Inorganic carbon fluxes across the vadose zone of planted and unplanted soil mesocosms

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Abstract

The efflux of carbon dioxide (CO$_2$) from soils influences atmospheric CO$_2$ concentrations and thereby climate change. The partitioning of inorganic carbon fluxes in the vadose zone between emission to the atmosphere and to the groundwater was investigated. Carbon dioxide partial pressure in the soil gas ($p$CO$_2$), alkalinity, soil moisture and temperature were measured over depth and time in unplanted and planted (barley) mesocosms. The dissolved inorganic carbon (DIC) percolation flux was calculated from the $p$CO$_2$, alkalinity and the water flux at the mesocosm bottom. Carbon dioxide exchange between the soil surface and the atmosphere was measured at regular intervals. The soil diffusivity was determined from soil radon-222 ($^{222}$Rn) emanation rates and soil air Rn concentration profiles, and was used in conjunction with measured $p$CO$_2$ gradients to calculate the soil CO$_2$ production. Carbon dioxide fluxes were modelled using the HP1 module of the Hydrus 1-D software.

The average CO$_2$ effluxes to the atmosphere from unplanted and planted mesocosm ecosystems during 78 days of experiment were $0.1 \pm 0.07$ and $4.9 \pm 0.07$ µmol carbon (C) m$^{-2}$ s$^{-1}$, respectively, and largely exceeded the corresponding DIC percolation fluxes of $0.01 \pm 0.004$ and $0.06 \pm 0.03$ µmol C m$^{-2}$ s$^{-1}$. Post-harvest soil respiration ($R_s$) was only 10% of the $R_s$ during plant growth, while the post-harvest DIC percolation flux was more than one third of the flux during growth. The $R_s$ was controlled by production and diffusivity of CO$_2$ in the soil. The DIC percolation flux was largely controlled by the $p$CO$_2$ and the drainage flux due to low solution pH. Plant biomass and soil $p$CO$_2$ were high in the mesocosms as compared to a standard field situation. Our results indicate no change of the cropland C balance under elevated atmospheric CO$_2$ in a warmer future climate, in which plant biomass and soil $p$CO$_2$ are expected to increase.
1 Introduction

The global flux of carbon dioxide (CO\textsubscript{2}) from the soil to the atmosphere amounts to 59–76.5 Gt carbon (C) yr\textsuperscript{-1} and is one of the largest fluxes in the global C budget (Raich and Potter, 1995; Houghton, 2007). Agriculture strongly enhances this flux, accounting for 10–12% of global anthropogenic emissions (Robertson et al., 2000; Barker et al., 2007; Vermeulen et al., 2012). The flux of CO\textsubscript{2} from the soil to the groundwater as dissolved inorganic carbon (DIC) is estimated at 0.2 Gt C yr\textsuperscript{-1} and hence much less than the upward flux of CO\textsubscript{2} (Kessler and Harvey, 2001). Agriculture enhances the DIC percolation flux by up to 4 times compared to undisturbed systems (Barnes and Raymond, 2009). Although numerous measurements have been made of either gas or aqueous phase CO\textsubscript{2} emission from cropland to the atmosphere and groundwater, respectively, few studies have investigated the total CO\textsubscript{2} emission with regard to its controls. In the light of the climate change induced by the present atmospheric concentration of CO\textsubscript{2} of 400 ppm and its increment rate of \sim 2 ppm yr\textsuperscript{-1} (IPCC, 2007; Lal, 2011), the magnitudes and underlying mechanisms of the soil CO\textsubscript{2} effluxes to atmosphere and groundwater from agricultural systems are of crucial importance for prediction of the climate forcing. The residence time of DIC in groundwater is at least as long as the residence time of groundwater which may be in the order of hundreds to thousands of years (Kessler and Harvey, 2001). The atmospheric residence time of CO\textsubscript{2} however may be as low as 5 years\textsuperscript{1} (Solomon et al., 2007; Archer and Brovkin, 2008), implying that even small changes in the C emission balance can have important effects on the atmospheric CO\textsubscript{2} concentration (Schimel, 1995). The present study explores the total CO\textsubscript{2} emission for a cropland mesocosm system and investigates the underlying mechanisms.

Dissolved inorganic C is the sum of C in carbonic acid, H\textsubscript{2}CO\textsubscript{3}\textsuperscript{*} (where H\textsubscript{2}CO\textsubscript{3}\textsuperscript{*} = CO\textsubscript{2(aq)} + H\textsubscript{2}CO\textsubscript{3}), bicarbonate, HCO\textsubscript{3}\textsuperscript{-}, and carbonate, CO\textsubscript{3}\textsuperscript{2−}. The DIC per-

\textsuperscript{1}No single lifetime can be defined for CO\textsubscript{2} because of the different rates of uptake by different removal processes (Solomon et al., 2007).
culation flux to the groundwater is closely linked to the soil partial pressure of CO₂ ($p$CO₂) via Henry’s law. In addition, the DIC percolation flux depends on the soil solution chemistry because of the pH-dependent solubility of inorganic C species, and is as such largely influenced by processes that increase soil alkalinity, e.g. the weathering of carbonate and silicate minerals (Appelo and Postma, 2005; Walmsley et al., 2011). The soil CO₂ efflux to the atmosphere, also referred to as the soil respiration, $R_s$, is a function of the soil diffusivity and the $p$CO₂. The $R_s$ integrates complex biological activity and a limited contribution from mineral reactions via the carbonate system (Kuzyakov, 2006; Trumbore, 2006). The magnitudes of biotic and abiotic production of CO₂ and DIC and their transport within the soil are therefore crucial for the determination of the total inorganic C flux from the soil.

The DIC percolation flux to the groundwater can be described by multiplying the concentration of DIC, [DIC], by the recharge flux (Appelo and Postma, 2005; Thaysen et al., 2014). The activity of DIC species in the soil solution governs precipitation and dissolution of carbonate minerals and is affected by other ions and mutually dependent chemical processes such as complexation reactions, cation exchange, mineral precipitation and dissolution, and redox reactions (Appelo and Postma, 2005). The DIC percolation flux is a function of soil type because the processes governing the chemical composition of the soil solution depend on the intrinsic soil material and climatic factors (Nordt et al., 2000).

Current knowledge describes the soil $p$CO₂ as a function of the combined respiration of microorganisms and roots and the soil gas diffusivity. Soil temperature and moisture are the main abiotic factors controlling the biological production of CO₂ (Schlesinger, 1973; Maier et al., 2011). Biological CO₂ production increases with temperature and peaks at an optimum soil moisture (Larcher, 2003) where the limiting effects of O₂ supply by gaseous diffusion and nutrient supply by aqueous phase diffusion are equal (Skopp et al., 1990). Further factors such as the overall soil nutrient content, soil mineralogy, land use history and plant phenology also play an important role for the magnitude of soil respiration (Lohila et al., 2003; Trumbore, 2006).
Diffusion of CO\(_2\) in air is about 10\(^4\) times faster than in water (Suarez and Šimůnek, 1993). Hence, frequent and heavy rains lower the gas diffusivity due to a resulting high soil water content, leading to accumulation of CO\(_2\) in air-filled pores and a reduced \(R_s\). Less intensive rains increase the \(R_s\) due to a stimulation of microbial respiration (Jassal et al., 2005; Zhang et al., 2010). Fine-textured soils have a higher water holding capacity than coarse-textured soils, and reduced gas diffusion will therefore lead to the highest \(p\)CO\(_2\) in fine-textured soils at equal water management (Suarez and Šimůnek, 1993; Lohila et al., 2003).

Plants impact the CO\(_2\) fluxes in the vadose zone in at least five ways: (1) through root respiration, (2) through release of labile organic C that in turn can stimulate or suppress microbial respiration (priming) (e.g. Kuzyakov, 2002), (3) through a changed pH in the rhizosphere (Marschner, 1995), (4) through a change in the moisture content (Sophocleous and McAllister, 1987) and (5) through binding of fine particles that changes soil physical properties (Drever, 1994). Reports on the contribution of root respiration to \(R_s\) show considerable variation, ranging from 10 to 90\% (Hanson et al., 2000).

Here, we measured upward and downward CO\(_2\) transport in both gas- and aqueous phases in unplanted and planted mesocosms to quantify the total CO\(_2\) emission from these ecosystems. The mesocosms, established to simulate the top 0–80 cm soil profile of a barley cropland, were incubated under controlled environmental conditions, allowing a model-based investigation (HP1 module, Hydrus 1-D) of the biogeochemical controls on CO\(_2\) production and transport in the soil profile prior to seeding, during growth and after harvest. Mesocosms have been shown to provide useful environments for conducting process-related research in unsaturated soil (Hendry et al., 2001; Thaysen et al., 2014). Reactive transport modelling may further increase the understanding of the coupled physical, chemical, and biological processes influencing CO\(_2\) transport within soils (Steefel et al., 2005). HP1 allows for the complex biogeochemical modelling of CO\(_2\) transport in the vadose zone by providing options for simulation of soil water content, root growth, root water and -solute uptake, as well as for gas diffusion
Emissions of CO$_2$ and DIC from unplanted and planted soil profiles may be directly compared in equally structured and textured soil maintained under controlled environmental conditions. In this study, seven mesocosms were constructed and incubated in a climate chamber. A detailed description of the experimental set-up and filling of mesocosms is given in Thaysen et al. (2014). Soil was collected from the A and C horizon of an experimental field site located in an agricultural area (Voulund, Denmark, 56°2′35.7″ N, 9°8′101.1″ E) characterized as a coarse-sandy alluvial sediment (Podzol). The soil was sieved (6 mm) and packed into plexiglas cylinders (length: 85 cm, diameter: 19 cm) (Fig. 1a). The A and C horizons were located at 0–30 and 30–78.5 cm depth, respectively. The bottom plate of the mesocosms at 82–85 cm had an embedded suction disc (thickness of 10 mm) and the hydraulic connection between the C horizon and the suction disc was optimized by means of a thin layer of quartz flour (∼ 81.5–82 cm) and a layer of quartz flour mixed with C horizon (∼ 78.5–81.5 cm).

The mesocosms were subjected to different treatments (Table 1). In mesocosms 1–3, barley (Hordeum vulgare L. cv. Anakin) was sown and CO$_2$ fluxes were investigated during growth (days 14 to 58 after sowing) and after harvest (days 58–117). In mesocosms 4 and 5, the growth period of barley was extended to 100 days with monitoring up to 78 days after sowing. Mesocosms 6 and 7 remained unplanted. In each planted mesocosm, 15 barley seeds were sown at 3 cm depth, and upon germination the seedlings were thinned to eight per mesocosm, corresponding to 280 plants m$^{-2}$.

For all planted mesocosms, frequency and amount of irrigation were adjusted to serve the need of the plants while maintaining a downward leaching. Prior to packing of and geochemical reactions of all possible chemical species, the latter being a novelty amongst vadose zone models.
mesocosms 1–3, basal nutrients were mixed into the upper 9 cm of the A horizon in the following amounts (mg kg\(^{-1}\) soil): \(\text{NH}_4\text{NO}_3\), 30; \(\text{K}_2\text{SO}_4\), 75; \(\text{CaCl}_2\), 75; \(\text{MgSO}_4 \cdot 7\text{H}_2\text{O}\), 45; \(\text{MnSO}_4 \cdot \text{H}_2\text{O}\), 10.5; \(\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}\), 5.4; \(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\), 2.1; \(\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}\), 0.2; \(\text{CoSO}_4 \cdot 7\text{H}_2\text{O}\), 0.4. Mesocosms 1–3 were irrigated with milli-Q water throughout the experiment. Mesocosms 4–7 were irrigated with milli-Q water prior to germination of barley and subsequently with a 50% strength Hoagland nutrient solution (Hoagland and Amon, 1950) with an alkalinity of 0.05 meqL\(^{-1}\). The different mode of fertilizer application in mesocosms 4–7 was implemented in order to avoid nutrient depletion of the soil during the longer duration of the experiment. Plants in mesocosms 1–3 were irrigated at 1–2 days intervals. Plants in mesocosms 4–5 were irrigated in the same manner before day 56 and thereafter daily. Unplanted mesocosms were initially irrigated in a similar way as planted mesocosms to compare the magnitude of soil respiration in unplanted and planted soil. Irrigation amounts were decreased after 24 days due to observed water logging at the mesocosm bottoms, but topsoil volumetric water content (VWC) was maintained at approximately the same level as in barley mesocosms. Maintenance of mesocosms was as in Thaysen et al. (2014).

2.2 Sampling and calculations

Due to the limited amount of replicates in this study, we report data ranges instead of averages. Ranges represent either the smallest and highest measured/calculated value for mesocosms 1–3 or both values for mesocosms 4–5.

2.2.1 Alkalinity, \(p\text{CO}_2\), temperature, water content, speciation calculations and DIC percolation

Soil water alkalinity (\(\sim\) sum of \([\text{HCO}_3^-]\) and \(2 \times [\text{CO}_3^{2-}]\)), soil \(p\text{CO}_2\), soil temperature and moisture content were determined as function of depth and time, as described in Thaysen et al. (2014). Speciation of DIC was calculated from the \(p\text{CO}_2\), alkalinity and soil temperature using PHREEQC (Parkhurst and Appelo, 2011). The weekly DIC
percolation flux in each mesocosm was estimated from calculated [DIC] at the lowest sampling depth and the measured drainage flux. When low \( p\text{CO}_2 \) was measured at the mesocosm bottoms due to high water content, the upper next sampler was used to obtain the \( p\text{CO}_2 \) value.

2.2.2 CO\(_2\) exchange

The exchange of \( \text{CO}_2 \) between the soil surface of the mesocosms and the atmosphere was measured using the static closed chamber technique (Ambus et al., 2007). A transparent cylindrical chamber \((V = 22.6 \text{ L})\) was carefully mounted gas-tight (Tersstat sealant) on the mesocosm tops. Before deployment, the chamber was filled with air of ambient \( \text{CO}_2 \) concentration. During measurement, the \( p\text{CO}_2 \) in the chamber space was closed-loop analyzed continuously with an environmental gas monitor (EGM-2, PP-Systems, Amesbury, MA, USA) (Fig. 1b) and the flux estimated from the concentration change, volume and measurement time. Carbon dioxide exchange in barley mesocosms was measured under light and in the dark to quantify net ecosystem exchange (NEE) and ecosystem respiration (ER, soil + canopy respiration), respectively. The barley plant canopy occupied an area that was approx. four times the surface area of the mesocosm, which implied careful insertion of shoots into the measurement chamber (Fig. 1). For unplanted mesocosms, only \( R_s \) was measured.

2.2.3 Radon profiles

Sedimentary produced radon-222 \((^{222}\text{Rn})\) was measured at different VWCs for each mesocosm, in order to determine the soil diffusivity. Evacuated ZnS(Ag)-scintillation cells \((V = 200 \text{ mL})\) equipped with a manometer were attached to the mesocosm gas sampling ports. Cells were removed when their inside pressure had increased to 1013 hPa. Samples were analyzed on a scintillation counter (EDA-200, CAN). The background activity of Rn-222 inside the climate chamber was measured with an Alphaguard PQ-2000 (Alphaguard, Genitron, DE) and was about 100 Bq m\(^{-3}\). Radon em-
anations rates of each soil horizon were determined in the laboratory from 5 replicate soil aliquots of 200 g through incubation in a closed container for two months and subsequent scintillation counting of an air sample from the container. Experimentally determined Rn profiles were modelled with the RnMod3d software (Andersen, 2001) using measured VWCs and Rn emanation rates, and assuming homogeneity within each soil horizon. Resulting bulk diffusivities were then used in the modeling of the CO$_2$ (Sect. 2.3), and to estimate the soil CO$_2$ production rate, $R_{CO_2}$, ($\mu$mol m$^{-2}$ s$^{-1}$) using the simplified approach of Fierer et al. (2005):

$$R_{CO_2} = \frac{D_{soil} \cdot (C_T - C_B)}{z}$$  

(1)

where $D_{soil}$ ($m^2 s^{-1}$) is the bulk CO$_2$ diffusion coefficient in the A horizon soil, $C_T$ is the concentration of CO$_2$ at the mesocosm surface ($\mu$mol m$^{-3}$), $C_B$ is the concentration of CO$_2$ at the first sampling depth ($\mu$mol m$^{-3}$), and $z$ is the depth interval (m). The variable $D_{soil}$ was determined by dividing the CO$_2$ diffusion coeffient in air with the ratio between the Rn diffusion coefficient in air and the Rn bulk diffusion coefficient for the A horizon. Equation (1) assumes isobaric conditions, no downward flux of CO$_2$ beyond the peak $pCO_2$ (located deeper than $C_B$), and CO$_2$ transport by gaseous diffusion only. It also neglects the effect of spatial differences in VWC.

2.2.4 Evapotranspiration

Weekly evapotranspiration was estimated from the difference between calculated and measured mesocosm weights. The calculated weight of a given mesocosm was obtained by subtracting the water removal due to effluent and sampling, from the sum of the mesocosm weight and the volume of irrigation water.

2.3 Modelling of CO$_2$ fluxes

In order to, determine the controls on gaseous and dissolved CO$_2$ fluxes, results from mesocosms 4–5 were modelled using the HP1 module of the Hydrus software.
(Šimůnek et al., 2006; Jacques et al., 2008). Only simulation results from mesocosm 5 (days 15–56) are presented herein. Besides the coupling between variably-saturated water flow, multicomponent transport, heat transport and biogeochemistry, particular features of the conceptual model are (i) CO$_2$ production accounting for respiration of both soil organisms and plant roots based on the SOILCO2 model (Šimůnek and Suarez, 1993; Suarez and Šimůnek, 1993), linking explicitly root respiration to root growth, (ii) cation exchange reactions and geochemical buffering by minerals, and (iii) root growth and root solute uptake.

### 2.3.1 Model setup

The mesocosm model contained three materials. The first two materials represented the A- and C horizons, respectively (Fig. 1a). The suction plate at the bottom of the mesocosm, the quartz flour layer and the layer of quartz flour mixed with the C horizon were lumped in the third material at 80–83 cm depth. The model domain was discretized in 157 nodes with the highest node densities at the mesocosm top and at the interfaces of the soil materials. Water flow was described by the Richards equation (Richards, 1931) and the constitutive relations of the van Genuchten–Mualem model without hysteresis (Mualem, 1978; van Genuchten, 1980). Upper boundary conditions for the water flow accounted for temporally-variable irrigation rates and potential evapotranspiration, which was modelled using weekly estimates (Sect. 2.2.5). At the domain bottom, a variable pressure head boundary condition was used to account for the applied suction range of −0.1 to −0.75 bar relative to atmospheric pressure (Thaysen et al., 2014). The root depth was fixed at 30 cm throughout the experiment, corresponding to a measured root depth of 30 cm on simulation day 0 (day 15 after sowing) and allocation of ~ 90 % of the root mass in the A horizon at the end of the experiment (Table 3). A normalized exponential root distribution function was employed to describe the vertical root distribution within the A horizon (Hoffmann and van Genuchten, 1983). Root water uptake was modelled using the root distribution and the S-shaped water uptake model without solute stress and default parameterization (van Genuchten, 1987).
Water retention parameters were obtained from inverse modelling of the water flow in an unplanted mesocosm (data not shown) using Hydrus 1-D (Šimůnek et al., 2013) and a global stochastic optimization algorithm (Vrugt et al., 2009).

Solute transport was modelled with the advection-dispersion equation. CO₂ transport processes included in HP1 are diffusion in the gas phase and advective-hydrodynamic dispersion in the aqueous phase. Carbon dioxide diffusion in the water and gas phase, respectively, was modelled by scaling the CO₂ diffusion coefficient in water and air with the Millington and Quirk tortuosity (Millington and Quirk, 1961). The boundary layer height was set at 0.02 m. Equilibrium CO₂ distribution between the gas and the water phase is described in HP1 by Henry’s law. More details are available in Šimůnek et al. (2006) and Jacques et al. (2008).

Heat transport was also described with an advection-dispersion equation using thermal conductivity data for sand (Chung and Horton, 1987). Soil temperatures of 22 and 18°C were chosen for the upper and lower boundary conditions, respectively, corresponding to the measured temperature decline from the top to the bottom of the mesocosm (Sect. 3.1). Day and night cycles were modelled with temperature amplitudes of 5°C.

### 2.3.2 CO₂ production and root growth

Soil CO₂ production was modelled through implementation of equations and parameters from the SOILCO2 model (Šimůnek and Suarez, 1993; Suarez and Šimůnek, 1993), making a few modifications. The total CO₂ production rate, \( S \) (mol m\(^{-2}\) s\(^{-1}\)), is considered as the sum of the production by the soil microorganisms, \( \gamma_s \) (mol m\(^{-2}\) s\(^{-1}\) g\(_{\text{DWroot}}^{-1}\) (g\(_{\text{DWroot}}^{-1}\), grams dry weight root biomass)), and the production by plant roots, \( \gamma_p \) (mol m\(^{-2}\) s\(^{-1}\) g\(_{\text{DWroot}}^{-1}\)), according to

\[
S = (\gamma_s + \gamma_p) \text{RMI}
\]  

where the subscripts s and p refer to soil microorganisms and plant roots, respectively, and RMI is the root mass index in the system (g DW). Both \( \gamma_p \) and \( \gamma_s \) were linked to
the root distribution, since microbial respiration is primed by root mass (Schlesinger, 2000; Kuzyakov, 2002; Cheng and Kuzyakov, 2005; Zhu and Cheng, 2011). It is assumed that individual CO$_2$ producing processes are additive and that it is possible to superpose individual mechanisms that reduce production from the optimal value. The production rates for microbial and root respiration at any given point in time and space are described by Eqs. (3)–(5)

\[
\gamma_s = \gamma_{s0} \prod_i f_{si} \tag{3}
\]

\[
\gamma_p = \gamma_{p0} \prod_i f_{pi} \tag{4}
\]

\[
\prod_i f_i = f(h) f(T) f_{CO_2}(c_a) f(h_\theta) f(z) \tag{5}
\]

where $\gamma_{s0}$ and $\gamma_{p0}$ are the optimum respiration rates for microorganisms and roots (mol m$^{-2}$ s$^{-1}$ g$_{DWroot}^{-1}$), respectively, and the term $\prod f_i$ multiplies all reduction coefficients. The coefficient $f(h)$ is the reduction coefficient as a function of pressure head (unitless), $f(T)$ is the reduction coefficient as a function of temperature (unitless) and $f_{CO_2}(c_a)$ is the reduction coefficient as a function of CO$_2$ concentration (reduced oxygen availability) (unitless). These coefficients are assumed to be equal for $\gamma_{s0}$ and $\gamma_{p0}$. The coefficient $f(h_\theta)$ is the reduction coefficient as a function of osmotic head (unitless) which is set to 1 for $\gamma_{s0}$ (no reduction). Expressions for all reduction coefficients except for the reduction coefficient as a function of depth in the soil profile (m$^{-1}$), $f(z)$, are identical to those in SOILCO$_2$, more details are available in Šimůnek and Suarez (1993). The coefficient $f(z)$ is described differently for $\gamma_{s0}$ and $\gamma_{p0}$, as defined below. All reduction terms have values between 0 and 1, except the $f(T)$ which is higher than 1 above 20 °C and smaller than 1 below 20 °C.
Increasing respiration and CO$_2$ production due to the evolving root mass, RMI, is described by a linear biomass increase with time:

$$\text{RMI} = R_{\text{init}} + (\text{time} \cdot r)$$ (6)

where $R_{\text{init}}$ is the initial root mass at simulation time zero (g DW root), and $r$ is the root growth rate (g s$^{-1}$).

The depth reduction factor for root respiration, $f_p(z)$, is directly linked to the modelled vertical root distribution. For the soil respiration, $f_s(z)$ is described with an exponential function (see Šimůnek and Suarez, 1993) with the $a$ parameter having a value of 0.0015 m$^{-1}$.

In SOILCO2, there is no time dependency of microbial respiration (i.e. $\gamma_s$ is not linked to RMI), and the Verhulst–Pearl logistic growth function is used to describe root growth from differences in vertical root penetration depth. The use of these assumptions revealed a poor fit to our dataset. For our simulations, $R_{\text{init}}$ and $r$ were set to 2 g DW and $2.4 \times 10^{-6}$ g s$^{-1}$, respectively, as calculated from the measured root biomass in a similar mesocosm experiment ($\sim 13.7$ g, Table 3) at 65 days after plant emergence (70 days after sowing), under assumption of linear root growth. The $\gamma_{p0}$ and $\gamma_{s0}$ parameters were set to 0.8 µmol m$^{-2}$ s$^{-1}$ g$_{\text{DW root}}^{-1}$, assuming equal contributions of microbial and root respiration (mean of reported contributions of root respiration to the total ecosystem respiration of 10–90 %, Swinnen, 1994; Hanson et al., 2000; Kocyigit and Rice, 2006; Moyano et al., 2007). When multiplied by the root mass at the end of the experiment, the sum of $\gamma_{p0}$ and $\gamma_{s0}$ resulted in a CO$_2$ production of 16 µmol m$^{-2}$ s$^{-1}$ which was within the range of the average CO$_2$ production of 15–31 µmol m$^{-2}$ s$^{-1}$ in planted mesocosms (Sect. 4.3.2). An overview of all applied parameters is given in the Supplement, Table S1.

The simulated CO$_2$ efflux from the ecosystem to the atmosphere is essentially the soil respiration, $R_s$, because there is no plant module in this conceptual model. Hence, our ER measurements could not be directly compared to the simulated CO$_2$ efflux. Anticipating that (1) canopy respiration was roughly 50 % of the total plant respiration
(Poorter et al., 1990; Loveys et al., 2002), and (2) root respiration accounted for 50% of the total $R_s$ (see above), we corrected the ER by a factor of 0.67 to get an estimate of the $R_s$.

2.3.3 Root solute uptake

Root solute uptake was simulated (not measured) based on literature values on the average plant content of major ions. Average plant nutrient contents were ($\mu$mol gDWplant$^{-1}$, from Marschner, 1995): K$^+$, 250; Ca$^{2+}$, 125; Mg$^{2+}$, 80; PO$_4^{3-}$, 60; SO$_4^{2-}$, 30; Na$^+$, 0; total N (modelled as NO$_3^-$), 1000. The daily nutrient influx per g DW root, $J$, was calculated by multiplying the average the plant nutrient content by the rate of total plant biomass increase over the experiment ($1.05 \text{gd}^{-1}$) and dividing by the total root mass at the end of the experiment ($\sim 13.7$ g, Table 3). The root mass dependent nutrient influx, $J_{\text{TIME}}$ (mol s$^{-1}$), was then obtained by multiplication of $J$ with the RMI and the normalized vertical root distribution, $f_p(z)$, (Eq. 7).

$$J_{\text{TIME}} = J \times \text{RMI} \times f_p(z)$$

Because the root length was fixed at 30 cm (Sect. 2.3.1) but the root mass within this depth increased by the RMI, root solute uptake was simulated to increase linearly over time within the A horizon.

Root cation uptake was described by simulatanous excretion of protons, except for K$^+$ for which Na$^+$ was assumed to be excreted. Anion uptake was modelled by OH$^-$ excretion. This approach for root solute uptake modelling is in agreement with general knowledge on root nutrient uptake mechanisms (Marschner, 1995).

2.3.4 Geochemistry

Aqueous speciation and complexation were accounted for using PHREEQC (Parkhurst and Appelo, 2011) and the wateq4f.dat database. Cation exchange capacities and initial compositions were as measured from soil extractions (Kjøller et al., 2004). Initial
exchanger compositions were equilibrated with a solution composition in contact with a $pCO_2$ of 1% and with 0.3 meq L$^{-1}$ alkalinity, as measured on day 15 after sowing. Charge balance of the initial solution was achieved using Li$^+$ and an equilibrium constant for the exchange reaction of log $k = -100$. Nutrient irrigation was modelled using the half-strength Hoagland solution composition.

### 2.4 Calculation of the CO$_2$ budget and the net ecosystem C balance

A CO$_2$ budget for unplanted and planted mesocosms 4–5 was calculated from the CO$_2$ flux measurements during the 78 days of experiments (non-steady state). Post-harvest CO$_2$ fluxes from mesocosms 1–3 were considered, but marked as indicative due to a shorter growth period. The cumulative ER or $R_s$ was calculated by linear interpolation between measurements. The ER was separated into soil and leaf respiration as described in Sect. 2.3.2. Total CO$_2$ production and DIC percolation fluxes were calculated by summing weekly estimates and measurements. The net ecosystem C balance, excluding C leaching losses, was calculated from the difference between NEE and harvested aboveground biomass (e.g. Kindler et al., 2011). For the calculation of the amount of biomass on day 78, a linear biomass increase with time was anticipated. Total CO$_2$ fixed by photosynthesis (GPP) was estimated using above- and belowground vegetation biomass as proxies.

### 3 Results

#### 3.1 Profiles of $pCO_2$, water content, temperature, alkalinity, DIC and pH

Levels of $pCO_2$, VWC, temperature, alkalinity, DIC and pH vs. time are shown in Fig. 2 for mesocosms, 5 (barley growth), 1 (post-harvest) and 7 (unplanted). The selected data are representative for all replicate mesocosms (see Table 1, Supplement Fig. S1). The $pCO_2$ increased steadily with plant age, peaked at 5–9% between day 40 and 60 and subsequently decreased before plants reached maturity (Fig. 2a). Post-harvest
\( p\text{CO}_2 \) declined until day 88 and then stabilized at \( \sim 1\% \) (Fig. 2b). The \( p\text{CO}_2 \) in unplanted mesocosms varied between 0.2–1.2\%, depending on depth and the highest values were about one order of magnitude lower than in barley mesocosms (Fig. 2c). Within the depth range of 25–56 cm the \( p\text{CO}_2 \) was similar, regardless of treatment (Fig. 2a–c). The \( p\text{CO}_2 \) at the top (5–7 cm) was low due to loss by diffusion to the atmosphere.

The VWC at a given depth was fairly stable throughout the experiment in all treatments (Fig. 2). The topsoil and subsoil had VWCs in the ranges 20–27\% and 7–15\%, respectively, except for the mesocosm bottom (73–76 cm) where near saturation VWCs of around 27\% were caused by water logging.

The soil temperatures declined from the top to the bottom of the mesocosms (Fig. 2) due to the proximity of heat emitting lamps at the mesocosm tops, high VWC in the A horizons and the higher heat capacity of water compared to air. The soil temperature also declined during plant growth (Fig. 2a), probably due to increased shading of the soil by a growing plant canopy. After harvest, soil temperature slowly increased again (Fig. 2b). In unplanted mesocosms, a slight decline of the soil temperature over time was also observed, probably due to slightly decreasing topsoil VWC (Fig. 2c).

The alkalinity of unplanted mesocosms remained low (0.1–0.4 meqL\(^{-1}\)) and decreased slightly towards the end of the experiment (Fig. 2c) while the alkalinity of barley mesocosms increased over time and the highest values from 0.16 to 1.9 meqL\(^{-1}\) were measured at 13–16 cm depth (Fig. 2a). Post-harvest alkalinity decreased towards the level of the unplanted mesocosms (Fig. 2b). Alkalinity was lowest in uppermost samples (5–7 cm) and in samples from the lower part of mesocosm (55–75 cm).

Changes in the [DIC] with time and depth were similar to those described for alkalinity and \( p\text{CO}_2 \). The pH remained within the range 5.7–7.0 throughout depth in all mesocosms.
3.2 Distribution of inorganic carbon between gas and aqueous phase species

The total inorganic C, distributed between gaseous and aqueous phase species (i.e. CO$_2$(g) and DIC), increased during barley growth and decreased after harvest (Fig. 3a and b, Supplement Fig. S2). Throughout time inorganic C was mainly found as CO$_2$(g) and changed little beyond 20 cm depth. A downward moving front of elevated [DIC] was not visible. The latter was expected in the middle to bottom range of the C horizon due to the downward movement of initially present pore water. In unplanted mesocosms, the distribution and amount of inorganic C hardly changed over the course of the experiment (Fig. 3c).

3.3 CO$_2$ exchange and aboveground biomass

The ER increased with time during plant growth (Fig. 4a). After harvest of the aboveground biomass, the $R_s$ declined logarithmically (Fig. 4a). The $R_s$ was much lower from unplanted than from barley mesocosms both before and after harvest and was relatively constant. The NEE increased (became more negative) with plant age up to day 54 after which it decreased to less negative values similar to those observed 20 days after sowing (Fig. 4b). Soil surface temperatures were 20–23°C during measurements (Fig. 2). The aboveground biomass in mesocosms 4–5 was 2918 ± 83 g m$^{-2}$.

3.4 DIC percolation

The cumulative amount of DIC that leached from barley mesocosms 1–3 during growth and harvest was 303–311 mmol C m$^{-2}$ at a cumulative drainage of 212–234 mm (Fig. 4c and d). This drainage corresponded to an estimated 1.8–2.0 times the initially water-filled pore volumes, with 0.6–0.7 times the water-filled pore volumes flushed during growth. The average [DIC] during the pre-harvest and post-harvest periods was 1.8–2.0 and 1.1–1.3 mmol L$^{-1}$, respectively.
In barley mesocosms 4–5, the cumulative amount of DIC leached was 344–420 mmol C m$^{-2}$ and significantly higher than the 66–82 mmol C m$^{-2}$ leached from the corresponding unplanted mesocosms (Fig. 4c and d). The cumulative drainage for barley mesocosms 4–5 and unplanted mesocosms was 139–168 mm and 141–158 mm, respectively (Fig. 4d) and corresponded to 1.3–1.5 and 1.1–1.3 times the initially water-filled pore volumes. The average [DIC] in barley mesocosms 4–5 and unplanted mesocosms was 2.5 and 0.4–0.5 mmol L$^{-1}$, respectively. The cumulative DIC percolation fluxes from planted mesocosms were highly correlated with cumulative drainage (Fig. 4d; $R^2 = 0.96–0.99$).

3.5 CO$_2$ budgets and net ecosystem C balances

The cumulative CO$_2$ efflux to the atmosphere during 78 days of experiment was 0.4–1.1 and 32.8–33.4 mol C m$^{-2}$ from unplanted and planted soil, respectively (Fig. 5). The corresponding cumulative DIC percolation fluxes of 0.080–0.082 and 0.36–0.44 mol C m$^{-2}$, respectively, were small compared to the aboveground CO$_2$ efflux. The cumulative post-harvest CO$_2$ efflux to the atmosphere during 60 days of experiment was just 2.4–2.7 mol C m$^{-2}$ at a cumulative DIC percolation flux of 0.15–0.16 mol C m$^{-2}$, increasing the relative magnitude of the cumulative DIC percolation flux compared to the cumulative CO$_2$ efflux to the atmosphere from 1.6–2.0 % during growth to 5.6–6.7 % post-harvest.

The net ecosystem C balance of the mesocosm system (i.e. the amount of C captured in total biomass minus the ER minus the harvested aboveground biomass, but excluding leaching losses) was 1 to $\sim$10.8 mol C m$^{-2}$ during 78 days of growth and 60 days of post-harvest (Fig. 5). This corresponds to an estimated annual net C loss of 12 to $\sim$130 g C m$^{-2}$. The estimated annual DIC percolation flux (based on 138 days) of 6.1–7.2 g C m$^{-2}$ yr$^{-1}$ (0.5–0.6 mol C m$^{-2}$ yr$^{-1}$) amounted to 5–60 % of the net ecosystem C balance. The net ecosystem C loss for unplanted soil during a similar period of
138 days was 0.7–1.9 mol C m\(^{-2}\) and the cumulative DIC percolation flux amounted to 7–20 % of that.

### 3.6 Soil diffusivity and CO\(_2\) production

The Rn emanation rates of the soil A and C horizons were 4.93 ± 0.46 atoms s\(^{-1}\) kg\(^{-1}\) and 2.65 ± 0.13 atoms s\(^{-1}\) kg\(^{-1}\), respectively. At a VWC of ~ 20 % in the A horizon, the Rn concentration, [Rn], in unplanted mesocosms was 1.5 times larger than in planted mesocosms, with a difference of ~ 1000 Bqm\(^{-3}\) (Fig. 6). The bulk soil diffusivity was determined by comparing measured [Rn] profiles at a given VWC with modelled [Rn] at different bulk diffusivities. The code RnMod3d could reproduce the Rn profiles in unplanted mesocosms using bulk diffusivities of 0.6 \(\times 10^{-6}\) m\(^2\) s\(^{-1}\) and 2.0 \(\times 10^{-6}\) m\(^2\) s\(^{-1}\) for the A and C horizon, respectively. For barley mesocosms, the bulk diffusivities for the A and C horizon were 2.1 \(\times 10^{-6}\) m\(^2\) s\(^{-1}\) and 1.9 \(\times 10^{-6}\) m\(^2\) s\(^{-1}\), respectively (Fig. 6).

The confidence intervals in Fig. 6 mark the range of diffusivities at which agreement between measured and modelled [Rn] could be achieved. Modelled soil bulk diffusivities of the unplanted A and C horizons showed reasonable agreement with bulk diffusivities of 0.44 \(\times 10^{-6}\) and 0.9 \(\times 10^{-6}\) m\(^2\) s\(^{-1}\), respectively, calculated from empirical formulas in Rogers and Nielson (1991) and Andersen (2000) (see Supplement, Text S1).

The CO\(_2\) diffusion coefficient in unplanted and barley mesocosms was estimated to 1.2–2.3 \(\times 10^{-6}\) m\(^2\) s\(^{-1}\) and 1.8–6.8 \(\times 10^{-6}\) m\(^2\) s\(^{-1}\), respectively, using the Rn bulk diffusivities (Eq. 1). Average soil CO\(_2\) production as calculated from the range for the A horizon bulk diffusivities was 1.0–1.8 and 15.1–31.1 µmol m\(^{-2}\) s\(^{-1}\) for unplanted and barley mesocosms 4–5, respectively, where CO\(_2\) production during barley growth increased from ~ 5 to 59 µmol m\(^{-2}\) s\(^{-1}\) (confidence intervals: 3.5–7.4 to 30–87 µmol m\(^{-2}\) s\(^{-1}\)).

### 3.7 Modelling of CO\(_2\) fluxes

The CO\(_2\) diffusivity and production estimates (Sect. 3.6) were used to simulate the measured CO\(_2\) fluxes in mesocosm 5 (barley growth). Different geochemical con-
straints were applied in three scenarios: in scenario 1 root nutrient uptake was coupled to cation exchange. Scenario 2 had cation exchange and equilibrium (saturation index = 0) for amorphous aluminium hydroxide, Al(OH)$_3$(a), as the soil solution chemistry in the mesocosms revealed a possible control by Al(OH)$_3$(a) (Supplement Fig. S3). Scenario 3 was equal to scenario 2 except that root nutrient uptake was included. The fit of scenarios 2 and 3 to measured parameters was poor (not shown) and hence the discussion of our modelling is limited to scenario 1.

Due to the dependency of the $p$CO$_2$ and the $R_s$ on the VWC, a correct description of the VWC in the mesocosms at any given point in time was crucial. The dependency of the DIC percolation flux on drainage flux implied a need for an exact simulation of the drainage flux. Both water flow and drainage flux were generally well described (Supplement Fig. S6, forward simulation from fitted parameters in unplanted mesocosm 6).

The temporal variation of the simulated $p$CO$_2$ and $R_s$ captured the main trends in the observations (Fig. 7a and 8a). However, in the upper part of the mesocosm, the simulated $p$CO$_2$ was somewhat higher than the measured up to day 36 despite a good agreement between simulated and observed topsoil water content (Supplement Fig. S6) and the $R_s$ (Fig. 8a).

A general increase in alkalinity over time was caused by the high root uptake of NO$_3^-$ that exceeded uptake of any other plant nutrients (Supplement Fig. S4) and caused a net excretion of OH$^-$. This counteracted the pH drop caused by CO$_2$ dissolution and buffered the pH around 5.6–6.0 (Fig. 7c). Mismatch between the simulated and the calculated pH were largely caused by differences between measured and simulated alkalinity and $p$CO$_2$. In addition, the $p$CO$_2$ was low due to diffusional loss of CO$_2$ which caused the near-surface pH to increase (Fig. 7c).

Scenario 1 simulated increasing [Al$^{3+}$] and [Ca$^{2+}$] with time that approached the measurement on day 71 (Fig. 7d and 8g, respectively). Increasing [Al$^{3+}$] resulted from displacement of exchanger-bound Al by cations in the incoming nutrient solution. Low pH and high [Al$^{3+}$] led to supersaturation of Al(OH)$_3$(a) (not shown), in accordance with Supplement Fig. S3. Calcium was displaced on the A horizon exchanger as well.
(Fig. 7e), resulting in increasing $[\text{Ca}^{2+}]$ with time. However, the largest increase in $[\text{Ca}^{2+}]$ resulted from irrigation with nutrient solution and subsequent upconcentration due to evapotranspiration (Fig. 7g). Hence, near the soil surface, evaporation processes increased ion concentrations (see tracer simulation, Supplement Fig. S5). Root uptake rates of $\text{Ca}^{2+}$ (and other nutrients) were small compared to $[\text{Ca}^{2+}]$ in the soil solution (Fig. 7h, Supplement Fig. S3) but the accompanying release/uptake of protons had a big impact on the soil alkalinity and pH (Fig. 7b and c). Exchanger-bound Al and Ca were displaced by K (not shown), probably due to higher $[\text{K}^+]$ in the nutrient solution compared to other ions, and the high ionic strength of the nutrient solution (13.9 mmol kg$^{-1}$ water) (Appelo and Postma, 2005).

4 Discussion

In this work, we have quantified the inorganic C dynamics in planted and unplanted soil mesocosms representing the vadose zone of a cultivated podzol. The data were generated from a detailed collection of gaseous and aqueous samples and from subsequent modelling enabled by the novel implementation of SOILCO2 into HP1. We show that inorganic C dynamics in ecosystems are not well described from measurements of the CO$_2$ pools and fluxes alone, and that biogeochemistry has a potentially major impact on the movement of dissolved CO$_2$ in the vadose zone. In the following section, our results are discussed in the context of soil type effects on CO$_2$ fluxes and differences between mesocosm and field studies are addressed.

4.1 Soil respiration: gaseous CO$_2$ efflux and soil pCO$_2$

In general, there was a good agreement between measurements on soil pCO$_2$ and $R_s$ from the same treatment (i.e. growth period, post-harvest or unplanted). Also, the soil pCO$_2$ showed similar development over time as the ER and $R_s$ (Fig. 4a), and the CO$_2$ production estimates (Sect. 3.6) matched the measured ER and $R_s$. 

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Soil respiration in unplanted mesocosms (−3 to 3.2 μmol m$^{-2}$ s$^{-1}$) and pCO$_2$ (0.2–1.2 %) was generally in agreement with field studies on a range of different arable soils (Table 2a). In barley mesocosms, the pCO$_2$ (0.2–8.8 %) and the ER (0.8 to 52 μmol m$^{-2}$ s$^{-1}$) were generally higher than in published field studies (Table 2b) but were in accordance with pot-grown barley in humic clay (Simojoki et al., 1991). Higher respiration rates in mesocosms were probably a function of a larger plant biomass than in the field, as also observed by Simojoki et al. (1991). The aboveground biomass was elevated ~3–4 times (Lohila et al., 2003; Walmsley et al., 2011) and the root biomass, as determined in another series of mesocosm experiments with barley (Table 3), was ~2–5 times the values reported from field studies (Barraclough and Leigh, 1984; Xu and Juma, 1992; Malhi and Gill, 2002). The higher biomass in mesocosms probably resulted from ideal growth conditions. In addition, fewer neighbouring plants in mesocosm experiments triggered tillering and horizontal leaf orientation due to the plant-light response (Taiz and Zeiger, 2002) and decreased mutual shading of the leaves on a bigger area. As a result, the area of canopy surface coverage of the aboveground biomass was visually estimated to be approximately four times larger than the mesocosm surface from which the ER was calculated (Sect. 2.2.1, Fig. 1). The high ER (and pCO$_2$) were a function of the accelerated plant growth as photosynthesis increases with increasing leaf area (Lohila et al., 2003) and light exposure (Taiz and Zeiger, 2002) and as the magnitude of the ER depends on the photosynthesis (Kuzyakov and Cheng, 2001; Vargas et al., 2010). In addition, soil respiration will also have been influenced by the 3 to 5 °C higher day- and night time temperatures in the growth room than present in the field (e.g. Kotroczo et al., 2008).

The soil pCO$_2$ and CO$_2$ efflux to the atmosphere were about one order of magnitude higher in planted mesocosms than in unplanted mesocosms at peak time (Figs. 2a, b, and 4a). As previously shown by Lee (1997) this revealed a strong impact of vegetation on CO$_2$ dynamics in the unsaturated zone. Post-harvest pCO$_2$ and $R_s$ were higher than from unplanted soil, indicating a stimulation of microbial respiration by root-derived substrates (Kuzyakov, 2002). Respiration rates after harvest were within the range of
previously reported $R_s$ from sandy soil ($\sim 0.5 \mu$molCm$^{-2}$s$^{-1}$) (Heitkamp et al., 2012) and silty clay loam (1–11 μmolm$^{-2}$s$^{-1}$) (Moyano et al., 2007). The relatively high post-harvest $R_s$ and its rapid decline are in accordance with the high root biomass in mesocosms combined with a fast depletion of labile C from sandy soil (Heitkamp et al., 2012).

4.2 Percolation: DIC fluxes and soil alkalinity

The DIC percolation flux was calculated from the alkalinity, the $p$CO$_2$ at the mesocosm bottom and the drainage flux and was primarily a function of the latter two variables. The smaller effect of alkalinity on the downward DIC flux was caused by the low soil pH that shifted DIC primarily towards H$_2$CO$_3^-$ (Fig. 3). The absence of a downward moving DIC front was caused by the fact that H$_2$CO$_3^-$ is a direct function of the $p$CO$_2$ that was constant with depth (Fig. 2a–c).

The higher $p$CO$_2$ in barley mesocosms caused about four times higher DIC percolation flux than in unplanted mesocosms at similar drainage (Fig. 4c and d). Average post-harvest [DIC] were significantly higher than the average [DIC] in the percolation water from unplanted soil but may have partly been influenced by high [DIC] during plant growth due to incomplete exchange of the initial water-filled pore volume of during barley growth in mesocosms 1–3. The latter implies that high [DIC] arising from high $p$CO$_2$ conditions at the mesocosm top during barley growth was not transported all the way to the mesocosm outlet.

The measured alkalinity in mesocosms was typical for streams fed by leachates from sandy soils in western Denmark (−0.2 to 1.6 meqL$^{-1}$) (Rebsdorf et al., 1991). The mean [DIC] in these streams of 0.74 mmolL$^{-1}$ was at the lower range of our results, probably due to degassing of CO$_2$ from streams and/or lower $p$CO$_2$ in field than in planted mesocosms.

The DIC percolation flux and the average [DIC] under barley were within the range of reported values for cropland soil (Table 4). Further comparison of the [DIC] in the
percolation water is impeded by the numerous factors influencing soil $pCO_2$ and the [DIC] (see Sects. 1 and 4.1). The DIC percolation flux from unplanted soil was similar to the previously reported percolation fluxes from sandy forest soils (Kindler et al., 2011).

4.3 CO$_2$ budgets, net ecosystem C balances and controls on CO$_2$ fluxes in the vadose zone

CO$_2$ budgets were estimated to outline the main tendencies in the relative magnitudes of CO$_2$ fluxes in and from cropland prior to seeding, during growth, and after harvest, (Fig. 5). The budgets revealed a pivotal influence of vegetation on CO$_2$ fluxes in the vadose zone as both upward and downward transport of CO$_2$ was strongly increased in planted mesocosms. The cumulative DIC percolation flux was small relative to the cumulative $R_s$. Results from planted mesocosms (1.6–2.0 %) were higher than the global emission flux partitioning (0.26 %) (Raich and Potter, 1995; Kessler and Harvey, 2001) but lower than a 2.5 % fraction reported for an onion field (Sawamoto et al., 2003). The relatively higher ratio between cumulative DIC percolation flux and the cumulative $R_s$ in unplanted mesocosms (Fig. 5) resulted from lower cumulative $R_s$ in unplanted soil that was further decreased by periods of net uptake of CO$_2$ (Fig. 4a). Net uptake also caused the disagreement between the CO$_2$ production estimate and the cumulative $R_s$.

The estimated net ecosystem C balance of 12 g C loss m$^{-2}$ yr$^{-1}$ to −130 g C gain m$^{-2}$ yr$^{-1}$ (1 to −10.8 mol C m$^{-2}$) in planted mesocosms was in agreement with reported field data (e.g. seven European croplands, 95 ± 87 g C m$^{-2}$ yr$^{-1}$ (Kutsch et al., 2010); 15 European croplands, 138 ± 239 g C m$^{-2}$ yr$^{-1}$, Ceschia et al., 2010). The cumulative DIC percolation flux constituted ~5–60 % of the net ecosystem C balance, in agreement with a reported 14–20 % for the field (Kindler et al., 2011). Percolation of dissolved organic C was not considered in our study but may be of similar magnitude as DIC percolation (Kindler et al., 2011) and thus might have increased the role of the C emission flux to the groundwater.
Our findings are important in the context of climate change. In a future with elevated atmospheric $p$CO$_2$ and global warming, plant biomass and soil $p$CO$_2$ can be expected to increase (Dieleman et al., 2012). Our findings indicate that increased plant biomass and soil $p$CO$_2$ induce no change of the net C balance of croplands. Increased weathering of soil minerals by elevated $p$CO$_2$ (Karberg et al., 2005) can be expected to have only marginal effects on DIC export to groundwater beneath cropped acidic soils, but the process can be expected to gain significance in carbonated soils. The potential for increasing the DIC export to the groundwater by irrigation is substantial after harvest where the absence of plant transpiration facilitates fast percolation of water through the soil and where relatively high soil $p$CO$_2$ may transmit to increases in the [DIC].

The interpretation of CO$_2$ fluxes in mesocosms needs to take into account the high plant biomass density in mesocosms, the constant summer conditions in the climate chamber and the coarse-sanded, acidic soil of this study. Elevated biomass of plants grown at relatively high temperature increased the soil respiration which again increased both upward and downward flux of CO$_2$. Smaller [Rn] in barley mesocosms (Fig. 6) indicated that root growth and decay increased the soil diffusivity (by $\sim 1.5 \times 10^{-6}$ m$^{-2}$ s$^{-1}$). This may have enhanced the $R_s$, implying a decreased net uptake of atmospheric CO$_2$ (NEE) by the plant-soil ecosystem. Increased diffusivity due to the presence of biopores and cracks has indeed been reported (Holford et al., 1993; Hoff, 1997). However, some reduction in the [Rn] in planted soil may have been caused by Rn removal via plant transpiration (Lewis and MacDonell, 1990; Jayaratne et al., 2011). In any case, the high soil diffusivity of the coarse sand and the relatively low soil pH of $\sim 6$ caused much less downward transport of DIC compared to the CO$_2$ loss to the atmosphere (Fig. 5).

Modelling of the CO$_2$ fluxes was a valuable tool for narrowing down the number of processes behind the observed evolution in the dissolved CO$_2$ fluxes. Scenario 1 (root nutrient uptake coupled to cation exchange) was in accordance with previous demonstrations of slight soil alkalization when nitrate is the dominating inorganic N species (Marschner et al., 1991; Weligama et al., 2010). However, our modelling of
the nutrient uptake remains somewhat uncertain due to lack of data for actual nutrient uptake. Other buffering processes e.g. by dissolution of pieces of lime (Fig. S3) are possible.

5 Conclusions

The DIC percolation flux of \(\sim 5 \text{ mmol C m}^{-2} \text{ d}^{-1}\) during barley growth was \(\sim 1.6–2.0\,\%\) of the \(R_s\) at increased plant biomass and elevated soil \(p\text{CO}_2\) compared to the field situation. After harvest, the magnitude of the DIC percolation flux was lowered to \(\sim 2.5 \text{ mmol C m}^{-2} \text{ d}^{-1}\) but the importance of DIC percolation flux for the overall cropland \(\text{CO}_2\) emission increased to \(\sim 6–7\,\%\) of the \(R_s\). At constant conditions of temperature and water content, the \(R_s\) was controlled by the production and diffusivity of \(\text{CO}_2\) in the soil, both of which were increased by plant growth. The DIC percolation flux was primarily controlled by the recharge flux and the \(p\text{CO}_2\) due to the low soil pH in the acidic soil of our study.

Our findings indicate that the \(\text{CO}_2\) emission partitioning between \(R_s\) and DIC percolation, and the net C balance of croplands do not change in response to increased atmospheric \(p\text{CO}_2\) and global warming. In regions of high precipitation after crop harvest climate change may be mitigated by an increase in the DIC percolation flux. Further research is needed to support our findings. Our study showed that the integration of experimental and modelling work is a powerful tool in advancing process-understanding of \(\text{CO}_2\) fluxes in the vadose zone.

Supplementary material related to this article is available online at http://www.biogeosciences-discuss.net/11/4251/2014/bgd-11-4251-2014-supplement.pdf.
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References


Inorganic carbon fluxes across the vadose zone

E. M. Thaysen et al.


Hoff, A.: Radon transport in fractures soil: laboratory experiments and modelling, Risø-R-975(EN), Risø National Laboratory, Roskilde, Denmark, 1997.


Table 1. Overview over mesocosm experiments. Periods in brackets for the post-harvest experiment indicate that the experiment was the consecutive of the barley growth experiment.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Mesocosm</th>
<th>Duration of experiment (days)</th>
<th>Fertilization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barley growth</td>
<td>1–3</td>
<td>58</td>
<td>Addition to soil prior to experiments</td>
</tr>
<tr>
<td></td>
<td>4–5</td>
<td>78</td>
<td>Nutrient irrigation</td>
</tr>
<tr>
<td>Post-harvest</td>
<td>1–3</td>
<td>60 (days 59–118 after sowing)</td>
<td>Addition to soil prior to experiments</td>
</tr>
<tr>
<td>Unplanted</td>
<td>6–7</td>
<td>78</td>
<td>Nutrient irrigation</td>
</tr>
</tbody>
</table>
Table 2a. Ranges of $pCO_2$ and soil respiration ($R_s$) in unplanted mesocosms as compared to other studies (one in pots, four in the field). NA = Not available, VWC = Volumetric water content.

<table>
<thead>
<tr>
<th>$pCO_2$ (%)</th>
<th>$R_s$ (µmol m$^{-2}$ s$^{-1}$)</th>
<th>Crop</th>
<th>Soil type</th>
<th>Soil texture</th>
<th>Soil surface temperature (°C)</th>
<th>Daytime air temperature (°C)</th>
<th>VWC (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2–1.2</td>
<td>−3.0–3.2</td>
<td>Fallow</td>
<td>Podzol</td>
<td>Coarse sand</td>
<td>22–23</td>
<td>18</td>
<td>20–25</td>
<td>This study (mesocosms)</td>
</tr>
<tr>
<td>NA</td>
<td>~0.7–1.5</td>
<td>Fallow</td>
<td>Gleyic Cambisol</td>
<td>Sandy soil</td>
<td>18–22</td>
<td>NA</td>
<td>NA</td>
<td>Weihermüller et al. (2009) (pot experiment)</td>
</tr>
<tr>
<td>NA</td>
<td>~0.05–3.7</td>
<td>Fallow</td>
<td>Arenosol</td>
<td>Sandy soil</td>
<td>3–20</td>
<td>−10–28</td>
<td>10–25</td>
<td>Herbst et al. (2008)</td>
</tr>
<tr>
<td>0.5 ± 0.1</td>
<td>NA</td>
<td>Fallow</td>
<td>Fine montmorillonitic, mesic Udolic Pchraqualfs</td>
<td>Silt loam</td>
<td>15–20</td>
<td>13–15</td>
<td>27–30</td>
<td>Buyanovsky and Wagner (1983)</td>
</tr>
<tr>
<td>NA</td>
<td>1.5–8</td>
<td>Fallow</td>
<td>Orthic Humic Gleysol</td>
<td>Loam</td>
<td>10–26</td>
<td>NA</td>
<td>25–40</td>
<td>Rochette et al. (1992)</td>
</tr>
</tbody>
</table>
Table 2b. Ranges of $pCO_2$ and ecosystem respiration (ER) during growth in barley mesocosms as compared to field studies. NA = Not available, VWC = Volumetric water content.

<table>
<thead>
<tr>
<th>$pCO_2$ (%)</th>
<th>ER (µmol m$^{-2}$ s$^{-1}$)</th>
<th>Crop</th>
<th>Soil type</th>
<th>Soil texture</th>
<th>Soil surface temperature (°C)</th>
<th>Daytime air temperature (°C)</th>
<th>VWC (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2–8.8</td>
<td>0.8–52</td>
<td>Barley</td>
<td>Podzol</td>
<td>Coarse sand</td>
<td>20–24</td>
<td>18</td>
<td>20–25</td>
<td>This study (mesocosms)</td>
</tr>
<tr>
<td>2–6</td>
<td>NA</td>
<td>Barley</td>
<td>Podzol</td>
<td>Coarse sand</td>
<td>~7 to 29 (mean ~ 8)</td>
<td>8 (mean)</td>
<td>6–34</td>
<td>Our field site</td>
</tr>
<tr>
<td>0.3–2</td>
<td>NA</td>
<td>Barley</td>
<td>Eutric Cambisol</td>
<td>Coarse sandy loam over gravelly sand</td>
<td>NA</td>
<td>~ 9.3 (mean)</td>
<td>~ 17–33</td>
<td>Walmsley et al. (2011)</td>
</tr>
<tr>
<td>NA</td>
<td>0.2–16</td>
<td>Barley</td>
<td>Haplic Phaeozem</td>
<td>Silty clay loam</td>
<td>~2 to 22</td>
<td>NA</td>
<td>21–27</td>
<td>Moyano et al. (2007)</td>
</tr>
<tr>
<td>NA</td>
<td>2.3–7.5</td>
<td>Barley</td>
<td>Orthic humic Gleysol.</td>
<td>Loam</td>
<td>10–19</td>
<td>NA</td>
<td>10–35</td>
<td>Rochette et al. (1992)</td>
</tr>
</tbody>
</table>
Table 3. Root mass distribution as a function of depth in mesocosms measured 70 days after sowing in a later experiment.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Root mass (g DW) (means ± SE)</th>
<th>Root mass per soil horizon (%)</th>
<th>Root mass density (g m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–10</td>
<td>8.1 ± 0.5</td>
<td>91.7 ± 0.9</td>
<td>527.4 ± 14.7</td>
</tr>
<tr>
<td>10–20</td>
<td>3.5 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20–30</td>
<td>2.6 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30–42</td>
<td>0.5 ± 0.1</td>
<td>8.3 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>42–58</td>
<td>0.3 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>58–80</td>
<td>&lt; 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crop</td>
<td>Annual DIC Percolation (g C m⁻² yr⁻¹)</td>
<td>Drainage (mm yr⁻¹)</td>
<td>Average DIC (mmol L⁻¹)</td>
</tr>
<tr>
<td>--------------------------</td>
<td>----------------------------------------</td>
<td>--------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>Soybean/winter wheat</td>
<td>7.6–8.0</td>
<td>782</td>
<td>0.8–0.9 (dissolved CO₂ only)</td>
</tr>
<tr>
<td>Onion</td>
<td>13.2</td>
<td>1200</td>
<td>0.9</td>
</tr>
<tr>
<td>Cropland, not further specified</td>
<td>~1.9–10.2 (estimated from figure)</td>
<td>241–537</td>
<td>~0.7–1.6 (estimated from figure)</td>
</tr>
<tr>
<td>Cropland, not further specified</td>
<td>19.4</td>
<td>975</td>
<td>1.7</td>
</tr>
<tr>
<td>Maize</td>
<td>9.2–18</td>
<td>~250–400 (estimated from figure)</td>
<td>3–3.8</td>
</tr>
<tr>
<td>Winter wheat/winter barley</td>
<td>2.0</td>
<td>88</td>
<td>1.9</td>
</tr>
<tr>
<td>Spring barley</td>
<td>20.1</td>
<td>603</td>
<td>2.8</td>
</tr>
<tr>
<td>Barley</td>
<td>4.3–5.3*</td>
<td>139–168</td>
<td>2.5</td>
</tr>
<tr>
<td>Cropland, not further specified</td>
<td>13.3</td>
<td>189</td>
<td>5.9</td>
</tr>
</tbody>
</table>

* DIC percolation fluxes in mesocosms 4–5 during a growth period of 78 days.
Fig. 1. Mesocosm system with barley plants and sampling ports for gas and water sample collection, soil moisture and temperature measurement (A) and setup for CO₂ exchange measurements (B). During experiments, mesocosms were shaded from light with dark plastic bags (B).
Fig. 2. Time course of \( p\text{CO}_2 \), volumetric water content (VWC), temperature, alkalinity (Alk.), DIC and pH on measurement days throughout depth in barley mesocosms (exemplified by mesocosm 5) (A), after harvest (mesocosm 1) (B), and in unplanted mesocosm 7 (C). Measurements at 45 and 63 cm depth were excluded for clarification of the figure but followed the same trends as measurements at 13–56 cm. Note the different x axis scale for the subfigures.
Fig. 3. Distribution of DIC species and CO$_2$(g) at the start (day 15 AS; AS = after sowing) and the end (day 71 AS of the experiments) in mesocosms with barley as exemplified by mesocosm 5 (A), just after harvest (day 4 AH; AH = after harvest) and at the end (day 60 AH) of the harvest in mesocosm 1 (B), and at the start (day 15) and the end (day 71 of the experiments) in unplanted mesocosm 7 (C). The concentration of carbonate was negligible compared to the other species and is not shown. Note different x axis scale for unplanted mesocosms.
Fig. 4. Gaseous and dissolved CO₂ fluxes from mesocosms. (A) Ecosystem respiration (ER) from barley mesocosms 1–5 during growth (black) and soil respiration (Rₛ) from barley mesocosms 1–3 after harvest and unplanted mesocosms (grey tones). (B) Net ecosystem exchange (NEE) from mesocosms with barley. (C and D) Cumulative DIC percolation flux as a function of time and cumulative drainage, respectively.
**Fig. 5.** Estimated CO$_2$ budget for unplanted and cropped soil. Ranges result from estimates for the two replicate mesocosms and, for CO$_2$ production, from the confidence interval of the diffusion coefficient. Figures in parenthesis are estimates for post-harvest CO$_2$. Post-harvest CO$_2$ production was unknown (“X”). All figures in mol C m$^{-2}$. $R_s =$ soil respiration.
Fig. 6. Measured and modelled Rn profiles in planted mesocosms and unplanted mesocosms. Open symbols indicate Rn measurements taken at lower volumetric water content (VWC) than the remaining samples. Grey shaded areas designate model calculations carried out with diffusivities within the stated confidence intervals (see text).
Fig. 7. Measured (full lines) and simulated (dashed lines) temporal variation of soil air $pCO_2$ (A), alkalinity (B), pH (C), $Al^{3+}$ (D), $CaX_2$ (E), $AlX_3$ (F), $Ca^{2+}$ (G), and $Ca^{2+}$ root uptake (H) in barley mesocosm 5. Geochemical reactions in simulations were described by root nutrient uptake and cation exchange (scenario 1).
Fig. 8. Measured and modelled time course of soil respiration ($R_s$) (A) and cumulative DIC percolation flux in barley mesocosm 5 modelled with root nutrient uptake and cation exchange (B). Small fluctuations in the simulated $R_s$ around the baseline arise from diurnal temperature variations. Large peaks in the simulated $R_s$ arise from irrigation that causes a stimulation of microbial respiration and displaces CO$_2$ rich air in the soil. Measurements of $R_s$ were carried out more than 3 h after irrigation events where the effect of irrigation was expected to have ceased. Hence it is the simulated baselines of the $R_s$ that should be compared to measurements.