

Dissolved carbon leaching from soil is a crucial component of the net ecosystem carbon balance

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Abstract

Estimates of carbon leaching losses from different land use systems are few and their contribution to the net ecosystem carbon balance is uncertain. We investigated leaching of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and dissolved methane (CH₄), at forests, grasslands, and croplands across Europe. Biogenic contributions to DIC were estimated by means of its $\delta^{13}\text{C}$ signature. Leaching of biogenic DIC was $8.3 \pm 4.9 \text{ g m}^{-2} \text{ yr}^{-1}$ for forests, $24.1 \pm 7.2 \text{ g m}^{-2} \text{ yr}^{-1}$ for grasslands, and $14.6 \pm 4.8 \text{ g m}^{-2} \text{ yr}^{-1}$ for croplands. DOC leaching equalled $3.5 \pm 1.3 \text{ g m}^{-2} \text{ yr}^{-1}$ for forests, $5.3 \pm 2.0 \text{ g m}^{-2} \text{ yr}^{-1}$ for grasslands, and $4.1 \pm 1.3 \text{ g m}^{-2} \text{ yr}^{-1}$ for croplands. The average flux of total biogenic carbon across land use systems was $19.4 \pm 4.0 \text{ g C m}^{-2} \text{ yr}^{-1}$. Production of DOC in topsoils was positively related to their C/N ratio and DOC retention in subsoils was inversely related to the ratio of organic carbon to iron plus aluminium (hydr)oxides. Partial pressures of CO₂ in soil air and soil pH determined DIC concentrations and fluxes, but soil solutions were often supersaturated with DIC relative to soil air CO₂. Leaching losses of biogenic carbon (DOC plus biogenic DIC) from grasslands equalled 5–98% (median: 22%) of net ecosystem exchange (NEE) plus carbon

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inputs with fertilization minus carbon removal with harvest. Carbon leaching increased the net losses from cropland soils by 24–105% (median: 25%). For the majority of forest sites, leaching hardly affected actual net ecosystem carbon balances because of the small solubility of CO₂ in acidic forest soil solutions and large NEE. Leaching of CH₄ proved to be insignificant compared with other fluxes of carbon. Overall, our results show that leaching losses are particularly important for the carbon balance of agricultural systems.

Keywords: carbon cycle, carbon sequestration, CH₄, DIC, dissolved inorganic carbon, dissolved organic carbon, DOC, methane, net biome productivity, net ecosystem exchange

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Introduction

Uptake and release of CO₂ by terrestrial ecosystems are crucial modulators of the climate system (e.g., Heimann & Reichstein, 2008). Reliable estimates of net ecosystem carbon balances (Chapin *et al.*, 2006) are therefore fundamental to our understanding of global climate change and the development of appropriate mitigation strategies. Net ecosystem carbon balances can be determined by assessing changes in ecosystem carbon stocks over time (e.g., Liski *et al.*, 2002; Sleutel *et al.*, 2003). This approach is associated with large uncertainties, because annual changes are small compared with stock size, because of error propagation of measurements, spatial heterogeneity within ecosystems, and temporal or spatial extrapolation. A possible strategy to validate large-scale estimates of net ecosystem carbon balances is to compare them with independent estimates of carbon uptake derived from inverse modelling of CO₂ transport in the atmosphere (Janssens *et al.*, 2003; Schulze *et al.*, 2009). Such comparisons are hampered by the differing and uncertain system boundaries and the differing types of carbon fluxes measured. Atmosphere-based estimates of carbon uptake rates are often larger than increases in ecosystem carbon stocks because part of the carbon is exported in plant products (e.g. wood, grains, or forage), lost to the atmosphere in volatile organic forms, or leached in soluble forms (Janssens *et al.*, 2003; Ciais *et al.*, 2008).

Siemens (2003) hypothesized that the leaching of dissolved inorganic and organic carbon from soils can explain a large part of the difference between atmosphere- and land-based estimates of the carbon uptake of European terrestrial ecosystems. Similarly, Richey *et al.* (2002), Cole *et al.* (2007), and Battin *et al.* (2009) argued that consideration of inland waters as components of terrestrial carbon budgets is necessary to assess the carbon cycle at the landscape scale. In line with these views, current estimates of carbon balances of European terrestrial ecosystems assume an average loss of 7 g C m⁻² yr⁻¹ with drainage, based on measurements of riverine fluxes (Schulze *et al.*, 2009). Linking riverine carbon fluxes to those in terrestrial ecosystems is difficult because measurements of riverine fluxes not

only integrate over a number of transformation processes in aquifers and surface waters, they often also average carbon fluxes from various land use systems within a particular catchment. Thus, better data on leaching from soils could considerably improve estimates of carbon budgets of terrestrial ecosystems. Such data are also essential to further assess the active processing of land-borne carbon in aquifers and inland waters (Cole *et al.*, 2007; Battin *et al.*, 2009).

There is evidence that carbon leaching from terrestrial ecosystems varies systematically with land use. Brye *et al.* (2001) reported a more than fivefold increase in dissolved carbon leaching during 4 years after the conversion of native tall-grass prairie to maize cultivation with fertilization and ploughing. Parfitt *et al.* (1997) found losses of dissolved inorganic carbon (DIC) of 14.7 g m⁻² yr⁻¹ from pasture and 0.7 g m⁻² yr⁻¹ from a pine forest under similar climatic conditions, along with a drop in soil pH(H₂O) from 5.6–5.9 under pasture to 5.3–5.5 under pine as result of more intense acidification in the forest. Leaching of dissolved organic carbon (DOC) seems to be affected by ploughing and crop type (Vinther *et al.*, 2006). A better understanding of land use effects on dissolved carbon leaching is important because (i) net ecosystem carbon balances are often grouped according to land use classes (e.g., cropland, grassland, forest; Janssens *et al.*, 2003) and (ii) trends in riverine dissolved carbon fluxes seem to be related to land use (e.g., Raymond & Cole, 2003).

Carbon is dissolved in water not only as DOC and DIC but also as dissolved methane (CH₄). Despite its high global warming potential, dissolved CH₄ is commonly not included in measurements of dissolved carbon concentrations and has only been investigated in a small number of studies. For the Brockly Burn moorland catchment in Scotland, CH₄–C fluxes with stream water were <0.04% of CO₂–C fluxes (Dawson *et al.*, 2004). Even when considering a global warming potential factor of 25 for CH₄ (IPCC, 2007), its contribution to fluxes of CO₂–C equivalents was smaller than 1%. Fiedler *et al.* (2006) found that CH₄ export (in CO₂–C equivalents) from a catchment in the Black Forest, Germany, was approximately 8% of the CO₂ export. The small contribution of CH₄ to overall carbon losses with

stream water or spring water is due its poor solubility in water ($1.5 \times 10^{-5} \text{ mol L}^{-1} \text{ kPa}^{-1}$ at 20°C).

The goal of the present work was (i) to determine leaching losses of DIC and DOC from soils of typical European land use systems and to relate them to the respective net ecosystem carbon balances and (ii) to identify major factors controlling carbon leaching. In order to achieve a full carbon perspective, determinations of DOC and DIC leaching losses were complemented by analyses of CH_4 in soil air and soil water. Our hypothesis was that carbon leaching from soils considerably reduces net carbon uptake of terrestrial ecosystems.

Materials and methods

Instrumentation and sampling

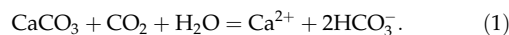
Twenty glass suction cups with a pore size $<1 \mu\text{m}$ for soil water collection (ecoTech, Bonn, Germany) and eight Teflon suction cups (ecoTech) for soil gas collection were installed at each of 12 European sites under different land use (Table 1, Fig. 1). Most of these sites were verification sites of the CarboEurope project (<http://www.carboeurope.org>) and/or flux sites of the NitroEurope project (Skiba *et al.*, 2009). The probes were divided into two sets of 10 suction cups and four gas probes, which allowed for sampling of different treatments (e.g., intensive and extensive grazing at Laqueuille) or different landscape positions (e.g., slope and hollow at Easter Bush). Suction cups and gas probes were installed horizontally from a soil pit by inserting them into boreholes. Half the number of probes were installed beneath the A horizon (at approximately 30 cm depth), the other half was installed as deep as possible (65–120 cm depth; Table 1). Suction cups were connected to 2 L glass bottles in an insulated aluminium box placed into the soil pit. Soil water was extracted by applying a vacuum of 40 kPa to the glass bottles after each sampling. In order to correctly measure DIC, 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 first flows through a 20 mL gas-tight vial before entering the evacuated 2 L bottle via a cannula, which penetrates the septum of the vials just deep enough to allow for outflow of solution. At the Hainich and Wetzstein sites, soil water was additionally collected from two glass suction plates installed at 20 cm depth.

Sample collection started at different points of time. Here, we present and discuss data from samples collected at least four weeks after sampler installation. These data span the period from October 1, 2006 until March 31, 2008 at all sites except for the Irish sites where soil water sampling commenced until March 31, 2009. Samples were collected fortnightly, except for periods when sites could not be reached due to snow or when the soil was frozen. Fluxes were calculated separately for summer (April 1 until September 30) and winter (October 1 until March 31).

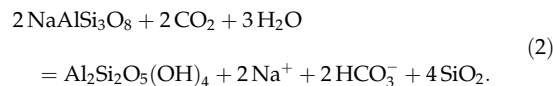
Determination of soil solution pH, DIC, and CH_4 concentrations in soil water

Soil solution pH was determined using a micro glass electrode (blueLine 16pH, Schott, Mainz, Germany) in the gas-tight 20 mL vials before DIC analysis. Concentrations of DIC of samples taken during the first winter 2006/2007 were analysed with a TOC-5050A analyser (Shimadzu Corp., Kyoto, Japan). Inorganic carbon was determined by acidification and sparging solution samples with CO_2 -free synthetic air and subsequently detecting the evolving CO_2 . Samples from summer 2007 and winter 2007/2008 were analysed using a gas chromatograph for simultaneous detection of CH_4 and CO_2 . The Shimadzu GC-2014AF gas chromatograph was equipped with an AOC-5000 autosampler, a $1 \text{ m} \times 1/8''$ HayeSep Q 80/100-mesh column, an electron capture detector and two flame ionization detectors, with one of them being coupled to a methanizer. Gas concentrations and total pressure were analysed in the headspace after shaking solutions at 90°C for 20 min. The gas concentrations in soil water were calculated from the headspace concentrations by applying Henry's law. Results were corrected for temperature, pressure-dependent residual gas concentrations and pH-dependent carbonate equilibrium (only for DIC). Tests with standard solutions showed that the Shimadzu TOC-5050A method and the GC method yielded comparable results for DIC.

DIC in soil water derives from either respiration, dissolution of carbonate minerals, or atmospheric CO_2 . Because partial pressures of CO_2 in soil air are much higher than atmospheric partial pressures, the direct influence of atmospheric CO_2 on DIC concentrations in soil water is negligible. According to the stoichiometry of the reaction of respiratory CO_2 with calcium or magnesium carbonate [Eqn (1)], the fraction of carbonate-borne DIC in calcareous soils should approach 50% if chemical equilibrium is reached within the residence time of percolating water in the soil (e.g., Amiotte-Suchet *et al.*, 1999).



In carbonate-free soils, respiratory CO_2 will react with silicates (e.g., feldspars) to form clay minerals and bicarbonate, which in this case is solely from soil respiration [e.g., Eqn (2); Amiotte-Suchet *et al.*, 1999]. In these soils, the fraction of DIC from respiration should therefore be close to 100%.



Since the $\delta^{13}\text{C}$ values of limestones are close to zero ($+2\%$ to -5%) and the $\delta^{13}\text{C}$ signature of CO_2 from soil respiration typically ranges from -21% to -25% , the fraction of biogenic and respiratory DIC can be inferred from $\delta^{13}\text{C}$ values of DIC (Pawellek & Veizer, 1994; Amiotte-Suchet *et al.*, 1999), taking into account the isotopic fractionation during the dissolution of CO_2 in water (Zhang *et al.*, 1995). The enrichment of ^{13}C in soil air CO_2 compared with biomass ($\delta^{13}\text{C}$ of C3 plants: $\sim -28\%$) is the result of isotopic enrichment during litter decay and enrichment of CO_2 during diffusion out of the soil into the atmosphere (Amiotte-Suchet *et al.*, 1999). To account

Table 1 Land use, soil characteristics, instrumentation, and mean temperature of the investigated sites

Site	Land use	Soil type (WRB)	Soil texture	Soil organic carbon (kg m ⁻²)	pH of topsoil	Sampling depth (cm)	Mean temperature in observed period (°C)	Mean annual temperature in observed period (°C)
Hainich (slope and valley)	Beech forest	Cambisols	Loamy clay	11.9*	5.7	20, 75	7.6	9.2
Sorø (near and far from tree)	Beech forest	Stagnic Luvisols	Loamy sand	9.8*	4.6	15, 100	8.2	9.6
Laois	Spuce forest	Stagnosols	Clay	2.2†	5.1	15, 70	9.1	10.9
Loobos	Pine forest	Haplic Arenosols	Sand	7.7‡	4.0	5, 120	9.5	10.9
Wetzstein	Spuce forest	Podzols	Sandy loam	8.7†	3.8	20, 90	5.6	7.3
Laqueuille (intensive and extensive use)	Grassland	Andosols	Silt loam	23.1‡	5.4	30, 90	6.6	7.9
Carlow (g) (slope and valley)	Grassland	Calcic Luvisols	Sandy loam	2.3†	7.5	20, 65	9.4	9.3
Easter Bush (slope and hollow)	Grassland	Gleyic Cambisols	Sandy loam	12.3*	5.4	30, 100	8.1	9.0
Früebüel	Grassland	Endogleyic Cambisols	Loamy clay	5.8†	5.5	30, 100	6.6	8.1
Grignon	Cropland	Calcic Cambisols	Silt loam	10.5*	7.3	40, 90	9.9	11.2
Klingenberg	Cropland	Stagnosols	Silt loam	9.7*	6.4	35, 75	7.1	8.8
Carlow (c)	Cropland	Eutric Cambisols	Sandy loam	7.3*	6.9	40	9.0	9.3

*Down to 60 cm depth.

†Down to 50 cm depth. Soil organic carbon data for Früebüel from Roth (2006).

‡Down to 30 cm depth.

Carlow (g): Carlow grassland, Carlow (c): Carlow cropland.

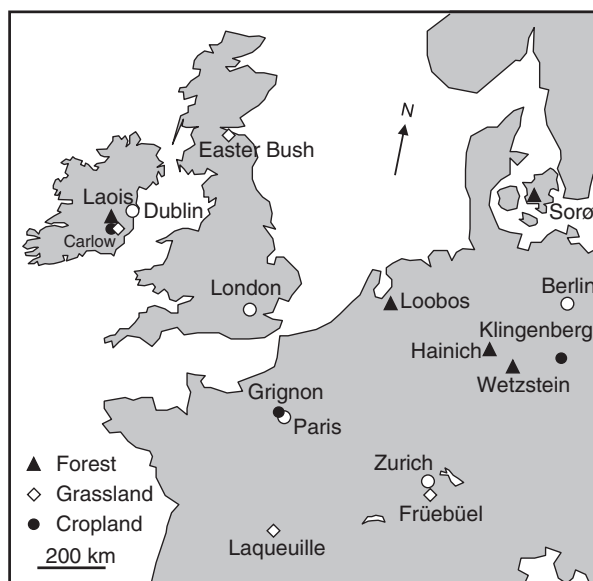


Fig. 1 Map of the research sites and their land use.

for the uncertainty caused by the enrichment of ^{13}C in soil air CO_2 , we used a value of -28‰ to calculate a minimum fraction of biogenic DIC and the measured $\delta^{13}\text{C}$ of soil air CO_2 to calculate a maximum biogenic fraction. A value of 0‰ was used for carbonate carbon. In addition, a value of -5‰ was used to assess the sensitivity of the calculated biogenic fraction to variations of this parameter.

The application of a mixing model with carbonates and CO_2 from soil respiration as the two end-members to derive the fraction of carbonate DIC relies on the assumption that the influence of isotopic exchange of DIC with atmospheric air ($\delta^{13}\text{C} \approx -8.5\text{‰}$) can be neglected. Isotopic exchange of DIC with atmospheric CO_2 would shift the $\delta^{13}\text{C}$ of DIC towards less negative values, which would cause a systematic overestimation of the carbonate-borne fraction of DIC when applying the two end-member mixing model mentioned above.

Delta ^{13}C values of DIC were determined using a Delta Plus XL isotope ratio mass spectrometer with GasBench II interface (Thermo-Finnigan MAT, Bremen, Germany, equipped with a Pal-80 autosampler, CEC Analytics, Zwingen, Switzerland), with an average deviation of 2‰ between replicate measurements. Samples for the determination of $\delta^{13}\text{C}$ values were collected between September 19, 2007 and October 31, 2007 from all sites. Measured DIC were corrected for isotopic fractionation during the dissolution of 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. Samples for the determination of $\delta^{13}\text{C}$ values of DIC were collected in October 2007. Insufficient sample volume was collected during this time as a consequence of drought at Grignon, so no $\delta^{13}\text{C}$ data are available for DIC samples from that site. Therefore, the biogenic fraction of DIC was calculated as the difference between the concentrations of DIC and the sum of Ca^{2+} and Mg^{2+} (in mmol L^{-1}) based on the stoichiometry of carbonate dissolution [Eqn (1)], assuming (i) that carbonate dissolution is the main source of Ca^{2+} and Mg^{2+} in

the calcareous soil and (ii) that chemical equilibrium is reached. A comparison of the method used for the Grignon site and the isotope method did not always yield identical results for the other sites. The release of Ca^{2+} and Mg^{2+} from litter in deciduous forests or fertilization of cropland with $\text{Ca}(\text{NO}_3)_2$ caused overestimates of the carbonate-borne DIC fraction, exceeding 100%.

Analysis of DOC concentrations

DOC concentrations of soil water samples were analysed using Pt-catalysed, high-temperature combustion (680°C) with a TOC-5050A analyser (Shimadzu Corp.). Before analysis, inorganic carbon was stripped off by adjusting the pH to 2 with HCl and sparging with CO_2 -free synthetic air.

Determination of iron and aluminium (hydr)oxide concentrations in soil horizons

Concentrations of poorly crystalline iron and aluminium oxides in the bulk soils at Wetzstein, Sorø, Laqueuille, Easter Bush, Hainich, and Grignon were determined by ammonium oxalate extraction (pH 3) in the dark according to Schwertmann (1964) and determination of iron and aluminium concentrations in extracts by ICP-OES.

Analysis of CO_2 and CH_4 in the gas phase

Gas samples were analysed with the GC-2014AF gas chromatograph used for determination of DIC concentrations. The $\delta^{13}\text{C}$ values of CO_2 in soil air samples were analysed using a HP 6890 gas chromatograph equipped with a BPX-5 column ($50\text{ m} \times 0.32\text{ mm} \times 0.5\text{ }\mu\text{m}$), linked via a combustion interface to a MAT 252 isotope ratio mass spectrometer (Thermo-Finnigan MAT, Bremen, Germany).

Calculation of fluxes

Fluxes of dissolved C were calculated by multiplying concentrations of DOC, DIC, and CH_4 , with the volume of leached water, which was derived from a soil water model. We used a capacity or 'bucket' model which assumes that leaching from a soil layer commences when the field capacity (FC in mm) is exceeded,

$$\text{if } \text{SWC}_i \leq \text{FC}, \text{ then } D_i = 0, \text{ else } D_i = c(\text{SWC}_i - \text{FC}), \quad (3)$$

with SWC_i denoting the soil water content at day i (mm), D_i the drainage volume at day i (mm day^{-1}), and c a rate constant (day^{-1}) defining the fraction of excess water that can drain per day. Changes in soil water contents over time were calculated from the soil water balance according to the following equation.

$$\text{SWC}_i = \text{SWC}_{i-1} + \text{INF}_i - \text{ET}_i, \quad (4)$$

with SWC_{i-1} indicating the soil water content of the preceding day (mm), INF_i denoting the infiltration at day i (mm), and ET_i the evapotranspiration at day i (mm). The soil water content was allowed to vary between the total pore volume of the soil (mm) and the water content at a soil metric potential of pF 4.2

(mm, wilting point). To this end, infiltration into the A horizon was restricted and diverted as 'rapid runoff' when the amount of precipitation exceeded the available pore volume of the soil matrix (mm) or the infiltration capacity (mm day^{-1}). This 'rapid runoff' might be discharged as surface runoff or flow through cracks and macropores. We did not consider carbon transport with this rapid runoff because the concentrations of DOC, DIC, and CH_4 therein were unknown. Water was replenished by capillary rise when SWC dropped below the soil water content at pF 4.2.

The model subdivided the soil pore volume into a fast and a slowly draining pool, each characterized by a specific total pore volume, FC and water content at pF 4.2. The proportion of precipitation entering the fast and the slow pool was assumed constant over time for each site. The model subdivided the soil profile into a topsoil layer and a subsoil layer. The fraction of water taken up by the plants from the subsoil was assumed constant over time and was set equal to the fraction of roots below the A horizon. An exception was the Carlow cropland for which only one soil layer above the gravelly subsoil was considered.

Values for total pore volume, FC, and water content at wilting point for the sum of the two soil water pools of each soil layer were matched to tabulated values (Boden, 1994), according to soil texture. In addition, the model parameters mentioned above were adjusted manually in a way that modelled soil water contents fitted *in situ* measured soil water contents. Input variables were precipitation, air temperature, and latent heat flux, which derived from eddy covariance measurements, either taken from the CarboEurope database (<http://gaia.agraria.unitus.it/database/carboeuropeip/>) or provided by the managers of the CarboEurope and NitroEurope sites. Actual evapotranspiration was calculated by dividing the latent heat flux derived from the database by the temperature-adjusted heat of evaporation. For the sites at Carlow and Laois, evapotranspiration was calculated according to approaches of Allen *et al.* (1998), Priestley & Taylor (1972), and Teklehaimanot & Jarvis (1991) because the gaps in eddy covariance data were too large to allow for calculation of reasonable evapotranspiration estimates. Details regarding the calculations of evapotranspiration at these sites are given in Walmsley (2009).

Statistics

Differences between land use types were tested for statistical significance using the nonparametric Kruskal–Wallis test, differences between sampling depths or terrain positions were analysed with the nonparametric Mann–Whitney *U*-test. The tests were carried out with the STATISTICA (version 8) software (Statsoft, Tulsa, OK, USA).

Results

Concentrations of DOC and DIC in soil water

DIC concentrations at shallow depths of forest sites ($2.5\text{--}23.9\text{ mg L}^{-1}$; mean: 8 mg L^{-1} , median: 4 mg L^{-1} ;

Fig. 2a) tended to be smaller than those of cropland ($22.7\text{--}50.5\text{ mg L}^{-1}$; mean: 35 mg L^{-1} , median: 33 mg L^{-1} ; Fig. 2c, $P = 0.09$, Kruskal–Wallis test). No significant differences were found between mean concentrations of forests and grasslands ($6\text{--}70\text{ mg L}^{-1}$; mean: 28 mg L^{-1} , median: 17 mg L^{-1} ; Fig. 2b, $P = 0.2$, Kruskal–Wallis test). Differences between subsoil DIC concentrations of forests ($2.5\text{--}67.7\text{ mg L}^{-1}$; mean: 34 mg L^{-1} , median: 33 mg L^{-1}), grasslands ($8.0\text{--}90.9\text{ mg L}^{-1}$; mean: 42 mg L^{-1} , median: 34 mg L^{-1}), and croplands ($28.3\text{--}84.8\text{ mg L}^{-1}$; mean: 57 mg L^{-1} , median: 57 mg L^{-1}) were not significant due to large variability within land use classes (Kruskal–Wallis test). DIC concentrations were insensitive to management intensity at Laqueuille (Fig. 2b) or topography at Hainich, Sorø (Fig. 2a), and Carlow grassland (Fig. 2b). Topography was important at Easter Bush, with significantly larger concentrations at the bottom of the valley than at the elevated position (Fig. 2b, shallow cups: $P = 0.009$; deep cups: $P = 0.075$, Mann–Whitney *U*-test).

Theoretical concentrations of DIC can be calculated from the partial pressures of soil air CO_2 and soil solution pH by applying Henry's law and assuming chemical equilibrium between CO_2 in the gas phase and solution H_2CO_3^* , HCO_3^- , and CO_3^{2-} . Total concentrations of DIC were close to equilibrium with partial pressures of soil air CO_2 for the Loobos, Wetzstein, Hainich, and Sorø forest sites (Fig. 3). Soil waters from all other sites were supersaturated with DIC relative to soil air CO_2 , especially in subsoils, which might be partly due to selective sampling of CO_2 -poor soil air from larger pores. Overall, the measured DIC concentrations were nearly equal to or greater than theoretical concentrations, indicating that outgassing of soil water samples was successfully minimized by the sampling method.

DIC concentrations were commonly much larger than DOC concentrations, particularly in subsoils (Fig. 2). Exceptions were the acidic soils at the Wetzstein and Loobos forest sites, with DIC representing $<10\%$ of the total dissolved carbon leached from topsoils and 16–30% in subsoils. Concentrations of DOC leached from topsoils of grasslands (median: 7 mg L^{-1} , mean: 8 mg L^{-1} ; range $1.9\text{--}17.1\text{ mg L}^{-1}$, Fig. 2b), croplands (median: 14 mg L^{-1} , mean: 12 mg L^{-1} , range: $3.9\text{--}17.3\text{ mg L}^{-1}$, Fig. 2c), and forests (median: 24 mg L^{-1} , mean: 23 mg L^{-1} ; range: $7.1\text{--}43.1\text{ mg L}^{-1}$, Fig. 2a) did not differ significantly due to large variation within land use classes ($P = 0.16$, Kruskal–Wallis test). A close positive relationship was observed between DOC concentrations at shallow sampling depths and topsoil C/N ratios (Fig. 4). We found no relationship between DOC concentrations and soil organic matter concentrations.

Differences between average subsoil DOC concentrations of land use systems were rather small: 11 mg L^{-1}

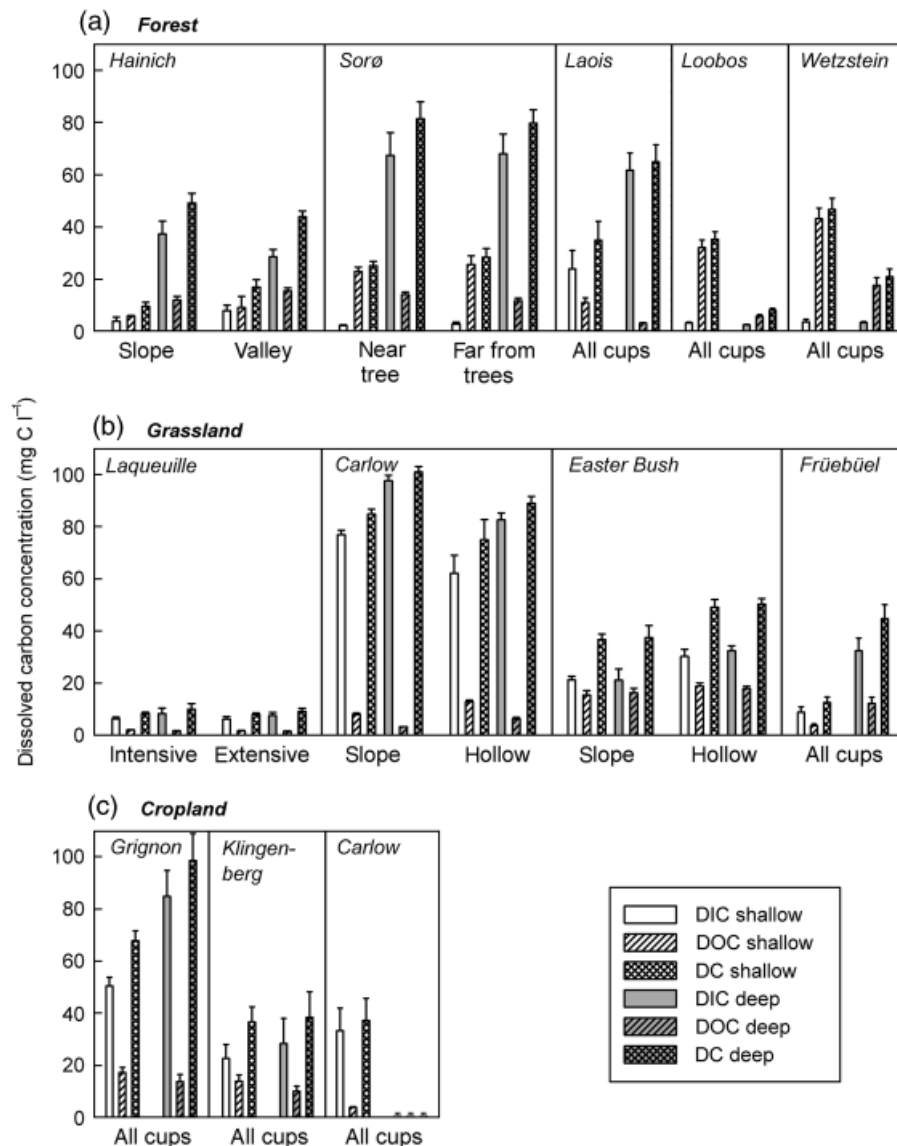


Fig. 2 Concentrations of total dissolved inorganic carbon (DIC, open), dissolved organic carbon (DOC, hatched), and total dissolved carbon (DC, crosshatched) below the soil A horizon (white) and below the main rooting zone (gray). Concentrations represent the arithmetic mean of the median concentrations of all suction cups in one depth over time. Error bars represent the standard error of five suction cups (terrain positions) or 10 suction cups (all cups) and indicate the uncertainty due to spatial variability of concentrations.

for forests (median: 13 mg L^{-1}), 12 mg L^{-1} for arable fields (median: 14 mg L^{-1}), and 9 mg L^{-1} for grasslands (median: 8 mg L^{-1}), with the latter value being somewhat lower due to small DOC concentrations in the Laqueuille Andosols (Fig. 2b).

Isotopic signature and sources of DIC

The $\delta^{13}\text{C}$ signatures of DIC in samples collected from subsoils clustered into two groups. Samples from the Hainich, Sorø, Laois, and Carlow grassland were all

characterized by $\delta^{13}\text{C}$ values close to -15‰ , with little variation between different suction cups (Fig. 5b). At Fräebüel, samples from eight suction cups were close to -15‰ , while the sample from one cup showed a value of -22‰ (Fig. 5b). Soils at Hainich, Sorø, Laois, Carlow, and Fräebüel all developed from carbonate-containing parent materials, which is Muschelkalk limestone at the Hainich site and glacial till at the other sites. Average $\delta^{13}\text{C}$ values of DIC were all below -20‰ at the Wetzstein, Laqueuille, Easter Bush, and Klingenberg sites (Fig. 5b). Soils at the Loobos, Wetzstein, Laqueuille,

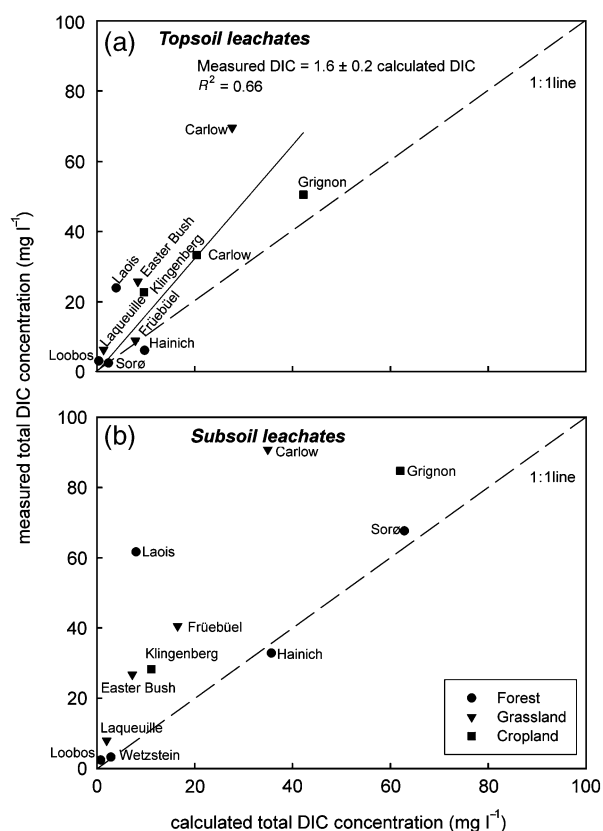


Fig. 3 Comparison of measured average total dissolved inorganic carbon (DIC) concentrations with average concentrations calculated from average partial pressures of soil air CO_2 and average soil solution pH using Henry's law. No calculated concentration can be given for topsoil leachates of the Wetzstein site, because wild boars destroyed the shallow soil air samplers.

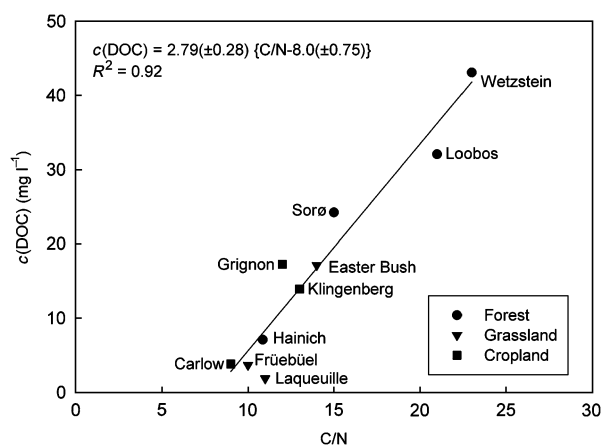


Fig. 4 Average concentrations of dissolved organic carbon (DOC) leached from topsoils as a function of topsoil C/N ratio. All sites for which C/N ratios were available were included into the relationship. Averages were calculated as the arithmetic mean of median concentrations of suction cups and suction plates over time. Topsoils reach down to the shallow depth of instrumentation given in Table 1.

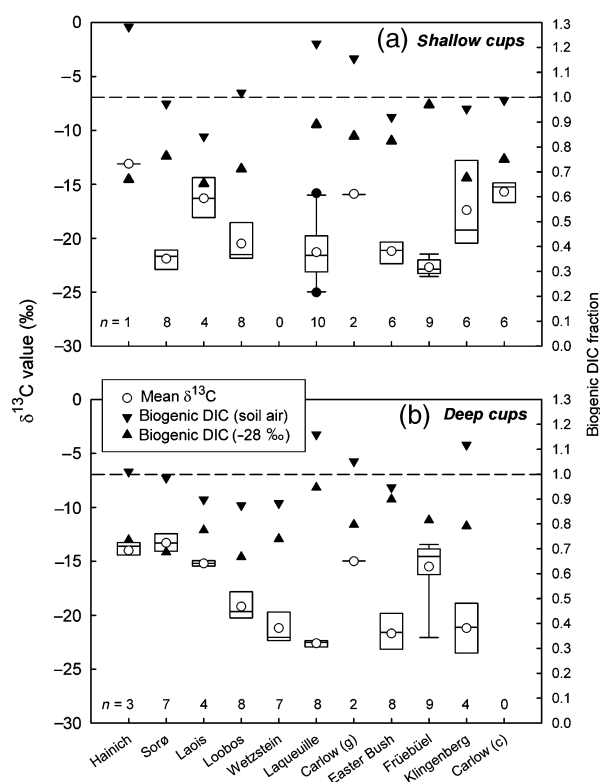


Fig. 5 $\delta^{13}\text{C}$ values (box plots and arithmetic mean as white dot) and the biogenic fraction of dissolved inorganic carbon (DIC, black triangles). The lower value of the biogenic fraction was calculated using a $\delta^{13}\text{C}$ of -28‰ for the biogenic end-member and a $\delta^{13}\text{C}$ of 0‰ for carbonates. The upper value of the biogenic fraction was calculated using the $\delta^{13}\text{C}$ of value of soil air CO_2 at the time of soil water collection and a $\delta^{13}\text{C}$ of 0‰ for carbonates. Use of a $\delta^{13}\text{C}$ of -5‰ for carbonate carbon reduced the calculated biogenic fraction on average by 5% (biogenic end-member of -28‰).

Easter Bush, and Klingenberg sites developed from carbonate-free parent material. Less negative values were found in the subsoil at the Loobos site. In contrast to subsoils, DIC from shallow depths of the Sorø and Frübüel sites had more negative $\delta^{13}\text{C}$ values below -20‰ , reflecting the dissolution of carbonates in topsoils during soil development (Fig. 5a).

Using a value of -28‰ for the biogenic end-member and a value of 0‰ for carbonate carbon, a biogenic DIC fraction of 74–82% was calculated for the calcareous subsoils of the Hainich, Sorø, Laois, and Frübüel sites and used to estimate leaching losses of total biogenic carbon (Fig. 5b, upright triangles). The fraction was reduced by 1–11% if an extreme value of -5‰ was assumed for carbonate carbon. Use of the measured $\delta^{13}\text{C}$ of soil air CO_2 increased the calculated biogenic fraction for DIC from the calcareous subsoils to 90–105%. An extreme value of 293% was calculated for the

Früebüel site, but this implausible value likely resulted from a contamination of soil air samples with atmospheric air during the extraction of air samples from the wet Früebüel soil.

Contrary to geochemical theory [Eqn (2)], the biogenic DIC fractions calculated for the carbonate-free subsoils at the Loobos, Wetzstein, and Klingenberg sites, using the end-members -28‰ and 0‰ , were much lower than the expected 100%. This might be caused by more intense isotopic exchange of soil air and DIC with atmospheric air. Indeed, when using measured $\delta^{13}\text{C}$ values of soil air CO_2 in the calculation, the estimated biogenic fraction was $>100\%$ for the Klingenberg site. For the Lobos and Wetzstein sites, however, calculated biogenic fractions remained below

100%, which might indicate a contamination of the little DIC pool in the acidic samples from these sites with atmospheric CO_2 during sampling and sample handling. In line with geochemical theory [Eqn (2)], we used a biogenic DIC fraction of 100% for calculating the total biogenic carbon leaching loss from the carbonate-free Loobos, Wetzstein, Laqueuille, Easter Bush, and Klingenberg soils.

Water balance of the study sites

Mean annual precipitation during our study period ranged from 710 mm yr^{-1} at Grignon to 1771 mm yr^{-1} at Früebüel, with an average of 1009 mm yr^{-1} across all sites (Table 2). The average loss of water by evapotran-

Table 2 Water balance of the research sites during the investigated period

						Average relative deviation of modelled water contents from measured ones	
Site	Precipitation	Evapotranspiration	Rapid runoff	Drainage		Shallow	Deep
				From A-horizon	From soil profile		
<i>Cumulative water fluxes during period of observations (mm)</i>							
Hainich	1363	374	589	572	326	14	No sensor
Sorø	1345	318	141	1086	915	20	No sensor
Laois	2594	1192	944*	542†	441	12	8
Loobos	1452	819	59	1036	646	24	No sensor
Wetzstein	1358	466	335	790	508	7	No sensor
Laqueuille	1757	997	62	952	720	5	4
Carlow (g)	2236	753	0	1627	1515	14	6
Easter Bush	966	250	13	752	695	14	No sensor
Früebüel	2178	797	449	1061	941	5	2
Grignon	1027	662	189	438	189	17	8
Klingenberg	1307	289	40	1038	975	17	No sensor
Carlow (c)	2236	669	0	1595	–	13	–
<i>Mean annual water fluxes (mm yr⁻¹)</i>							
Hainich	1008	346	489	335	166	–	–
Sorø	928	287	112	688	531	–	–
Laois	1040	561	357‡	202†	149	–	–
Loobos	982	609	33	683	406	–	–
Wetzstein	966	428	252	498	259	–	–
Laqueuille	1295	773	55	670	486	–	–
Carlow (g)	894	345	0	620	569	–	–
Easter Bush	735	141	13	610	584	–	–
Früebüel	1711	666	399	751	651	–	–
Grignon	710	523	132	266	95	–	–
Klingenberg	950	242	33	713	652	–	–
Carlow (c)	894	308	0	598	–	–	–

Drainage from A-horizon denoted fluxes deeper than the upper instrumentation depth given in Table 1, drainage from soil profile refers to water fluxes deeper than the lower instrumentation depth of Table 1.

*Total rapid runoff including surface runoff of 349 mm .

†Infiltration into B horizon excluding rapid lateral runoff.

‡Total rapid runoff including surface runoff of 135 mm yr^{-1} .

spiration was 436 mm yr^{-1} . The average relative deviation of modelled soil water contents from measured ones was 14% for the shallow depths and 6% for subsoils (Table 2). Figure 6c and d provides a visual impression of the goodness of fit between measured and modelled soil water contents for the Carlow grassland site, where the quality of the model fit was exactly the average of all sites.

Especially at the sites with clayey soils (Hainich, Laois, and Fr  eb  el), modelled water contents could only be matched to measured ones when large volumes of water ($357\text{--}489 \text{ mm yr}^{-1}$) were discharged by rapid runoff via surface flow or preferential flow paths in the calibrated water balance model (Table 2). On average 429 mm yr^{-1} of water were left over for drainage from the soil profile after subtracting evapotranspiration and rapid runoff from precipitation (Table 2).

Leaching losses of dissolved carbon

Across all sites, an average of $4.2 \text{ g DOC m}^{-2} \text{ yr}^{-1}$ was leached from soils, with rather small differences between land use systems (Table 3). Subtracting DOC leached from subsoils from DOC fluxes from topsoils indicated that as much as 17 (Wetzstein) to $20 \text{ g m}^{-2} \text{ yr}^{-1}$ (Loobos) of DOC was retained in acidic forest B horizons (Table 3). Other forest B horizons retained only 2 (Laois) to $9 \text{ g DOC m}^{-2} \text{ yr}^{-1}$ (Sor  ) and retention in the B horizons of grasslands or arable fields was generally smaller than $5.5 \text{ g DOC m}^{-2} \text{ yr}^{-1}$ (Table 3). Retention of DOC in B horizons decreased exponentially with increasing ratio of organic carbon to the sum of oxalate-extractable iron and aluminium present in the bulk soil (Fig. 7).

The average loss of DIC from forest topsoils was significantly smaller than DIC leaching from grassland topsoils ($P = 0.03$) and tended also to be smaller than leaching from cropland topsoils ($P = 0.09$, Table 4). Leaching losses of DIC from subsoils, however, did not differ significantly between land use types ($P = 0.31$, Kruskal–Wallis test).

As a result of the strong retention of DOC and the low DIC concentrations, total biogenic dissolved carbon (DOC plus biogenic DIC) leaching from forest soils tended to be smaller than leaching from grasslands or arable fields (Table 5). Differences, however, were not significant ($P = 0.23$, Kruskal–Wallis test) because the variability between sites under similar land use was large. The overall average biogenic dissolved carbon loss from soils was $19.3 \text{ g m}^{-2} \text{ yr}^{-1}$. This value was strongly influenced by large losses from the forest at Sor   and the grasslands at Easter Bush and Carlow. Consequently, the median flux across all sites was smaller ($15.2 \text{ g C m}^{-2} \text{ yr}^{-1}$).

CH₄ concentrations in soil air and its leaching losses

CH₄ concentrations in soil air at shallow depths were mostly smaller than global average atmospheric concentrations of $1.7 \mu\text{L L}^{-1}$, indicating that most sites could have acted as sinks for atmospheric CH₄ (Table 6). Exceptions were the Laois and Klingenberg Stagnosols. In subsoils, CH₄ concentrations larger than atmospheric ones were only found in the Laois Stagnosols and in the Easter Bush Gleyic Cambisols at the hollow terrain position.

Leaching losses of CH₄ were $<5 \text{ mg CH}_4\text{--C m}^{-2} \text{ yr}^{-1}$ at most sites. Even the largest loss of $26 \pm 2 \text{ mg CH}_4\text{--C m}^{-2} \text{ yr}^{-1}$, measured at Klingenberg, was equivalent to a loss of only $0.23 \text{ g CO}_2\text{--C}_{\text{eq}} \text{ m}^{-2} \text{ yr}^{-1}$ when applying a warming potential of 25 (Table 6). Leaching of CH₄ was therefore not relevant for the greenhouse gas budget of the investigated sites.

Discussion

Uncertainties of calculated leaching losses

The errors for the estimates of leaching losses, indicated in brackets in Tables 3–6, only reflect the uncertainty caused by the spatial variation of DIC, DOC, and dissolved CH₄ concentrations. Additional uncertainties arise from the modelling of the water balance, the spatial variation of water fluxes, and the calculation of the biogenic fraction of DIC from its $\delta^{13}\text{C}$ signature.

We assessed the uncertainty of evapotranspiration measurements using the eddy covariance method by analysing the energy balance of the Klingenberg site for the years 2006 and 2007 (Vowinkel, 2008). A regression between net radiation and the sum of sensible and latent heat flux (assuming a negligible net soil heat flux over long-term periods) showed that approximately 68% of the available energy was consumed by turbulent heat fluxes only. Using the slope of this regression and monthly means of the Bowen ratio as well as the available energy, measured latent heat fluxes were subsequently corrected. Monthly correction factors ranged from 1.01 to 1.89 and averaged 1.66, which means an underestimation of the eddy covariance-based evapotranspiration at the Klingenberg site during our study period from October 2006 to March 2008 by approximately 182 mm.

This systematic underestimation of evapotranspiration is roughly compensated by a systematic underestimation of precipitation by standard rainfall collectors due to evaporation from the wet funnel surface and wind turbulence (Richter, 1995). Applying the empirical correction of Richter (1995) to precipitation data of the Klingenberg site (assuming that

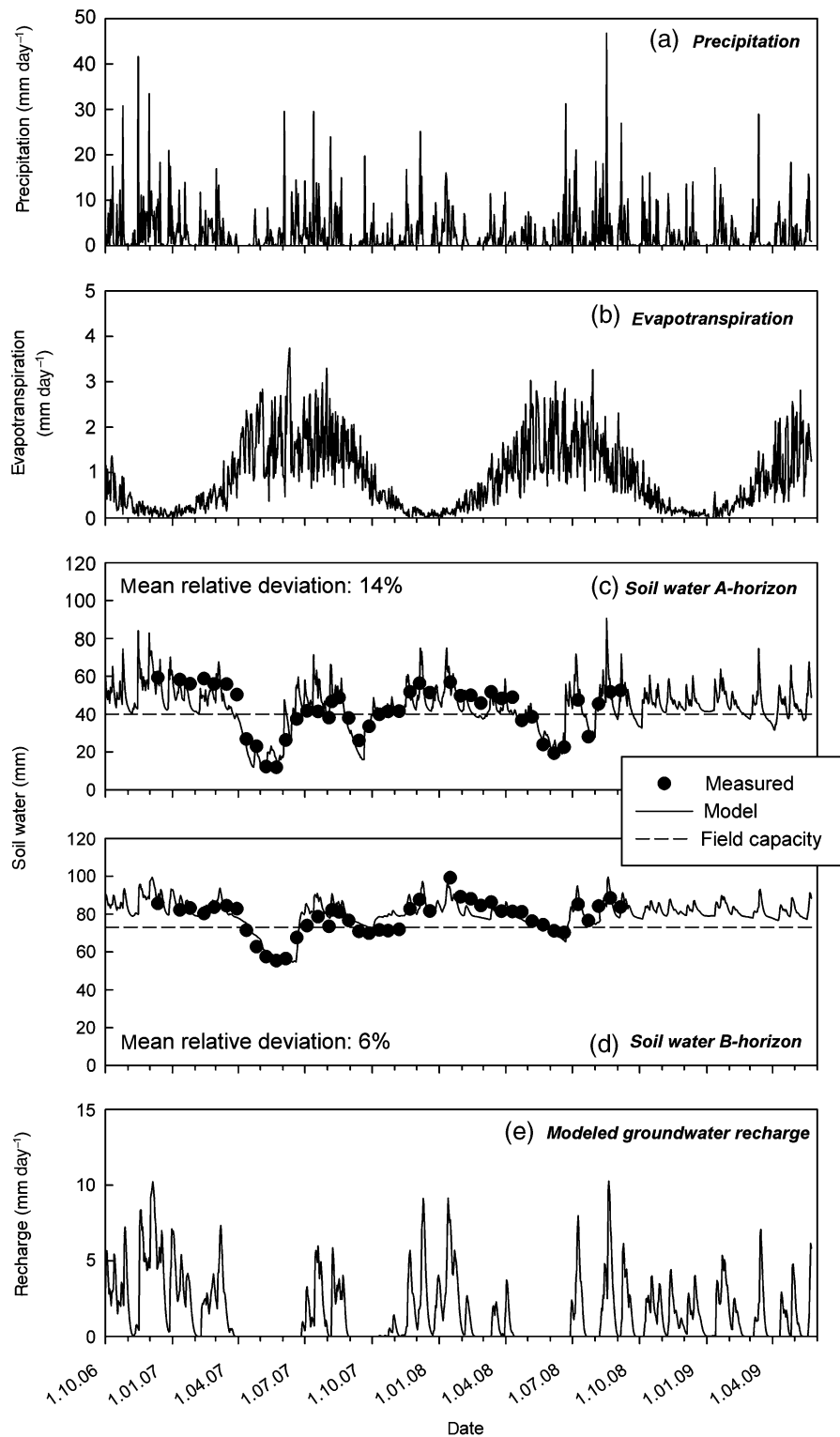


Fig. 6 Precipitation (a), evapotranspiration (b), measured and modelled soil water volumes (c and d), and modelled groundwater recharge (e) for the Carlow grassland. The average relative deviation of the modelled soil water volume was 14% for the A horizon and 6% for the B horizon (Table 2).

Table 3 Leaching losses of dissolved organic carbon (DOC) from topsoils and subsoils of the research sites

Site	Loss from topsoils						Loss from subsoils					
	Winter (g C m ⁻²)		Summer (g C m ⁻²)		Total (g C m ⁻² yr ⁻¹)		Winter (g C m ⁻²)		Summer (g C m ⁻²)		Total (g C m ⁻² yr ⁻¹)	
Hainich												
Slope	1.3	(0.1)	0.7	(0.0)	2.0	(0.1)	2.6	(0.0)	0.0	(0.0)	2.6	(0.0)
Valley	1.8	(0.1)	1.4	(0.0)	3.2	(0.1)	1.9	(0.0)	0.0	(0.0)	1.9	(0.0)
Sorø												
Near tree	8.7	(0.3)	7.5	(0.3)	16.2	(0.4)	5.7	(0.5)	2.7	(0.2)	8.3	(0.5)
Between trees	9.3	(0.5)	8.4	(0.4)	17.8	(0.6)	4.7	(0.2)	2.6	(0.1)	7.3	(0.3)
Laois	1.8	(0.8)	1.0	(0.4)	2.8*	(0.9)	0.6	(0.2)	0.0	(0.0)	0.6	(0.2)
Loobos	10.3	(0.5)	11.5	(0.9)	21.8	(1.1)	1.4	(0.1)	0.8	(0.1)	2.2	(0.1)
Wetzstein	11.3	(0.5)	10.0	(0.4)	21.3	(0.7)	4.5	(0.6)	0.3	(0.2)	4.7	(0.7)
<i>Average forest</i>	<i>6.8</i>	<i>(2.1)</i>	<i>6.3</i>	<i>(2.2)</i>	<i>13.1</i>	<i>(4.3)</i>	<i>2.8</i>	<i>(0.9)</i>	<i>0.8</i>	<i>(0.5)</i>	<i>3.5</i>	<i>(1.3)</i>
<i>Median forest</i>	<i>9.0</i>		<i>8.0</i>		<i>17.0</i>		<i>2.3</i>		<i>0.3</i>		<i>2.3</i>	
Laqueuille												
Intensive use	0.5	(0.0)	1.5	(0.1)	2.0	(0.1)	0.3	(0.0)	0.7	(0.0)	1.1	(0.0)
Extensive use	0.6	(0.0)	1.4	(0.1)	2.0	(0.1)	0.4	(0.0)	0.7	(0.0)	1.1	(0.0)
Carlow (g)												
Slope	3.1	(0.5)	2.2	(0.4)	5.3	(0.6)	1.3	(0.2)	0.7	(0.2)	2.0	(0.3)
Valley	5.1	(0.6)	3.7	(0.4)	8.8	(0.7)	2.2	(0.3)	1.1	(0.2)	3.3	(0.4)
Easter Bush												
Slope	6.4	(0.3)	4.9	(0.2)	11.2	(0.3)	5.0	(0.2)	3.8	(0.2)	8.7	(0.3)
alley	7.2	(0.4)	7.3	(0.7)	14.5	(0.8)	5.6	(0.1)	5.1	(0.3)	10.7	(0.3)
Früebüel	1.2	(0.1)	1.9	(0.2)	3.1	(0.2)	3.4	(0.3)	4.2	(0.4)	7.6	(0.5)
<i>Average grassland</i>	<i>3.2</i>	<i>(1.4)</i>	<i>3.1</i>	<i>(1.0)</i>	<i>6.3</i>	<i>(2.5)</i>	<i>2.7</i>	<i>(1.1)</i>	<i>2.6</i>	<i>(1.0)</i>	<i>5.3</i>	<i>(2.0)</i>
<i>Median grassland</i>	<i>2.7</i>		<i>2.4</i>		<i>5.1</i>		<i>2.6</i>		<i>2.6</i>		<i>5.1</i>	
Grignon	3.6	(0.1)	0.1	(0.0)	3.7	(0.1)	2.8	(0.1)	ND	–	2.8	(0.1)
Klingenberg	4.0	(0.2)	3.4	(0.2)	7.4	(0.3)	3.2	(0.3)	2.1	(0.1)	5.3	(0.3)
Carlow (c)	1.7	(0.4)	0.9	(0.2)	2.6	(0.5)	–	–	–	–	–	–
<i>Average cropland</i>	<i>3.1</i>	<i>(0.7)</i>	<i>1.5</i>	<i>(1.0)</i>	<i>4.6</i>	<i>(1.4)</i>	<i>3.0</i>	<i>(0.2)</i>	<i>1.1</i>	<i>(1.1)</i>	<i>4.1</i>	<i>(1.3)</i>
<i>Median cropland</i>	<i>3.6</i>		<i>0.9</i>		<i>3.8</i>		<i>3.0</i>		<i>2.1</i>		<i>4.1</i>	
<i>Total average DOC flux</i>	<i>4.7</i>	<i>(1.1)</i>	<i>4.0</i>	<i>(1.1)</i>	<i>8.7</i>	<i>(2.2)</i>	<i>2.8</i>	<i>(0.5)</i>	<i>1.6</i>	<i>(0.5)</i>	<i>4.2</i>	<i>(0.9)</i>
<i>Median DOC flux</i>	<i>3.8</i>		<i>2.4</i>		<i>5.4</i>		<i>2.8</i>		<i>0.9</i>		<i>2.8</i>	

The winter period is from October 1 until March 30. Winter data are the average of winters 2006/2007 and 2007/2008 (and 2008/2009 for Irish sites). The summer period started on April 1 and ended on September 30. For Irish sites, the summer value is the average of summers 2007 and 2008, for all other sites it is the value for summer 2007.

The numbers in italics are averages, medians, and standard deviations. Numbers in brackets indicate standard deviations due to spatial variability of concentrations for individual sites and the standard error of the average across sites with the same land use system or across all sites. ND, not detectable.

*Excluding lateral runoff of 3.0 g DOC m⁻² yr⁻¹. Topsoils reach down to the shallow instrumentation depth, subsoil reach down to the deeper instrumentation depth given in Table 1.

precipitation at temperatures <0 °C occurs as snow) indicated an underestimation of the rainfall by 216 mm.

A major uncertainty of the soil water model is the calculated rapid runoff. At Laois, the relevance of lateral water flows could easily be deduced from the clayey soil texture and the occurrence of drainage ditches on the plot. Here, micro-catchments were constructed by separating areas of 10–12 m² by trenches and wooden boards in a way that lateral runoff could be collected in a down slope trench, so that modelled lateral flows could be matched to measured water

volumes (Walmsley, 2009). No micro-catchments were available at Früebüel and Hainich, which were also characterized by clayey soils and rapid runoff. For these sites, the results of our water balance model were compared with results of the BLAU 'bucket' model of Huwe (1991), which was extended with a surface runoff routine. For Früebüel, the results of the BLAU model deviated from the results in Table 2 by only 2% for surface/rapid runoff (440 vs. 449 mm) and by 0.3% for drainage from the soil profile (944 vs. 941 mm). A good agreement between results of the two models was also

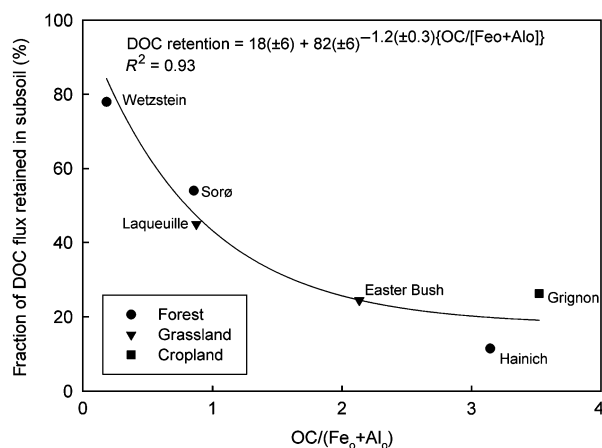


Fig. 7 Retention of dissolved organic carbon (DOC) in B horizons of soils related to the ratio of organic carbon (OC) and the sum of oxalate-extractable iron (Fe_o) and aluminium (Al_o) of B horizons. Data for oxalate-extractable iron and aluminium were only available for the displayed sites.

found for the Hainich site; rapid/surface runoff and drainage from the soil profile deviated by only 4%.

Dissolved carbon fluxes associated with rapid runoff could not be calculated because concentrations in that runoff were not assessed. According to Kaiser *et al.* (2000), leaching losses of DOC from shallow forest soils (Rendzic Leptosols) via preferential flow paths during heavy rainstorms were similar to mean annual fluxes as determined for soil matrix flow. This potential underestimation of DOC losses due to preferential flow and rapid runoff of soil water might partly have been compensated for in our study by an overestimation of DIC losses since DIC concentrations in soil water rapidly draining through large pores are probably smaller than concentrations in water in slowly draining pores of the soil matrix. We are not aware of any study that has analysed concentrations of DIC in preferential flow.

Biogenic DIC concentrations are also subjected to an error associated with the determination of the fraction of carbonate-borne DIC using the DIC $\delta^{13}\text{C}$ signature. The largest source of error is contamination or isotopic exchange of DIC with atmospheric air. Contamination and isotopic exchange with atmospheric air would shift the measured $\delta^{13}\text{C}$ values to less negative values, resulting in systematic underestimation of biogenic DIC concentrations. According to the stoichiometry of carbonate dissolution, the fraction of biogenic DIC in soil water of calcareous soils must exceed 50% and, of course, it should be smaller than 100%. This limits the potential underestimation of biogenic DIC concentrations and fluxes from calcareous soils to 18–31%. The potential overestimation of biogenic DIC concentrations resulting from the assumption of an average $\delta^{13}\text{C}$ value

of 0‰ for carbonates was 1–11% (average 5%). Our results indicated greater isotopic exchange between DIC and atmospheric air for samples from carbonate-free subsoils, especially for the acidic forest subsoils at Loobos and Wetzstein. For these subsoils, however, the assumption of 100% biogenic DIC according to the stoichiometry of weathering reactions is safe and the relevance of the small DIC concentrations at these sites for total carbon leaching is limited.

Factors controlling dissolved carbon concentrations and leaching losses

The positive correlation between soil C/N ratios and DOC concentrations and fluxes in terrestrial ecosystems across biomes was first published by Aitkenhead & McDowell (2000). In contrast to the observation of Aitkenhead & McDowell (2000), DOC concentrations and fluxes in our study correlated only to topsoil C/N ratios (upper 5–40 cm, Table 1) and not to C/N ratios of the entire soils down to 65–100 cm depth. Due to the accumulation of organic matter, topsoils and organic layers are regarded as the soil compartments that are the most important for the generation of DOC (e.g., Guggenberger & Kaiser, 2003). The topsoil C/N ratio is indicative of the litter quality and the intensity of microbial transformation processes. Large C/N ratios indicate poorly degradable litter and a slow transformation and recycling of organic matter. Studies using $\delta^{13}\text{C}$ or ^{14}C to track sources and turnover of DOC (Schiff *et al.*, 1997; Flessa *et al.*, 2000; Hagedorn *et al.*, 2004; Fröberg *et al.*, 2007) suggest that dissolved organic matter, which is transported over decimetres or metres down into subsoils, mainly represents highly altered residues of organic matter processing. Processing of nitrogen-poor organic matter seems to result in production of more soluble residues, which explains the positive correlation between soil C/N ratios and DOC concentrations. A positive correlation between DOC production and C/N ratios of soil organic matter was also observed in laboratory experiments (Gödde *et al.*, 1996; Kalbitz & Knappe, 1997). A hypothesis put forward by Gödde *et al.* (1996) to explain this relationship was that microbial communities in soils with large C/N ratios have to process more organic matter to satisfy their nitrogen requirements than communities in soils with small C/N ratios. In this way, more DOC is produced as leftover of soil organic matter degradation in nitrogen-poor soils. At C/N ratios $\ll 10$, most carbon associated with processed soil organic matter is either respired or re-assimilated so that only small amounts of DOC are produced. The regression equation in Fig. 4 suggests that above a critical C/N ratio of approximately eight increasing amounts of soluble

Table 4 Leaching losses of total dissolved inorganic carbon from topsoils and subsoils of the research sites

Site	Loss from topsoils						Loss from subsoils					
	Winter (g C m ⁻²)		Summer (g C m ⁻²)		Total (g C m ⁻² yr ⁻¹)		Winter (g C m ⁻²)		Summer (g C m ⁻²)		Total (g C m ⁻² yr ⁻¹)	
Hainich												
Slope	1.5	(0.2)	0.6	(0.1)	2.1	(0.3)	9.1	(0.0)	0.4	(0.0)	9.4	(0.0)
Valley	2.5	(0.1)	1.2	(0.0)	3.6	(0.1)	5.9	(0.1)	0.4	(0.0)	6.2	(0.1)
Sorø												
Near tree	1.4	(0.1)	1.3	(0.2)	2.7	(0.2)	22.4	(1.1)	22.5	(4.4)	44.9	(4.6)
Between trees	1.8	(0.2)	1.6	(0.2)	3.4	(0.3)	19.4	(0.8)	14.5	(1.5)	33.9	(1.7)
Laois	4.4	(2.5)	2.1	(1.4)	6.5*	(2.7)	8.5	(1.2)	0.5	(0.1)	9.1	(1.2)
Loobos	0.7	(0.0)	1.3	(0.2)	2.0	(0.2)	0.4	(0.0)	0.4	(0.0)	0.8	(0.0)
Wetzstein	2.3	(0.0)	1.4	(0.1)	3.7	(0.1)	0.9	(0.1)	0.1	(0.0)	1.0	(0.1)
<i>Average forest</i>	2.2	(0.4)	1.4	(0.2)	3.6	(0.8)	7.6	(3.7)	4.0	(3.6)	11.6	(7.2)
<i>Median forest</i>	2.0		1.4		3.1		7.5		0.4		7.8	
Laqueuille												
Intensive use	2.4	(0.3)	6.3	(0.6)	8.7	(0.7)	1.7	(0.3)	4.4	(1.3)	6.1	(1.3)
Extensive use	2.3	(0.2)	6.2	(0.6)	8.4	(0.6)	2.0	(0.2)	2.7	(0.7)	4.7	(0.7)
Carlow (g)												
Slope	30.6	(1.7)	17.1	(0.7)	47.7	(1.8)	32.5	(2.4)	16.9	(1.6)	49.5	(2.9)
Valley	25.7	(3.2)	13.3	(1.9)	39.1	(3.7)	31.4	(1.3)	14.7	(0.9)	46.1	(1.7)
Easter Bush												
Slope	9.8	(0.5)	6.3	(0.7)	16.1	(0.9)	8.7	(0.5)	4.4	(0.3)	13.1	(0.6)
Valley	15.5	(0.7)	10.5	(1.7)	26.0	(1.8)	18.5	(0.7)	9.0	(0.7)	27.5	(1.0)
Früebüel	3.9	(0.4)	5.0	(0.4)	8.8	(0.6)	13.4	(1.1)	30.3	(2.0)	43.6	(2.3)
<i>Average grassland</i>	11.8	(5.9)	8.7	(2.3)	20.5	(8.2)	14.5	(6.3)	12.6	(4.7)	27.1	(9.2)
<i>Median grassland</i>	8.3		7.3		14.9		12.2		11.3		27.6	
Grignon	7.8	(0.2)	0.2	(0.0)	8.0	(0.2)	13.3	(0.3)	0.0	(0.0)	13.3	(0.3)
Klingenberg	12.6	(0.8)	5.5	(0.3)	18.0	(0.8)	12.8	(1.0)	6.6	(0.6)	19.4	(1.2)
Carlow (c)	13.2	(4.2)	7.9	(2.9)	21.1	(5.1)	–	–	–	–	–	–
<i>Average cropland</i>	11.2	(1.7)	4.5	(2.3)	13.7	(3.0)	11.3	(1.3)	3.3	(2.7)	16.4	(2.5)
<i>Median cropland</i>	12.6		5.5		15.2		11.3		3.3		16.4	
<i>Total average DIC flux</i>	7.6	(2.3)	4.6	(1.3)	12.3	(3.5)	11.1	(2.7)	7.0	(2.2)	18.1	(4.6)
<i>Median DIC flux</i>	4.2		3.6		8.3		10.7		3.6		13.3	

The winter period is from October 1 until March 30. Winter data are the average of winters 2006/2007 and 2007/2008 (and 2008/2009 for Irish sites). The summer period started on April 1 and ended on September 30. For Irish sites, the summer value is the average of summers 2007 and 2008, for all other sites it is the value for summer 2007.

The numbers in italics are averages, medians, and standard deviations. Numbers in brackets indicate standard deviations due to spatial variability of concentrations for individual sites and the standard error of the average across sites with the same land-use system or across all sites; the errors do not reflect uncertainties associated with the calculation of the biogenic fraction of DIC with the isotope method (see text).

*Excluding lateral runoff of 3.7 g DIC m⁻² yr⁻¹ (Walmsley, 2009). Topsoils reach down to the shallow instrumentation depth, subsoil reach down to the deeper instrumentation depth given in Table 1.

carbon residues are produced with increasing C/N ratio of soil organic matter. It is plausible to expect that DOC leaching from topsoils only occurs if a critical C/N ratio is exceeded.

Leaching of DOC from subsoils was controlled by retention in B horizons, with this retention being related to the ratio of organic carbon to the sum of oxalate-extractable iron plus aluminium (Fig. 7). Oxalate-extractable iron and aluminium are a measure of the concen-

tration of poorly crystalline iron and aluminium (hydr)oxides with a high specific surface area in soils. These iron and aluminium(hydr)oxides are considered to be the most important sorbents for dissolved organic matter in soils (e.g., Kaiser *et al.*, 1996). The ratio of organic carbon to the concentration of iron and aluminium (hydr)oxides in B horizons is therefore an indicator of the saturation of the available capacity of subsoils to sorb the DOC they receive from topsoils.

Table 5 Leaching losses of dissolved organic carbon (DOC) plus biogenic dissolved inorganic carbon (DIC) in relation to the net ecosystem exchange (NEE) and net ecosystem carbon balance (NECB) of the study sites

Site	Leaching loss from (sub)soils			Average multiyear NEE* (g C m ⁻² yr ⁻¹)	NEE + fertilization – harvest		NECB	
	Winter (g C m ⁻²)	Summer (g C m ⁻²)	Total (g C m ⁻² yr ⁻¹)		Excluding leaching (g C m ⁻² yr ⁻¹)	Leached fraction of balance (%)		Including leaching (g C m ⁻² yr ⁻¹)
Hainich	7.6 (0.1)	0.3 (0.0)	8.0 (0.1)	+ 294†	+ 294†	3	+ 286	
Sorø	19.8 (1.2)	15.5 (3.9)	35.2 (4.1)	+ 143‡	+ 143‡	25	+ 108	
Laos	7.0 (1.1)	0.4 (0.1)	7.4 (1.1)	+ 873§	+ 873§	1	+ 866	
Loobos	1.8 (0.1)	1.2 (0.1)	3.0 (0.1)	+ 402¶	+ 402¶	1	+ 399	
Wetzstein	5.4 (0.6)	0.3 (0.2)	5.7 (0.7)	+ 177	+ 177	3	+ 171	
Average forest	8.3 (3.0)	3.5 (3.0)	11.9 (5.9)	378(132)	378(132)	6(5)	366(134)	
Median forest	7.0	0.4	7.4	294	294	3	286	
Laqueuille	2.2 (0.3)	4.3 (1.4)	6.5 (1.5)	+ 181**	+ 141**	5	+ 135	
Carlow (g)	25.8 (2.2)	12.6 (1.6)	38.4 (2.7)	+ 185**	–40**	98	–79	
Easter Bush	18.9 (0.9)	11.1 (0.8)	30.0 (1.3)	+ 221**	+ 212**	14	+ 182	
Früebühl	14.1 (1.1)	28.4 (1.9)	42.5 (2.1)	+ 320††	+ 146††	29	+ 104	
Average grassl.	15.3 (5.0)	14.1 (5.1)	29.4 (8.0)	227(32)	115(54)	36(21)	85(57)	
Median grassland	16.5	11.9	34.2	203	144	22	119	
Grignon	12.5 (0.3)	ND	12.5 (0.3)	+ 472‡‡	–51‡‡	25	–64	
Klingenberg	16.0 (1.1)	8.7 (0.6)	24.7 (1.2)	+ 64§§	–103§§	24	–128	
Carlow (c)	11.2 (3.4)	6.6 (2.3)	17.8 (4.1)	+ 222§	–17§	105	–35	
Average cropland	13.2 (1.4)	7.7 (1.1)	18.3 (3.5)	253(119)	–57(25)	51(27)	–75(27)	
Median cropland	12.5	7.7	17.8	222	–51	25	–64	
Total average	11.9 (2.1)	8.1 (2.8)	19.4 (4.0)	296(61)	181(76)	28(10)	162(78)	
Lower quartile	6.6	0.8	7.2	180	–23	3	–42	
Upper quartile	16.7	11.9	31.3	340	232	26	208	
Total median	11.9	6.6	15.2	222	145	19	121	

The numbers in italics are averages, medians, and standard deviations. Positive numbers indicate net uptake from atmosphere, negative numbers net release of carbon.

*Net ecosystem exchange = gross primary productivity – ecosystem respiration, excluding C deprivation with harvest, fires, etc. Numbers in brackets indicate standard deviations due to spatial variability of concentrations for individual sites and the standard error of the average across sites with the same land use system or across all sites.

†Mean 2000–2007, W. Kutsch, M. Aubinet, N. Buchmann, P. Smith, B. Osborne, W. Eugster, M. Wattenbach, E. D. Schulze, E. Tommelli, E. Ceschia, C. Bernhofer, P. Béziat, A. Carrara, P. Di Tommasi, T. Grünwald, M. Jones, V. Magliulo, O. Marilhoie, A. Olioso, M. J. Sanz, M. Saunders, H. Søgaard & W. Ziegler (unpublished results).

‡Mean 1997–2008, K. Pilegaard (personal communications).

§Mean 2003–2007, P. Davis, M. Saunders, D. C. Walmsley, M. Jones & B. Osborne (unpublished results).

¶Mean 1997–2008, E. J. Moors, J. A. Elbers, W. W. P. Jans, C. M. J. Jacobs, B. Kruijt, P. C. Stok, R. W. A. Hutjes, H. ter Maat & A. J. Dolman (unpublished results).

||Mean 2002–2007, Rebmann *et al.* (2010).

**Laqueuille: 2003–2006; Easter Bush: 2004–2007; Carlow: 2003–2007, K. Klumpp, N. Guix, T. Tallec & J. F. Soussana (unpublished results).

††Mean 2006–2007, Zeeman *et al.* (2010).

‡‡Mean 2005–2008, S. Lehuget, B. Gabrielle, P. Cellier, B. Loubet, E. Roche, P. Béziat, E. Ceschia & M. Wattenbach (unpublished results).

§§Mean of four crop periods 2004/2005–2008; a net loss of -255 g m⁻² yr⁻¹ was observed when the application of organic fertilizer to rape in 2004 is excluded from the balance, Prescher *et al.* (2010). ND, not detectable.

Table 6 Concentrations of methane (CH₄) in soil air and leaching losses of dissolved CH₄

	pCH ₄ beneath topsoil (μL L ⁻¹)		pCH ₄ subsoil (μL L ⁻¹)		CH ₄ leaching (g CO ₂ -C _{eq} m ⁻² yr ⁻¹)			
					From topsoil		From subsoil	
Hainich	1.20	(0.13)	0.86	(0.15)	0.005	(0.000)	0.001	(0.000)
Sorø	0.56	(0.08)	0.66	(0.11)	0.004	(0.001)	0.002	(0.000)
Laois	4.82	(1.34)	3.26	(0.54)	0.037	(0.045)	0.018	(0.053)
Loobos	1.18	(0.11)	0.73	(0.06)	0.007	(0.000)	0.004	(0.001)
Wetzstein	–	–	0.77	(0.06)	0.007	(0.000)	0.002	(0.000)
Laqueuille								
Intensive	1.76	(0.11)	1.53	(0.01)	0.009	(0.001)	0.007	(0.000)
Extensive	1.73	(0.01)	1.73	(0.01)	0.005	(0.000)	0.004	(0.000)
Carlow (g)	1.51	(0.34)	1.45	(0.43)	0.002	(0.000)	0.002	(0.000)
Easter Bush								
Slope	1.09	(0.03)	1.71	(0.01)	0.012	(0.002)	0.007	(0.000)
Hollow	1.63	(0.13)	29.45	(27.08)	0.031	(0.006)	0.038	(0.005)
Früebühl	1.66	(0.11)	2.04	(0.16)	0.014	(0.001)	0.011	(0.000)
Grignon	0.92	(0.11)	0.69	(0.11)	0.002	(0.000)	0.002	(0.000)
Klingenberg	5.36	(2.27)	2.04	(0.41)	0.147	(0.008)	0.233	(0.009)
Carlow (c)	0.78	(0.09)	–	–	0.001	(0.001)	–	–

Numbers in brackets indicate standard deviations due to spatial variability of concentrations. No data can be given for soil air concentration beneath the Wetzstein topsoil because wild boars destroyed the shallow soil air samplers. Topsoils reach down to the shallow instrumentation depth, subsoil reach down to the deeper instrumentation depth given in Table 1.

Hence, the relationship presented in Fig. 7 suggests that the concept of a sorptive control on DOC output from mineral soils (e.g., Guggenberger & Kaiser, 2003) seems to apply for a wide range of soils and land use systems. Where sorptive retention of DOC occurs, it contributes to carbon accumulation in subsoils due to the stabilization of sorbed dissolved organic matter against biological degradation (Kalbitz & Kaiser, 2008).

The close relationship between measured and calculated DIC concentrations leached from topsoils indicates that the partial pressure of CO₂ in soil air and the pH of soil solution control DIC concentrations (and fluxes), according to carbonate equilibrium. The almost constant degree of supersaturation of soil waters with respect to equilibrium concentrations probably reflects the diffusion gradient of CO₂ from microbial habitats through soil air into the atmosphere or the kinetic retardation of CO₂ outgassing from soil water into soil air. For subsoils, the degree of supersaturation was larger and more variable than for topsoils, which might reflect the longer diffusion path into the atmosphere and therefore the stronger build-up of disequilibria between CO₂ production in moist soil zones and the partial pressure of CO₂ in soil air in drier zones. On the other hand, any contamination of soil air samples with atmospheric air during sampling or sample handling would probably also lead to an underestimation of equilibrium DIC concentrations because CO₂ concen-

trations in soil air are commonly much larger than atmospheric concentrations.

We did not observe any relationship between the absolute or relative excess of measured compared with calculated DIC concentrations with mean annual precipitation, clay content, air capacity of the soils (air-filled pore volume at FC), soil water content, or water-filled pore space. Likely, the connectivity and spatial arrangement of soil (macro)pores rather than bulk soil properties control gas exchange with the atmosphere (Lange *et al.*, 2009) and the degree of supersaturation of soil waters (Walmsley, 2009).

Relevance of DOC plus biogenic DIC leaching for the net ecosystem carbon balance

Plot-scale balances of carbon fluxes of four forest sites in our study were not significantly affected by carbon leaching (Table 5). Only for the beech forest at Sorø, carbon leaching equalled 25% of the balance of atmospheric CO₂ fluxes (Table 5). Reasons for this large fraction are the comparably small net ecosystem exchange (NEE) and high leaching losses of biogenic DIC due to the high pH of the calcareous subsoil. Neglecting leaching losses would lead to a substantial overestimation of the net ecosystem carbon balance of the Sorø forest (+ 145 g C m⁻² yr⁻¹ instead of + 108 g C m⁻² yr⁻¹, Table 5). For forest ecosystems, in particular, the tem-

poral scale of balances is extremely important for estimating the magnitude of carbon sequestration. The forest ecosystem carbon balances in Table 5 cover only few years (<13 years), which is short in relation to a forest's life cycle. Therefore, carbon release as a result of logging or catastrophic events like fire or wind storms are not included. According to the latest estimates, logging reduces the average net carbon uptake of European forests by $63 \pm 11 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Schulze *et al.*, 2009). Another $5 \pm 1 \text{ g C m}^{-2} \text{ yr}^{-1}$ are lost through fires. Owing to these losses, the long-term average net biome productivity of European forests, excluding leaching losses, is estimated to $82 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Schulze *et al.*, 2009). The average leaching loss of $12 \text{ g C m}^{-2} \text{ yr}^{-1}$ we observed for forests equals 14% of the average net biome productivity of forests.

Grasslands differed with regard to their balance of aboveground carbon fluxes (Table 5). While the grasslands at Laqueuille, Easter Bush, and Fr  b  el were characterized by a positive balance of NEE, fertilizer addition and carbon removal with harvest (indicating a carbon sink), the Carlow grassland showed a net negative balance due to large harvest of biomass. At Carlow, net carbon losses nearly doubled from 40 to $79 \text{ g C m}^{-2} \text{ yr}^{-1}$ when leaching losses were considered. At the other sites, 5–29% of the net inputs of carbon into soil were leached. The estimated average net biome productivity of European grasslands, excluding leaching losses, is $64 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Schulze *et al.*, 2009). Our average leaching loss for grasslands of $29 \text{ g C m}^{-2} \text{ yr}^{-1}$ is almost 50% of that estimate.

In contrast to forests or grasslands, all studied croplands were net sources of carbon (Table 5). Carbon losses with drainage were 24–105% of the sum of NEE plus fertilization minus harvest (median: 25% Table 5). W. Kutsch, M. Aubinet, N. Buchmann, P. Smith, B. Osborne, W. Eugster, M. Wattenbach, E. D. Schulze, E. Tommellieri, E. Ceschia, C. Bernhofer, P. B  ziat, A. Carrara, P. Di Tommasi, T. Gr  nwald, M. Jones, V. Magliulo, O. Marloie, A. Olioso, M. J. Sanz, M. Saunders, H. S  gaard & W. Ziegler (unpublished results) found an average net biome productivity (excluding leaching losses) of $-97 \text{ g C m}^{-2} \text{ yr}^{-1}$ for five temperate European croplands (including the Carlow and Klingenberg sites) based on eddy covariance measurements and carbon fluxes with organic fertilizers and harvested biomass. The average leaching loss of $18 \text{ g C m}^{-2} \text{ yr}^{-1}$ we found equals 19% of the net carbon loss as determined by W. Kutsch, M. Aubinet, N. Buchmann, P. Smith, B. Osborne, W. Eugster, M. Wattenbach, E. D. Schulze, E. Tommellieri, E. Ceschia, C. Bernhofer, P. B  ziat, A. Carrara, P. Di Tommasi, T. Gr  nwald, M. Jones, V. Magliulo, O. Marloie, A. Olioso, M. J. Sanz, M. Saunders, H. S  gaard & W. Ziegler

(unpublished results). According to Schulze *et al.* (2009), European croplands are a smaller net source of carbon ($17 \text{ g C m}^{-2} \text{ yr}^{-1}$ on average, excluding leaching losses), which is of a similar magnitude to the average leaching losses found in this study.

Downstream fate of dissolved carbon

The estimates of Schulze *et al.* (2009) for average greenhouse gas balances of European land use systems accounted for leaching losses of DOC and DIC by assuming a constant average loss of $7 \text{ g C m}^{-2} \text{ yr}^{-1}$ for all land use systems, which is close to the losses of $5.9 \text{ g C m}^{-2} \text{ yr}^{-1}$ reported by Ciais *et al.* (2008). Both estimates are considerably smaller than the average ($19.5 \text{ g C m}^{-2} \text{ yr}^{-1}$) and the median ($15.2 \text{ g C m}^{-2} \text{ yr}^{-1}$) of leaching losses we found (Table 5). This difference is related to the fact that the losses given by Ciais *et al.* (2008) and Schulze *et al.* (2009) represent the carbon export with rivers to oceans since these studies aimed at the carbon budget of the whole continent. In the studies of Ciais *et al.* (2008) and Schulze *et al.* (2009), the riverine carbon export was divided by the area of the river catchments to derive an average loss per m^2 , whereas our study directly determined leaching from the soil into groundwater. A comparison of our results with the estimates of Ciais *et al.* (2008) and Schulze *et al.* (2009) is therefore only possible when considering the downstream fate of dissolved carbon after being leached from soil.

DOC leached from soil may partly be retained in the vadose zone before reaching aquifers (Guggenberger & Kaiser, 2003; Siemens & Kaupenjohann, 2003; Mikutta *et al.*, 2007; Kalbitz & Kaiser, 2008; Scheel *et al.*, 2008). As a result of retention in the vadose zone, DOC concentrations in groundwater are often smaller than 5 mg L^{-1} (e.g., Siemens & Kaupenjohann, 2003). For the range of groundwater recharge of $95\text{--}652 \text{ mm yr}^{-1}$ we found in our study, these concentrations would lead to a small ($<0.5\text{--}3.3 \text{ g DOC m}^{-2} \text{ yr}^{-1}$), albeit constant flux of DOC into surface waters. In lakes and rivers, allochthonous dissolved organic matter will be partly processed by aquatic organisms and finally mineralized biologically and/or photochemically to DIC (Tranvik, 1993; Tranvik & Bertilsson, 2001).

The discharge of DIC-rich soil water and groundwater supersaturated with CO_2 (Stets *et al.*, 2009), together with the oxidation of dissolved organic matter in surface waters, results in a large supersaturation of river and lake water relative to the atmosphere (e.g., Duarte & Prairie, 2005). Efficient outgassing of CO_2 has been observed from headwaters with a large fraction of young groundwater (e.g., Fiedler *et al.*, 2006) and from estuaries (Frankignoulle *et al.*, 1998; Ciais *et al.*, 2008).

The resulting evolution of CO₂ from inland waters and estuaries into the atmosphere was estimated to equal ~40% of carbon inputs from land on a global scale (Cole *et al.*, 2007) and ~66% of the carbon European rivers receive from terrestrial ecosystems (Ciais *et al.*, 2008). Multiplication of these estimates with our mean carbon leaching loss gives an evolution of 8–13 and of 6–10 g C m⁻² yr⁻¹ when using the median. Subtraction of this evolution from surface waters from our dissolved carbon flux from soils gives a flux of 5–12 g C m⁻² yr⁻¹ from the continent into the ocean.

A fraction of the carbon that is transferred from terrestrial ecosystems to inland waters is buried in the sediments of lakes and reservoirs. Burial of carbon in the sediments of inland waters has been estimated to equal 12% of inputs from land on a global scale (Cole *et al.*, 2007) and 21% of the net ecosystem carbon transfer from European terrestrial ecosystems into rivers (Ciais *et al.*, 2008). Since we did not include fluxes of organic matter with eroded soil material in our study, the estimates of carbon burial of Cole *et al.* (2007) and Ciais *et al.* (2008) are difficult to relate to the fluxes of dissolved carbon reported here. Assuming that all carbon buried in the sediments of lakes and reservoirs derived from dissolved carbon indicates that <2–4 g m⁻² yr⁻¹ of DOC and DIC leached from soils are probably stored in the sediments of inland waters, which would reduce the carbon released from soils that reaches the ocean with rivers to 1–10 g C m⁻² yr⁻¹, but this reduction is uncertain. Overall, the carbon leaching losses reported here correspond to a riverine flux of DOC and biogenic DIC of 5.5 g m⁻² yr⁻¹ reported for Europe by Ludwig *et al.* (1998) and the river carbon fluxes of 5.9 and 7 g m⁻² yr⁻¹ given by Ciais *et al.* (2008) and Schulze *et al.* (2009), respectively, when considering outgassing from inland waters and potential burial in sediments.

In summary, leaching represents a comparatively small, but continuous loss of carbon from terrestrial ecosystems. Considering these losses for ecosystem greenhouse gas balances is increasingly important when long time periods are examined and net changes of biomass stocks are small. Leaching losses are especially important to local and plot-scale studies, because outgassing of carbon into the atmosphere from surface waters probably occurs outside the boundaries of the studied systems. Leaching losses are particularly important for the net ecosystem carbon balance of grasslands and croplands where dissolved carbon leaching roughly equalled 25% of NEE plus fertilizer carbon minus harvested carbon. Topsoil C/N ratio, the saturation of the subsoils' sorption capacity for organic carbon, and its carbonate content were important factors controlling the magnitude of carbon leaching losses.

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