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

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Keywords:	carbon sequestration, carbon cycle, net biome productivity, net ecosystem exchange, methane, dissolved inorganic carbon, dissolved organic carbon
Abstract:	<p>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 (CH<sub>4</sub>), at five forests, four grasslands, and three croplands across Europe. Biogenic contributions to DIC were estimated by means of its <math>\delta^{13}\text{C}</math> signature. Leaching of DOC plus biogenic DIC was <math>11.9 \pm 5.9 \text{ g C m}^{-2} \text{ yr}^{-1}</math> for forests (median: <math>7.4 \text{ g C m}^{-2} \text{ yr}^{-1}</math>), <math>29.4 \pm 8.0</math> for grasslands (median: <math>34.2 \text{ g C m}^{-2} \text{ yr}^{-1}</math>), and <math>18.3 \pm 3.5 \text{ g C m}^{-2} \text{ yr}^{-1}</math> for croplands (median: <math>17.8 \text{ g C m}^{-2} \text{ yr}^{-1}</math>). The average flux across land use systems was <math>19.4 \pm 4.0 \text{ g C m}^{-2} \text{ yr}^{-1}</math> (median: <math>15.2 \text{ g C m}^{-2} \text{ yr}^{-1}</math>). Production of DOC in topsoils was positively related to their C/N ratio and its retention in B horizons of subsoils was inversely related to the ratio of organic carbon to iron plus aluminium (hydr)oxides. Partial pressures of CO<sub>2</sub> in soil air and soil pH determined DIC concentrations and fluxes, but soil solutions were often supersaturated with DIC in relation to soil air CO<sub>2</sub>. Leaching losses of biogenic carbon from grasslands equalled 5–98% (median: 22%) of net ecosystem exchange (NEE) plus carbon 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 CO<sub>2</sub> in acidic forest soil solutions and large net ecosystem exchange. Leaching of CH<sub>4</sub> proved to be insignificant compared with other fluxes of carbon or CO<sub>2</sub>-C equivalents. Overall, our results show that leaching losses are particularly important for the carbon balance of agricultural systems.</p>

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For Review Only

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3 **1 Dissolved carbon leaching from soil is a crucial component of the net ecosystem carbon**  
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10 Running title: Dissolved carbon leaching  
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59 53 *Keywords: dissolved organic carbon, DOC, dissolved inorganic carbon, DIC, methane, CH<sub>4</sub>,*  
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54 *net biome productivity, net ecosystem exchange, carbon cycle, carbon sequestration*

**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 ( $\text{CH}_4$ ), at five forests, four grasslands, and three croplands across Europe. Biogenic contributions to DIC were estimated by means of its  $\delta^{13}\text{C}$  signature. Leaching of DOC plus biogenic DIC was  $11.9 \pm 5.9 \text{ g C m}^{-2} \text{ yr}^{-1}$  for forests (median:  $7.4 \text{ g C m}^{-2} \text{ yr}^{-1}$ ),  $29.4 \pm 8.0$  for grasslands (median:  $34.2 \text{ g C m}^{-2} \text{ yr}^{-1}$ ), and  $18.3 \pm 3.5 \text{ g C m}^{-2} \text{ yr}^{-1}$  for croplands (median:  $17.8 \text{ g C m}^{-2} \text{ yr}^{-1}$ ). The average flux across land use systems was  $19.4 \pm 4.0 \text{ g C m}^{-2} \text{ yr}^{-1}$  (median:  $15.2 \text{ g C m}^{-2} \text{ yr}^{-1}$ ). Production of DOC in topsoils was positively related to their C/N ratio and its retention in B horizons of subsoils was inversely related to the ratio of organic carbon to iron plus aluminium (hydr)oxides. Partial pressures of  $\text{CO}_2$  in soil air and soil pH determined DIC concentrations and fluxes, but soil solutions were often supersaturated with DIC in relation to soil air  $\text{CO}_2$ . Leaching losses of biogenic carbon from grasslands equalled 5–98% (median: 22%) of net ecosystem exchange (NEE) plus carbon 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  $\text{CO}_2$  in acidic forest soil solutions and large net ecosystem exchange. Leaching of  $\text{CH}_4$  proved to be insignificant compared with other fluxes of carbon or  $\text{CO}_2$ -C equivalents. Overall, our results show that leaching losses are particularly important for the carbon balance of agricultural systems.

## 76 **Introduction**

77 Uptake and release of CO<sub>2</sub> by terrestrial ecosystems are crucial modulators of the climate  
78 system (e.g., Heimann & Reichstein, 2008). Reliable estimates of net ecosystem carbon  
79 balances (Chapin *et al.*, 2006) are therefore fundamental to our understanding of global  
80 climate change and the development of appropriate mitigation strategies. Net ecosystem  
81 carbon balances can be determined by assessing changes in ecosystem carbon stocks over  
82 time (e.g., Liski *et al.*, 2002; Sleutel *et al.*, 2003). This approach is associated with large  
83 uncertainties, because annual changes are small compared to stock size, because of error  
84 propagation of measurements, spatial heterogeneity within ecosystems, and temporal or  
85 spatial extrapolation. A possible strategy to validate large-scale estimates of net ecosystem  
86 carbon balances is to compare them with independent estimates of carbon uptake derived  
87 from inverse modelling of CO<sub>2</sub> transport in the atmosphere (Janssens *et al.*, 2003; Schulze *et*  
88 *al.*, 2009). Such comparisons are hampered by the differing and uncertain system boundaries  
89 and the differing types of carbon fluxes measured. Atmosphere-based estimates of carbon  
90 uptake rates are often larger than increases in ecosystem carbon stocks because part of the  
91 carbon is exported in plant products (e.g. wood, grains, or forage), lost to the atmosphere in  
92 volatile organic forms, or leached in soluble forms (Janssens *et al.*, 2003; Ciais *et al.*, 2008).  
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94 Siemens (2003) hypothesized that the leaching of dissolved inorganic and organic carbon  
95 from soils can explain a large part of the difference between atmosphere- and land-based  
96 estimates of the carbon uptake of European terrestrial ecosystems. Similarly, Ritchey *et al.*  
97 (2002), Cole *et al.* (2007), and Battin *et al.* (2009) argued that consideration of inland waters  
98 as components of terrestrial carbon budgets is necessary to assess the carbon cycle at the  
99 landscape scale. In line with these views, current estimates of carbon balances of European  
100 terrestrial ecosystems assume an average loss of 7 g C m<sup>-2</sup> yr<sup>-1</sup> with drainage, based on  
101 measurements of riverine fluxes (Schulze *et al.*, 2009). Linking riverine carbon fluxes to those

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3 102 in terrestrial ecosystems is difficult because measurements of riverine fluxes not only  
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5 103 integrate over a number of transformation processes in aquifers and surface waters, they often  
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8 104 also average carbon fluxes from various land use systems within a particular catchment. Thus,  
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10 105 better data on leaching from soils could considerably improve estimates of carbon budgets of  
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12 106 terrestrial ecosystems. Such data are also essential to further assess the active processing of  
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15 107 land-borne carbon in aquifers and inland waters (Cole *et al.*, 2007; Battin *et al.*, 2009).  
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20 109 There is evidence that carbon leaching from terrestrial ecosystems varies systematically with  
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22 110 land use. Brye *et al.* (2001) reported a more than five-fold increase in dissolved carbon  
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24 111 leaching during four years after the conversion of native tall-grass prairie to maize cultivation  
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26 112 with fertilization and ploughing. Parfitt *et al.* (1997) found losses of dissolved inorganic  
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28 113 carbon (DIC) of  $14.7 \text{ g m}^{-2} \text{ yr}^{-1}$  from pasture and  $0.7 \text{ g m}^{-2} \text{ yr}^{-1}$  from a pine forest under  
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30 114 similar climatic conditions, but a reduction in soil pH(H<sub>2</sub>O) from 5.6–5.9 under pasture to  
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32 115 5.3–5.5 under pine as a result of more intense acidification in the forest. Leaching of  
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34 116 dissolved organic carbon (DOC) seems to be affected by ploughing and crop type (Vinther *et*  
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36 117 *al.*, 2006). A better understanding of land use effects on dissolved carbon leaching is  
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38 118 important because i) net ecosystem carbon balances are often grouped according to land use  
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40 119 classes (e.g., cropland, grassland, forest; Janssens *et al.*, 2003) and ii) trends in riverine  
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42 120 dissolved carbon fluxes seem to be related to land use (e.g., Raymond & Cole, 2003).  
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50 122 Carbon is dissolved in water not only as DOC and DIC but also as dissolved methane (CH<sub>4</sub>).  
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52 123 Despite its high global warming potential, dissolved CH<sub>4</sub> is commonly not included in  
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54 124 measurements of dissolved carbon concentrations and has only been investigated in a small  
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56 125 number of studies. For the Brocky Burn moorland catchment in Scotland, CH<sub>4</sub>-C fluxes with  
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58 126 stream water were less than 0.04% of CO<sub>2</sub>-C fluxes (Dawson *et al.*, 2004). Even when  
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60 127 considering a global warming potential factor of 25 for CH<sub>4</sub> (IPCC, 2007), its contribution to



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3 128 fluxes of CO<sub>2</sub>-C equivalents was smaller than 1%. Fiedler *et al.* (2006) found that CH<sub>4</sub> export  
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5 129 (in CO<sub>2</sub>-C equivalents) from a catchment in the Black Forest, Germany, was approximately  
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8 130 8% of the CO<sub>2</sub> export. The small contribution of CH<sub>4</sub> to overall carbon losses with stream  
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10 131 water or spring water is due its poor solubility in water ( $1.5 \cdot 10^{-5} \text{ mol l}^{-1} \text{ kPa}^{-1}$  at 20°C).  
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15 133 The goal of the present work was i) to determine leaching losses of DIC and DOC from soils  
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17 134 of typical European land use systems and to relate them to the respective net ecosystem  
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20 135 carbon balances and ii) to identify major factors controlling carbon leaching. In order to  
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22 136 achieve a full carbon perspective, determinations of DOC and DIC leaching losses were  
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25 137 complemented by analyses of CH<sub>4</sub> in soil air and soil water.  
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3 138 **Materials and Methods**  
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5 139 *Instrumentation and Sampling*  
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8 140 Twenty glass suction cups with a pore size  $<1 \mu\text{m}$  for soil water collection (ecoTech, Bonn,  
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10 141 Germany) and eight Teflon suction cups (ecoTech, Bonn, Germany) for soil gas collection  
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12 142 were installed at each of twelve European sites under different land use (Table 1, Fig. 1).  
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14 143 Most of these sites were verification sites of the CarboEurope project ([www.carboeurope.org](http://www.carboeurope.org))  
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16 144 and/or flux sites of the NitroEurope project (Skiba *et al.*, 2009). The probes were divided into  
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18 145 two sets of 10 suction cups and 4 gas probes, which allowed for sampling of different  
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20 146 treatments (e.g., intensive and extensive grazing at Laqueuille) or different landscape  
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22 147 positions (e.g., slope and hollow at Easter Bush). Suction cups and gas probes were installed  
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24 148 horizontally from a soil pit by inserting them into boreholes. Half the number of probes were  
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26 149 installed beneath the A horizon (at approximately 30 cm depth), the other half was installed as  
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28 150 deep as possible (65–120 cm depth; Table 1). Suction cups were connected to 2-liter glass  
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30 151 bottles in an insulated aluminium box placed into the soil pit. Soil water was extracted by  
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32 152 applying a vacuum of 40 kPa to the glass bottles after each sampling. In order to correctly  
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34 153 measure DIC, degassing of  $\text{CO}_2$  was minimized by using a headspace-free sample collection  
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36 154 system similar to the one described by Suarez (1986). In this system, the soil water from the  
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38 155 suction cup first flows through a 20-ml gas-tight vial before entering the evacuated 2-l bottle  
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40 156 via a cannulae, which penetrates the septum of the vials just deep enough to allow the outflow  
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42 157 of solution. At the Hainich and Wetzstein sites, soil water was additionally collected from two  
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44 158 glass suction plates installed at 20 cm depth.  
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55 160 Sample collection started at different dates. Here, we present and discuss data that span the  
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57 161 period from 1 October 2006 until 31 March 2008 at all sites except the Irish sites where soil  
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59 162 water sampling commenced until 31 March 2009. Fluxes were calculated separately for  
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163 summer (1 April until 30 September) and winter (1 October until 31 March).

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6 165 *Determination of soil solution pH, DIC, and CH<sub>4</sub> concentrations in soil water*  
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8 166 Soil solution pH was determined using a micro glass electrode (blueLine 16pH, Schott, Mainz,  
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10 167 Germany) in the gas-tight 20 ml vials prior to DIC analysis. Concentrations of DIC of  
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12 168 samples taken during the first winter 2006/2007 were analysed with a TOC-5050A analyser  
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15 169 (Shimadzu Corp., Kyoto, Japan). Inorganic carbon was determined by acidification and  
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17 170 sparging solution samples with CO<sub>2</sub>-free synthetic air and subsequently detecting the evolving  
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20 171 CO<sub>2</sub>. Samples from summer 2007 and winter 2007/2008 were analysed using a gas  
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22 172 chromatograph for simultaneous detection of CH<sub>4</sub> and CO<sub>2</sub>. The Shimadzu GC-2014AF gas  
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24 173 chromatograph was equipped with an AOC-5000 autosampler, a 1 m × 1/8" HayeSep Q  
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26 174 80/100-mesh column, an electron capture detector and two flame ionization detectors, with  
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28 175 one of them being coupled to a methanizer. Gas concentrations and total pressure were  
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30 176 analysed in the headspace after shaking solutions at 90°C for 20 minutes. The gas  
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32 177 concentrations in soil water were calculated from the headspace concentrations by applying  
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34 178 Henry's law. Results were corrected for temperature, pressure-dependent residual gas  
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36 179 concentrations and pH-dependent carbonate equilibrium (only for DIC). Tests with standard  
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38 180 solutions showed that the Shimadzu TOC-5050A method and the GC method yielded  
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40 181 comparable results for the DIC detection.  
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48 183 Dissolved inorganic carbon in soil water derives from either respiration, dissolution of  
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50 184 carbonate minerals, or atmospheric CO<sub>2</sub>. Because partial pressures of CO<sub>2</sub> in soil air are much  
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52 185 higher than atmospheric partial pressures, the direct influence of atmospheric CO<sub>2</sub> on DIC  
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54 186 concentrations in soil water is negligible. According to the stoichiometry of the reaction of  
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56 187 respiratory CO<sub>2</sub> with calcium or magnesium carbonate (eq. [1]), the fraction of carbonate-  
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58 188 borne DIC in calcareous soils should approach 50% if chemical equilibrium is reached within  
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60 189 the residence time of percolating water in the soil (e.g., Amiotte-Suchet *et al.*, 1999).

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193 In carbonate-free soils, respiratory  $\text{CO}_2$  will react with silicates (e.g., feldspars) to form clay  
194 minerals and bicarbonate, which in this case is solely from soil respiration (e.g., eq. [2];  
195 Amiotte-Suchet *et al.*, 1999). In these soils, the fraction of DIC from respiration should  
196 therefore be close to 100%.



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200 Since the  $\delta^{13}\text{C}$  values of limestones are close to zero (+2 to  $-5\text{‰}$ ) and the  $\delta^{13}\text{C}$  signature of  
201  $\text{CO}_2$  from soil respiration typically ranges from  $-21\text{‰}$  to  $-25\text{‰}$ , the fraction of biogenic and  
202 respiratory DIC can be inferred from  $\delta^{13}\text{C}$  values of DIC (Pawellek & Veizer, 1994; Amiotte-  
203 Suchet *et al.*, 1999), taking into account the isotopic fractionation during the dissolution of  
204  $\text{CO}_2$  in water (Zhang *et al.*, 1995). The enrichment of  $^{13}\text{C}$  in soil air  $\text{CO}_2$  compared to biomass  
205 ( $\delta^{13}\text{C}$  of C3-plants:  $\sim -28\text{‰}$ ) is the result of isotopic enrichment during litter decay and  
206 enrichment of  $\text{CO}_2$  during diffusion out of the soil into the atmosphere (Amiotte-Suchet *et al.*,  
207 1999). To account for the uncertainty caused by the enrichment of  $^{13}\text{C}$  in soil air  $\text{CO}_2$ , we used  
208 a value of  $-28\text{‰}$  to calculate a minimum fraction of biogenic DIC and the measured  $\delta^{13}\text{C}$  of  
209 soil air  $\text{CO}_2$  to calculate a maximum biogenic fraction. A value of  $0\text{‰}$  was used for  
210 carbonate-C. In addition, a value of  $-5\text{‰}$  was used to assess the sensitivity of the calculated  
211 biogenic fraction to variations of this parameter.

212  
213 The application of a mixing model with carbonates and  $\text{CO}_2$  from soil respiration as the two  
214 end-members to derive the fraction of carbonate DIC relies on the assumption that the  
215 influence of isotopic exchange of DIC with atmospheric air ( $\delta^{13}\text{C} \approx -8.5\text{‰}$ ) can be neglected.

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3 216 Isotopic exchange of DIC with atmospheric CO<sub>2</sub> would shift the  $\delta^{13}\text{C}$  of DIC towards less  
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5 217 negative values, which would cause a systematic overestimation of the carbonate-borne  
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8 218 fraction of DIC when applying the two end-member mixing model mentioned above.  
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12 220 Delta  $^{13}\text{C}$  values of DIC were determined using a Delta Plus XL isotope ratio mass  
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15 221 spectrometer with GasBench II interface (Thermo-Finnigan MAT, Bremen, Germany,  
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17 222 equipped with a Pal-80 autosampler, CEC Analytics, Zwingen, Switzerland), with an average  
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19 223 deviation of 2% between replicate measurements. Measured  $\delta^{13}\text{C}$  values of DIC were  
20  
21 224 corrected for isotopic fractionation during the dissolution of CO<sub>2</sub> in water according to Zhang  
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23 225 *et al.* (1995), considering the speciation of total dissolved CO<sub>2</sub> (H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) as a  
24  
25 226 function of pH. Samples for the determination of  $\delta^{13}\text{C}$  values of DIC were collected in  
26  
27 227 October 2007. Because insufficient sample volume was collected during this time as a  
28  
29 228 consequence of drought at Grignon, no  $\delta^{13}\text{C}$  data are available for DIC samples from that site.  
30  
31 229 Therefore, the biogenic fraction of DIC was calculated as the difference between the  
32  
33 230 concentrations of DIC and the sum of Ca<sup>2+</sup> and Mg<sup>2+</sup> (in mmol l<sup>-1</sup>) based on the stoichiometry  
34  
35 231 of carbonate dissolution (eq. [1]), assuming i) that carbonate dissolution is the main source of  
36  
37 232 Ca<sup>2+</sup> and Mg<sup>2+</sup> in the calcareous soil and ii) that chemical equilibrium is reached. A  
38  
39 233 comparison of the method used for the Grignon site and the isotope method did not always  
40  
41 234 yield identical results at the other sites. The release of Ca<sup>2+</sup> and Mg<sup>2+</sup> from litter in deciduous  
42  
43 235 forests or fertilization of cropland with Ca(NO<sub>3</sub>)<sub>2</sub> caused overestimates of the carbonate-borne  
44  
45 236 DIC fraction exceeding 100%.  
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### 53 237 54 55 238 *Analysis of DOC concentrations*

56  
57 239 Dissolved organic carbon concentrations of soil water samples were analysed using Pt-  
58  
59 240 catalysed, high-temperature combustion (680°C) with a TOC-5050A analyser (Shimadzu  
60

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2  
3 241 Corp., Kyoto, Japan). Prior to analysis, inorganic carbon was stripped off by adjusting the pH  
4  
5 242 to 2 with HCl and sparging with CO<sub>2</sub>-free synthetic air.  
6  
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8 243

9  
10 244 *Determination of iron and aluminium (hydr)oxide concentrations in soil horizons*

11  
12 245 Concentrations of poorly-crystalline iron and aluminium oxides in the bulk soils at Wetzstein,  
13  
14 246 Sorø, Laqueuille, Easter Bush, Hainich, and Grignon were determined by ammonium-oxalate  
15  
16 247 extraction (pH 3) in the dark after Schwertmann (1964) and measurement of iron and  
17  
18 248 aluminium concentrations in extracts with ICP-OES.  
19

20 249

21  
22 250 *Analysis of CO<sub>2</sub> and CH<sub>4</sub> in the gas phase*

23  
24  
25 251 Gas samples were analysed with the GC-2014AF gas chromatograph used for determination  
26  
27 252 of DIC concentrations (see above). The  $\delta^{13}\text{C}$  values of CO<sub>2</sub> in soil air samples were analysed  
28  
29 253 using a HP 6890 gas chromatograph equipped with a BPX-5 column (50 m × 0.32 mm × 0.5  
30  
31 254  $\mu\text{m}$ ), linked via a combustion interface to a MAT 252 isotope ratio mass spectrometer  
32  
33  
34 255 (Thermo-Finnigan MAT, Bremen, Germany).  
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256 *Calculation of fluxes*

257 Fluxes of dissolved C were calculated by multiplying concentrations of DOC, DIC, and CH<sub>4</sub>,  
258 with the volume of leached water, which was derived from a soil water model. We used a  
259 capacity or "bucket" model which assumes that leaching from a soil layer commences when  
260 the field capacity (FC in mm), is exceeded (eq. [3]),

$$261$$
$$262 \text{ if } SWC_i \leq FC, \text{ then } D_i = 0, \text{ else } D_i = c(SWC_i - FC) \quad [3],$$

263

264 with  $SWC_i$  denoting the soil water content at day  $i$  (mm),  $D_i$  the drainage volume at day  $i$  (mm  
265  $d^{-1}$ ), and  $c$  a rate constant ( $d^{-1}$ ) defining the fraction of excess water that can drain per day.

266 Changes in soil water contents over time were calculated from the soil water balance  
267 according to eq. [4].

$$268$$
$$269 SWC_i = SWC_{i-1} + INF_i - ET_i \quad [4]$$

270

271 with  $SWC_{i-1}$  indicating the soil water content of the preceding day (mm),  $INF_i$  denoting the  
272 infiltration at day  $i$  (mm), and  $ET_i$  the evapotranspiration at day  $i$  (mm). The soil water content  
273 was allowed to vary between the total pore volume of the soil (mm) and the water content at a  
274 soil matric potential of pF 4.2 (mm, wilting point). To this end, infiltration into the A horizon  
275 was restricted and diverted as "rapid runoff" when the amount of precipitation exceeded the  
276 available pore volume of the soil matrix (mm) or the infiltration capacity ( $mm d^{-1}$ ). This  
277 "rapid runoff" might be discharged as surface runoff or flow through cracks and macropores.  
278 We did not consider carbon transport with this rapid runoff because the concentrations of  
279 DOC, DIC, and CH<sub>4</sub> therein were unknown. Water was replenished by capillary rise when  
280  $SWC$  dropped below the soil water content at pF 4.2.

281

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2  
3 282 The model subdivided the soil pore volume into a fast and a slowly draining pool, each  
4  
5 283 characterized by a specific total pore volume, field capacity and water content at pF 4.2. The  
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7  
8 284 proportion of precipitation entering the fast and the slow pool was assumed constant over time  
9  
10 285 for each site. The model subdivided the soil profile into a topsoil layer and a subsoil layer.  
11  
12 286 The fraction of water taken up by the plants from the subsoil was assumed constant over time  
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14  
15 287 and was set equal to the fraction of roots below the A horizon. An exception was the Carlow  
16  
17 288 cropland for which only one soil layer above the gravelly subsoil was considered.  
18

19  
20 289  
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22 290 Values for total pore volume, field capacity, and water content at wilting point for the sum of  
23  
24 291 the two soil water pools of each soil layer were matched to tabulated values (AG Boden,  
25  
26 292 1994), according to soil texture. In addition, the model parameters mentioned above were  
27  
28 293 adjusted manually in a way that modelled soil water contents fitted *in situ* measured soil water  
29  
30 294 contents. Input variables were precipitation, air temperature, and latent heat flux, which  
31  
32 295 derived from eddy covariance measurements, either taken from the CarboEurope database  
33  
34 296 (<http://gaia.agraria.unitus.it/database/carboeuropeip/>) or provided by the managers of the  
35  
36 297 CarboEurope and NitroEurope sites. Actual evapotranspiration was calculated by dividing the  
37  
38 298 latent heat flux derived from the database by the temperature-adjusted heat of evaporation.  
39  
40 299 For the sites at Carlow and Laois, evapotranspiration was calculated according to approaches  
41  
42 300 of Allen *et al.* (1998), Priestley & Taylor (1972), and Teklehaimanot & Jarvis (1991) because  
43  
44 301 the gaps in eddy covariance data were too large to allow for calculation of reasonable  
45  
46 302 evapotranspiration estimates. Details regarding the calculations of evapotranspiration at these  
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48 303 sites are given in Walmsley (2010).  
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### 305 *Statistics*

306 Differences between land use types were tested for statistical significance using the non-  
307 parametric Kruskal-Wallis test, differences between sampling depths or terrain positions were



1  
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3 308 analyzed with the non-parametric Mann-Whitney *U*-test. The tests were carried out with the  
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5 309 Statistica version 8 software (Statsoft, Tulsa, USA).  
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## 310 **Results**

### 311 *Concentrations of DOC and DIC in soil water*

312 Dissolved inorganic carbon concentrations beneath topsoils of forest sites (2.5–23.9 mg l<sup>-1</sup>;  
313 mean: 8 mg l<sup>-1</sup>, median: 4 mg l<sup>-1</sup>; Fig. 2a) tended to be smaller than those of cropland (22.7–  
314 50.5 mg l<sup>-1</sup>; mean: 35 mg l<sup>-1</sup>, median: 33 mg l<sup>-1</sup>; Fig 2c,  $p = 0.09$ , Kruskal-Wallis test). No  
315 significant differences were found between mean concentrations of forests and grasslands (6–  
316 70 mg l<sup>-1</sup>; mean: 28 mg l<sup>-1</sup>, median: 17 mg l<sup>-1</sup>; Fig. 2b,  $p = 0.2$ , Kruskal-Wallis test). Also  
317 subsoil water DIC concentrations tended to increase in the order forest (2.5–67.7 mg l<sup>-1</sup>;  
318 mean: 34 mg l<sup>-1</sup>, median: 33 mg l<sup>-1</sup>) < grassland (8.0–90.9 mg l<sup>-1</sup>; mean: 42 mg l<sup>-1</sup>, median 34  
319 mg l<sup>-1</sup>) < cropland (28.3–84.8 mg l<sup>-1</sup>; mean: 57 mg l<sup>-1</sup>, median: 57 mg l<sup>-1</sup>), but these  
320 differences were not statistically significant (Kruskal-Wallis test). Dissolved inorganic carbon  
321 concentrations were insensitive to management intensity at Laqueuille (Fig. 2b) or topography  
322 at Hainich, Sorø (Fig 2a), and Carlow grassland (Fig 2b). However, topography was important  
323 at Easter Bush, with significantly larger concentrations at the bottom of the valley than at the  
324 elevated position (Fig. 2b, shallow cups:  $p = 0.009$ ; deep cups:  $p = 0.075$ , Mann-Whitney  $U$ -  
325 test).

326  
327 Theoretical concentrations of DIC can be calculated from the partial pressures of soil air CO<sub>2</sub>  
328 and soil solution pH by applying Henry's law and assuming chemical equilibrium between  
329 CO<sub>2</sub> in the gas phase and solution H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>. Total concentrations of DIC  
330 were close to equilibrium with partial pressures of soil air CO<sub>2</sub> for the Loobos, Wetzstein,  
331 Hainich and Sorø forest sites (Fig. 3). Soil waters from all other sites were supersaturated with  
332 DIC relative to soil air CO<sub>2</sub>, especially in subsoils, which might be partly due to selective  
333 sampling of CO<sub>2</sub>-poor soil air from larger pores. Overall, the measured DIC concentrations  
334 were nearly equal to or greater than theoretical concentrations, indicating that outgassing of  
335 soil water samples was successfully minimized by the sampling method.

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3 336  
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6 337 Dissolved inorganic carbon concentrations were commonly much larger than DOC  
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8 338 concentrations, particularly in subsoils (Fig. 2). Exceptions were the acidic soils at the  
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10 339 Wetzstein and Loobos forest sites, with DIC representing less than 10% of the total dissolved  
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12 340 carbon leached from topsoils and 16–30% in subsoils. Concentrations of DOC leached from  
13  
14 341 topsoils of grasslands (median: 7 mg l<sup>-1</sup>, mean: 8 mg l<sup>-1</sup>; range 1.9–17.1 mg l<sup>-1</sup>, Fig 2b) and  
15  
16 342 arable fields (median: 14 mg l<sup>-1</sup>, mean: 12 mg l<sup>-1</sup>, range: 3.9–17.3 mg l<sup>-1</sup>, Fig 2c) tended to be  
17  
18 343 smaller than those leached from forest topsoils (median: 24 mg l<sup>-1</sup>, mean: 23 mg l<sup>-1</sup>; range:  
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20 344 7.1–43.1 mg l<sup>-1</sup>, Fig. 2a), but the differences were not statistically significant ( $p = 0.16$ ,  
21  
22 345 Kruskal Wallis test). A close positive relationship was observed between DOC concentrations  
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24 346 at shallow sampling depths and topsoil C/N ratios (Fig. 4).  
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32 348 Differences between average subsoil DOC concentrations were rather small between the  
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34 349 different land use systems: 11 mg l<sup>-1</sup> for forests (median: 13 mg l<sup>-1</sup>), 12 mg l<sup>-1</sup> for arable  
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36 350 fields (median: 14 mg l<sup>-1</sup>), and 9 mg l<sup>-1</sup> for grasslands (median: 8 mg l<sup>-1</sup>), with the latter value  
37  
38 351 being somewhat lower due to small DOC concentrations in the Laqueuille Andosol (Fig. 2b).  
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#### 43 353 *Isotopic signature and sources of dissolved inorganic carbon*

44  
45 354 The  $\delta^{13}\text{C}$  signatures of DIC in samples collected from subsoils clustered into two groups.  
46  
47 355 Samples from the Hainich, Sorø, Laois, and Carlow grassland were all characterized by  $\delta^{13}\text{C}$   
48  
49 356 values close to  $-15\text{‰}$ , with little variation between different suction cups (Fig. 5b). At  
50  
51 357 Frübüel, samples from eight suction cups were close to  $-15\text{‰}$ , while the sample from one  
52  
53 358 cup showed a value of  $-22\text{‰}$  (Fig. 5b). Soils at Hainich, Sorø, Laois, Carlow, and Frübüel  
54  
55 359 all developed from carbonate-containing parent materials, which is Muschelkalk limestone at  
56  
57 360 the Hainich site and glacial till at the other sites. Soils at the Loobos, Wetzstein, Laqueuille,  
58  
59 361 Easter Bush, and Klingenberg sites developed from carbonate-free parent material. Average  
60

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3 362  $\delta^{13}\text{C}$  values of DIC were all below  $-20\text{‰}$  at the Wetzstein, Laqueuille, Easter Bush and  
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5 363 Klingenberg sites (Fig. 5b). Less negative values were found in the subsoil at the Loobos site.  
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8 364 In contrast to subsoil, dissolved inorganic carbon from shallow depths of the Sorø and  
9  
10 365 Frübüel sites had more negative  $\delta^{13}\text{C}$  values below  $-20\text{‰}$ , reflecting the dissolution of  
11  
12 366 carbonates in topsoils during soil development (Fig. 5a).  
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15 367  
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17 368 Using a value of  $-28\text{‰}$  for the biogenic end-member and a value of  $0\text{‰}$  for carbonate-C, a  
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19 369 biogenic DIC fraction of 74–82% was calculated for the calcareous subsoils of the Hainich,  
20  
21 Sorø, Laois, and Frübüel sites and used to estimate leaching losses of total biogenic carbon  
22  
23 370 (Fig. 5b, upright triangles). The fraction was reduced by 1–11% if an extreme value of  $-5\text{‰}$   
24  
25 371 was assumed for carbonate-C. Use of the measured  $\delta^{13}\text{C}$  of soil air  $\text{CO}_2$  increased the  
26  
27 372 calculated biogenic fraction for DIC from the calcareous subsoils to 90–105%. An extreme  
28  
29 373 value of 293% was calculated for the Frübüel site, but this unpalatable value likely resulted  
30  
31 374 from a contamination of soil air samples with atmospheric air during the difficult abstraction  
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33 375 of air samples from the wet Frübüel soil.  
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35 376  
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41 378 Contrary to geochemical theory (eq. [2]), the biogenic DIC fractions calculated for the  
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43 379 carbonate-free subsoils at the Loobos, Wetzstein, and Klingenberg sites, using the end-  
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45 380 members  $-28\text{‰}$  and  $0\text{‰}$ , were much lower than the expected 100%. This might be caused by  
46  
47 381 more intense isotopic exchange of soil air and DIC with atmospheric air. Indeed, when using  
48  
49 382 measured  $\delta^{13}\text{C}$  values of soil air  $\text{CO}_2$  in the calculation, the estimated biogenic fraction was  
50  
51 383  $>100\%$  for the Klingenberg site. For the Lobos and Wetzstein sites, however, calculated  
52  
53 384 biogenic fractions remained below 100%, which might indicate a contamination of the little  
54  
55 385 DIC pool in the acidic samples from these sites with atmospheric  $\text{CO}_2$  during sampling and  
56  
57 386 sample handling. In line with geochemical theory (Eq [2]), we used a biogenic DIC fraction of  
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3 387 100% for calculating the total biogenic carbon leaching loss from the carbonate-free Loobos,  
4  
5 388 Wetzstein, Laqueuille, Easter Bush, and Klingenberg soils.  
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10 390 *Water balance of the research sites*

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12 391 Mean annual precipitation during our study period ranged from 710 mm yr<sup>-1</sup> at Grignon to

13 392 1771 mm yr<sup>-1</sup> at Frübüel with an average of 1009 mm yr<sup>-1</sup> across all sites (Table 2). The

14  
15 393 average loss of water by evapotranspiration equalled 436 mm yr<sup>-1</sup>. The average relative

16  
17 394 deviation of modelled soil water contents from measured ones was 14% for the shallow

18  
19 395 depths and 6% for subsoils (Table 2). Figure 6 (c, d) provides a visual impression of the

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21 396 goodness of fit between measured and modelled soil water contents for the Carlow grassland

22  
23 397 site, where the quality of the model fit was exactly the average of all sites.  
24  
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28 399 Especially at the sites with clayey soils (Hainich, Laois, and Frübüel), modelled water

29  
30 400 contents could only be matched to measured ones when large volumes of water (357–489 mm

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32 401 yr<sup>-1</sup>) were discharged by rapid runoff via surface flow or preferential flow paths in the

33  
34 402 calibrated water balance model (Table 2). On average 429 mm yr<sup>-1</sup> of water were left over for

35  
36 403 drainage from the soil profile after subtracting evapotranspiration and rapid runoff from

37  
38 404 precipitation (Table 2).  
39  
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43 406 *Leaching losses of dissolved carbon*

44  
45 407 Across all sites, an average of 4.2 g DOC m<sup>-2</sup> yr<sup>-1</sup> was leached from soils, with rather small

46  
47 408 differences between land use systems (Table 3). Subtracting DOC leaching from subsoils

48  
49 409 from DOC fluxes from topsoils indicated that as much as 17 (Wetzstein) to 20 g m<sup>-2</sup> yr<sup>-1</sup>

50  
51 410 (Loobos) of DOC was retained in acidic forest B horizons (Table 3). Other forest B horizons

52  
53 411 retained only 2 (Laois) to 9 g DOC m<sup>-2</sup> yr<sup>-1</sup> (Sorø) and retention in the B horizons of

54  
55 412 grasslands or arable fields was generally smaller than 5.5 g DOC m<sup>-2</sup> yr<sup>-1</sup> (Table 3).  
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3 413 Retention of DOC in B horizons decreased exponentially with increasing ratio of organic  
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5 414 carbon to the sum of oxalate-extractable iron and aluminium present in the bulk soil (Fig. 7).  
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10 416 The average loss of DIC from forest topsoils was significantly smaller than DIC leaching  
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12 417 from grassland topsoils ( $p = 0.03$ ) and tended also to be smaller than leaching from cropland  
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14 418 topsoils ( $p = 0.09$ , Table 4). Leaching losses of DIC from subsoils, however, did not differ  
15  
16 419 significantly between land use types ( $p = 0.31$ , Kruskal Wallis test).  
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20 420  
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22 421 As a result of the strong retention of DOC and the low DIC concentrations, total biogenic  
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24 422 dissolved carbon leaching from forest soils tended to be smaller than leaching from grasslands  
25  
26 423 or arable fields (Table 5). Differences, however, were not significant ( $p = 0.23$ , Kruskal  
27  
28 424 Wallis test) because the variability between sites under similar land use was large. The overall  
29  
30 425 average biogenic dissolved carbon loss from soils was  $19.3 \text{ g C m}^{-2} \text{ yr}^{-1}$ . This value was  
31  
32 426 strongly influenced by large losses from the forest at Sorø and the grasslands at Easter Bush  
33  
34 427 and Carlow. Consequently, the median flux across all sites was smaller ( $15.2 \text{ g C m}^{-2} \text{ yr}^{-1}$ ).  
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39 428  
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41 429 *Methane concentrations in soil air and its leaching losses*  
42

43 430 Methane concentrations in soil air at shallow depths were mostly smaller than global average  
44  
45 431 atmospheric concentrations of  $1.7 \mu\text{l l}^{-1}$ , indicating that most sites could have acted as sinks  
46  
47 432 for atmospheric  $\text{CH}_4$  (Table 6). Exceptions were the Laois and Klingenberg Stagnosols. In  
48  
49 433 subsoils,  $\text{CH}_4$  concentrations larger than atmospheric ones were only found in the Laois  
50  
51 434 Stagnosol and the Easter Bush Gleyic Cambisol in the hollow terrain position.  
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55 435  
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57 436 Leaching losses of  $\text{CH}_4$  were  $<5 \text{ mg CH}_4\text{-C m}^{-2} \text{ yr}^{-1}$  at most sites. Even the largest loss of 26  
58  
59 437  $\pm 2 \text{ mg CH}_4\text{-C m}^{-2} \text{ yr}^{-1}$ , measured at Klingenberg, was equivalent to a loss of only 0.23 g  
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3 438  $\text{CO}_2\text{-C}_{\text{eq}} \text{ m}^{-2} \text{ yr}^{-1}$  when applying a warming potential of 25 (Table 6). Leaching of  $\text{CH}_4$  was  
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5  
6 439 therefore not relevant for the greenhouse gas budget of the investigated sites.  
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3 440 **Discussion**  
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8 442 *Uncertainties of calculated leaching losses*  
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10 443 The errors in the estimates of leaching losses, indicated in brackets in tables 3–7, only reflect  
11  
12 444 the uncertainty caused by the spatial variation of DIC, DOC, and dissolved CH<sub>4</sub>  
13  
14  
15 445 concentrations. Additional uncertainties arise from the modelling of the water balance, the  
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17 446 spatial variation of water fluxes, and the calculation of the biogenic fraction of DIC from its  
18  
19 447  $\delta^{13}\text{C}$  signature.  
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22 448  
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24 449 We assessed the uncertainty of evapotranspiration measurements using the eddy covariance  
25  
26 450 method by analyzing the energy balance of the Klingenberg site for the years 2006 and 2007  
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28 451 (Vowinckel, 2008). A regression between net radiation and the sum of sensible and latent heat  
29  
30 452 flux (assuming a negligible net soil heat flux over long-term periods) showed that  
31  
32 453 approximately 68% of the available energy was consumed by turbulent heat fluxes only.  
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34 454 Using the slope of this regression and monthly means of the Bowen ratio as well as the  
35  
36 455 available energy, measured latent heat fluxes were subsequently corrected. Monthly  
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38 456 correction factors ranged from 1.01 to 1.89 and averaged 1.66, which means an  
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40 457 underestimation of the eddy covariance-based evapotranspiration at the Klingenberg site  
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42 458 during our study period from October 2006 to March 2008 by approximately 182 mm.  
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50 460 This systematic underestimation of evapotranspiration is roughly compensated by a  
51  
52 461 systematic underestimation of precipitation by standard rainfall collectors due to evaporation  
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54 462 from the wet funnel surface and wind turbulence (Richter, 1995). Applying the empirical  
55  
56 463 correction of Richter (1995) to precipitation data of the Klingenberg site (assuming that  
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58 464 precipitation at temperatures  $<0^{\circ}\text{C}$  occurs as snow) indicated an underestimation of the  
59  
60 465 rainfall by 216 mm.



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6 467 A major uncertainty of the soil water model is the calculated rapid runoff. At Laois, the  
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8 468 relevance of lateral water flows could easily be deduced from the clayey soil texture and the  
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10 469 occurrence of drainage ditches on the plot. Here, micro-catchments were constructed by  
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12 470 separating areas of 10–12 m<sup>2</sup> by trenches and wooden boards in a way that lateral runoff  
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14  
15 471 could be collected in a down slope trench, so that modelled lateral flows could be matched to  
16  
17 472 measured water volumes (Walsmley, 2010). No micro-catchments were available at Frübüel  
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19  
20 473 and Hainich, which were also characterized by clayey soils and rapid runoff. For these sites,  
21  
22 474 the results of our water balance model were compared with results of the BLAU “bucket”  
23  
24 475 model of Huwe (1991), which was extended with a surface runoff routine. For Frübüel, the  
25  
26 476 results of the BLAU model deviated from the results in Table 2 by only 2% for surface/rapid  
27  
28 477 runoff (440 vs. 449 mm) and by 0.3% for drainage from the soil profile (944 vs. 941 mm). A  
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30  
31 478 good agreement between results of the two models was also observed for the Hainich site;  
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33  
34 479 rapid/surface runoff and drainage from the soil profile deviated by only 4%.

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36 480  
37  
38 481 Dissolved carbon fluxes associated with rapid runoff could not be calculated because  
39  
40 482 concentrations in that runoff were not assessed. According to Kaiser *et al.* (2000), leaching  
41  
42 483 losses of DOC from a shallow forest soil (Rendzic Leptosol) via preferential flow paths  
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44 484 during heavy rainstorms were similar to mean annual fluxes as determined for soil matrix  
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46 485 flow. This potential underestimation of DOC losses due to preferential flow and rapid runoff  
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48 486 of soil water might partly have been compensated for in our study by an overestimation of  
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51 487 DIC losses since DIC concentrations in soil water rapidly draining through large pores are  
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53 488 probably smaller than concentrations in water in slowly draining pores of the soil matrix. We  
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56 489 are not aware of any study that has analysed concentrations of DIC in preferential flow.  
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3 491 Biogenic DIC concentrations are also subjected to an error associated with the determination  
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5 492 of the fraction of carbonate-borne DIC using the DIC  $\delta^{13}\text{C}$  signature. The largest source of  
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8 493 error is contamination or isotopic exchange of DIC with atmospheric air. Contamination and  
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10 494 isotopic exchange with atmospheric air would shift the measured  $\delta^{13}\text{C}$  values to less negative  
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12 495 values, leading to systematic underestimation of biogenic DIC concentrations. According to  
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14  
15 496 the stoichiometry of carbonate dissolution, the fraction of biogenic DIC in soil water of  
16  
17 497 calcareous soils must exceed 50% and, of course, it should be smaller than 100%. This limits  
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19 498 the potential underestimation of biogenic DIC concentrations and fluxes from calcareous soils  
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21 499 to values of 18–31%. The potential overestimation of biogenic DIC concentrations resulting  
22  
23 500 from the assumption of an average  $\delta^{13}\text{C}$  value of 0‰ for carbonates was 1–11% (average  
24  
25 501 5%). Our results indicated greater isotopic exchange between DIC and atmospheric air for  
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27 502 samples from carbonate-free subsoils, especially for the acidic forest subsoils at Loobos and  
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29 503 Wetzstein. For these subsoils, however, the assumption of 100% biogenic DIC according to  
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31 504 the stoichiometry of weathering reactions is safe and the relevance of the small DIC  
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33 505 concentrations at these sites for total carbon leaching is limited.  
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#### 41 507 *Factors controlling dissolved carbon concentrations and leaching losses*

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43 508 The positive correlation between soil C/N ratios and DOC concentrations and fluxes in  
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45 509 terrestrial ecosystems across biomes was first published by Aitkenhead & McDowell (2000).  
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47 510 In contrast to the observation of Aitkenhead & McDowell (2000), DOC concentrations and  
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49 511 fluxes in our study correlated only to topsoil C/N ratios (upper 5–40 cm, Table 1) and not to  
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51 512 C/N ratios of the entire soils down to 65–100 cm depth. Due to the accumulation of organic  
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53 513 matter, topsoils and organic layers are regarded as the soil compartments that are the most  
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55 514 important for the generation of DOC (e.g., Guggenberger & Kaiser, 2003). The topsoil C/N  
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57 515 ratio is indicative of the litter quality and the intensity of microbial transformation processes.  
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60 516 Large C/N ratios indicate poorly degradable litter and a slow transformation and recycling of

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3 517 organic matter. Studies using  $\delta^{13}\text{C}$  or  $^{14}\text{C}$  to track sources and turnover of DOC (Schiff *et al.*,  
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5 518 1997; Flessa *et al.*, 2000; Hagedorn *et al.*, 2004; Fröberg *et al.*, 2007) suggest that dissolved  
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7 519 organic matter, which is transported over decimetres or metres down into subsoils, mainly  
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10 520 represents highly altered residues of organic matter processing. Processing of N-poor organic  
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12 521 matter seems to result in production of more soluble residues, which explains the positive  
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15 522 correlation between soil C/N ratios and DOC concentrations. A positive correlation between  
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17 523 DOC production and C/N ratios of soil organic matter was also observed in laboratory  
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19 524 experiments (Gödde *et al.*, 1996; Kalbitz & Knappe, 1997). A hypothesis put forward by  
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21 525 Gödde *et al.* (1996) to explain this relationship was that microbial communities in soils with  
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23 526 large C/N ratios have to process more organic matter to satisfy their N requirements than  
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26 527 communities in soils with small C/N ratios. At C/N ratios  $\ll 10$ , most carbon associated with  
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28 528 processed soil organic matter is either respired or re-assimilated so that only small amounts of  
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30 529 DOC are produced. The regression equation in Fig. 4 suggests that above a critical C/N ratio  
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32 530 of approximately 8, increasing amounts of soluble C residues are produced with increasing  
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34 531 C/N ratio of soil organic matter. It is plausible to expect that DOC leaching from topsoils only  
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36 532 occurs if a critical C/N ratio is exceeded.  
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42 534 Leaching of DOC from subsoils was controlled by retention in B horizons, with this retention  
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44 535 being related to the ratio of organic carbon to the sum of oxalate-extractable iron plus  
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46 536 aluminium (Fig. 7). Oxalate-extractable iron and aluminium are a measure of the  
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48 537 concentration of poorly crystalline iron and aluminium (hydr)oxides with a high specific  
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50 538 surface area in soils. These iron and aluminium(hydr)oxides are considered to be the most  
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52 539 important sorbents for dissolved organic matter in soils (e.g., Kaiser *et al.*, 1996). The ratio of  
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54 540 organic carbon to the concentration of iron and aluminium (hydr)oxides in B horizons is  
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56 541 therefore an indicator of the saturation of the available sorption capacity of subsoils for the  
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58 542 DOC they receive from topsoils. Hence, the relationship presented in Fig. 7 suggests that the

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3 543 concept of a sorptive control on DOC output from mineral soils (e.g., Guggenberger &  
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5 544 Kaiser, 2003) seems to apply for a wide range of soils and land use systems.  
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10 546 The close relationship between measured and calculated DIC concentrations leached from  
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12 547 topsoils indicates that the partial pressure of CO<sub>2</sub> in soil air and the pH of soil solution control  
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14 548 DIC concentrations (and fluxes), according to carbonate equilibrium. The almost constant  
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16 549 degree of supersaturation of soil waters with respect to equilibrium concentrations probably  
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18 550 reflects the diffusion gradient of CO<sub>2</sub> from microbial habitats through soil air into the  
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20 551 atmosphere or the kinetic retardation of CO<sub>2</sub> outgassing from soil water into soil air. For  
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22 552 subsoils, the degree of supersaturation was larger and more variable than for topsoils, which  
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24 553 might reflect the longer diffusion path into the atmosphere and therefore the stronger build-up  
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26 554 of disequilibria between CO<sub>2</sub> production in moist soil zones and the partial pressure of CO<sub>2</sub> in  
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28 555 soil air in drier zones. On the other hand, any contamination of soil air samples with  
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30 556 atmospheric air during sampling or sample handling would probably also lead to an  
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32 557 underestimation of equilibrium DIC concentrations because CO<sub>2</sub> concentrations in soil air are  
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34 558 commonly much larger than atmospheric concentrations.  
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43 560 We did not observe any relationship between the absolute or relative excess of measured  
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45 561 compared to calculated DIC concentrations with mean annual precipitation, clay content, air  
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47 562 capacity of the soils (air-filled pore volume at field capacity), soil water content, or water-  
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49 563 filled pore space. Likely, the connectivity and spatial arrangement of soil (macro)pores rather  
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51 564 than bulk soil properties control gas exchange with the atmosphere (Lange *et al.*, 2009) and  
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53 565 the degree of supersaturation of soil waters (Walmsley, 2010).  
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60 567 *Relevance of DOC plus biogenic DIC leaching for the net ecosystem carbon balance*

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3 568 Plot-scale balances of carbon fluxes of four forest sites in our study were not significantly  
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5 569 affected by carbon leaching (Table 5). Only for the beech forest at Sorø, carbon leaching  
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7 570 equalled 25% of the balance of atmospheric CO<sub>2</sub> fluxes (Table 5). Reasons for this large  
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9 571 fraction are the comparably small NEE and high leaching losses of biogenic DIC due to the  
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11 572 high pH of the calcareous subsoil. Neglecting leaching losses would lead to a substantial  
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13 573 overestimation of the net ecosystem carbon balance of the Sorø forest (+145 g C m<sup>-2</sup> yr<sup>-1</sup>  
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15 574 instead of +108 g C m<sup>-2</sup> yr<sup>-1</sup>, Table 5). For forest ecosystems, in particular, the temporal scale  
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17 575 of balances is extremely important for estimating the magnitude of carbon sequestration. The  
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19 576 forest ecosystem carbon balances in Table 5 cover only few years (<13 years) in relation to a  
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21 577 forest's life cycle. Therefore, carbon release as a result of logging or catastrophic events like  
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23 578 fire or wind storms are not included. According to the latest estimates, logging reduces the  
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25 579 average net carbon uptake of European forests by 63 ± 11 g m<sup>-2</sup> yr<sup>-1</sup> (Schulze *et al.*, 2009).  
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27 580 Another 5 ± 1 g C m<sup>-2</sup> yr<sup>-1</sup> are lost through fires. Due to these losses, the long-term average  
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29 581 net biome productivity of European forests, excluding leaching losses, is estimated to 82 g C  
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31 582 m<sup>-2</sup> yr<sup>-1</sup> (Schulze *et al.*, 2009). The average leaching loss of 12 g C m<sup>-2</sup> yr<sup>-1</sup> we observed for  
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33 583 forests equals 14% of the average net biome productivity of forests.  
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37 585 Grasslands strongly differed with regard to their balance of aboveground carbon fluxes (Table  
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39 586 5). While the grasslands at Laqueuille, Easter Bush, and Frübüel were characterized by a  
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41 587 positive balance of NEE, fertilizer addition and carbon removal with harvest (indicating a  
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43 588 carbon sink), the Carlow grassland showed a net negative balance due to large harvest of  
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45 589 biomass (for silage). At Carlow, net carbon losses nearly doubled from 40 g m<sup>-2</sup> yr<sup>-1</sup> to 79 g  
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47 590 m<sup>-2</sup> yr<sup>-1</sup> when leaching losses were considered. At the other sites, 5–29% of the net inputs of  
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49 591 carbon into soil were leached. The estimated average net biome productivity of European  
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51 592 grasslands, excluding leaching losses, is 64 g C m<sup>-2</sup> yr<sup>-1</sup> (Schulze *et al.*, 2009). Our average  
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53 593 leaching loss for grasslands of 29 g C m<sup>-2</sup> yr<sup>-1</sup> is almost 50% of that estimate.

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6 595 In contrast to forests or grasslands, all studied croplands were net sources of carbon (Table 5).  
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8 596 Carbon losses with drainage were 24–105% of the sum of NEE plus fertilization minus  
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10 597 harvest (median: 25% Table 5). Kutsch *et al.* (2010) reported an average net biome  
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12 598 productivity (excluding leaching losses) of  $-97 \text{ g C m}^{-2} \text{ yr}^{-1}$  for five temperate European  
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14 599 croplands (including the Carlow and Klingenberg sites) based on eddy covariance  
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16 600 measurements and carbon fluxes with organic fertilizers and harvested biomass. The average  
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18 601 leaching loss of  $18 \text{ g C m}^{-2} \text{ yr}^{-1}$  we found equals 19% of the net carbon loss as given by  
19  
20 602 Kutsch *et al.* (2010). According to Schulze *et al.* (2009), European croplands are a smaller net  
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22 603 source of carbon ( $17 \text{ g C m}^{-2} \text{ yr}^{-1}$  on average, excluding leaching losses), which is of a similar  
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24 604 magnitude to the average leaching losses found in this study.  
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### 32 606 *Downstream fate of dissolved carbon*

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34 607 The estimates of Schulze *et al.* (2009) for average greenhouse gas balances of European land  
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36 608 use systems accounted for leaching losses of DOC and DIC by assuming a constant average  
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38 609 loss of  $7 \text{ g C m}^{-2} \text{ yr}^{-1}$  for all land use systems, which is close to the losses of  $5.9 \text{ g C m}^{-2} \text{ yr}^{-1}$   
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40 610 reported by Ciais *et al.* (2008). Both estimates are considerably smaller than the average ( $19.5$   
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42 611  $\text{g C m}^{-2} \text{ yr}^{-1}$ ) and the median ( $15.2 \text{ g C m}^{-2} \text{ yr}^{-1}$ ) of leaching losses we found (Table 5). This  
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44 612 difference is related to the fact that the losses given by Ciais *et al.* (2008) and Schulze *et al.*  
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46 613 (2009) represent the carbon export with rivers to oceans because these studies aimed at the  
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48 614 carbon budget of the whole continent. In the studies of Ciais *et al.* (2008) and Schulze *et al.*  
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50 615 (2009), the riverine carbon export was divided by the area of the river catchments to derive an  
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52 616 average loss per  $\text{m}^2$ , whereas our study directly measured leaching from the soil into  
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54 617 groundwater. A comparison of our results with the estimates of Ciais *et al.* (2008) and  
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56 618 Schulze *et al.* (2009) is therefore only possible when considering the downstream fate of  
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58 619 dissolved carbon after being leached from soil.  
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6 621 Dissolved organic carbon leached from soil may partly be retained in the vadose zone before  
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8 622 reaching aquifers (Siemens & Kaupenjohann, 2003). Adsorption or precipitation of DOC may  
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10 623 slow down its biodegradation (Mikutta *et al.*, 2007; Kalbitz & Kaiser, 2008; Scheel *et al.*,  
11  
12 624 2008), but the extent of stabilization under field conditions is uncertain (Guggenberger &  
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14 625 Kaiser, 2003; Siemens & Kaupenjohann, 2003). As a result of retention in the vadose zone,  
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16 626 DOC concentrations in groundwater are often smaller than 5 mg l<sup>-1</sup> (e.g., Siemens &  
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18 627 Kaupenjohann, 2003). For the range of groundwater recharge of 95–652 mm yr<sup>-1</sup> we found in  
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20 628 our study, these concentrations would lead to a small (<0.5–3.3 g DOC m<sup>-2</sup> yr<sup>-1</sup>), albeit  
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22 629 constant flux of DOC into surface waters. Significant additional amounts of DOC reach  
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24 630 surface waters with runoff at or near the soil surface during storms (e.g., Hagedorn *et al.*,  
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26 631 2000) or with drainage water from peatlands (e.g., Dawson *et al.*, 2004). In lakes and rivers,  
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28 632 allochthonous dissolved organic matter will be partly processed by aquatic organisms and  
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30 633 finally mineralized to DIC (Tranvik, 1993; Tranvik & Bertilsson, 2001).  
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38 635 The discharge of DIC-rich soil water and groundwater supersaturated with CO<sub>2</sub> (Stets *et al.*,  
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40 636 2009), together with the oxidation of dissolved organic matter in surface waters, results in a  
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42 637 large supersaturation of river and lake water relative to the atmosphere (e.g., Duarte & Prairie,  
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44 638 2005). Efficient outgassing of CO<sub>2</sub> has been observed from headwaters with a large fraction  
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46 639 of young groundwater (e.g., Fiedler *et al.*, 2006) and from estuaries (Frankignoulle *et al.*,  
47  
48 640 1998; Ciais *et al.*, 2008). The resulting evasion of CO<sub>2</sub> from inland waters and estuaries into  
49  
50 641 the atmosphere was estimated to equal ~40% of carbon inputs from land on a global scale  
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52 642 (Cole *et al.*, 2007) and to ~66% of the carbon European rivers receive from terrestrial  
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54 643 ecosystems (Ciais *et al.*, 2008). Multiplication of these estimates with our mean carbon  
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56 644 leaching loss gives an evasion of 8–13 g C m<sup>-2</sup> yr<sup>-1</sup> and an evasion of 6–10 g C m<sup>-2</sup> yr<sup>-1</sup> when  
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3 645 using the median. Subtraction of this evasion from surface waters from our dissolved carbon  
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5 646 flux from soils gives a flux of  $5\text{--}12 \text{ g C m}^{-2} \text{ yr}^{-1}$  from the continent into the ocean.  
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8 647  
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10 648 A fraction of the carbon that is transferred from terrestrial ecosystems to inland waters is  
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12 649 buried in the sediments of lakes and reservoirs. Burial of carbon in the sediments of inland  
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14 650 waters has been estimated to equal 12% of inputs from land on a global scale (Cole *et al.*,  
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16 651 2007) and 21% of the net ecosystem carbon transfer from European terrestrial ecosystems into  
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18 652 rivers (Ciais *et al.*, 2008). Particulate organic matter washed into inland waters due to erosion  
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20 653 of soils certainly contributes to this burial of carbon in the sediments of lakes and reservoirs  
21  
22 654 (Stallard, 1998). Since we did not include fluxes of organic matter with eroded soil material in  
23  
24 655 our study, the estimates of carbon burial of Cole *et al.* (2007) and Ciais *et al.* (2008) are  
25  
26 656 difficult to relate to the fluxes of dissolved carbon reported here. Assuming that all carbon  
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28 657 buried in the sediments of lakes and reservoirs derived from dissolved carbon indicates that  
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30 658 less than  $2\text{--}4 \text{ g m}^{-2} \text{ yr}^{-1}$  of DOC and DIC leached from soils are probably stored in the  
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32 659 sediments of inland waters, which would reduce the carbon lost from soils that reaches the  
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34 660 ocean with rivers to  $1\text{--}10 \text{ g C m}^{-2} \text{ yr}^{-1}$ , but this reduction is uncertain. Overall, the carbon  
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36 661 leaching losses reported here correspond to a riverine flux of DOC and biogenic DIC of  $5.5 \text{ g}$   
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38 662  $\text{m}^{-2} \text{ yr}^{-1}$  reported for Europe by Ludwig *et al.* (1998) and the river carbon fluxes of 5.9 and  
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40 663  $7 \text{ g m}^{-2} \text{ yr}^{-1}$  given by Ciais *et al.* (2008) and Schulze *et al.* (2009), respectively, when  
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42 664 considering outgassing from inland waters and potential burial in sediments.  
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53 666 Our set of research sites did not include sites from southern, northern, and eastern Europe. In  
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55 667 the study of Ciais *et al.* (2008), the yield of river carbon fluxes reaching the continental shelf  
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57 668 was twice as large for southern Europe ( $<42^\circ \text{ N}$ ;  $10.8 \text{ g m}^{-2} \text{ yr}^{-1}$ ) than for temperate Europe  
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59 669 ( $42\text{--}50^\circ \text{ N}$ ;  $5.2 \text{ g m}^{-2} \text{ yr}^{-1}$ ). The rather good agreement of riverine carbon fluxes with carbon  
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61 670 leaching losses in our study when considering outgassing and sedimentation is probably due



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3 671 to the small effect of high C export from south European catchments on the overall export due  
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5 672 to their small area and small river discharge in relation to temperate and northern Europe.  
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10 674 In summary, leaching represents a comparatively small, but continuous loss of carbon from  
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12 675 terrestrial ecosystems. Considering these losses for ecosystem greenhouse gas balances is  
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15 676 increasingly important when long time periods are examined and net changes of biomass  
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17 677 stocks are small. Leaching losses are especially important to local and plot-scale studies,  
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20 678 because outgassing of carbon into the atmosphere from surface waters probably occurs  
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22 679 outside the boundaries of the studied systems. Leaching losses are particularly important for  
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24 680 the net ecosystem carbon balance of grasslands and croplands where dissolved carbon  
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27 681 leaching roughly equalled 25% of NEE plus fertilizer carbon minus harvested carbon. Topsoil  
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29 682 C/N ratio, the saturation of the subsoils sorption capacity for organic carbon, and its carbonate  
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32 683 content were important factors controlling the magnitude of carbon leaching losses.  
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4

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## Tables

**Table 1:** Land use, soil characteristics, instrumentation, and temperature, of the investigated sites. Mean annual temperatures, mean annual precipitation, and mean drainage is given for the period of the observations of this study. This period was from 1 October 2006 until 30 March 2009 for Laois and Carlow and from 1 October 2006 until 30 March 2008 for all other sites.

Site	Land use	Soil type (WRB)	Soil texture	Soil organic carbon (kg m <sup>-2</sup> )	pH of topsoil	Sampling depths (cm)	Mean temperature in observed period (°C)	Mean annual temperature in observed period (°C)
Hainich (slope and valley)	Beech forest	Cambisol	Loamy clay	11.9 <sup>1</sup>	5.7	20, 75	7.6	9.2
Sorø (near and far from tree)	Beech forest	Stagnic Luvisol	Loamy sand	9.8 <sup>1</sup>	4.6	15, 100	8.2	9.6
Laois	Spuce forest	Stagnosol	Clay	2.2 <sup>3</sup>	5.1	15, 70	9.1	10.9
Loobos	Pine forest	Haplic Arenosol	Sand	7.7 <sup>2</sup>	4.0	5, 120	9.5	10.9
Wetzstein	Spuce forest	Podzol	Sandy loam	8.7 <sup>3</sup>	3.8	20, 90	5.6	7.3
Laqueuille (intensive and extensive use)	Grassland	Andosol	Silt loam	23.1 <sup>2</sup>	5.4	30, 90	6.6	7.9
Carlow (g) (slope and valley)	Grassland	Calcic Luvisol	Sandy loam	2.3 <sup>3</sup>	7.5	20, 65	9.4	9.3
Easter Bush (slope and hollow)	Grassland	Gleyic Cambisol	Sandy loam	12.3 <sup>1</sup>	5.4	30, 100	8.1	9.0
Früebüel	Grassland	Endogleyic Cambisol	Loamy clay	5.8 <sup>3</sup>	5.5	30, 100	6.6	8.1
Grignon	Cropland	Calcaric Cambisol	Silt loam	10.5 <sup>1</sup>	7.3	40, 90	9.9	11.2
Klingenberg	Cropland	Stagnosol	Silt loam	9.7 <sup>1</sup>	6.4	35, 75	7.1	8.8
Carlow (c)	Cropland	Eutric Cambisol	Sandy loam	7.3 <sup>1</sup>	6.9	40	9.0	9.3

<sup>1</sup>down to 60 cm depth, <sup>2</sup>down to 30 cm depth, <sup>3</sup>down to 50 cm depth. Soil organic carbon data for Früebüel from Roth (2006). <sup>6</sup>Infiltration into B horizon excluding a lateral runoff of 287 mm. Carlow (g): Carlow grassland, Carlow (c): Carlow cropland

**Table 2:** Water balance of the research sites during the investigated period. 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.

site	Precipitation	Evapotranspiration	Rapid runoff	Drainage		Average relative deviation of modelled water contents from measured ones	
				from A-horizon	from soil profile	shallow	deep
<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 <sup>2</sup>	542 <sup>1</sup>	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<sup>-1</sup>)</i>							
Hainich	1008	346	489	335	166	–	–
Sorø	928	287	112	688	531	–	–
Laois	1040	561	357 <sup>3</sup>	202 <sup>1</sup>	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	–	–	–

<sup>1</sup>Total lateral runoff including surface runoff of 349 mm; <sup>2</sup>Infiltration into B horizon excluding lateral runoff; <sup>3</sup>Total lateral runoff including surface runoff of 135 mm yr<sup>-1</sup>.

**Table 3:** Leaching losses of dissolved organic carbon from topsoils and subsoils of the research sites. The winter period is from 1 October until 30 March. Winter data are the average of winters 2006/2007 and 2007/2008 (and 2008/2009 for Irish sites). The summer period started on 1 April and ended on 30 September. 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.

Site		Loss from topsoils			Loss from subsoils		
		winter (g C m <sup>-2</sup> )	summer (g C m <sup>-2</sup> )	total (g C m <sup>-2</sup> yr <sup>-1</sup> )	winter (g C m <sup>-2</sup> )	summer (g C m <sup>-2</sup> )	total (g C m <sup>-2</sup> yr <sup>-1</sup> )
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 <sup>1</sup> (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)
<b>Average forest</b>		<b>6.8 (2.1)</b>	<b>6.3 (2.2)</b>	<b>13.1 (4.3)</b>	<b>2.8 (0.9)</b>	<b>0.8 (0.5)</b>	<b>3.5 (1.3)</b>
<b>Median forest</b>		<b>9.0</b>	<b>8.0</b>	<b>17.0</b>	<b>2.3</b>	<b>0.3</b>	<b>2.3</b>
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)
	valley	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)
<b>Average grassland</b>		<b>3.2 (1.4)</b>	<b>3.1 (1.0)</b>	<b>6.3 (2.5)</b>	<b>2.7 (1.1)</b>	<b>2.6 (1.0)</b>	<b>5.3 (2.0)</b>
<b>Median grassland</b>		<b>2.7</b>	<b>2.4</b>	<b>5.1</b>	<b>2.6</b>	<b>2.6</b>	<b>5.1</b>
Grignon		3.6 (0.1)	0.1 (0.0)	3.7 (0.1)	2.8 (0.1)	n.d. -	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)	- -	- -	- -
<b>Average cropland</b>		<b>3.1 (0.7)</b>	<b>1.5 (1.0)</b>	<b>4.6 (1.4)</b>	<b>3.0 (0.2)</b>	<b>1.1 (1.1)</b>	<b>4.1 (1.3)</b>
<b>Median cropland</b>		<b>3.6</b>	<b>0.9</b>	<b>3.8</b>	<b>3.0</b>	<b>2.1</b>	<b>4.1</b>
<b>Total average DOC flux</b>		<b>4.7 (1.1)</b>	<b>4.0 (1.1)</b>	<b>8.7 (2.2)</b>	<b>2.8 (0.5)</b>	<b>1.6 (0.5)</b>	<b>4.2 (0.9)</b>
<b>Median DOC flux</b>		<b>3.8</b>	<b>2.4</b>	<b>5.4</b>	<b>2.8</b>	<b>0.9</b>	<b>2.8</b>

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; n.d.: not detectable; <sup>1</sup>excluding lateral runoff of 3.0 g DOC m<sup>-2</sup> yr<sup>-1</sup>.

Topsoils reach down to the shallow instrumentation depth, subsoil reach down to the deeper instrumentation depth given in Table 1.

**Table 4:** Leaching losses of total dissolved inorganic carbon from topsoils and subsoils of the research sites. The winter period is from 1 October until 30 March. Winter data are the average of winters 2006/2007 and 2007/2008 (and 2008/2009 for Irish sites). The summer period started on 1 April and ended on 30 September. 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.

Site		Loss from topsoils			Loss from subsoils		
		winter (g C m <sup>-2</sup> )	summer (g C m <sup>-2</sup> )	total (g C m <sup>-2</sup> yr <sup>-1</sup> )	winter (g C m <sup>-2</sup> )	summer (g C m <sup>-2</sup> )	total (g C m <sup>-2</sup> yr <sup>-1</sup> )
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 <sup>1</sup> (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)
<b>Average forest</b>		<b>2.2 (0.4)</b>	<b>1.4 (0.2)</b>	<b>3.6 (0.8)</b>	<b>7.6 (3.7)</b>	<b>4.0 (3.6)</b>	<b>11.6 (7.2)</b>
<b>Median forest</b>		<b>2.0</b>	<b>1.4</b>	<b>3.1</b>	<b>7.5</b>	<b>0.4</b>	<b>7.8</b>
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)
<b>Average grassland</b>		<b>11.8 (5.9)</b>	<b>8.7 (2.3)</b>	<b>20.5 (8.2)</b>	<b>14.5 (6.3)</b>	<b>12.6 (4.7)</b>	<b>27.1 (9.2)</b>
<b>Median grassland</b>		<b>8.3</b>	<b>7.3</b>	<b>14.9</b>	<b>12.2</b>	<b>11.3</b>	<b>27.6</b>
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)	-	-	-
<b>Average cropland</b>		<b>11.2</b> <b>1.7</b>	<b>4.5</b> <b>2.3</b>	<b>13.7</b> <b>3.0</b>	<b>11.3</b> <b>1.3</b>	<b>3.3</b> <b>2.7</b>	<b>16.4</b> <b>2.5</b>
<b>Median cropland</b>		<b>12.6</b>	<b>5.5</b>	<b>15.2</b>	<b>11.3</b>	<b>3.3</b>	<b>16.4</b>
<b>Total average DIC flux</b>		<b>7.6</b> <b>2.3</b>	<b>4.6</b> <b>1.3</b>	<b>12.3</b> <b>3.5</b>	<b>11.1</b> <b>2.7</b>	<b>7.0</b> <b>2.2</b>	<b>18.1</b> <b>4.6</b>
<b>Median DIC flux</b>		<b>4.2</b>	<b>3.6</b>	<b>8.3</b>	<b>10.7</b>	<b>3.6</b>	<b>13.3</b>

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); n.d.: not detectable; <sup>1</sup>excluding lateral runoff of 3.7 g DIC m<sup>-2</sup> yr<sup>-1</sup> (Walmsley, 2009). Topsoils reach down to the shallow instrumentation depth, subsoil reach down to the deeper instrumentation depth given in Table 1.

**Table 5:** Leaching losses of DOC plus biogenic DIC in relation to the net ecosystem exchange (NEE) and net ecosystem carbon balance (NECB) of the study sites. Positive numbers indicate net uptake from atmosphere, negative numbers net release of carbon.

Site	Leaching loss from (sub)soils			Average multi-year NEE <sup>1</sup> (g C m <sup>-2</sup> yr <sup>-1</sup> )	NEE + fertilization - harvest excluding leaching (g C m <sup>-2</sup> yr <sup>-1</sup> )	Leached fraction of balance (%)	NECB including leaching (g C m <sup>-2</sup> yr <sup>-1</sup> )
	Winter (g C m <sup>-2</sup> )	Summer (g C m <sup>-2</sup> )	Total (g C m <sup>-2</sup> yr <sup>-1</sup> )				
Hainich	7.6 (0.1)	0.3 (0.0)	8.0 (0.1)	+294 <sup>2</sup>	+294 <sup>2</sup>	3	+286
Sorø	19.8 (1.2)	15.5 (3.9)	35.2 (4.1)	+143 <sup>3</sup>	+143 <sup>3</sup>	25	+108
Laois	7.0 (1.1)	0.4 (0.1)	7.4 (1.1)	+873 <sup>4</sup>	+873 <sup>4</sup>	1	+866
Loobos	1.8 (0.1)	1.2 (0.1)	3.0 (0.1)	+402 <sup>5</sup>	+402 <sup>5</sup>	1	+399
Wetzstein	5.4 (0.6)	0.3 (0.2)	5.7 (0.7)	+177 <sup>6</sup>	+177 <sup>6</sup>	3	+171
<b>Average forest</b>	<b>8.3 (3.0)</b>	<b>3.5 (3.0)</b>	<b>11.9 (5.9)</b>	<b>378(132)</b>	<b>378(132)</b>	<b>6(5)</b>	<b>366(134)</b>
<b>Median forest</b>	<b>7.0</b>	<b>0.4</b>	<b>7.4</b>	<b>294</b>	<b>294</b>	<b>3</b>	<b>286</b>
Laqueuille	2.2 (0.3)	4.3 (1.4)	6.5 (1.5)	+181 <sup>7</sup>	+141 <sup>7</sup>	5	+135
Carlow (g)	25.8 (2.2)	12.6 (1.6)	38.4 (2.7)	+185 <sup>7</sup>	-40 <sup>7</sup>	98	-79
Easter Bush	18.9 (0.9)	11.1 (0.8)	30.0 (1.3)	+221 <sup>7</sup>	+212 <sup>7</sup>	14	+182
Früebüel	14.1 (1.1)	28.4 (1.9)	42.5 (2.1)	+320 <sup>8</sup>	+146 <sup>8</sup>	29	+104
<b>Average grassl.</b>	<b>15.3 (5.0)</b>	<b>14.1 (5.1)</b>	<b>29.4 (8.0)</b>	<b>227(32)</b>	<b>115(54)</b>	<b>36(21)</b>	<b>85(57)</b>
<b>Median grassland</b>	<b>16.5</b>	<b>11.9</b>	<b>34.2</b>	<b>203</b>	<b>144</b>	<b>22</b>	<b>119</b>
Grignon	12.5 (0.3)	n.d. -	12.5 (0.3)	+472 <sup>9</sup>	-51 <sup>9</sup>	25	-64
Klingenberg	16.0 (1.1)	8.7 (0.6)	24.7 (1.2)	+64 <sup>10</sup>	-103 <sup>10</sup>	24	-128
Carlow (c)	11.2 (3.4)	6.6 (2.3)	17.8 (4.1)	+222 <sup>4</sup>	-17 <sup>4</sup>	105	-35
<b>Average cropland</b>	<b>13.2 (1.4)</b>	<b>7.7 (1.1)</b>	<b>18.3 (3.5)</b>	<b>253(119)</b>	<b>-57(25)</b>	<b>51(27)</b>	<b>-75(27)</b>
<b>Median cropland</b>	<b>12.5</b>	<b>7.7</b>	<b>17.8</b>	<b>222</b>	<b>-51</b>	<b>25</b>	<b>-64</b>
<b>Total average</b>	<b>11.9 (2.1)</b>	<b>8.1 (2.8)</b>	<b>19.4 (4.0)</b>	<b>296(61)</b>	<b>181(76)</b>	<b>28(10)</b>	<b>162(78)</b>
<b>Lower quartile</b>	<b>6.6</b>	<b>0.8</b>	<b>7.2</b>	<b>180</b>	<b>-23</b>	<b>3</b>	<b>-42</b>
<b>Upper quartile</b>	<b>16.7</b>	<b>11.9</b>	<b>31.3</b>	<b>340</b>	<b>232</b>	<b>26</b>	<b>208</b>
<b>Total median</b>	<b>11.9</b>	<b>6.6</b>	<b>15.2</b>	<b>222</b>	<b>145</b>	<b>19</b>	<b>121</b>

<sup>1</sup>net ecosystem exchange = gross primary productivity minus 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; <sup>2</sup>mean 2000–2007 Kutsch et al. (in prep.), <sup>3</sup>mean 1997–2008 Pilegaard et al. (in prep.), <sup>4</sup>mean 2003–2007 Saunders et al. (in prep.), <sup>5</sup>mean 1997–2008 Moors et al. (unpublished data), <sup>6</sup>mean 2002–2007 Rebmann et al. (2009), <sup>7</sup>Laqueuille: 2003–2006; Easter Bush: 2004–2007, Carlow: 2003–2007 Klumpp et al. (in prep.), <sup>8</sup>mean 2006–2007 Zeeman et al. (2010), <sup>9</sup>mean 2005–2008 Lehuger et al. (2009), <sup>10</sup>mean of four crop periods 2004/2005–2008; a net loss of -255 g m<sup>-2</sup> yr<sup>-1</sup> was observed when the application of organic fertilizer to rape in 2004 is excluded from the balance, Prescher et al. (2010).

**Table 6:** Concentrations of methane (CH<sub>4</sub>) in soil air and leaching losses of dissolved CH<sub>4</sub>.

		pCH <sub>4</sub> beneath topsoil μl l <sup>-1</sup>	pCH <sub>4</sub> subsoil μl l <sup>-1</sup>	CH <sub>4</sub> leaching from topsoil (g CO <sub>2</sub> -C <sub>eq</sub> m <sup>-2</sup> yr <sup>-1</sup> )	CH <sub>4</sub> leaching from subsoil (g CO <sub>2</sub> -C <sub>eq</sub> m <sup>-2</sup> yr <sup>-1</sup> )
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)
Früebüel		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.

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3 **Figure captions**  
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5 Fig. 1: Map of the research sites and their land use.  
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3 Fig. 2: Concentrations of total dissolved inorganic carbon (open), dissolved organic carbon  
4 (hatched), and total dissolved carbon (crosshatched) below the soil A horizon (white) and  
5  
6 below the main rooting zone (gray). Concentrations represent the arithmetic mean of the  
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8 median concentrations of all suction cups in one depth over time. Error bars represent the  
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10 standard error of 5 suction cups (terrain positions) or 10 suction cups (all cups) and indicate  
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12 the uncertainty due to spatial variability of concentrations.  
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3 Fig. 3: Comparison of measured average total DIC concentrations with average  
4 concentrations calculated from average partial pressures of soil air CO<sub>2</sub> and average soil  
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6 concentrations calculated from average partial pressures of soil air CO<sub>2</sub> and average soil  
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8 solution pH using Henry's law. No calculated concentration can be given for topsoil leachates  
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10 of the Wetzstein site, because wild boars destroyed the shallow soil air samplers.  
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3 Fig. 4: Average concentrations of DOC leached from topsoils as a function of topsoil C/N  
4 ratio. All sites for which C/N ratios were available were included into the relationship.  
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6 Averages were calculated as the arithmetic mean of median concentrations of suction cups  
7 and suction plates over time. Topsoils reach down to the shallow depth of instrumentation  
8 given in Table 1.  
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3 Fig. 5:  $\delta^{13}\text{C}$  values (box plots and arithmetic mean as white dot) and the biogenic fraction of  
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6 DIC (black triangles). The lower value of the biogenic fraction was calculated using a  $\delta^{13}\text{C}$  of  
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8  $-28\text{‰}$  for the biogenic end-member and a  $\delta^{13}\text{C}$  of  $0\text{‰}$  for carbonates. The upper value of the  
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10 biogenic fraction was calculated using the  $\delta^{13}\text{C}$  of value of soil air  $\text{CO}_2$  at the time of soil  
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12 water collection and a  $\delta^{13}\text{C}$  of  $0\text{‰}$  for carbonates. Use of a  $\delta^{13}\text{C}$  of  $-5\text{‰}$  for carbonate-C  
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14 reduced the calculated biogenic fraction on average by 5% (biogenic end-member of  $-28\text{‰}$ ).  
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3 Fig. 6: Precipitation (a), evapotranspiration (b), measured and modeled soil water volumes (c,  
4 d), and modelled groundwater recharge (e) for the Carlow grassland. The average relative  
5 deviation of the modelled soil water volume was 14% for the A-horizon and 6% for the B-  
6 horizon (Table 2).  
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3 Fig. 7: Retention of DOC in B horizons of soils related to the ratio of organic carbon (OC)  
4 and the sum of oxalate-extractable iron ( $Fe_o$ ) and aluminium ( $Al_o$ ) of B horizons. Data for  
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8 oxalate-extractable iron and aluminium were only available for the displayed sites.  
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Figures

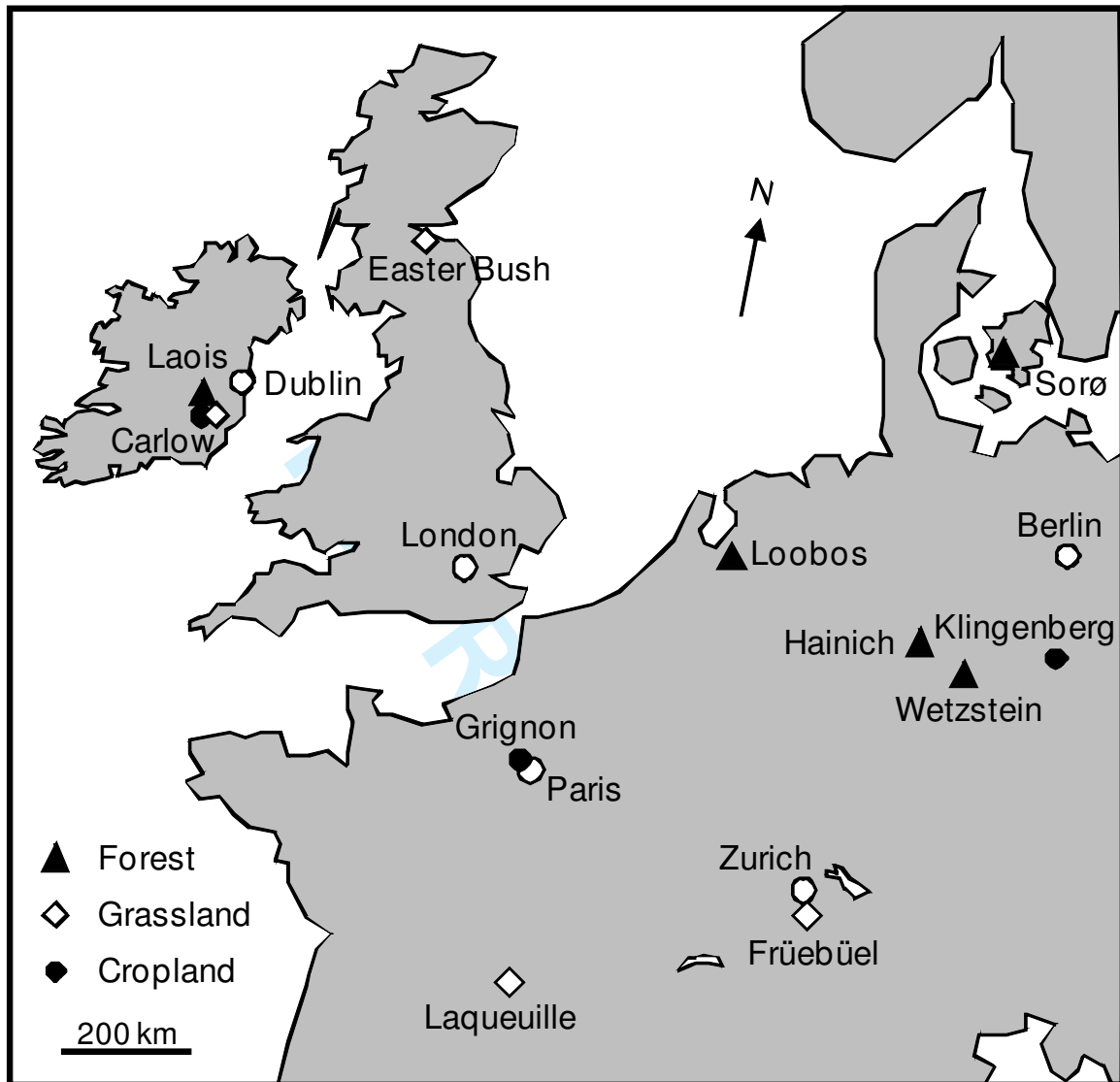


Figure 1

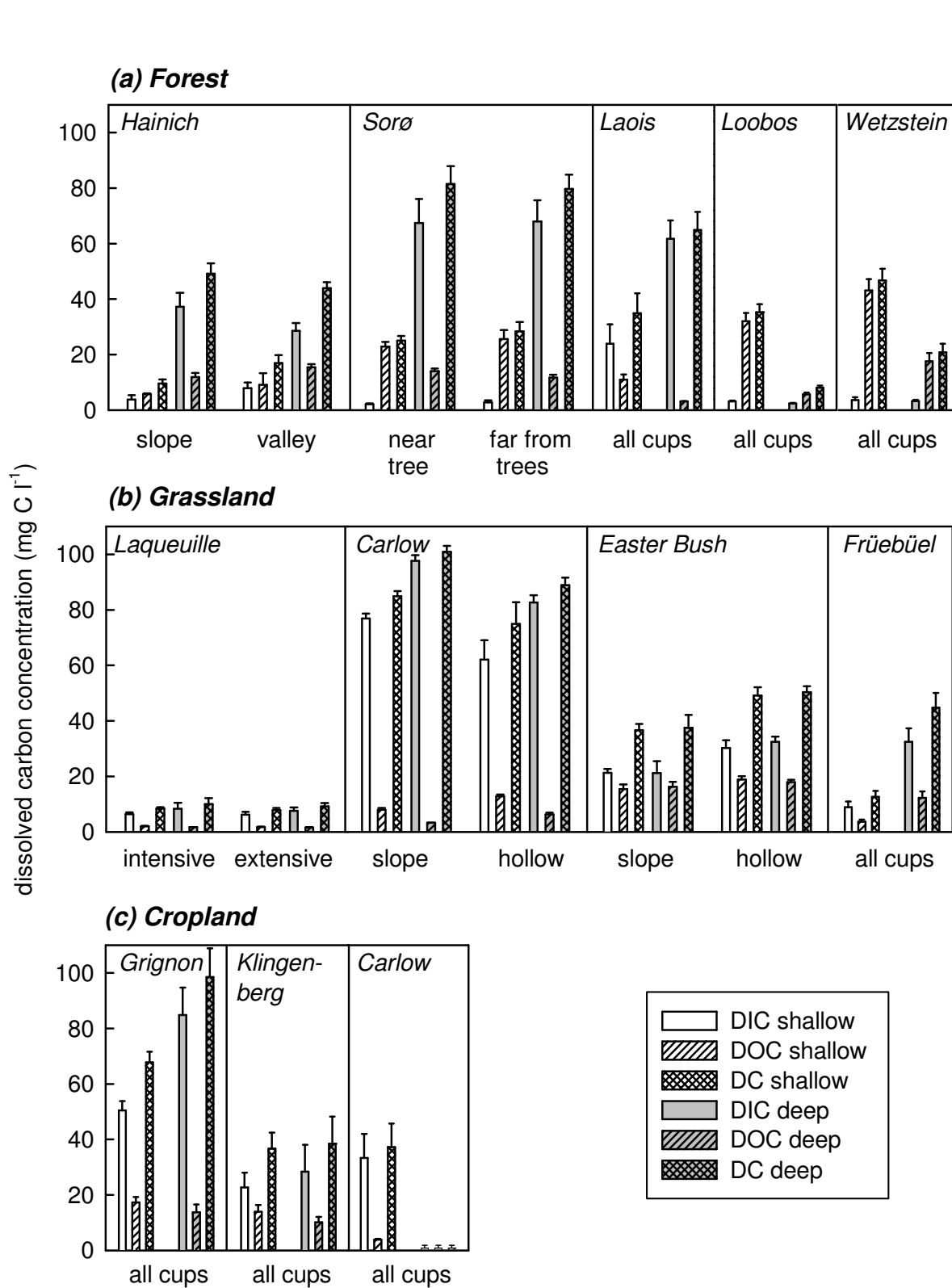


Figure 2



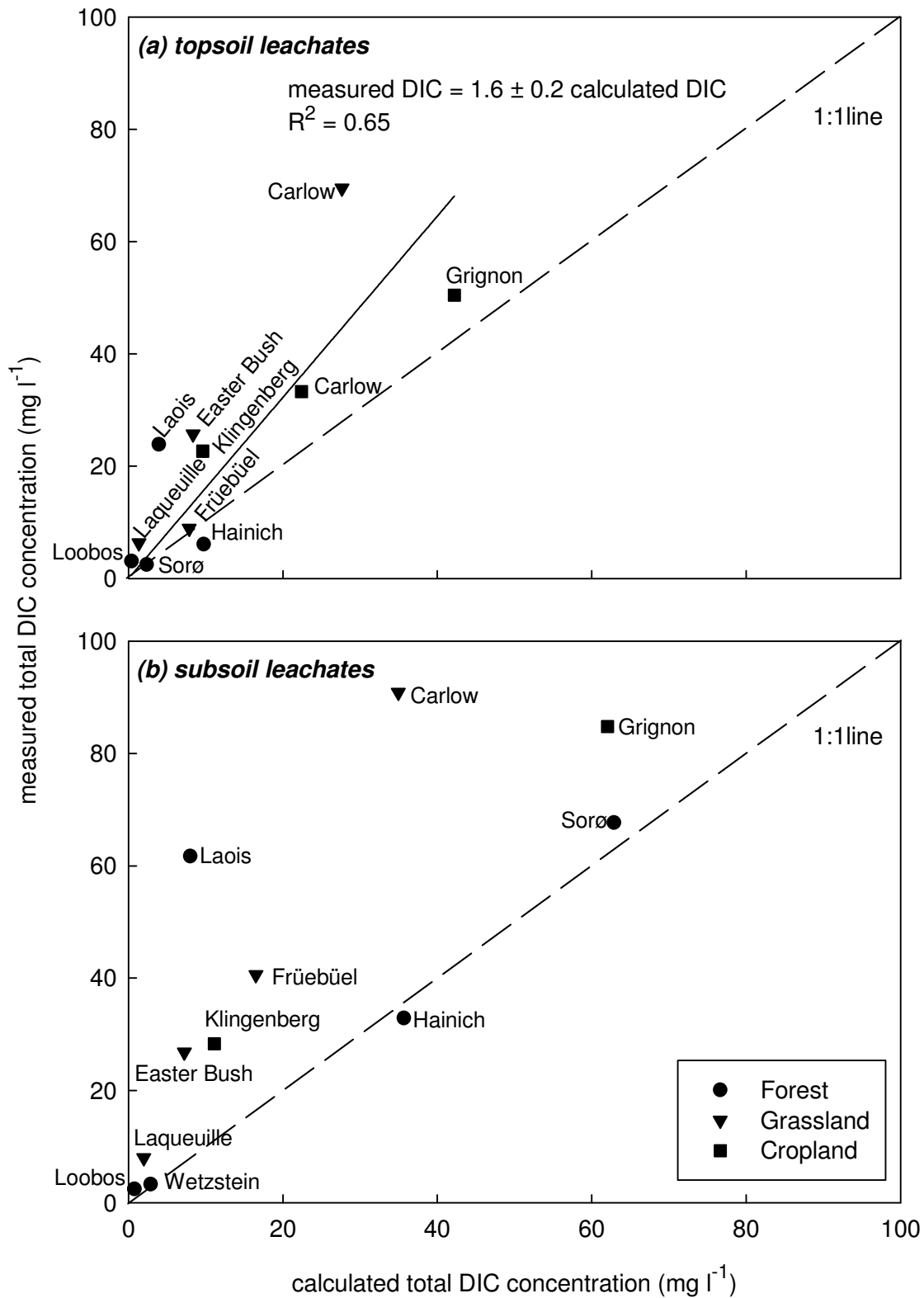


Figure 3

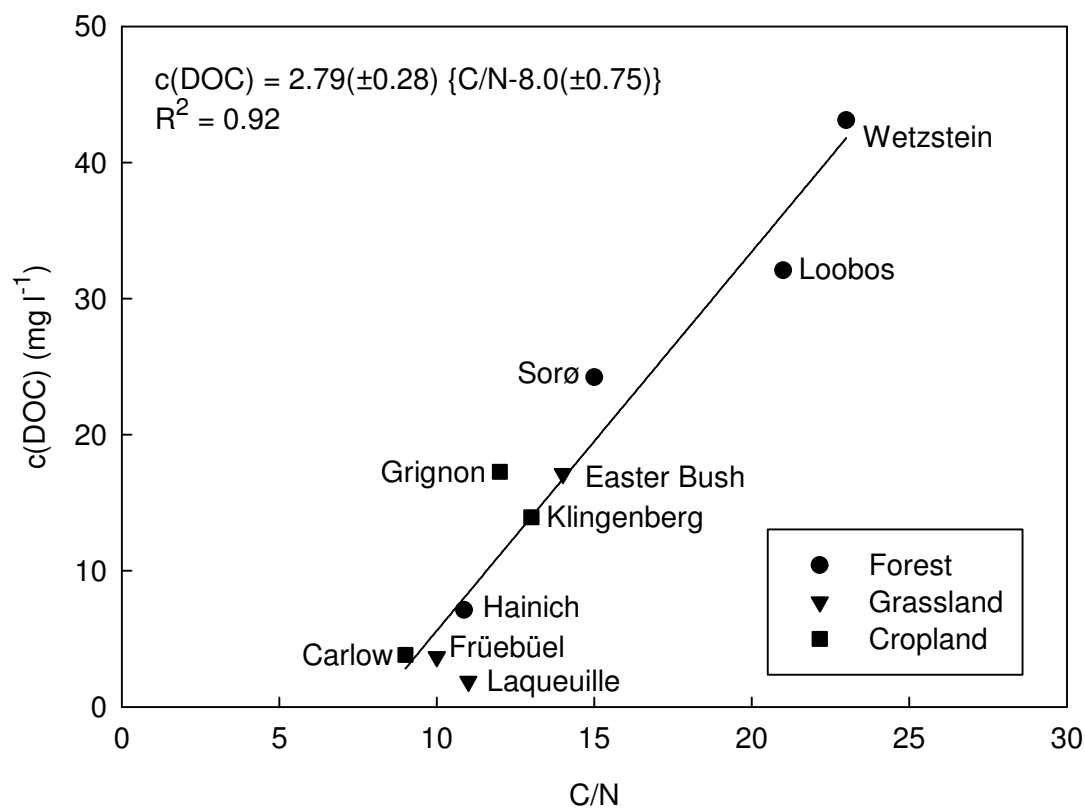


Figure 4

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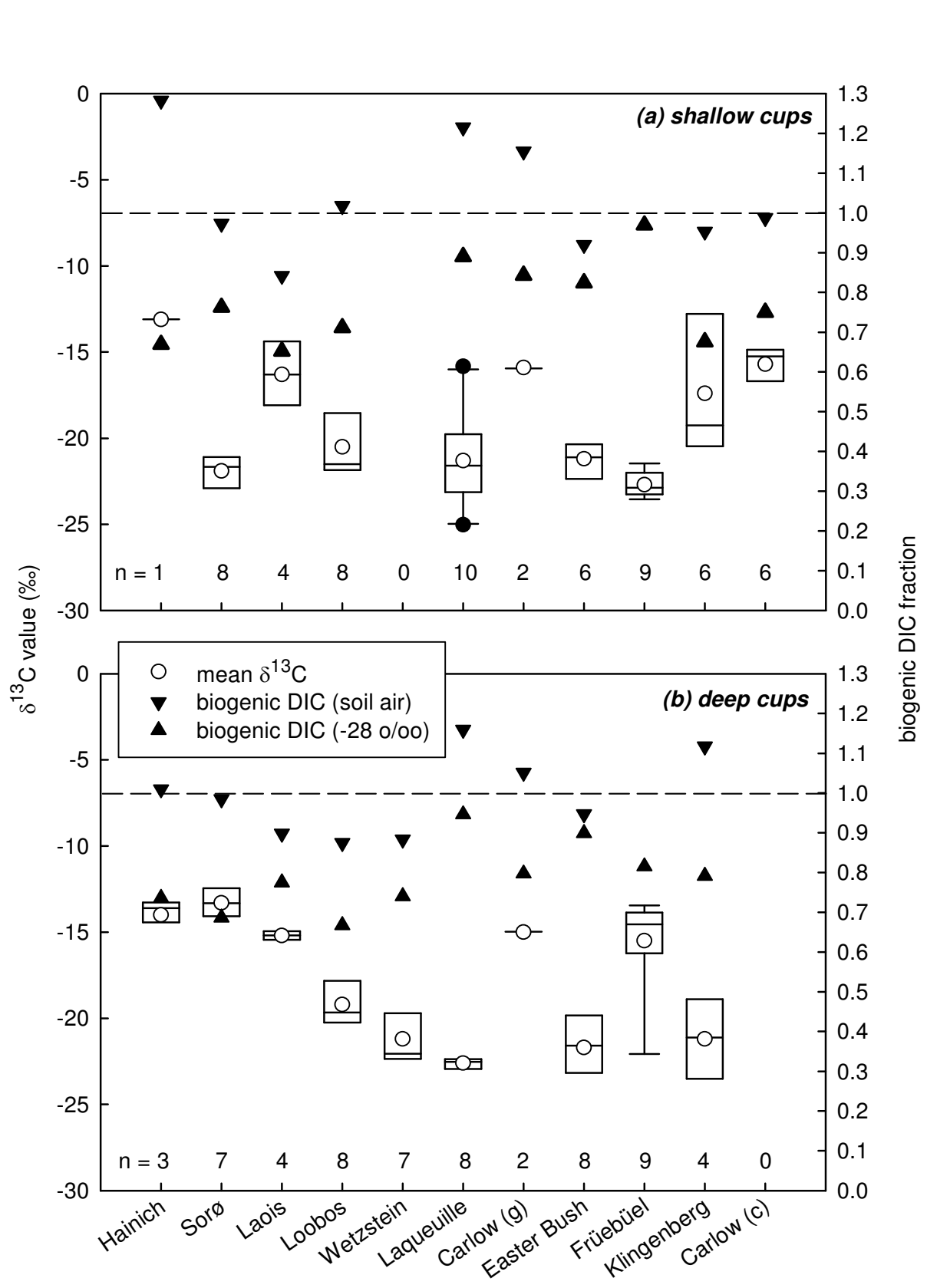


Figure 5

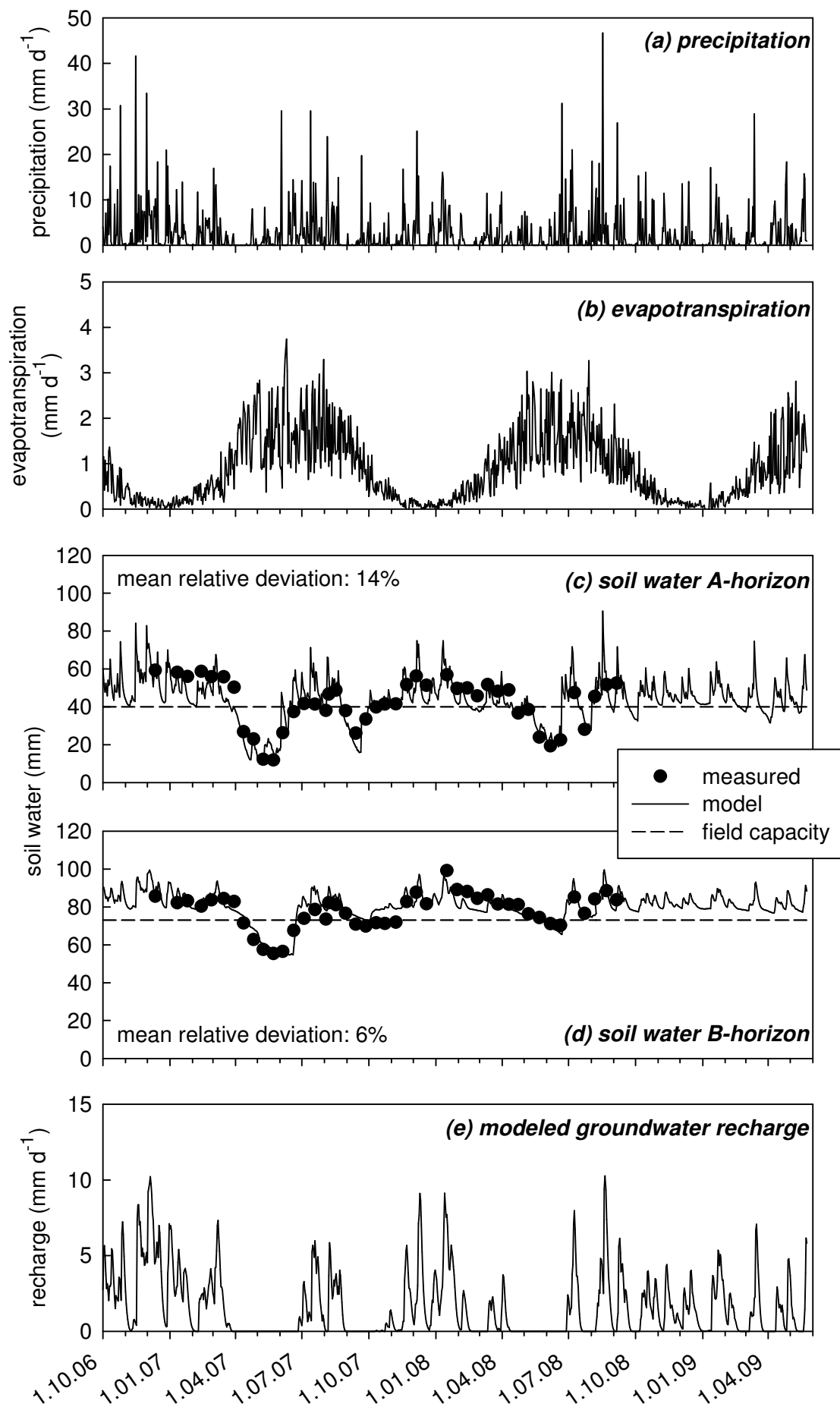


Figure 6

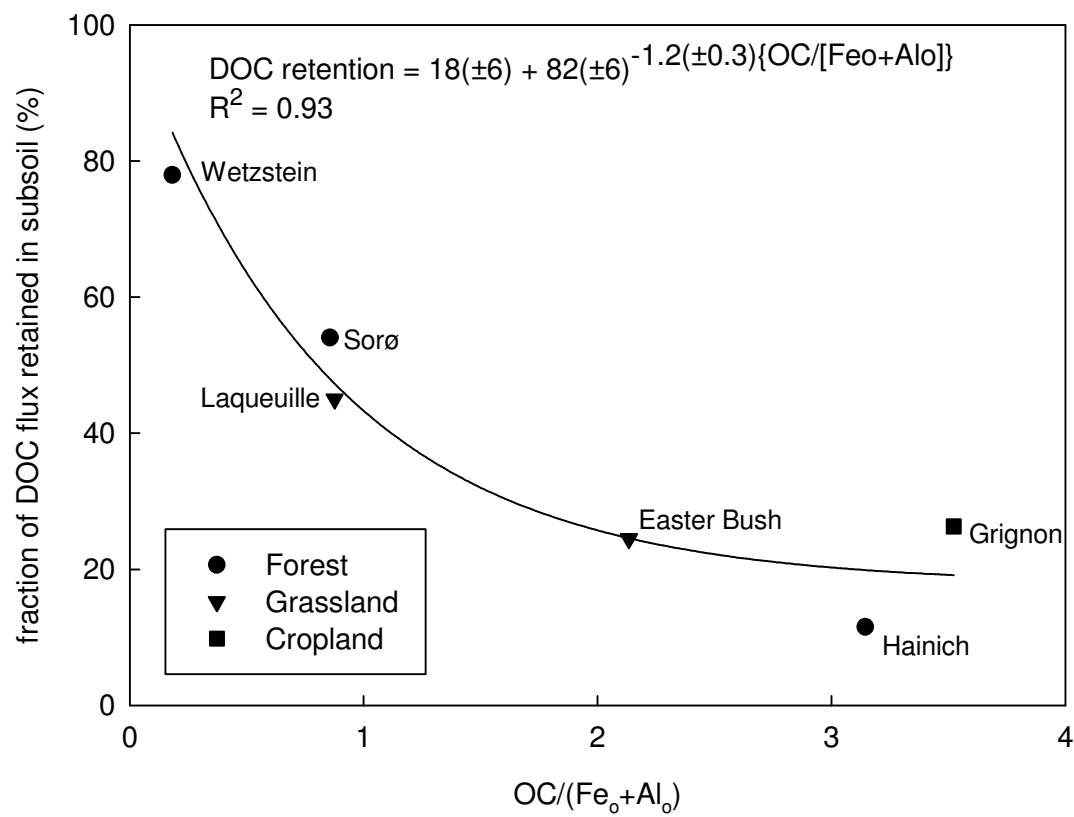


Figure 7