; see below), the soil-atmosphere system reached a new isotopic steadystate. Then, a step change in δ_{atm} in the opposite direction caused corresponding changes in the other isotopic direction (Fig. 4b), with an initial shift in δ_{efflux} to 26.2% more depleted values. Again, the system tended to a new steady-state (Fig. 4d).



These model results were derived from the independent consideration of ¹²CO₂ and ¹³CO₂ pools and fluxes (Fig. 4e-I; for clarity, the illustration is limited to the top soil layer). This included the following steps: (1) The change in $\delta_{\rm atm}$ from ambient to labelling (more ¹³C-depleted) conditions corresponded to an increase of 0.16 µmol mol⁻¹ of the atmospheric ${}^{12}CO_2$ pool and a decrease of 0.16 µmol mol⁻¹ of the atmospheric 13 CO₂ pool. (2) These changes of atmospheric CO₂ pool sizes caused changes in the differences between soil and atmospheric CO₂ pools, which led to a decreased ¹²CO₂ and an increased ¹³CO₂ diffusive soil efflux (Eq. 15). Although the changes in the CO₂ differences were small (0.16 μ mol mol⁻¹) compared to the CO₂ differences $(535 \,\mu\text{mol}\,\text{mol}^{-1}$ for ${}^{12}\text{CO}_2$ and $5.9 \,\mu\text{mol}\,\text{mol}^{-1}$ for ${}^{13}\text{CO}_2$), the relative changes in the 10 differences (and thus in the effluxes) differed for ¹²CO₂ and ¹³CO₂. This caused the change in δ_{efflux} of 26.2‰. (3) The altered fluxes, in turn, increased the soil pool of 12 CO₂ and decreased that of 13 CO₂. (4) After some time, the system attained a new steady-state with the original fluxes, but with altered ${}^{12}CO_2$ and ${}^{13}CO_2$ pool sizes. (5) The switch back to δ_{atm} of ambient air again changed the atmospheric CO₂ pool 15 sizes, in this case ${}^{12}CO_2$ was decreased and ${}^{13}CO_2$ was increased by 0.16 µmol mol⁻¹. (6) Accordingly, this led to an increased ${}^{12}CO_2$ and a decreased ${}^{13}CO_2$ soil efflux, changing δ_{efflux} to a more depleted value. Overall, this mechanism acted as a disequilibrium tracer flux: the δ^{13} C of the labelled CO₂ was transferred from the atmosphere into the soil (although both the ¹²CO₂ and the ¹³CO₂ fluxes were directed from the soil 20 to the atmosphere) and vice versa, respectively, via diffusion. It should be noted that the ¹²CO₂ and ¹³CO₂ pool sizes and fluxes changed, while total CO₂, which is the sum of both isotopologues, remained constant.

Dissolution of CO₂ in soil water delayed the attainment of the new steady-state following a change in δ_{atm} (Fig. 5). The δ_{efflux} reached δ_{resp} within 0.4‰ (corresponding to 1% of the difference between ambient and labelled CO₂) after 15.4 h when dissolution was included in the simulation, and after 49 min (19 times faster) when dissolution was excluded. This relationship of simulated equilibration times corresponded to the



ratio of total (gaseous+dissolved phase) CO_2 to gaseous CO_2 in the soil. In contrast, dissolution did not affect the magnitude of the initial change in soil CO_2 efflux. This was driven by the step change in δ_{atm} but was independent of the size of the soil CO_2 pool.

3.4 Simulated tracer time series of nocturnal ecosystem CO₂ efflux

⁵ Simulated δ_{efflux} (predicted by simulated Keeling plot intercepts; Fig. 6, dashed line) in the labelling experiment was depleted compared to δ_{resp} (Fig. 6, solid line, taken from Fig. 2). When simulations of the closed chamber measurements considered only the diffusion mechanism, then the predicted disequilibrium effect was 1.8‰ on average (Fig. 6a). When, in addition, downward advection of soil air during daytime tracer application was included, then the predicted disequilibrium effect increased to 3.6‰ (Fig. 6b). When dissolution of CO₂ in soil water was included in addition to diffusion, the predicted disequilibrium effect was 4.5‰ (Fig. 6c). When diffusion, advection and dissolution were all included in the simulation, the predicted disequilibrium effect was 9.5‰ (Fig. 6d). This largely agreed with the observed disequilibrium effect of 11.2‰ (Fig. 6, black squares; taken from Fig. 2).

The magnitude of the disequilibrium effect resulting from Keeling plot non-linearity was derived from simulations where δ_{atm} remained unchanged and advection was excluded. These conditions were met when Keeling plots were derived before the onset of labelling (see also Fig. 1). These Keeling plots yielded disequilibrium effects smaller than 0.05‰.

4 Discussion

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4.1 The mechanism underlying the ${}^{13}C/{}^{12}C$ disequilibrium between nocturnal ecosystem CO₂ efflux and ecosystem respiration

This work provides direct evidence for isotopic disequilibrium effects between nocturnal ecosystem δ_{efflux} and ecosystem δ_{resp} in a grassland tracer experiment. This



 13 CO₂/ 12 CO₂ flux disequilibrium was a transient feature. It occurred in closed chamber studies (in which the Keeling plot approach was used) and was induced by a change of δ_{atm} at the beginning of the closed chamber Keeling plot measurements. Simulations with a soil CO₂ transport model accounting for diffusion, advection and dissolution reproduced most (9.5‰) of the observed disequilibrium effect (11.2‰). In contrast, simu-

- ⁵ produced most (9.5‰) of the observed disequilibrium effect (11.2‰). In contrast, simulations excluding either dissolution or advection or both accounted for less than half of the observed disequilibrium effect. This strongly suggests that, besides diffusion, both dissolution and advection contributed significantly to the observed disequilibrium effect and, hence, that soil CO₂ pools and species other than gaseous CO₂ (e.g., dissolved)
- ¹⁰ bicarbonate) were involved. The disequilibrium effect strongly affected data interpretation in terms of ecosystem respiration, since its magnitude corresponded to ~30% of the tracer signal in our experimental study. If interpreted in terms of tracer content of soil respiration, the disequilibrium effect would have been even larger. A similar phenomenon (disequilibrium or "abiotic" tracer flux) was noted by Subke et al. (2009) ¹⁵ who used a diffusion model and a much stronger label (δ_{atm} ~23000‰ as compared to
 - -46.9‰ in our study).

The simulation of the tracer time series suggested that dissolution of CO_2 in soil water significantly influenced the magnitude of the disequilibrium effect in the present experimental study. Dissolved CO_2 represented a reservoir allowing storage of a large

- ²⁰ amount of label CO₂ in the soil in addition to CO₂ in soil air pores. Involvement of dissolved CO₂ in soil CO₂ transport processes delayed the equilibration between CO₂ in soil air and the overlying atmosphere and slowed re-equilibration of δ_{efflux} . Dissolved CO₂ was modelled as part of soil CO₂ transport assuming instantaneous exchange between gaseous and dissolved phase. This assumption was valid if the gaseous-²⁵ dissolved phase chemical equilibration was fast compared to the isotopic equilibration
- between soil air CO₂ and overlying atmosphere. The latter occured within hours to days. Presumably, gaseous-dissolved phase equilibration was much faster, as it was probably catalysed by carbonic anhydrase. Carbonic anhydrase was previously found in soil inhabitating organisms such as bacteria (Kusian et al., 2002; Mitsuhashi et al.,



2004) and fungi (Aguilera et al., 2005; Amoroso et al., 2005; Klengel et al., 2005; Mogensen et al., 2006), as well as in non-photosynthetic plant organs and tissues (Raven and Newman, 1994), particularly roots (Viktor and Cramer, 2005) and growing root tips (Chang and Roberts, 1992). Furthermore, Seibt et al. (2006) and Wingate et al.

- ⁵ (2008) provided evidence for the presence of carbonic anhydrase in the top soil, accelerating the hydration of bicarbonate by a factor of 80–1000 (which corresponded to equilibration within less than 1 s). Considering these timescales, participation of a major fraction of dissolved CO₂ in soil gas transport is likely, even if isotopic equilibrium was not fully reached. However, Reardon et al. (1979) found that δ^{13} C of CO₂ species in groundwater was consistent with complete isotopic equilibration of CO₂ in soil water
- with CO_2 in soil gas. In agreement with the suggestion of Högberg et al. (2008), the present findings provide strong evidence for (at least partial) isotopic equilibration of label CO_2 with CO_2 species dissolved in soil water.
- The capacity of the soil to store isotopically labelled CO₂ is expected to be largest ¹⁵ under alkaline conditions, as the amount of CO₂ in the dissolved phase increases with pH. At low pH values (below ~6), the concentration of dissolved carbon species is dominated by H₂CO₃(aq). The H₂CO₃(aq) concentration is constant for a given temperature and CO₂ concentration in the air, and approximately the same amount of carbon is dissolved as H₂CO₃(aq) and in the gaseous phase as CO₂, if volumes of water and air ²⁰ are equal. At pH values above ~6, HCO₃⁻ dominates the dissolved carbon species. As the HCO₃⁻ concentration increases exponentially with pH, the CO₂ storage capacity of soil water increases strongly under alkaline conditions. Then a multiple of the amount
- of carbon in the gaseous phase (CO₂) is dissolved in an equal volume of water. In the present study (pH=7.5) this factor was 12.4. In contrast, at the experimental site of Subke et al. (2009) the pH was low (4.5), indicating that dissolved CO₂ played a much
 - smaller role in that study than in our example.

Downward advection of soil air also affected our nighttime δ_{efflux} measurements, even when the measurements were performed after a phase of advective transport. Chamber headspace pressurisation during daytime tracer application (Gamnitzer et al., 2009)



presumably displaced soil air masses downwards (Lund et al., 1999), as the soil collars of the chambers restricted lateral movement.

Mechanisms which were not included in the simulation may have accounted for the residual disequilibrium effect of 1.7‰ between modelled and observed $\delta_{\rm efflux}.$ These

⁵ mechanisms included temporal changes of parameters (such as temperature, soil water content and respiration rate) during the course of the labelling experiment, diffusion in the dissolved phase, advection of soil water or incomplete isotopic equilibration between gaseous and dissolved CO₂.

4.2 Relevance to other experimental conditions

- ¹⁰ Isotopic labelling signals of similar magnitude are frequently applied in Free-Air CO₂ Enrichment (FACE) experiments, which are usually operated at δ^{13} C of elevated CO₂ between –15‰ and –20‰ (e.g., Nitschelm et al., 1997; Matamala et al., 2003; Asshoff et al., 2006; Keel et al., 2006; Pregitzer et al., 2006; Taneva et al., 2006). When FACE experiments are combined with measurements of δ_{efflux} (Torn et al., 2003; Søe et al.,
- ¹⁵ 2004; Pregitzer et al., 2006; Taneva et al., 2006) and fumigation with isotopically different CO₂ is restricted to daytime (e.g., Lewin et al., 1994; Zanetti et al., 1996; Miglietta et al., 1997; Hendrey et al., 1999; Dickson et al., 2000; Edwards et al., 2001; Miglietta et al., 2001; Reich et al., 2001; Pepin and Körner, 2002; Talhelm et al., 2007), the measurements are potentially affected by disequilibrium effects as observed in the present
- study, if these measurements are performed shortly after the nighttime switch-off of the fumigation. However, the timescale relevant for the detection of disequilibrium effects must be considered. It ranged from hours to days in our grassland experiment. This was consistent with observations in a boreal forest ecosystem, where the disequilibrium ("abiotic") tracer flux was significant for 48 h (Subke et al., 2009).
- ²⁵ In some instances chamber techniques have involved a lowering of the chamber headspace CO_2 concentration at the onset of the measurements (Flanagan et al., 1996; Buchmann and Ehleringer, 1998; Ohlsson et al., 2005). This procedure alters not only the soil-atmosphere CO_2 gradient but also the ¹²CO₂ and ¹³CO₂ gradients,



and thus δ_{efflux} , as shown by Ohlsson et al. (2005). In a theoretical investigation considering CO₂ in soil air, Nickerson and Risk (2009c) predicted a disequilibrium effect (deviation between δ_{resp} and δ_{efflux} observed with such chambers) of up to 15‰. This disequilibrium effect would be even larger when dissolution of CO₂ in soil water oc-

- ⁵ curred. This applies when the gaseous-dissolved phase chemical equilibration is fast compared to the isotopic equilibration between soil air CO₂ and overlying atmosphere (such as in the presence of carbonic anhydrase in the soil). Natural variability in atmospheric CO₂ would cause the same disequilibrium effect as a change of headspace CO₂ inside the chambers. Diurnal cycles of δ_{atm} can show amplitudes of ~10‰ (e.g.,
- ¹⁰ Schnyder et al., 2004). Using a diffusion-based model Nickerson and Risk (2009a) predicted a disequilibrium effect within 0.05‰ resulting from daytime-nighttime changes of both atmospheric CO₂ concentration and δ^{13} C. However, inclusion of the dissolution mechanism would likely multiply this disequilibrium effect.

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Table 1. Parameters characterising conditions for CO ₂ transport in the soil at the Grünschwaige ield site.				BGD 8, 83–119, 2011	
Parameter	Value (range)	Method of determination	Dap		
Porosity: Total Air-filled	0.57 (0.56–0.58) m ³ m ⁻³ 0.25 (0.23–0.27) m ³ m ⁻³	Estimated from measured wet and dry mass of defined volume of bulk soil (mean of the top 10 cm of soil layer) and an assumed density of $2.5 \mathrm{g}\mathrm{cm}^{-3}$ for solid matter	er Discus	Isotopic composition of soil respiration U. Gamnitzer et al.	
Soil CO ₂ production: Soil respiration rate	5.0 (4.0–6.0) μ mol m ⁻² s ⁻¹	Measurements of nocturnal ecosys-	sion Pap	Title	Page
Fraction produced in top 5 cm	0.8 (0.5–0.9)	Exponential distribution with depth, adapted to root mass distribution (Klapp, 1971)	er D	Conclusions	References
Temperature	16.5 (10–24) °C	Observed soil temperature (5 cm depth)	iscussi	14	▶
рН	7.5 (7.2–7.8)	K. Auerswald, unpublished data	on F		
Advection: Air volume flux per unit soil area	1.1 (0.5–5.8) 10 ^{–5} m s ^{–1}	Determined according to Eq. (10) from observed pressure difference (Gamnitzer et al., 2009) and assumed	^o aper	Back	Close
		air permeability of the soil of 10.1 $(4.85-52.5) \mu m^2$ (median and 25%-75% quantil; Ball et al., 1997; Fish and	Discus	Full Scree Printer-frier	een / Esc ndly Version
		Munkholm et al., 2005; Schjønning et al., 2007)		Interactive	Discussion



Fig. 1. Schematic sequence of labelling experiment, including chamber headspace conditions (cl.: closed) of air flow, CO_2 mole fraction and $\delta^{13}C$ of CO_2 . The latter are shown as averages observed during the labelling experiment, and were used as input parameters in the model simulation. For closed chamber headspace, values are given at chamber closure.











Fig. 3. Modelled depth profiles (thick black lines) of soil CO_2 mole fraction *C* (**a**, **c**) and isotopic composition $\delta^{13}C$ (**b**, **d**) under ambient conditions (the beginning of the labelling experiment) for soil conditions observed at the experimental field site. Sensitivity of each to variations in input parameters within the observed range (Table 1) is indicated by the thin dashed or dotted lines. Upper panels (**a**, **b**): depth profiles when depth distribution of CO_2 production in soil (dashed) and in soil respiration rate (dotted), respectively, were varied. Lower panels (**c**, **d**): depth profiles when soil porosity (dashed) and temperature (dotted), respectively, were varied.







Fig. 4. Conceptual model of the influence of a step change in δ_{atm} on δ_{efflux} . The δ_{atm} was switched from ambient (-8.5%) to labelling conditions (-46.9%) (left panels), and vice versa (right panels). (a, b) δ_{atm} (solid line) and δ_{resp} (dotted line, constant). (c, d) δ_{efflux} (solid line) and δ_{resp} (dotted line, constant). (e, f) ${}^{12}CO_2$ and (g, h) ${}^{13}CO_2$ mole fraction in the atmospheric and top soil layer, and the mole fraction difference between these two layers. Bottom (i-I): Schematic illustration of the mechanism underlying abiotic tracer diffusion, treating ${}^{12}CO_2$ and ¹³CO₂ as separate gases. Squares, atmospheric and soil CO₂ pools; arrows, CO₂ fluxes; dotted lines indicate pools and fluxes prior to the changes; numbered events in the bottom scheme (i–I) match with those in the upper panels (e–h). (i) Unlabelled system in steady-state. (j) Tracer application and associated transitions, namely (1) change in δ_{atm} to more depleted value (corresponding to more ¹²CO₂ and less ¹³CO₂), (2) change in CO₂ diffusive fluxes due to changes in soil-atmosphere CO₂ gradient, and (3) change in soil CO₂ pool due to altered fluxes. (k) Labelled system in steady-state with (4) fluxes exhibiting the original δ^{13} C. (I) Closed chamber measurement and associated transitions, namely (5) change in δ_{atm} to ambient value, (6) change in CO_2 diffusive fluxes due to changes in soil-atmosphere CO_2 gradient, and (7) change in soil CO₂ pool due to altered fluxes.













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Fig. 6. The δ_{resp} estimated from open chamber measurements (solid lines), and δ_{efflux} derived from measured (dots; error bars: SE, n=2-10) and modelled (dashed lines) Keeling plot intercepts in closed chambers. Simulations exclude (a, b) or include (c, d) dissolution of CO₂ in soil water, and exclude (a, c) or include (b, d) advection during daytime tracer application. The grey shaded areas indicate the sensitivity of modelled Keeling plot intercepts to variations of input parameters (see Table 1 for range).