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Elevated air carbon dioxide concentrations increase dissolved carbon leaching from a cropland soil

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Abstract Increasing leaching losses of carbon from soils due to accelerated weathering and increasing concentrations of dissolved carbon as a result of intensified soil respiration are suspected to provide a negative feedback on rising atmospheric CO_2 concentrations. We tested this hypothesis by studying concentrations of dissolved carbon and groundwater recharge at the Braunschweig free air carbon dioxide enrichment (FACE) experiment under winter wheat and winter barley. Dissolved carbon concentrations under elevated atmospheric CO_2 and ambient conditions were rather similar and not consistently higher under FACE. An analysis of δ^{13}C signatures suggested that dissolved organic and inorganic carbon contained 9–29% (DOC) and 26–49% (DIC) of "new" carbon originating from CO_2 added to the FACE rings. Dissolved inorganic carbon additionally contained 15–42% of carbonate-derived C. A 15% reduction in evapotranspiration under elevated CO_2 increased groundwater recharge by 60 mm or 55%, which was the main driver for an observed 81% increase in dissolved carbon leaching from 2.7 to 4.9 g C m^{-2} $year^{-1}$ at 90 cm depth. Our results suggest that future changes of dissolved carbon leaching losses will be mainly governed by changes in climate and groundwater recharge and to a lesser extent by increasing dissolved carbon concentrations.

Keywords Free air carbon dioxide enrichment · Dissolved organic carbon · Dissolved inorganic carbon · Net biome productivity · Net ecosystem carbon balance · Carbon sequestration

Introduction

Photosynthetic carbon fixation by ecosystems drives the accumulation of organic matter and weathering of minerals in soils (e.g., Chadwick et al. 1994). The

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subsequent leaching of dissolved inorganic carbon (DIC) during soil development diverts carbon from the fast cycling between atmosphere and biosphere into slower pedological and geological carbon cycles (Chadwick et al. 1994). The consumption of atmospheric CO_2 during weathering reactions of silicates and carbonates has been put forward as an (partial) explanation for long-term fluctuations of atmospheric CO_2 concentrations (e.g., Pagani et al. 2009) or large scale gradients of CO_2-exchange between continents, oceans and atmosphere (e.g., Aumont et al. 2001). In addition to long-term and large-scale carbon cycling, leaching losses of dissolved carbon from soils have recently been shown to affect annual carbon budgets of particularly croplands and grasslands (Kindler et al. 2011). Leaching losses of dissolved carbon represented on average 51% (croplands, median: 25%) or 36% (grasslands, median: 21%) of the balance between photosynthetic carbon uptake and carbon gains with organic fertilizers on the one hand and carbon losses with respiration and harvest on the other hand (Kindler et al. 2011).

The current trend of increasing concentrations of atmospheric CO_2 likely stimulates photosynthetic carbon fixation and plant biomass production (Burkhart et al. 2009; Leakey et al. 2009; Manderscheid et al. 2009). Increasing root respiration and rising inputs of litter and root exudates into soil under elevated CO_2 together with decreasing soil aeration due to higher water contents may cause increasing partial pressures of CO_2 in soil air (Bader and Körner 2010; Bernhardt et al. 2006; Karberg et al. 2005; King et al. 2001; Oh et al. 2005). According to Henry's law, rising partial pressures of soil air CO_2 will increase concentrations of carbonic acid (H_2CO_3) in soil solution, which accelerates soil acidification and mineral weathering (Oh and Richter 2004) and increases concentrations of DIC in leachate (Karberg et al. 2005). Accelerated weathering of minerals and increasing export of DIC from terrestrial ecosystems to surface waters and oceans have been suggested to slow down the rate by which the atmospheric CO_2 concentration is increasing over long time scales (Andrews and Schlesinger 2001; Karberg et al. 2005). For the study of Andrews and Schlesinger (2001), the reported increase of DIC concentrations and leaching under FACE was, however, later identified as an experimental artifact caused by the spatial heterogeneity of soil properties among the FACE rings (Oh et al. 2007). Oh et al. (2007) therefore conclude that the entirely plausible hypothesis of enhancement of chemical weathering and DIC leaching due to increasing concentrations of atmospheric CO_2 remains to be conclusively tested under field conditions. This is particularly true for agricultural ecosystems, which represent an important fraction of global land use and for which no study has yet investigated effects of atmospheric CO_2 concentrations on DIC dynamics. Such test is also desirable because larger-scale and long-term phenomena like increasing alkalinity and CO_2 concentrations of groundwater are potentially linked to interactions between atmospheric CO_2 concentrations and DIC (Macpherson et al. 2008).

Carbon is leached from soils not only as DIC but also as dissolved organic carbon (DOC). In the above mentioned forest FACE experiments, no CO_2-effect on DOC concentrations of soil solutions could be detected (King et al. 2001; Oh et al. 2007). Also Hagedorn et al. (2002, 2008) did not observe an effect of elevated atmospheric CO_2 on DOC concentrations in mineral soil horizons. In organic surface horizons (Hagedorn et al. 2008) and peat (Freeman et al. 2004), however, CO_2 enrichment increased DOC concentrations suggesting that sorption of DOC in mineral soils might dampen the positive CO_2-effect on DOC production (Hagedorn et al. 2008). Zhong et al. (2009) reported an increase of water extractable organic carbon concentrations by 25% (fertilization: 174 kg N ha^{-1}) or 31% (fertilization: 350 kg N ha^{-1}) as a consequence of FACE for a Chinese wheat field.

The added CO_2 in FACE experiments is commonly derived from burned natural methane gas, which is strongly depleted in ^{13}C. This depletion leads to an isotopic labeling of plants, soil organic matter, dissolved organic matter and DIC in these experiments. In addition to insights regarding the effect of elevated atmospheric CO_2 concentrations on the DOC- or DIC-concentrations in leaching water, the FACE experiments therefore allow the tracking of their sources by interpretation of their $\delta^{13}C$ signature (Andrews and Schlesinger 2001; Hagedorn et al. 2002; Karberg et al. 2005). The isotopic labeling allows the differentiation between dissolved carbon that is derived from "recently assimilated" carbon and "old" soil organic matter. "Recently assimilated" carbon has been photosynthetically assimilated since the start of fumigation in 1999 in the FACE experiment of this study, whereas carbon in "old" organic matter entered the soil before the start of CO_2 addition. For forest systems, insignificant effects of FACE on DOC concentrations have been assigned to a small fraction of "recently assimilated" carbon in DOC (Hagedorn et al. 2002).

To date the effect of elevated atmospheric CO_2 concentrations on evapotranspiration has been neglected in studies of CO_2-effects on carbon leaching. It is well known, however, that evapotranspiration is often reduced under FACE (Kimball et al. 2002; Weigel et al. 2005; Leakey et al. 2009; Burkhart et al. 2011), which can be expected to increase groundwater recharge in case that precipitation patterns remain unchanged. This physiological effect of increasing atmospheric CO_2 concentrations was put forward to explain increases in global continental runoff during the twentieth century (Gedney et al. 2006). Even if dissolved carbon concentrations were unaffected by increasing atmospheric CO_2, increasing runoff would rise leaching losses of carbon.

We investigated dissolved carbon concentrations, groundwater recharge, and carbon leaching during two winters and two summers after 5 years of FACE in a winter barley, sugar beet, winter wheat crop rotation in Northern Germany in the last winter wheat period (year 6) of the FACE experiment and the subsequent post-FACE winter barley period. Our hypothesis was that elevated atmospheric CO_2 concentrations increase carbon leaching due to increasing DIC and DOC concentrations combined with increasing groundwater recharge.

Materials and methods

The Braunschweig FACE experiment

The FACE experiment was established from 04.10.1999 until 20.07.2005 at a 24 ha field of the von Thünen Institute at Braunschweig. The soil at the site is a Luvisol with a sandy loam soil texture. It is important to note that the soil contains carbonate-C at the depths of soil water collection (Table 1), which affected concentrations and isotopic composition of DIC. Due to the occurrence of carbonates, pH values measured in water were close to neutral (Table 1). The site has a mean annual temperature of 8.8°C and a mean temperature in July of 17°C. Mean annual precipitation equals 618 mm. During the 605 day period of soil water collection from November 2004 until June 2006 (Table 1; Fig. 4), the cumulative precipitation including irrigation amounted to 890 mm, which roughly corresponds to an annual precipitation of only 540 mm. Thus considerably less precipitation fell during the study period than the long-term average of 618 mm.

Carbon dioxide was added to free air in two rings in order to achieve a target concentration of 550 $\mu l\ l^{-1}$ when temperatures were above 5°C and wind speed was less than 6.5 $m\ s^{-1}$. Fumigation was carried out with a circular FACE system equipped with 32 vertical vent pipes blowing CO_2 enriched air into the treatment area (20 m in diameter) as designed by Brookhaven National Laboratory (Lewin et al. 1992). The effect of ambient CO_2 concentrations were investigated in two identical systems supplied with ambient air ($\sim$380 $\mu l\ l^{-1}$ CO_2).

Table 1 Bulk soil pH and carbon contents of the plots at the two depths of soil water collection

Ring	Depth (cm)	pH (H_2O)	Carbonate-C (g kg^{-1})	Organic-C (g kg^{-1})
2 (ambient)	30–40	6.9 (0.1)	0.73 (0.09)	4.74 (0.24)
3 (ambient)	30–40	7.1 (0.2)	0.94 (0.53)	4.59 (0.66)
1 (FACE)	30–40	7.2 (0.1)	0.88 (0.45)	5.12 (1.44)
4 (FACE)	30–40	6.9 (0.3)	0.78 (0.40)	5.63 (2.46)
2 (ambient)	80–90	6.8 (0.5)	0.50 (0.04)	0.41 (0.04)
3 (ambient)	80–90	7.2 (0.1)	0.02 (–)	0.7 (–)
1 (FACE)	80–90	7.2 (0.0)	0.21 (–)	1.19 (–)
4 (FACE)	80–90	7.3 (0.0)	0.09 (0.09)	0.87 (0.12)

Numbers in brackets indicate standard deviations illustrating the spatial variability of soil properties. Data were determined for soil material that was collected during the installation of the suction cups ($n = 3$ for 30–40 cm depth; $n = 2$ for 80–90 cm depth)

The added CO_2 was derived from natural gas and strongly depleted in ^{13}C ($\delta^{13}C$: −48‰ to −45‰) which reduced the $\delta^{13}C$ signature of atmospheric air in the FACE rings to -20 ± 3‰ as compared to a value of −8‰ under ambient conditions (Giesemann and Weigel 2008). This isotopic label allowed us to trace the carbon fixed under FACE in the dissolved organic and inorganic carbon pools. In order to avoid water stress and thus, unwanted interactions between CO_2 treatments and soil water supply, all plots were irrigated when the soil water content dropped to less than 50% of the plant available water capacity in one plot with a roving line sprinkler. For this purpose volumetric water contents were recorded at 10 cm depth and 35 cm depth with six time domain reflectometry (TDR) probes per ring per depth (IMKO, Ettlingen, Germany and Easy-test, Lublin, Poland). A detailed description of the experimental setup can be found in Weigel et al. (2006). The crop rotation was typical for the North German region with winter barley (*Hordeum vulgare* L.), followed by ryegrass (*Lolium multiflorum* Lam.) as cover crop, followed by sugar beet (*Beta vulgaris* ssp. *altissima* Döll) and finally winter wheat (*Triticum aestivum* L.). Carbon dioxide enrichment was maintained for two rotation cycles (6 years).

Instrumentation and sampling

Five glass suction cups with a pore size <1 µm for soil water collection (Robu, Hattert, Germany) were installed at each of two control plots with ambient atmospheric CO_2 concentrations and the two FACE plots. The suction cups were divided into two sets of 3 and 2 suction cups. Three suction cups were installed right below the plough layer and two cups were installed at 90 cm depth by inserting them into boreholes. The effective rooting depth at the study site is 80 cm. Suction cups were connected to 2-l glass bottles in an insulated wooden box placed in a soil pit. Soil water was extracted by applying a vacuum that was adjusted electronically to the soil matric potential (Siemens and Kaupenjohann 2004) with an offset equivalent to the difference in height between the suction cup and the inlet into the collection bottle plus 0.2 kPa. In order to correctly measure DIC concentrations, degassing of CO_2 was minimized by using a headspace-free sample collection system similar to the one described by Suarez (1986). In this system, the soil water from the suction cup flows through a 12-ml gas-tight vial before entering the evacuated 2-l bottle via a cannula, which penetrated the septum of the vials just deep enough to allow the outflow of solution.

Soil water collection started in autumn 2004 after sugar beet harvest under winter wheat and continued under winter barley until summer 2006. Soil water samples were collected at weekly intervals. While winter wheat included CO_2 fumigation treatments, winter barley in 2005/06 was grown in the former FACE treatment plots without CO_2 enrichment and without installation of the FACE systems. Timing of crop management, CO_2 addition and soil water collection are specified in detail in Table 2.

Analysis of DOC concentrations and isotopic signature

Dissolved organic carbon concentrations of soil water samples were analyzed using Pt-catalyzed, high-temperature combustion (680°C) with a TOC-5050A analyzer (Shimadzu Corp., Kyoto, Japan). Prior to analysis, inorganic C was stripped off by adjusting the pH to 2 with HCl and sparging with CO_2-free synthetic air. At different points of time, soil water samples were spiked with K_2SO_4 (suprapur, Merck, Darmstadt, Germany) and lyophilized. The $\delta^{13}C$ ratio of the salt containing the formerly DOC was subsequently determined with an isotope ratio mass spectrometer (Thermofinigan, DeltaPlus) at the von Thünen Institute in Braunschweig and expressed as ‰ relative to the PeeDee belemnite standard. The fraction of "new", recently assimilated organic carbon was calculated with a two end-member mixing model (Eq. 1), with $f(DOC)_{new}$ denoting the fraction of new carbon, $\delta^{13}C(DOC)_{FACE}$ indicating the $\delta^{13}C$ value of DOC from the FACE plots, $\delta^{13}C(DOC)_{ambient}$ indicating the $\delta^{13}C$ value of DOC from the plots under ambient atmospheric CO_2, and $\delta^{13}C(biomass)_{FACE}$ denoting the $\delta^{13}C$ value of biomass and litter from the FACE plots. For this purpose average $\delta^{13}C$-values of aboveground biomass and belowground plant biomass (roots, tubers) from the FACE plots for the period from 06.06.2004 until 27.07.2005 were calculated from unpublished data of Giesemann. These values were −42.1‰ (16 samples, standard deviation: 1.24‰) for aboveground biomass and −40.61‰ (14 samples, standard deviation: 1.40‰) for belowground biomass. Confidence

Table 2 Agricultural management and timing of CO_2 addition and soil water collection

Crop	Sowing date	Harvest date	N-fertilization (kg N ha^{-1})	Start of CO_2 addition	Start of soil water collection	End of soil water collection
FACE experiment						
Winter barley	23.09.1999	22.06.2000	264	04.10.1999	–	–
Ryegrass	26.07.2000	12.10.2000	197	05.08.2000	–	–
Sugar beet	11.04.2001	24.09.2001	126	14.05.2001	–	–
Winter wheat	06.11.2001	31.07.2002	181	22.01.2002	–	–
winter barley	27.09.2002	26.06.2003	179	10.10.2002	–	–
Ryegrass	21.08.2003	14.10.2003	72	01.09.2003	–	–
Sugar beet	14.04.2004	28.09.2004	156	14.05.2004	–	–
Winter wheat	26.10.2004	27.07.2005	168	12.01.2005	22.11.2004	27.05.2005
Post FACE						
Winter barley	19.09.2005	11.07.2006	137	–	14.06.2005	30.06.2006

intervals for $f(DOC)_{new}$ were derived assuming that DOC is either derived exclusively from aboveground biomass (lower 95% limit) or entirely from belowground biomass (upper 95% limit). Confidence intervals of $f(DOC)_{new}$ were calculated according to Phillips and Gregg (2001) using their ISOERROR 1.04 Microsoft Excel spreadsheet.

$$f(DOC)_{new} = \frac{(\delta^{13}C(DOC)_{FACE} - \delta^{13}C(DOC)_{ambient})}{(\delta^{13}C(biomass)_{FACE} - \delta^{13}C(DOC)_{ambient})} \quad (1)$$

Analysis of DIC concentrations and isotopic composition in soil water

Concentrations of DIC of soil water were analyzed with a TOC-5050A analyzer (Shimadzu Corp., Kyoto, Japan). After acidification and sparging the sample with CO_2-free synthetic air, the stripped inorganic C was determined as CO_2 by infrared detection. DIC in soil water may derive from respiration, dissolution of carbonate minerals, or atmospheric CO_2. Because partial pressures of CO_2 in soil air are commonly much higher than atmospheric partial pressures, the direct influence of atmospheric CO_2 on DIC concentrations in soil water is negligible. The fraction of biogenic DIC was therefore calculated from δ^{13}C values of DIC with a two end-member mixing model considering carbonates and respiration (Amiotte-Suchet et al. 1999; Eq. 2). In Eq. 2 $f(DIC)_{carb}$ denotes the fraction of DIC derived from dissolution of carbonates, $\delta^{13}C_{DIC}$ is the measured δ^{13}C value of DIC, $\delta^{13}C_{bio}$ is the measured δ^{13}C of biomass or soil organic matter, and $\delta^{13}C_{carb}$ is the δ^{13}C value of carbonates. The δ^{13}C of carbonates is close to zero (range +2‰ to −5‰; Pawellek and Veizer 1994; Amiotte-Suchet et al. 1999) and a value of zero was used as end-member for our calculations. Kindler et al. (2011) found a potential overestimation of the carbonate-C fraction by on average 5% associated with the assumption of a value of 0‰ for carbonates in a sensitivity analysis when using an extreme value of −5‰ for carbonate-C.

$$f(DIC)_{carb} = \frac{(\delta^{13}C_{DIC} - \delta^{13}C_{carb})}{(\delta^{13}C_{bio} - \delta^{13}C_{carb})} \quad (2)$$

For the calculations end-member δ^{13}C values of −28‰ (biomass, minimum estimate) and −27‰ (soil organic matter, maximum estimate) were used for ambient conditions (Giesemann and Weigel 2008). The end-member δ^{13}C values for CO_2 derived from mineralization of biomass or soil organic matter were corrected for isotopic fractionation during the dissolution CO_2 in water according to Zhang et al. (1995), considering the speciation of total dissolved CO_2 (H_2CO_3*, HCO_3^-, CO_3^{2-}) as a function of pH. We neglected isotope exchange between soil air CO_2 and atmospheric CO_2, because we collected samples for the determination of the isotopic composition of DIC during spring and summer when CO_2 production in soils is high, leading to strong CO_2 diffusion out of soil and δ^{13}C values of soil air CO_2 close the ones of soil organic matter and biomass (Amiotte-Suchet et al. 1999).

The application of a simple two-end member mixing model is not possible for the FACE rings, because CO_2 from root respiration of labeled plants and the mineralization of labeled plant litter produced in the 5 years preceding the experiment added a third source of isotopically different carbon to the system (in addition to the two end-members carbonate-C and biomass-C). The analysis of DIC sources in the FACE rings therefore either requires an additional isotopic signal (^{14}C) or the assumption of a certain continuous CO_2 production from the mineralization of "old" soil organic matter. Since ^{14}C labeling data were not available and the assumption of a continuous CO_2 production was deemed too inaccurate and speculative, we used the approach of Phillips and Gregg (2003) and computed confidence intervals of the fractions of C derived from carbonates, "old" soil organic matter, or "new" organic matter that has been assimilated since the start of the FACE experiment with their IsoSource 1.3.1 software. For "old" soil organic matter we used the average $\delta^{13}C$ of soil organic matter of the ambient plots in the years 2004 and 2005 of −27‰ (Giesemann and Weigel 2008). For "new" organic matter we used an overall average of biomass from the FACE plots of −41‰ determined by repeated samplings in the years 2004 and 2005 (see above). Again these values were corrected for isotopic fractionation during gas exchange between soil air and soil solution using the equations of Zhang et al. (1995).

$\delta^{13}C$ values of DIC were determined at the Institute of Geology, Mineralogy and Geophysics of the Ruhr Universität Bochum using a gasbench II coupled to a delta S mass spectrometer (Finnigan MAT, Bremen, Germany). Samples for the determination of $\delta^{13}C$ of DIC were collected six times during the vegetation period 2005 on 28 April, 4 May, 14 May, 14 June, 25 July, 25 July, and 2 August. As not all suction cups yielded sufficient amounts of soil solution for isotope analysis at all points of time, averaged $\delta^{13}C$ values over these sampling dates were used for calculations.

Water balance and calculation of fluxes

Fluxes of dissolved C were calculated by multiplying concentrations with the volume of leached water, which was derived from a water balance subroutine of a crop model (Kage and Stützel 1999; Henke et al. 2008). The water balance routine describes fluxes of water in soil using the Richards equation based on water contents. Soil water retention and the relationship between soil water content and unsaturated water conductivity are described according to the equations of van Genuchten (1980) in the revised form of Wösten and van Genuchten (1988). Soil hydraulic parameters were derived from an inverse simulation of an infiltration experiment at our research site (Trockel 2007). The soil was discretized in layers of 10 cm thickness for modeling the water balance. Potential evapotranspiration was calculated using the Penman–Monteith equation (Monteith 1973) using a standard stomata resistance of 55 s m^{-1} for winter wheat and 50 m s^{-1} for winter barley, which were based on studies by the German Agricultural Meteorological Service at our research site and literature data (Zenker 2003). The standard stomata resistance was converted into a canopy resistance using the approach of Stockle et al. (1994). To account for lowered stomata conductivity under FACE conditions when modeling the effect of elevated atmospheric CO_2 concentrations on evapotranspiration, the stomata resistance parameter was increased for periods with CO_2 addition so that modeled soil water contents matched soil water contents in 0–60 cm depth (unpublished data, German Agricultural Meteorological Service). The fitting of the model was done by inverse simulation using the Levenberg–Marquardt algorithms implemented in the HUME modeling environment (Kage and Stützel 1999; Henke et al. 2008).

Statistics

Two-way nested designs with two FACE rings and two ambient rings, such as the one chosen in the Braunschweig FACE experiment (with only one N fertilization level considered), are a common solution to cope with the trade-off between statistical power and the cost for infrastructure, gas and manpower in FACE experiments (e.g. Filion et al. 2000). Søe et al. (2004) regarded replicate measurements of soil respiration and microbial biomass within the experimental rings as statistically independent. Adapting the approach of Søe et al. (2004), we used the results of single suction cups of FACE rings or ambient rings for an analysis of variance (ANOVA). To this end, monthly averages of dissolved carbon concentrations of suction cups were analyzed using a repeated measures ANOVA with the Statistica 8.0 software (Statsoft, Tulsa, USA) after data gaps in the time series for individual cups were filled by linear interpolation between sampling dates. Since the suction cups were removed from soil before the harvest of winter wheat and re-installed after sowing of winter barley in 2005, the repeated-measures ANOVA was performed separately for the two measurement periods depicted in Table 2.

In addition to the ANOVA, Monte Carlo–Markov Chain analyses were performed to detect differences between DIC or DOC concentrations of FACE plots and ambient plots. To account for the temporal variation of concentrations, the data series was subdivided into five periods, which were 22.11.2004–16.2.2005 (winter season, FACE often switched off due to low temperatures), 02.03.2005–14.06.2005 (growing season, FACE), 25.07.2005–17.11.2005 (growing season, post FACE), 22.11.2005–22.02.2006 (winter season, post FACE), and 23.03.2006–30.06.2006 (growing season, Post FACE). The Monte Carlo–Markov chain analyses were conducted with the software WINBUGS 1.4 (Spiegelhalter et al. 2003) using the original measurements without data interpolation.

Results

Concentrations of DOC and DIC in soil water

Until May 2005 concentrations of DOC in 30 cm depth under FACE plots and ambient plots were similar. Over the whole measurement period, the ANOVA did not indicate significant differences between the treatments (Fig. 1). The Monte Carlo–Markov Chain analysis, however, revealed significantly higher ($P < 0.05$) concentrations in 30 cm depth of the FACE plots than in ambient plots for the period from 25.07.2005 until 17.11.2005. Yet, this significant difference was based on only two samples with high concentrations of DOC collected on plot 4 on the 17.11.2005, and the difference disappeared when the boundaries of season 3 were slightly changed. For samples collected from 90 cm depth, the Monte Carlo–Markov Chain analysis indicated significantly larger DOC concentrations under ambient conditions for the period from 22.11.2005 until 22.02.2005. Average DIC concentrations under elevated CO_2 exceeded concentrations under ambient conditions at several points of time during the FACE period and at the beginning of the *post-FACE* period. According to the Monte Carlo–Markov Chain analysis these differences were significant for samples from 30 cm depth for the period 25.07.2005 until 22.02.2006 ($P < 0.05$). For samples from 90 cm depth, DIC concentrations under FACE exceeded those under ambient conditions significantly for the periods 02.03.2005 until 14.06.2005 and 23.03.2006 until 30.06.2006. These differences between the treatments must, however, be interpreted with caution because a closer inspection of the data revealed that only DIC concentrations under ring 1 were significantly larger than those under the ambient rings 2 and 3, not those of the second FACE ring 4. A stronger influence of the FACE on DIC under ring 1 than under ring 4 was also reflected in the $\delta^{13}C$ signature of DIC (see next paragraph). The ANOVA did not indicate significant differences between DIC concentrations under FACE and ambient conditions.

Isotopic signature of DOC and DIC

The $\delta^{13}C$ values of DOC collected from the ambient plots ranged from −28.8 to −27.7‰, those of DOC from the FACE plots were more negative, ranging from −31.1 to −29.4‰ (Table 3). The application of a two end-member mixing model showed that 9–29% of the DOC collected under the FACE rings at 30 cm depth was derived from biomass or soil organic matter assimilated and accumulated since the start of the FACE experiment in 1999. For samples from 90 cm depth, this fraction was 15–25% (Table 3).

The isotopic signature of DIC collected under ambient conditions was less negative than the signature of DOC (−15.1 to −12.5‰, Table 4), most probably due to carbonate dissolution and isotopic fractionation during gas exchange between soil air and water. After correcting for this fractionation, a fraction of 21–42% of carbonate-derived DIC could be calculated. Under elevated atmospheric CO_2, $\delta^{13}C$ values of DIC decreased to values of −23.0 to −18.3‰ (Table 4). With respect to its $\delta^{13}C$ ratio DIC at 30 cm depth differed significantly between the two FACE rings (Table 4). Using the approach of Phillips and Gregg (2003), a fraction of 46–49% of “new” DIC derived from recently fixed carbon can be calculated for ring 1. For ring 4 this fraction is smaller (27–30%, Table 4).

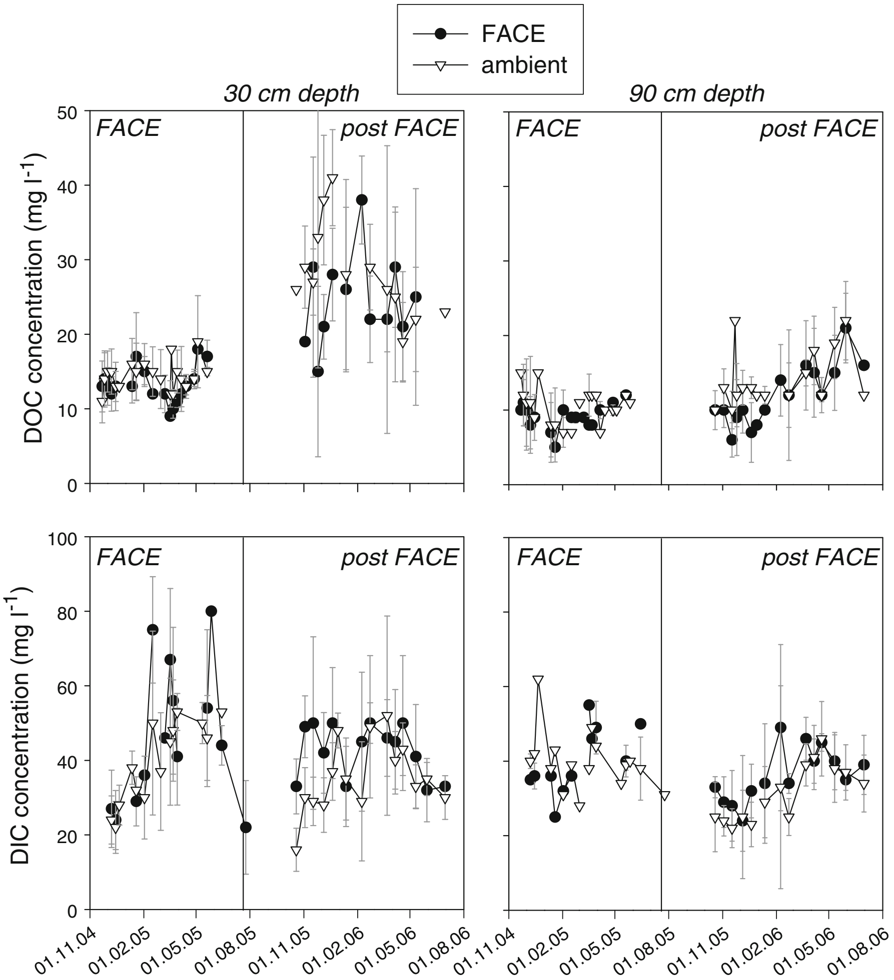

Fig. 1 Concentrations of dissolved organic carbon (DOC, *top panels*) and dissolved inorganic carbon (DIC, *bottom panels*) over time under ambient and elevated atmospheric CO_2 concentrations. *Error bars* show the standard deviations to indicate the spatial variability of concentrations. The gap of data in summer 2005 is due to drought and the de-installation of suction cups before harvest and plowing. Suction cups were re-installed in October 2005

Table 3 δ^{13}C signature of DOC at different points of time and fraction of "new" recently assimilated carbon in DOC

Date	Ambient	FACE	Ambient	FACE	*f(DOC)* $f(DOC)_{new}$ (Eq. 1)	
	30 cm (‰)	35 cm (‰)	90 cm (‰)	90 cm (‰)	35 cm (%)	90 cm (%)
February 2005	−28.8 (0.1)	−31.1 (0.3)	–	–	9[a]–29[b]	–
May 2005	−28.5 (0.2)	−30.9 (0.2)	–	–	10–26	–
November 2005	−28.4 (0.0)	−31.0 (0.1)	−27.8 (0.2)	−29.4 (0.3)	10–26	19–25
March 2006	−27.7 (–)	–	−28.2 (–)	30.2 (–)	–	15[c]–16[d]

Numbers in brackets indicate the standard error of the mean δ^{13}C signature (unit: ‰) or the confidence interval of the estimated fraction of DOC_{new} (unit: %)

[a] Lower 95% limit calculated assuming that all DOC_{new} is derived from aboveground biomass

[b] upper 95% limit calculated assuming that all DOC_{new} is derived from below-ground plant biomass

[c] average fraction based on one DOC sample and the average δ^{13}C of aboveground plant biomass

[d] average fraction based on one DOC sample and the average δ^{13}C of belowground plant biomass

Table 4 δ^{13}C signature of DIC under ambient and elevated atmospheric CO_2 concentrations and fractions of biogenic DIC that can be calculated from isotopic mixing

	30 cm depth				90 cm depth			
	δ^{13}C (‰)	Carbonate DIC (Eq. 2) (%)	"Old" DIC (%)	"New" DIC (%)	δ^{13}C (‰)	Carbonate DIC (Eq. 2) (%)	"Old" DIC (%)	"New" DIC (%)
Ambient								
Ring 2	−14.3 (0.2)	30–35	65–70	–	−12.5 (1.9)	39–42	58–61	–
Ring 3	−14.7 (0.3)	25–30	70–75	–	−15.1 (2.2)	21–24	76–79	–
Mean	−14.5	27–33	67–73	–	−13.8	30–33	67–70	–
FACE								
Ring 1	−23.0 (1.7)	15[a]–17[b]	35–39	46–49	−19.8 (2.3)	19–21	45–50	31–33
Ring 4	−19.9 (1.0)	21–23	46–51	27–30	−18.3 (–)	23–25	46–51	26–29
Mean	–	–	–	–	−19.1	21–23	46–51	28–31

Samples were collected on 28.04.2005, 04.05.2005, 14.05.2005, 14.06.2005, 25.07.2005, and 02.08.2005. Brackets indicate the standard deviation caused by temporal variability

δ^{13}C values of rings 1 and 4 for the depth of 30 cm differ significantly ($P = 0.01$; Mann–Whitney U-test). "Old" DIC denotes the sum of DIC from root respiration plus DIC from mineralization of litter and soil organic matter under ambient atmospheric CO_2 and DIC from the mineralization of litter and soil organic matter older than the start of the FACE experiment under elevated CO_2. "New" DIC denotes DIC from carbon that has been assimilated since the start of the FACE experiment in 1999.

[a] Lower 95% limit of confidence interval according to Phillips and Gregg (2003) and [b] upper 95% limit of confidence interval

At 90 cm depth, differences between the fractions of recently assimilated DIC of ring 1 and 4 were less pronounced; the estimated fraction of "new" carbon in DIC was roughly one third (Table 4).

Water balance and leaching losses of dissolved carbon

From the start of soil water collection in November 2004 until the end of the FACE experiment on the 20th of July 2005, elevated atmospheric CO_2 concentrations reduced the modeled evapotranspiration of wheat plants by 60 mm or 15% with the majority of this reduction being due to less intensive transpiration between March and July 2005. The reduction of evapotranspiration was reflected in higher volumetric water contents (Fig. 2) and smaller soil matric potentials under elevated CO_2 especially during summer 2005 (pF, Fig. 3). Less intensive evapotranspiration caused larger drainage volumes until May 2005 and less capillary rise of soil water between May and July 2005 (Fig. 4), so that the cumulative groundwater recharge under elevated CO_2 exceeded recharge under ambient CO_2 by 22 mm or 35% by the end of CO_2 addition on the 20th of July. Because soil water contents were closer to field capacity under elevated CO_2, leaching started earlier in late summer 2005 after the harvest of winter wheat at the former FACE rings (Fig. 4). As a result, total groundwater recharge under the FACE rings was 69 mm (55%) higher than recharge under ambient conditions.

During winter and spring 2004/2005, 3.0 g of total carbon per square meter were leached below 90 cm depth under ambient conditions (Table 5). Subtraction of the fraction of carbonate-borne DIC from the DIC flux resulted in a leaching loss of 2.1 g m^{-2} of dissolved biogenic carbon. Under elevated CO_2 the downward flux of total dissolved carbon increased to 3.8 g m^{-2}, the loss of biogenic carbon increased to 2.4 g m^{-2} (Table 5). Capillary rise of soil water due to intensive plant transpiration caused a small net upward flux of 0.6 g C m^{-2} under ambient conditions during summer 2005 (Table 5). Under elevated CO_2, the early start of groundwater recharge after the harvest of wheat in July caused a small net loss of 0.4 g C m^{-2} in this period. For the winter period 2005/2006 following the FACE experiment, leaching losses of total dissolved carbon from the former FACE rings of 5.3 g m^{-2} exceeded losses from the former ambient rings by 1.6 g m^{-2} (Table 5). Summing up the summer flux with the average of the winter fluxes gave a mean annual total dissolved carbon flux of

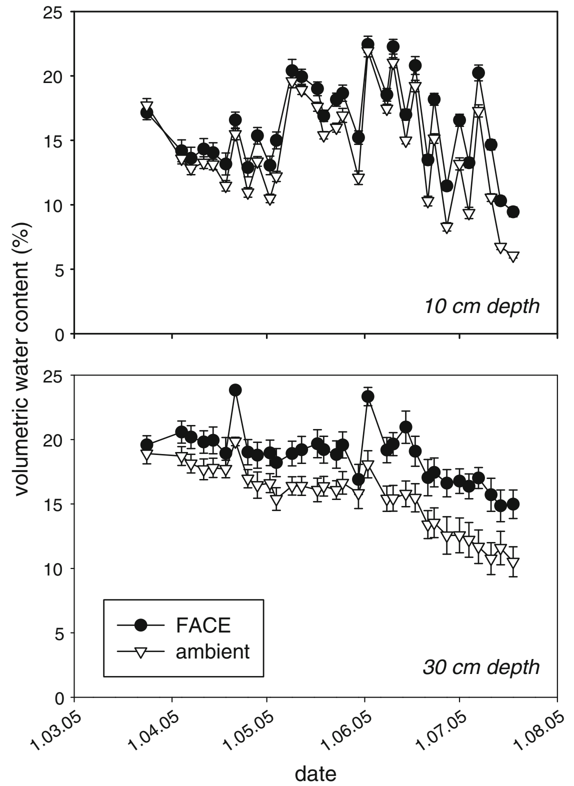

Fig. 2 Volumetric water content at 10 cm depth and 35 cm depth measured with TDR probes. *Error bars* represent the standard error of the mean

2.7 g m^{-2} $year^{-1}$ for ambient conditions and a loss of 4.9 g m^{-2} $year^{-1}$ (+81%) under elevated CO_2 for our measurement period. Biogenic carbon leaching under elevated CO_2 increased by 65% (3.3 vs. 2.0 g m^{-2} $year^{-1}$, Table 5). Irrespective of atmospheric CO_2 concentration, dissolved carbon was mainly leached as DIC, which represented 77% of total dissolved carbon losses under ambient conditions and 76% of the total dissolved carbon flux under elevated CO_2. Even after subtracting its carbonate-derived fraction, DIC losses accounted for 63% (FACE) or 70% (ambient) of total biogenic carbon leaching.

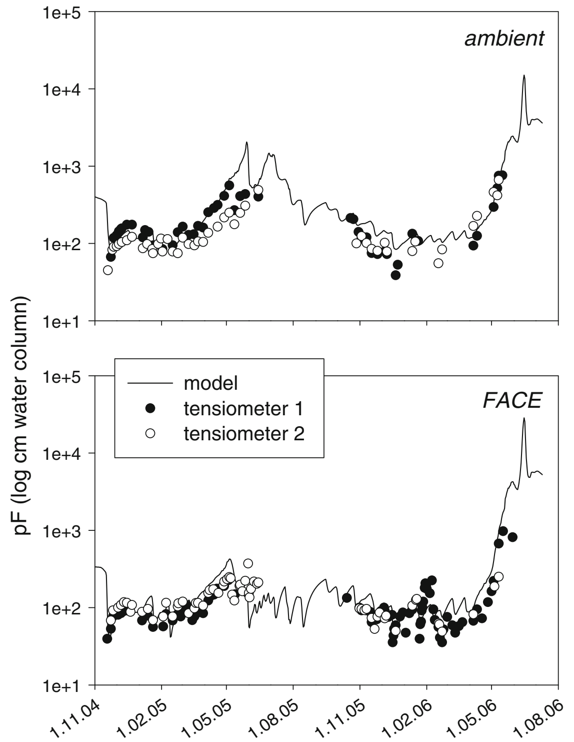

Fig. 3 Comparison of measured versus modeled soil matric potentials (pF) at 30 cm depth over time for the plots under ambient atmospheric CO_2 concentration (*top panel*) and under elevated atmospheric CO_2 concentration (*bottom panel*). One tensiometer was installed at each of the four research plots. Note that the matric potentials were not used for calibration of the soil water model, so that they allow an independent judgment of the model quality

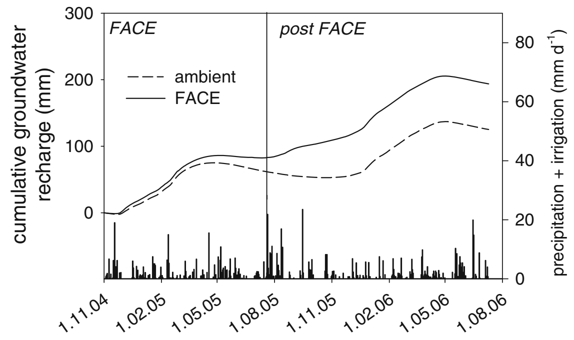

Fig. 4 Modeled cumulative groundwater recharge at 90 cm depth and sum of precipitation plus irrigation (*bars*)

Discussion

Concentrations and isotopic composition of dissolved carbon

Dissolved organic and inorganic carbon concentrations found at the Braunschweig site are within the range of concentrations that Kindler et al. (2011) report for other European arable sites. In line with the results of King et al. (2001), Oh et al. (2007), and Hagedorn et al. (2002, 2008), DOC concentrations

Table 5 Leaching losses of dissolved carbon at 90 cm depth

Suction cups of ring	DOC (g m^{-2})	DIC (g m^{-2})	Biogenic DIC[a] (g m^{-2})	Total dissolved C (g m^{-2})	Total biogenic C[b] (g m^{-2})
01.11.2004–30.04.2005					
2 (ambient)	0.6 (–)[c]	2.7 (–)[c]	1.6	3.3	2.2
3 (ambient)	0.3 (0.1)	2.5 (0.1)	1.9	2.8	2.2
All ambient	0.4 (0.1)	2.6 (0.1)	1.7	3.0	2.1
1 (FACE)	0.8 (0.1)	3.2 (0.3)	1.9	4.0	2.7
4 (FACE)	0.6 (–)[c]	2.9 (–)[c]	1.6	3.5	2.2
All FACE	0.7 (0.1)	3.1 (0.2)	1.7	3.8	2.4
01.05.2005–31.10.2005					
2 (ambient)	−0.1 (–)[c]	−0.4 (–)[c]	−0.2	−0.5	−0.3
3 (ambient)	0.0 (0.0)	−0.5 (0.0)	−0.4	−0.5	−0.4
All ambient	−0.1 (0.0)	−0.5 (0.1)	−0.3	−0.6	−0.4
1 (FACE)	0.2 (0.0)	0.3 (0.0)	0.2	0.5	0.4
4 (FACE)	0.1 (–)[c]	0.2 (–)[c]	0.1	0.3	0.2
All FACE	0.1 (0.0)	0.3 (0.0)	0.2	0.4	0.3
01.11.2005–30.04.2006					
2 (ambient)	1.1 (0.1)	2.9 (0.2)	1.7	4.0	2.8
3 (ambient)	0.9 (0.1)	2.5 (0.5)	1.9	3.4	2.8
All ambient	1.0 (0.1)	2.7 (0.4)	1.8	3.7	2.8
1 (FACE)	1.3 (0.3)	4.2 (0.4)	2.4	5.5	3.7
4 (FACE)	1.6 (0.1)	3.3 (0.7)	1.8	4.9	3.4
All FACE	1.5 (0.2)	3.8 (0.5)	2.1	5.3	3.6
Mean annual flux 01.11.2004–30.04.2006[d]					
2 (ambient)	0.7	2.4	1.4	3.1	2.1
3 (ambient)	0.6	2.0	1.5	2.6	2.1
All ambient	0.6	2.1	1.4	2.7	2.0
1 (FACE)	1.2	4.0	2.3	5.2	3.5
4 (FACE)	1.2	3.4	1.8	4.6	3.0
All FACE	1.2	3.7	2.1	4.9	3.3

Numbers in brackets indicate standard deviation of the mean flux across suction cups caused by the spatial variation of dissolved carbon concentrations

[a] Calculated by subtracting the fraction of carbonate DIC from Table 4

[b] Sum of DOC plus biogenic DIC

[c] No standard deviation could be calculated because one of the two suction cups in the experimental ring failed

[d] Average of winter fluxes (2004/2005 and 2005/2006) plus flux in summer 2005

were hardly affected by elevated atmospheric CO_2 concentrations for most of the time. Hagedorn et al. (2002) argued that this lack of response can be explained by the small fraction of "new", recently assimilated carbon in DOC, which was smaller than 8% after 4 years of CO_2 enrichment in their lysimeter study with small trees. For the agricultural system in Braunschweig, this fraction of "new" carbon in DOC was larger (9–29%, Table 3). A considerably larger fraction of "new" carbon in DOC from our agricultural system did, therefore, not lead to a significant increase in DOC concentrations under FACE. In contrast to the results of Zhong et al. (2009), the Monte Carlo Markov Chain analysis indicated even smaller DOC concentrations in 90 cm depth under FACE than under ambient conditions, which might be related to dilution effects caused by higher soil water contents and larger groundwater recharge.

The fraction of 21–45% carbonate-borne DIC that we calculated for the ambient plots corresponds to fractions reported by Kindler et al. (2011) for other European arable sites. According to the stoichiometry of the dissolution of carbonate minerals with carbonic acid the fraction of carbonate-borne HCO_3^-, which is the dominant DIC species at close to neutral pH, should approach 50% at chemical equilibrium (e.g. Amiotte-Suchet et al. 1999). Values smaller than 50% indicate that this chemical equilibrium is not reached completely at our research site because (i) the residence time of soil water within the soil profile is not sufficient and/or (ii) the spatial distribution of carbonates in the soil is too heterogeneous to allow a reaction of all soil water with these minerals. This spatial variability of carbonate contents is also reflected in coefficients of variation of up to 100% of the carbonate C contents shown in Table 1. Using the approach of Phillips and Gregg (2003), a contribution of 26–49% of "new" carbon to DIC could be calculated for the FACE plots. This fraction of "new" carbon in DIC is smaller than the large proportion of recently fixed carbon (70%) that was determined by Søe et al. (2004) for CO_2 from soil respiration for the Braunschweig site under sugar beet. Hagedorn et al. (2004) reported a fraction of roughly 50% of "new" carbon in CO_2 produced in incubation experiments with forest soils from a four-year FACE experiment. The significant deviation between $\delta^{13}C$ values of DIC from 30 cm depth between the two of FACE rings, however, suggests that the calculated fractions of "new" carbon in DIC should be interpreted with caution.

Contrary to our expectation, differences between DIC concentrations under elevated CO_2 and ambient conditions were rather small and not consistent. Whilst the ANOVA did not show a significant effect of elevated atmospheric CO_2 concentrations, the Monte Carlo–Markov Chain analysis suggested that DIC concentrations were significantly larger during certain periods of time. However, larger DIC concentrations were only found for ring 1, not for ring 4. Similar to the results of Oh et al. (2007), this indicates that effects of spatial variability of soil properties and crop stands might override effects of elevated atmospheric CO_2 concentrations. The difference between ring 1 and ring 4 is also reflected in the $\delta^{13}C$ signature of DIC (Table 4). To date, the reasons for the observed differences between rings 1 and 4 remain unclear. The most obvious factors, soil pH and the presence of carbonates, are similar for rings 1 and 4, and thus do not provide an explanation for the observed differences. Overall, our results do not provide unequivocal evidence supporting the positive effect of elevated atmospheric CO_2 concentrations on DIC concentrations in soil water as reported by Andrews and Schlesinger (2001) and Karberg et al. (2005).

Water balance and dissolved carbon leaching

The cumulative drainage under winter wheat calculated by our soil water model for the period November 2004 until April 2005 (main drainage period) was smaller (75 mm) than the groundwater recharge determined with lysimeters for the Braunschweig site under triticale (91 mm, German Meteorological Service, unpublished data), indicating a potential underestimation of drainage by approximately 20%. For the period from November 2005 until April 2006, measured groundwater recharge under bare soil equaled 95 mm (German Meteorological Service, unpublished data), whilst modeled drainage under winter barley was 84 mm. The comparison of lysimeter drainage with the model results thus supports the overall plausibility of the modeled groundwater recharge, but suggests a potential systematic underestimation of true recharge and related carbon leaching by 10–20%.

The 15% reduction in evapotranspiration under elevated CO_2 as derived from inverse simulation of the soil water balance is well within the range of reductions in crop transpiration of 18% (sugar beet) and 12% (wheat) that were found by Burkhart et al. (2011) using direct measurements in the Braunschweig FACE experiment. A reduction in evapotranspiration of 5–20% has also been reported from other FACE experiments for wheat (Leakey et al. 2009). The good agreement between modeled and measured effects of elevated atmospheric CO_2 concentrations on evapotranspiration indicates that the relative differences between calculated groundwater recharge and dissolved carbon leaching between FACE plots and ambient plots are reliable. Less depletion of soil water under elevated CO_2 during the summer of 2005 due to reduced transpiration increased groundwater recharge under the former FACE plots even after the end of the FACE experiment in fall 2005.

The considerable increase of cumulative groundwater recharge by 55% as a result of reduced evapotranspiration was the major driver for the observed 81% increase in dissolved carbon leaching from the FACE rings at 90 cm depth. However, due to dry weather conditions, this large relative increase in groundwater recharge and carbon leaching can also be attributed to small absolute groundwater recharge and carbon leaching during our study period.

As a result of exceptionally dry conditions, the mean annual fluxes of 2.0 (ambient) or 3.3 (FACE) g of biogenic carbon m^{-2} $year^{-1}$ are small compared to leaching losses found at other arable sites. In a study on carbon leaching from soils of various land use systems across Europe, Kindler et al. (2011)

determined leaching losses of 18 (Carlow, Ireland), 13 (Grignon, France), and 25 g dissolved biogenic carbon m^{-2} $year^{-1}$ (Klingenberg, Germany) from cropland soils. It is well possible that relative increases in carbon leaching due to increasing atmospheric CO_2 at sites with larger drainage will be smaller than those we observed in Braunschweig.

Conclusions

The results of our study do not support our hypothesis that elevated atmospheric CO_2 concentrations cause an increase of DOC and DIC concentrations in soil water. They confirm, however, the proposed positive effect of elevated atmospheric CO_2 on groundwater recharge and dissolved carbon leaching. Elevated atmospheric CO_2 concentrations hence led to increased dissolved carbon leaching mainly due to increased drainage volumes and to a lesser extent due to higher concentrations of DOC and DIC. This hydrologic control of dissolved carbon leaching suggests that future exports of dissolved carbon from soils to the groundwater under elevated atmospheric CO_2 concentrations will mainly depend on future climatic conditions, especially precipitation patterns, and to a smaller extent on changes in weathering rates and DIC concentrations.

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