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A comparative study of dissolved organic carbon transport and stabilization in California forest and grassland soils

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Abstract For soil carbon to be effectively sequestered beyond a timescale of a few decades, this carbon must become incorporated into passive reservoirs or greater depths, yet the actual mechanisms by which this occurs is at best poorly known. In this study, we quantified the magnitude of dissolved organic carbon (DOC) leaching and subsequent retention in soils of a coniferous forest and a coastal prairie ecosystem. Despite small annual losses of DOC relative to respiratory losses, DOC leaching plays a significant role in transporting C from surface horizons and stabilizing it within the mineral soil. We found that DOC movement into the mineral soil constitutes 22% of the annual C inputs below 40 cm in a coniferous forest, whereas only 2% of the C inputs below 20 cm in a prairie soil could be accounted for by this process. In line with these C input estimates, we calculated advective transport velocities of 1.05 and 0.45 mm year^{-1} for the forested and prairie sites, respectively. Radiocarbon measurements of field-collected DOC interpreted with a basic transport-turnover model indicated that DOC which was transported and subsequently absorbed had a mean residence time of 90–150 years. Given these residence times, the process of DOC movement and retention is responsible for 20% of the total mineral soil C stock to 1 m in the forest soil and 9% in the prairie soil. These results provide quantitative data confirming differences in C cycles in forests and grasslands, and suggest the need for incorporating a better mechanistic understanding of soil C transport, storage and turnover processes into both local and regional C cycle models.

Keywords Carbon sequestration · Dissolved organic carbon · Mean residence time · Radiocarbon · Soil organic matter · Transport modeling

Introduction

Globally, the top meter of soil stores ~1,500 Pg of carbon (C), approximately twice the C as found in the atmospheric CO_2 pool, with approximately 60% of this C found at depths greater than 20 cm (Jobbagy and Jackson 2000), though the amounts and residence times vary enormously with depth and climate zone/ecosystem. For soil C to be effectively sequestered

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beyond a timescale of a few decades, C must become physically stabilized, commonly by association with clay surfaces and in subsurface mineral horizons. Yet, the rates of this process are poorly known. Within the upper 10 cm of soil, biological metabolism and physical mixing are too rapid for large quantities of C to become effectively protected against mineralization (Baisden et al. 2002a; Ewing et al. 2006). Carbon at the soil surface originating from litterfall can be incorporated into the mineral horizons by (1) leaching of dissolved organic carbon (DOC) and/or (2) biological and physical mixing, with root turnover and exudation representing direct inputs of C. The relative magnitude of these processes, and how they vary from forests to grasslands, has been difficult to determine.

The relative importance of DOC compared with direct root inputs and biogenic mixing in redistributing C within the soil profile will depend on several factors. These include climate (amount and timing of rainfall), edaphic conditions (soil structure/texture, nutrient status and pH), and vegetation type (root distribution and litter quality). Grasslands with large net primary productivity (NPP) allocations to root growth commonly are assumed to be dominated by direct root inputs (Jackson et al. 1996), though the data to compare to leaching is unavailable. In contrast, coniferous forests produce higher fractions of C inputs as annual litter fall, and fine roots are concentrated in the litter or in the near soil layers (Nadelhoffer and Reich 1992; Uselman et al. 2007). The acidic litter makes the soil inhospitable to many soil fauna, and the absence of biological mixing in conjunction with organic acid leaching leads to distinct soil horizonation (Schaetzl 2002; Vance et al. 1986). Here, DOC leaching is commonly assumed to be a significant means of transporting carbon into the mineral soil (Michalzik et al. 2003).

The O horizons common to forests have been shown to be a large source of DOC to the mineral soil, with annual fluxes ranging from 100 to 500 kgC ha^{-1} -year^{-1} (see literature summaries by Michalzik et al. 2001 and Neff and Asner 2001). In contrast, the DOC fluxes leaving the B horizons of these soils are often one or two orders of magnitude lower (Michalzik et al. 2001; Neff and Asner 2001). The fate of this "missing" leached C (i.e. sorption and stabilization or decomposition) is critical to understanding the relative importance of DOC fluxes in the belowground C cycle. Laboratory experiments typically indicate that most mineral soils have a high tendency to absorb DOC (Dalva and Moore 1991; Kaiser et al. 1996; Qualls and Haines 1992b), yet decomposition of the DOC is slow and only partial (Qualls and Haines 1992a; Yano et al. 1998) especially after absorption to mineral surfaces (Kalbitz et al. 2005). Additionally, it has been shown that DOC collected within the mineral soil is chemically much more similar to soil OM than to fresh litter leachates (Froberg et al. 2006, 2007; John et al. 2003; Kaiser and Guggenberger 2000; Kalbitz et al. 2007; Karltun et al. 2005), suggesting significant sorption and exchange as water percolates through the soil (Sanderman et al. 2008).

The purpose of this study is to examine the importance of DOC in transporting and sequestering C in the mineral soil in two strongly contrasting ecosystems. DOC and CO_2 fluxes, laboratory sorption and biomineralization rates, and soil C stocks from a coniferous forest and prairie soil were measured in order to compare the magnitude of DOC transport and retention relative to the other major C transport processes. The data are interpreted in terms of a soil C transport-turnover model in order to place DOC transport and reaction processes into a more general framework of soil C cycling.

Methods

Study sites

The research was conducted at two contrasting coastal northern California ecosystems which are part of a larger watershed-scale investigation of DOC fluxes and chemistry (Sanderman 2007). *Tennessee Valley*, located in the rolling soil-mantled sandstone hills of coastal Marin County, California, is a coastal prairie ecosystem with current vegetation dominated by a mixture of European annual grasses, various forbs, and, to a lesser extent, native perennial grasses. Soils are classified as Typic Haplustolls that possess dark, well-mixed A horizons residing above a clayey, organic-poor, relatively unmixed horizon (Table 1). The A horizons are mixed by gophers and ground squirrels, which is the key biological sediment transport mechanism in the area (Heimsath et al. 1997; Yoo et al. 2005). *Caspar Creek*, located in the coastal Redwood zone of Mendocino County, CA, is dominated by a nearly 100-year-old second growth

Table 1 Selected properties of the two soils examined in the study

Horizon	Depth cm	Bulk density[a] Mg/m^3	Texture[b]			Gravel%	pH 1:1 H_2O	CEC[c] cmol+/kg	BS[d] %	Org C[e] %	$Fe^{f}_{d\text{-}ox}$ g/kg	$(Fe + Al)^{g}_{ox\text{-}py}$ g/kg	OC^{h}_{py} g/kg
			Sand%	Silt%	Clay%								
Forest soil													
Oi	6–3	0.04								46.07			
Oe	3–0	0.18								35.19			
A1	0–7	0.75	32.4	26.0	41.7	25	6.1	30.8	46.6	3.38	7.54	4.10	5.52
A2	7–15	1.07	31.9	22.1	46.0	15	6.0	20.6	44.3	2.28	8.07	4.56	5.23
AB	15–21	1.27	32.3	17.6	50.1	15	5.9	19.7	36.8	1.30	9.21	4.26	2.67
Bt1	21–37	1.40	35.7	16.8	47.6	20	5.8	21.8	29.3	0.90	10.10	2.77	1.09
Bt2	37–68	1.55	44.2	13.4	42.4	20	5.8	15.4	32.3	0.47	9.35	3.78	2.08
BC	68–120	1.63	50.5	10.2	39.3	30	5.7	18.2	23.5	0.39	11.90	1.67	1.23
Cr	120+	1.41	60.4	12.6	27.0	70	5.7	n.d.	n.d.	0.31	n.d.	n.d.	n.d.
Grassland soil													
A1	0–10	0.86	41.1	22.4	36.5	50	6.2	33.5	50.3	3.97	19.01	1.59	6.86
A2	10–27	1.12	40.2	25.3	34.6	40	6.2	26.8	56.2	2.31	19.67	1.36	5.84
A3	27–40	1.15	40.2	25.2	34.7	20	6.4	26.6	62.1	1.68	20.13	2.43	4.39
AC	40–60	1.21	38.2	22.0	39.9	50	6.7	26.9	74.4	1.14	25.16	2.62	2.85
Cr	60+	1.39	21.5	24.1	54.4	75	7.0	n.d.	n.d.	0.70	n.d.	n.d.	n.d.

[a] Bulk density measured in situ with a bulk density corer

[b] Clay determined by sedimentation (Gee and Bauder 1986), sand by sieving and silt by difference

[c] Cation exchange capacity determined following methods of Chapman (1965)

[d] Base saturation determined as difference between exchangeable bases and CEC

[e] Organic C determined on a Leico CHN autoanalyzer

[f] Crystalline Fe sesquioxides estimated as the difference between dithionite-citrate and NH_4 oxalate extractable Fe (McKeague and Day 1966)

[g] Amorphous Al and Fe hydroxides estimated as the difference between NH_4 oxalate and Na pyrophosphate extractable Al and Fe (McKeague et al. 1971)

[h] Na pyrophosphate extractable organic C

redwood-Douglas fir forest with well-weathered soils derived from greywacke sandstone, classified as Typic Haplohumults (Table 1). Both sites have a Mediterranean climate with warm dry summers and cool wet winters. Mean annual precipitation is 1,200 mm at Caspar Creek (Ziemer 1998) and 1,050 mm at Tennessee Valley (NCDC 2007). More detailed site descriptions can be found in Sanderman et al. (2008).

Field sampling and monitoring

Soils at both locations were excavated along a hillslope gradient from ridge to hollow, sampled by genetic horizon, and then instrumented for hydrometric monitoring and water collection before careful backfilling. In this paper, we only report results from the upper part of the hillslope transects, areas where water flow is predominantly vertical.

Volumetric water content (θ) was monitored continuously at 10, 20 and 50 cm using Decagon ECHO probes attached to Decagon EM5 dataloggers (Decagon Devices, Inc., Pullman, WA). Due to the clayey nature of these soils, specific calibration curves on intact cores were determined in the lab. Soil temperature and water potential (ψ_s) at the same depths as the ECHO probes was monitored continuously using Spectrum Watermark sensors attached to Watchdog dataloggers (Spectrum Technologies, Inc., Plainfield, IL). Ceramic cup tensiometers were also installed near each soil excavation at depths of 10, 25, 50, 75 and 100 cm, and these were monitored manually using a needle pressure transducer.

Zero-tension lysimeters (custom-built 150 cm^2 HDPE pans) were installed at 0 (below the forest floor), 3, 7, 15, and 30 cm at the forested site and at 10 cm in the grassland site. Prenart Super-quartz (Prenart AsP, Denmark) tension lysimeters were installed at 40, 70 and 120 cm in the forest soil and at 20, 50, 100 cm in the grassland soil. After a 3 month equilibration period, soil solution samples were collected approximately every 2 weeks from the tension lysimeters and after most large rain events for the zero-tension samplers for the 2005 and 2006 hydrologic years (HY2005 = Oct 1, 2004–Sept 30, 2005). Solution samples were filtered through Whatman GF/F filters (nominal pore size = 0.7 μm) and stored at 4°C until analyzed for DOC concentration on an OI Analytical model 1010 TOC/TIC analyzer (OI Analytical, College Station, TX) by persulfate oxidation following acidification with phosphoric acid.

Soil CO_2 concentrations at 10, 25, 50, 75 and 100 cm were measured in the field by sampling soil air from stainless steel gas wells (3 mm OD) capped with silicon septa at 18 sampling dates throughout HY2005. Samples were immediately analyzed on a portable Licor 6200 infrared gas analyzer (LI-COR biosciences, Lincoln, NE). Because $p\text{CO}_2$ levels can reach over 2% in soils, a small volume of soil air (5 cm^3) was injected into a much larger CO_2-free volume attached inline with the Licor unit (see Wang et al. 2000 for details of the instrumental setup) and CO_2 standards (Matheson Tri-Gas, Twinsburg, OH) of 500, 2,000 and 20,000 ppm (v) where run before and after each set of measurements for calibration.

Soil C inputs

At Tennessee Valley, annual aboveground productivity of the grasses was assessed by measuring the maximum standing biomass (as dry weight) in late April of each year in 0.25 m^2 quadrats. The root-to-shoot ratio of smaller subsamples next to each quadrat was used to estimate the belowground productivity. Root mass was determined by gently washing soil from roots and then measuring dry weight of samples.

At the forested Caspar Creek site, litterfall, as a proxy for aboveground C inputs to the soil system, was collected at approximately monthly intervals using 0.1 m^2 baskets ($n = 6$). The small size of these litter baskets excluded most coarse woody debris, thus underestimating the actual productivity. However, because the decomposition rate of coarse debris is often 2 orders of magnitude slower than the fine litter (Harmon et al. 1986; Spies et al. 1988), the exclusion of woody litter should have only a small impact on subsurface soil C cycling. Belowground inputs were not measured.

DOC flux

Vertically infiltrating DOC fluxes were calculated by multiplying the DOC concentration for each sampling period by the water flux through that section of soil for that period of time, and then summing to obtain annual values. Water fluxes were calculated using two methods: (1) a depth integrated water balance model was solved for drainage:

$$D_{t,z} = D_{t,z-1} - ET_{t,z} - \Delta S_{t,z}, \quad (1)$$

where D is drainage ($D_{z=0}$ = rainfall), rainfall and evapotranspiration (ET) are the main driving variables and storage (S) capacity is determined from measured soil properties; and (2) a Darcian-based model where water flux (J_w) is proportional to the potential gradient multiplied by the hydraulic conductivity (K_h):

$$J_w = K_h \frac{\partial h}{\partial z}. \quad (2)$$

Details of both of these approaches, along with parameter values, are presented in the appendix. For depths where we can compare the two methods, the mean relative standard deviation of daily flux at Tennessee Valley was 12.4 ± 5.5% and at Caspar Creek, the mean RSD was 8.7 ± 5.7%.

CO_2 flux

Fick's law was used to calculate CO_2 flux rates (umol CO_2 m^{-2} s^{-1}) from the soil pCO_2 profile measurements:

$$F_{co_2} = -D_s\left(\frac{dCO_2}{dz}\right), \quad (3)$$

where D_s is the diffusivity in soil (mm^2 s^{-1}) and dCO_2/dz is the concentration gradient (umol CO_2 m^{-3} m^{-1}). The Millington and Shearer (1971) model for gaseous diffusion in aggregated media was chosen to calculate D_s based on porosity and volumetric water content (θ). From the monthly pCO_2 measurements, empirical relationships were derived with day of year (DOY), soil temperature (T_s) and θ to predict dCO_2/dz on a daily basis. Combining these empirical relationships with the Millington and Shearer (1971) diffusion model allowed us to calculate daily CO_2 fluxes and production (as the difference between flux into and out of each layer) at ~20 cm depth increments. Details of model development and validation are presented in Sanderman (2007).

$\Delta^{14}C$ analysis

For $\Delta^{14}C$ analyses, soil organic C samples collected in 2003 were first converted to CO_2 by sealed tube combustion using CuO as a catalyst followed by cryogenic purification (Minagawa et al. 1984). This purified CO_2 was converted to graphite using a H_2 reduction method (Vogel et al. 1984) and loaded into targets for $\Delta^{14}C$ analysis at the Keck Center for Carbon Accelerator Mass Spectrometry, University of California, Irvine, in 2004. $\Delta^{14}C$ was calculated as:

$$\Delta^{14}C = \left(\frac{A_{sample}}{A_{abs}} - 1\right) \times 1{,}000, \quad (4)$$

where A_{sample} is the $^{14}C/^{12}C$ ratio of the sample normalized to a $\delta^{13}C$ value of −25‰ and A_{abs} is 0.95 times the $^{14}C/^{12}C$ ratio of the international standard corrected for radioactive decay, which represents the $^{14}C/^{12}C$ ratio of the pre-industrial atmosphere (Stuiver and Polach 1977). Dissolved samples for $\Delta^{14}C$ analysis collected in early 2005 were filtered, acidified to pH <2 using 5% phosphoric acid, concentrated to ~20 ml on a rotary-evaporator and then lyophilized to a powder. These powdered samples were then prepared for analysis in the same manner as the solid samples. The ^{14}C measurements were made in October of 2005.

Laboratory experiments

Sorption isotherms

The potential for the soils to adsorb or desorb C was assessed by a batch adsorption experiment (e.g. Nodvin et al. 1986). Briefly, triplicate 3 g samples of dried soil were equilibrated with 8 different DOC solutions with concentrations varying from 0 (deionized water) to 100 mgC l^{-1} overnight on a shaker table, centrifuged and then filtered to 0.45 µm. Fresh DOC stock was obtained for Caspar Creek by leaching ~1 kg of litter in 5 l of DI water overnight. For Tennessee Valley, stock solution was obtained by leaching ~1 kg of freshly collected surface soil containing live grass and roots. Stocks were either diluted with DI water or concentrated on a rotary evaporator to desired concentrations. Both stock solution and equilibrated soil solutions were immediately analyzed for DOC concentration, ^{13}C content and UV adsorption at 254 nm.

Organic C is present both in solution and bound to exchangeable sites on mineral surfaces. The batch adsorption results were therefore interpreted using equilibrium concepts in the initial mass isotherm of Nodvin et al. (1986):

$$RE = mX_i - b \quad (5)$$

where RE is the amount released or removed from solution (mgC g $soil^{-1}$) and X_i is initial DOC concentration (mgC g soil^{-1}). From the slope (m) and intercept (b), a distribution coefficient (K_d, cm^3 g^{-1}) and an estimate of the size of the reactive soil pool (RSP, mgC g^{-1} soil) were be obtained:

$$K_d = \left(\frac{m}{1-m}\right)\left(\frac{vol_{solution}}{mass_{soil}}\right), \tag{6}$$

and

$$RSP = \frac{b}{1-m}. \tag{7}$$

Lastly, the null-point DOC concentration was estimated from the intercept of a plot of the equilibrium DOC concentration (mgC l^{-1}) and RE.

Bioavailability experiment

Field-collected throughfall and soil water samples were incubated in the dark at lab temperature (~18°C) for 2 months similar to the methods of Qualls and Haines (1992a). In order to obtain enough fresh soil water (4 l was needed for 5 replicates), in March of 2005 we set up an artificial rainfall simulation over 30 × 30 cm metal pans inserted horizontally into the wall of a freshly evacuated trench. These large metal pans ensured that approximately 1 pore volume of soil water would be displaced. Field samples were filtered to 0.7 µm. Inoculum was obtained by shaking 200 g of field moist soil, from the same site as each soil water sample was collected, with 500 ml of DI water and then filtering to ~2.0 µm. About 10 ml of the inoculum, along with 12 hole-punches from a sterile glass fiber filter to provide a surface for microbial attachment, were added to 800 ml of each sample in autoclaved 1 l Ball preserve jars. Samples were kept aerated throughout the experiment by bubbling 100% RH air through the samples. At 1, 3, 7, 15, 29, 43 and 63 days, 15 ml of sample was removed for DOC analysis. Mass loss of C was corrected for changes in solution volume throughout the experiment.

The results from the bioavailability experiment were interpreted using a two-pool first-order decay model (Townsend et al. 1997) of the form:

$$\%DOC_{\text{remaining}} = Ce^{k_f t} + (100 - C)e^{k_s t}, \tag{8}$$

where C is the percent of the C in a fast cycling pool, t is time (days), and k is the decay constant (days^{-1}) for the fast and slow cycling pools. This model was chosen because it both generally provided a significantly improved fit over a single pool model and recognizes that that there are at least two slightly less heterogeneous C fractions within the DOM pool that have greatly differing decomposition rates.

Soil carbon modeling

Downward transport of soil C has been represented in simulation models by diffusive and/or advective processes (Baisden et al. 2002b; Elzein and Balesdent 1995; O'Brien and Stout 1978). Diffusive transport includes biophysical mixing by soil fauna and the shrink/swell action of certain soils. Advection refers to the vertical transport of a solute in the liquid phase. In this study, the relative importance of the two transport mechanisms is hypothesized to vary between site; and to begin we use a generalized soil C model (Fig. 1) where changes in C mass in a given horizon (z) over time is equal to the net addition/loss by diffusive processes minus net addition/loss by advective processes minus C lost to microbial respiration (kC) plus any input of C from plants (f_d):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - kC + f_d, \tag{9}$$

where D is the diffusion coefficient (mm^2 year^{-1}), v is the advective transport coefficient (mm year^{-1}), k is the decomposition constant (year^{-1}) and f_d represents the direct input of organic C via litterfall at the surface and via root turnover within the soil. In Eq. 9,

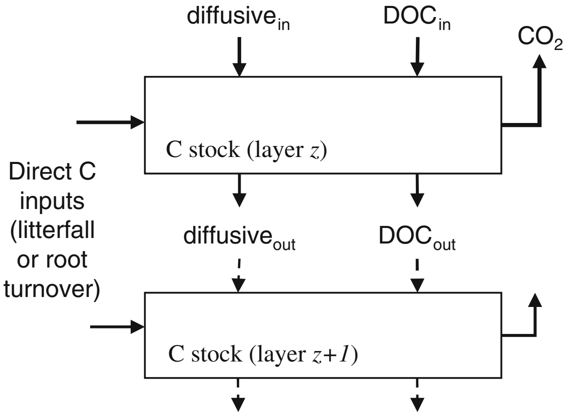

Fig. 1 Illustration of C transport-turnover model. For a given soil layer, the change in C over time is the difference between inputs and losses. Inputs include direct C inputs from litter or roots, diffusive mixing and DOC leaching. Outputs are dominated by microbial respiration

a single decay constant (k) is given to simply represent an aggregate of several C pools with differing turnover times. We hypothesize that the different input mechanisms have greatly differing turnover times and when we calculate k in Eqs. 10–11, this k (k_{RSP}) only refers to the portion of the entire C pool that is attributable to DOC movement and retention.

Carbon input calculation

We combined the in situ measurements of DOC and CO_2 fluxes to make an estimate of the relative importance of DOC movement as a C input mechanism. Carbon inputs to soil C pools include: (1) root turnover and exudation (F_{root}), (2) DOC leaching (DOC_{in}) and (3) diffusive mixing of C from above (Fig. 1, Eq. 9). C losses from this pool are (1) mineralization to CO_2, (2) DOC leaching (DOC_{out}) and (3) diffusive mixing to deeper horizons. Given that C fluxes of all types typically decrease with increasing depth, DOC leaching and diffusive mixing can be represented as net inputs (i.e. DOC retention $= DOC_{in} - DOC_{out}$). Therefore, assuming C stocks are close to steady state, C loss due to mineralization is equal to net inputs (F_{root}, DOC retention and net diffusive inputs). Net mineralization rates (i.e. CO_2 production) were calculated as the difference between CO_2 flux into and out of a given soil thickness after subtracting an estimated autotrophic contribution to total soil CO_2 flux. We estimated autotrophic respiration by assuming that on an annual basis total CO_2 efflux was an even mix of heterotrophic and autotrophic respiration (Hanson et al. 2000) and that the autotrophic contribution was then distributed with depth following the distribution of roots (exponential decline) in each soil. Given the constraints of DOC and CO_2 measurement depths in consideration with the hypothesized major source regions for DOC (the forest floor at Caspar Creek and the topsoil of at Tennessee Valley), we performed this calculation for the depth increments 0–40 and 40–100 cm in the forest soil and only for the 20–100 cm depth increment in the grassland soil.

Mean residence time of sorbed DOC

In order make an estimate of the proportion of C stocks attributable to DOC movement and retention, the mean residence time (τ) of adsorbed DOC must be calculated. To accomplish this goal, we combined measurements of the $\Delta^{14}C$ values of field-collected DOC, along with measured DOC flux rates and sorption parameters. A discrete transport-turnover model was constructed to describe changes in the ^{12}C and ^{14}C content of the reactive soil pool (*RSP*) over time, which we assume is both analogous to sorbed DOC and is in isotopic equilibrium with field-collected DOC (Sanderman et al. 2008). The measured DOC fluxes represent vertical transport (F_{DOC}), and turnover of this pool is represented by a single-pool first-order decay constant (k_{RSP}). For ^{12}C content:

$$RSP^{12C}_{t+1,z} = RSP^{12C}_{t,z} + F^{z-1}_{DOC} - F^{z}_{DOC} - k_{RSP}RSP^{12C}_{t,z}. \tag{10}$$

This equation was modified for ^{14}C content by including radioactive decay ($\lambda = 1.245 \times 10^{-4}$ year^{-1}) and by multiplying F_{DOC} by the ratio of $^{14}C/^{12}C$ in the respective RSP's:

$$RSP^{14C}_{t+1,z} = RSP^{14C}_{t,z} + \left(\frac{RSP^{14}}{RSP^{12}}\right)_{t,z-1} F^{z-1}_{DOC} - \left(\frac{RSP^{14}}{RSP^{12}}\right)_{t,z} F^{z}_{DOC} - (k_{RSP} + \lambda)RSP^{14C}_{t,z}. \tag{11}$$

The soils were divided into 10 cm increments down to 80 cm. To estimate fluxes into and out of each of these soil layers, measured DOC fluxes were then smoothed with depth using an exponential fit ($R^2 = 0.93$ and 0.96 for Caspar Creek and Tennessee Valley, respectively). In the uppermost soil box (0–10 cm), we assumed a small portion of the annual C inputs was transformed into potentially dissolvable C (i.e. the *RSP*) so that, at steady state, the size of the *RSP* in the surface horizon was equal to the measured values in Table 3. This quantity was added to either rainfall DOC for Tennessee Valley or throughfall DOC at Caspar Creek. In order to incorporate the effects of atmospheric weapons testing on $\Delta^{14}C$ values, the $^{14}C/^{12}C$ ratio of inputs to the upper soil box was set equal to the value of the atmosphere for that year (Cain and Suess 1976; Levin and Kromer 1997, 2004). The model was iterated for 5,000 annual time steps with a steady atmospheric $^{14}C/^{12}C$ ratio to achieve steady state, and then the measured atmospheric ^{14}C record was used starting in the year 1900 through 2006. Mean residence time (τ) for the *RSP* was then estimated by minimizing the sum of squares error between the measured and modeled $^{14}C/^{12}C$ ratios of DOC. After determining a τ value for the adsorbed DOC pool, we estimated the fraction of total C stocks attributable to this input mechanism by multiplying the DOC input rate (mgC m^{-2} $year^{-1}$) by τ (years) and dividing by C stock (mgC m^{-2}).

Results

Soil C cycle

Annual DOC fluxes, CO_2 fluxes and C inputs for HY2005, as well as soil C stocks for both sites are summarized in Fig. 2. DOC results are only presented for HY2005 in order to facilitate a direct comparison to CO_2 fluxes (differences between years varied from 6% to 15% at all depths). In the forest, the canopy was a large source of DOC, with an annual flux of 13.2 gC m^{-2} $year^{-1}$. This throughfall mobilized additional C as it percolates through the litter layers (O horizon leachate = 31.7 gC m^{-2} $year^{-1}$). The net loss of C as DOC from the litter layer was ~10% of the rate of annual C inputs due to litterfall (200 gC m^{-2} $year^{-1}$). DOC fluxes were rapidly attenuated below the C-rich surface horizons as water percolates through the underlying mineral soil. At the coastal prairie site, due to the nature of the soil and root structure, the shallowest depth we could install a lysimeter was 10 cm. While we cannot partition sources within or above this horizon, as a whole this C-rich biologically active zone was the dominant source of DOC production, with an annual flux of 8.6 gC m^{-2} $year^{-1}$, a value about 25% that of the

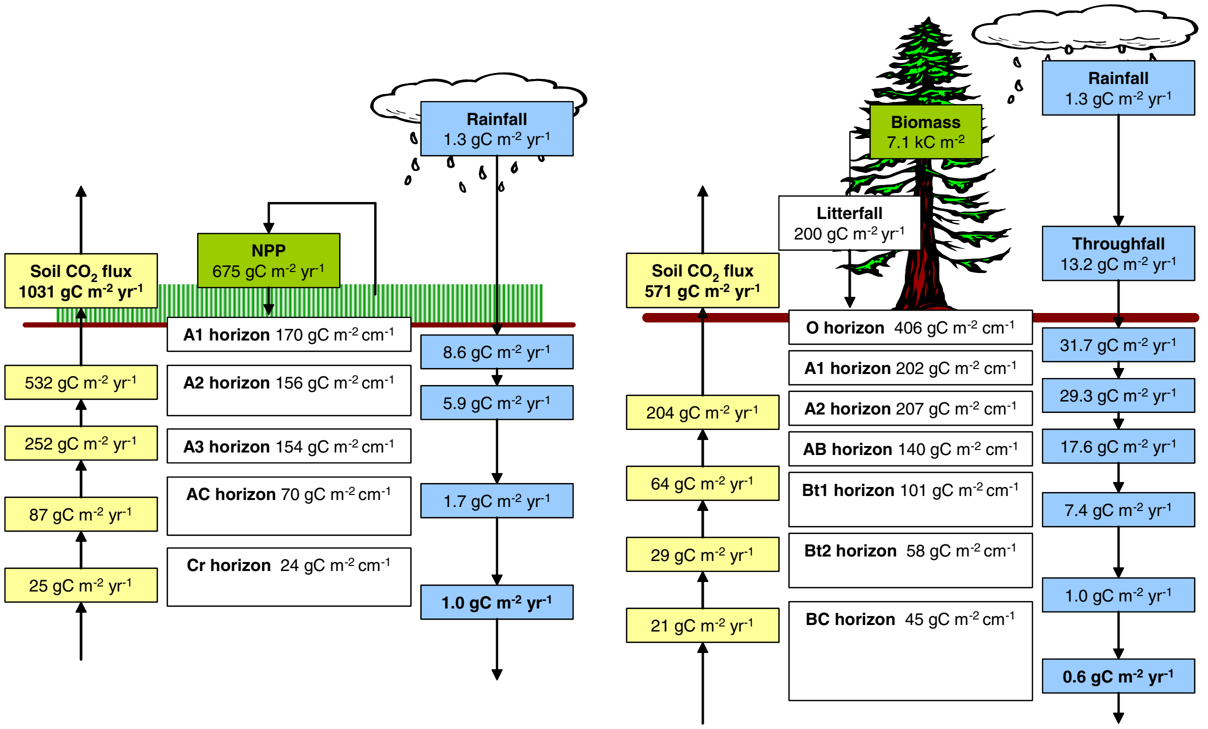

Fig. 2 Carbon budgets, annual CO_2 fluxes (yellow) and DOC fluxes (blue) at the grassland (left) and the forest (right) sites. NPP estimates at TV include aboveground and belowground inputs, whereas at CC, only litterfall was measured. Soil organic C stocks are reported on a per cm basis (see Table 1 for horizon thicknesses). Total C to 1 m depth at Tennessee Valley (TV) is 8.7 kgC m^{-2}; and at Caspar Creek (CC), 12.7 kgC m^{-2} in the mineral soil and an additional 1.8 kgC m^{-2} in the O horizon. CO_2 fluxes, which include both autotrophic and heterotrophic respiration, have been calculated at the soil surface and at depths of 18, 38, 63 and 88 cm. DOC fluxes at TV are reported at 10, 20, 50 and 100 cm; and at CC, DOC fluxes are reported at 0 (base of O horizon), 7, 15, 40, 70 and 120 cm

forest. As in the forest soil, DOC fluxes were rapidly attenuated with depth in the grassland.

At both sites the decline in DOC fluxes with depth was due a large decrease in DOC concentrations rather than a decrease in water flux. Water fluxes declined by a factor of 2, whereas DOC concentrations decreased by a factor of 20 or more, with increasing soil depth (Sanderman et al. 2008). Both soils were so effective at retaining DOC that concentrations and fluxes below 1 m were less than those in the measured rainwater. Thus, annual net C losses from these soils were dominated by respiratory losses as CO_2.

$\Delta^{14}C$ results

$\Delta^{14}C$ values for bulk soil C, water-extractable organic C (WEOC) and field-collected DOC are shown in Fig. 3. At both sites, litter had radiocarbon contents representative of the 2003 atmosphere (~80‰) while the mineral soil $\Delta^{14}C$ values declined rapidly with increasing depth, as is commonly observed (e.g. O'Brien and Stout 1978; Baisden et al. 2002b). WEOC generally had $\Delta^{14}C$ values similar to that of the bulk soil pool, while the field collected DOC samples were generally much younger than the bulk soil pool. Although DOC was younger than the mineral soil, these DOC values have been interpreted to be representative of OM that was considerably older than surface litter indicating that chemical exchange had occurred as water passed downward through the soil (Sanderman et al. 2008).

Sorption isotherms

For our range of X_i, linear regression coefficients ranged from 0.97 to 0.99 ($n = 8$) indicating that the initial mass isotherm model was indeed appropriate (Fig. 4). All the soils had a high propensity to adsorb DOC as indicated by the high m values, while the surface horizons also had a propensity to desorb C into solution as given by high intercept (b), RSP and $DOC_{null\text{-}pt}$ values (Table 2). The ability of these soils to both adsorb and desorb C resulted in a large gross exchange of C between the mineral surfaces and the soil solution regardless of net adsorption or desorption (Sanderman et al. 2008).

Bioavailability results

The two-pool model produced an excellent fit for the forest soil samples (Fig. 5, Table 3). The decay rates derived from this model did not change appreciably between samples ($k_f \approx 0.04$ days^{-1}), but the proportion of the DOC in a fast cycling pool in the forest declined from 36% to 27% to 20% passing from the throughfall, O horizon leachate and A horizon leachate, respectively (Table 3). In the prairie soil (Fig. 5a), the 2 month incubation period was not long enough to isolate a slow cycling pool of DOC, and the majority of DOC decayed at a moderate rate, with k values declining from 0.007 to 0.005 days^{-1} with increasing depth.

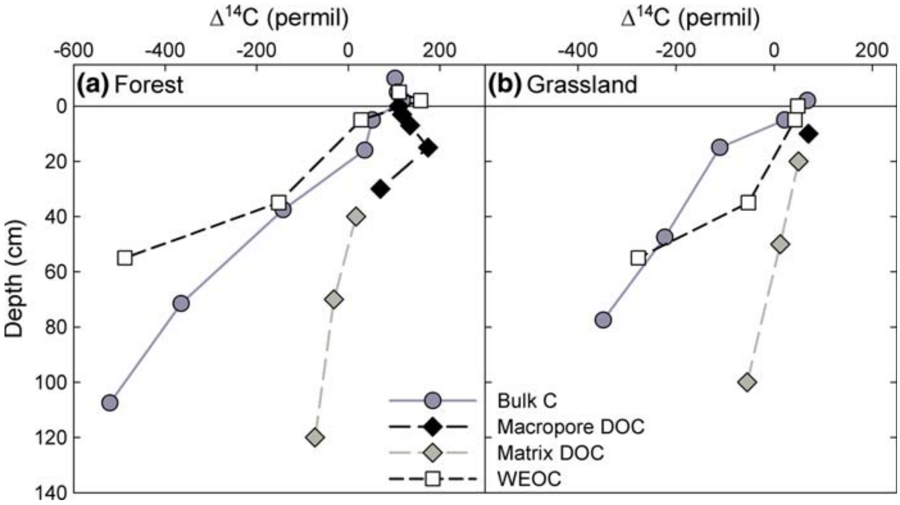

Fig. 3 $\Delta^{14}C$ values of bulk soil C (grey circles), water-extractable organic C (WEOC, open squares), field collected macropore DOC (black diamonds) and matrix water DOC (grey diamonds) for Caspar Creek (**a**) and Tennessee Valley (**b**). Macropore samples collected in zero-tension lysimeters and matrix water collected in tension lysimeters. In both plots, the mineral soil surface is at 0 cm

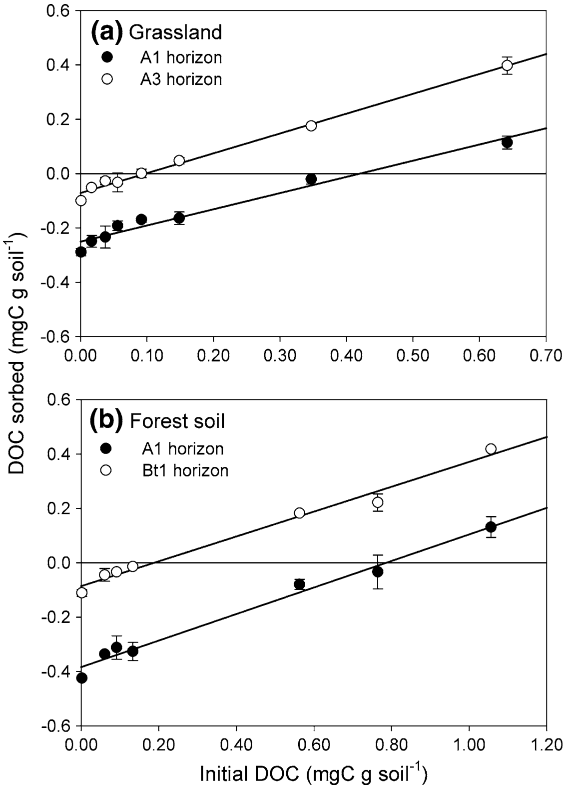

Fig. 4 DOC sorption isotherms for grassland (**a**) and forest soil (**b**). Error bars = 1 s.e. ($n = 3$). See Table 2 for regression summary

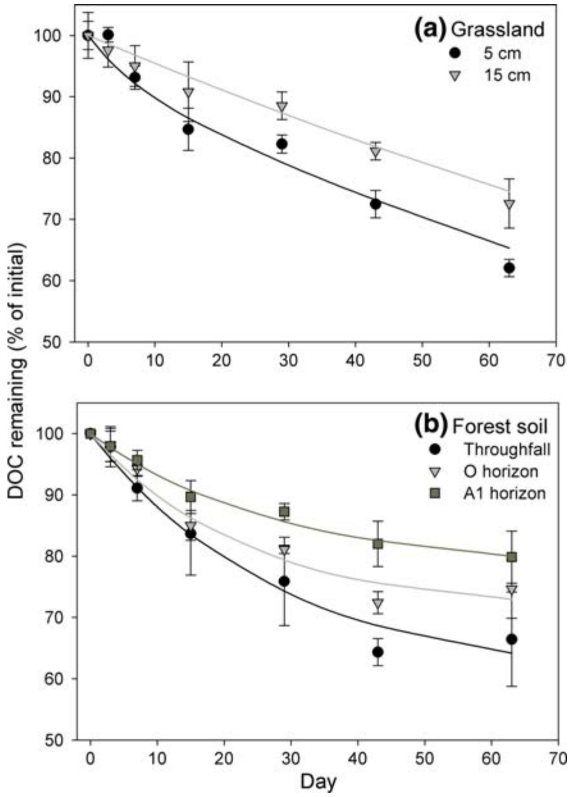

Fig. 5 DOC incubation results plotted as % of initial DOC concentration remaining for grassland (**a**) and forest soil (**b**). Error bars = 1 s.e. ($n = 5$). See Table 3 for regression summary

Discussion

The case for DOC retention

DOC concentrations declined with depth (Fig. 2), but are these patterns due to adsorption or decomposition? Kaiser and Zech (1998) found that in only 15 min, 60–90% of DOC added to a subsoil was retained by sorption. Our batch sorption results showed that 43–72% of added DOC was retained by the soils, with higher values correlated with finer textured subsurface horizons rich in Fe and Al sesquioxides. Under similar experimental conditions, Moore et al. (1992) and Kaiser et al. (1996) found comparable results.

The conditions under which the batch sorption experiments are conducted exposes more mineral surfaces and organic matter to water than would be expected in the field, leading to the potential over-estimation of both sorption (*m*) and desorption (*b*) parameters. The ^{14}C content of water-extractable

Table 2 DOC sorption isotherm parameters derived from lab experiments

Parameter	Units	Grassland		Forest	
		A1 horizon	A3 horizon	A1 horizon	Bt1 horizon
m	Unitless	0.60 (0.01)	0.73 (0.01)	0.47 (0.03)	0.46 (0.03)
b	mgC g^{-1}	0.25 (0.04)	0.07 (0.03)	0.39 (0.02)	0.09 (0.02)
K_d	cm^3 g^{-1}	14.7 (0.02)	27.1 (0.01)	8.85 (0.04)	8.63 (0.04)
RSP	mgC g^{-1}	0.62 (0.05)	0.26 (0.03)	0.73 (0.03)	0.16 (0.03)
$DOC_{\text{null-pt}}$	mgC l^{-1}	43.4 (0.08)	9.63 (0.04)	84.5 (0.08)	19.2 (0.03)

Standard error shown in parentheses. See text for definitions

Table 3 DOC decomposition experiment results

Parameter	Grassland		Forest		
	5 cm	15 cm	TF	O horizon	A horizon
Initial (DOC)	5.6	6.2	4.5	8.6	10.1
Initial SUVA[a]	6.6	7.0	2.9	4.1	6.1
% decay[b]	39.3 (3.7)	25.4 (7.0)	36.0 (2.0)	27.3 (2.1)	20.0 (0.8)
C^c	3.9	0.0	39.7	28.4	19.2
$1/k_f$ (days)	10.5	n.s.	28.1	22.9	24.8
$1/k_s$ (days)	136	215	4350	4020	2025
adj R^2	0.90	0.86	0.95	0.93	0.85

[a] SUVA = specific UV adsorption, the adsorption at $\lambda = 254$ nm normalized to DOC concentration (mgC l^{-1})

[b] Mean of five replicates (standard error in parentheses)

[c] Proportion of carbon in fast cycling pool

organic carbon (WEOC), i.e. the equilibrated soil solution from the control (DOC = 0 mgC l^{-1}) batch treatment, was very similar to that of the bulk soil C, but much older than field-collected DOC at the same depths (Fig. 3), indicating that the batch experiment exposed C that was not exchangeable in situ. Qualls and Haines (1992b) compared conventional batch sorption results to those obtained using continuous, unsaturated flow through intact soil cores for an AB horizon of a Typic Hapludult, a soil similar to those in this study. They found that the intact cores released less C into solution but retained slightly more DOC than the disturbed soil. Thus, it appears that although batch sorption experiments tend to overestimate the in situ desorption of C, they are fairly robust for estimating the sorption potential of undisturbed soils.

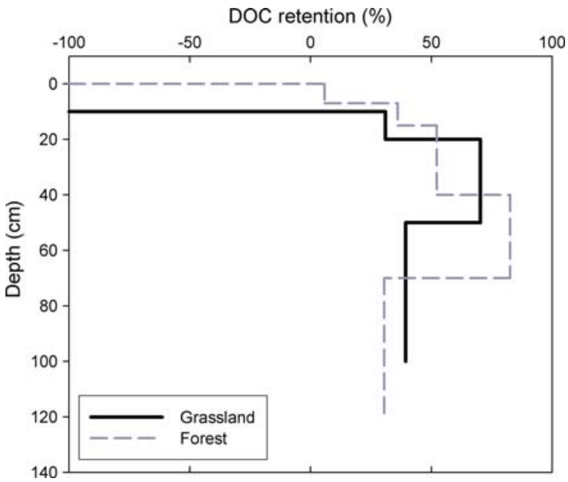

Fig. 6 The percent of DOC entering a soil layer that is retained within that layer calculated as the difference between the DOC flux entering and leaving a given layer adjusted for decomposition of a labile fraction. Decomposition rates for Caspar Creek were taken as the deepest k_f value in Table 3 and the proportion of DOC in this labile pool declined exponentially with increasing depth; while at Tennessee Valley, decomposition proceeded on the entire DOC pool with $k = 0.0047$ day^{-1}. We assumed soil water residence time increased linearly with depth (residence time (days) = 0.5 × depth (cm)) following the work of Asano et al. (2002) and McGuire et al. (2002)

During the 2 month incubation, only 20–40% of DOC was mineralized (Table 3). It has been proposed that the percent mineralized is representative of the size of the labile portion of the DOC (e.g. Qualls and Haines 1992a; Jandl and Sollins 1997; Yano et al. 1998), and both decreased with increasing depth in our experiments. In Fig. 6, the percent of DOC retained within each soil layer was calculated as the difference between the flux of DOC into and out of that layer minus the amount mineralized assuming reasonable soil water residence times (water residence time increased at the rate of 1 day per 2 cm depth following the work of Asano et al. (2002); McGuire et al. (2002)). Because soil water residence times are on the order of days to several weeks (Asano et al. 2002; McGuire et al. 2002), mineralization can account for just a small fraction of the DOC losses and adsorption therefore dominates the removal process. This is consistent with other work (summarized by Kalbitz et al. 2000) revealing that rates of absorption greatly exceed mineralization. Additionally, the net retention values calculated in Fig. 6 were similar to the maximum adsorption values obtained from the batch sorption experiment

(46–73% of DOC added) and showed subsurface maxima coinciding with the illuvial horizons where clay and sesquioxide content is greatest.

Stabilization upon sorption

What is the fate of DOC once it is adsorbed to the mineral soil? If sorbed C is mineralized rapidly, then DOC retention is of little importance to C stocks. However, there is evidence that that suggests the residence time for sorbed DOC is long. First, the bioavailability of DOC in the soil solution is low with a large fraction of the DOC having mean residence times of years to decades (Table 3). Second, the portion of DOC that is most likely to be adsorbed is the hydrophobic fraction, which is composed of more recalcitrant compounds with greatly reduced decay rates (Ciglasch et al. 2004; Marschner and Kalbitz 2003; Qualls 2005). Third, there is evidence that mineralization rates of DOC decline following sorption to mineral surfaces. Kalbitz et al. (2005) found that the amount of Spodosol DOC mineralized during a 1-year incubation dropped from 77% to 13% for an Oi solution, and from 28% to 5% for an Oa solution, following sorption to mineral soil. Kaiser et al. (2007) found that there was no detectable decomposition of Oa horizon leachates after sorption to fresh ferrihydrite and goethite minerals during a 3 year incubation. Mineralization rates for labile substrates are similarly affected. Van Hees et al. (2003) showed that mineralization rates of citrate, a low molecular weight organic acid, decreased between 35% and 99% depending on the nature of the sorption surface. This decline in mineralization rates was even more pronounced following sorption of citrate to ferrihydrite (Jones and Edwards 1998).

The ^{14}C results presented in Fig. 3 provide insights into the processes affecting DOC as water percolates through the soil. The finding that field-collected soil DOC is significantly aged (i.e. Δ^{14}C values much lower than current atmospheric values) indicates that DOC in solution is not simply the fraction of surficially derived DOC that has not been removed from solution and there must be exchange with an older C pool that has a residence time of decades to centuries. The presence of exchange was also demonstrated by changes in δ^{13}C values of DOC during the batch sorption experiment. Sanderman et al. (2008) found that even under conditions of strong net sorption (i.e. high initial DOC concentration), the δ^{13}C value of the equilibrated solution was shifted towards the higher soil value.

We were able to obtain satisfactory estimates of the mean residence time of sorbed DOC (Fig. 7) using the modeling approach outlined in the methods section. For the forest, where DOC was sampled at a greater depth resolution, we achieved a good fit (adj $R^2 = 0.91$ ($n = 6$)) with $\tau = 92$ years. At the grassland, τ was found to be 148 years (adj $R^2 = 0.78$ ($n = 4$)). Most of the lack of fit for both sites came in the uppermost horizon because, in this model, we are assuming that field-collected DOC is representative of the *RSP* for that horizon and it is likely that DOC collected in zero-tension lysimeters in the upper soil is actually a mixture of younger DOC leached from fresh litter and DOC desorbed from the *RSP* within that horizon (Sanderman et al. 2008). If DOC was a mixture of young and old C sources, then we have actually slightly underestimated the actual τ of the *RSP*. In this modeling exercise, we have not included the possibility of direct leaching of DOC from roots. If roots were a major source of DOC within the mineral soil, then we have further underestimated the actual τ of the *RSP* because root-derived DOC would also have a fairly young ^{14}C age (Gaudinski et al.

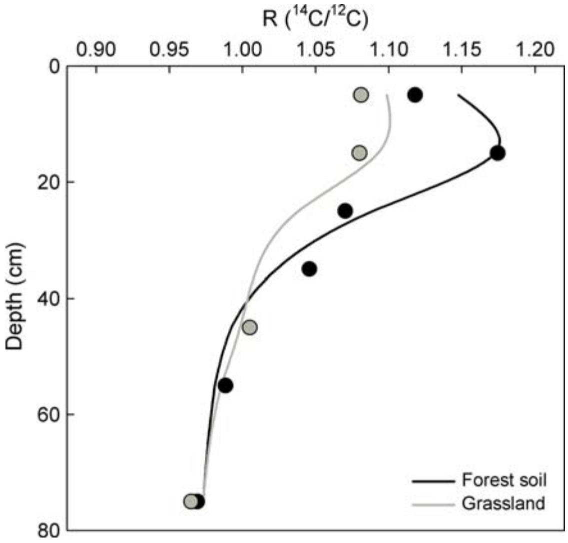

Fig. 7 Best fit curves (solid lines) used for calculating the mean residence time of the *RSP* based on the ^{14}C/^{12}C ratio of DOC for forest (black) and grassland (grey) soils. The depths used in this figure do not exactly match the depths in Fig. 4 because measurements were matched to the mid-points of the modeled 10 cm increments

2001). With these caveats in mind, these estimates of τ for the *RSP* compare favorably with an estimated τ of 91 years for DOC following sorption to a Bw horizon of a Spodosol (Kalbitz et al. 2005) and for DOC sorbed to various fresh mineral surfaces (Mikutta et al. 2007). Additionally, the greater residence time in the grassland soil agrees with results from numerous studies showing a close correlation between ^{14}C-derived τ values and the content of Fe and Al sesquioxides (Masiello et al. 2004; Mikutta et al. 2006; Torn et al. 1997).

C storage due to DOC retention

DOC transport and retention in deeper fine textured soil horizons where decomposition proceeds at much reduced rates represents a potential mechanism to effectively stabilize large quantities of C for significant periods of time. Kalbitz et al. (2005) estimated that 22% of the mineral soil C stock of a coniferous forest could be attributed to the stabilization of DOC on mineral surfaces. Neff and Asner (2001) incorporated measured DOC sorption and decomposition kinetics into a multilayered 3-pool soil C turnover model and found that 25% of the mineral soil C stock was due to DOC movement and retention, while direct root inputs supplied the remainder. Michalzik et al. (2003) modeled C transport and retention dynamics in 2 northern spodosols and found that between 73% and 89% of mineral soil C stocks was supplied by DOC. However, both the Neff and Asner (2001) and Michalzik et al. (2003) models only considered advective C transport, and thus possibly overestimated the role of DOC leaching and retention. Additionally, it was shown by Neff and Asner (2001) that DOC fluxes supported about a third of the microbial activity beneath 40 cm. Similarly, based on ^{14}C measurements of subsurface soil CO_2 production, Fierer et al. (2005) hypothesized that mineralization of recently-leached DOC supported a large fraction of this deep respiration.

In the present study, the proportion of total C inputs due to DOC differed greatly between the forest and grassland soils (Table 4). We found that 9% of C inputs in the top 40 cm and 22% of C inputs below 40 cm at the forested site were due to DOC transport. In contrast, in the grassland, only about 2% of the C inputs below 20 cm were attributable to DOC. These input rates can be used to calculate the fraction of the total soil C pool provided by DOC transport. This calculation was made by multiplying the net DOC retention (gC m^{-2} year^{-1}) by the estimated mean residence times (years) calculated above. In the forest, we found that 23% of organic C stock in the top 40 cm and 14% of the C in the next 60 cm (which comprises 20% of the total organic C found in the top meter) is driven by DOC movement and retention. Despite the low DOC fluxes in the grassland, 14% of the organic C below 20 cm and 8.6% of the entire profile C was controlled by DOC inputs due to the relatively slow decomposition rate of this adsorbed C pool.

Our finding that significant quantities of relatively young C (90–150 year residence time) can be rapidly

Table 4 Soil carbon input and loss rates as measured or modeled

Depth	CO_2 production[a]	DOC retention[b]	Unaccounted inputs[c] (root + net diffusive)		DOC retention[d]
cm	gC m^{-2} year^{-1}	gC m^{-2} year^{-1}	gC m^{-2} year^{-1}	% of total inputs	% of total inputs
Forest					
0–40	268	24.3	243.7	90.9	9.1
40–100	31	6.8	24.2	78.1	21.9
Grassland					
20–100	283	4.8	278.2	98.3	1.7

See text for details

[a] CO_2 production is for heterotrophic respiration only (estimated as 50% of total soil respiration with the autotrophic contribution exponentially decreasing similar to the observed drop in root abundance)

[b] DOC retention = DOC flux in − DOC flux out of given depth increment

[c] Unaccounted inputs = CO_2 production − DOC retention

[d] DOC retention as a percentage of total inputs

transported as DOC from the surface into deeper mineral horizons where sorption can stabilize this C for decades lends support to Baisden and Parfitt's (2007) conclusion that there exists a substantial decadally-reactive soil OM pool at depth in many soils. By comparing ^{14}C content of bulk soils collected in 1959, 1974 and 2002, Baisden and Parfitt (2007) found significant bomb-^{14}C enrichment below 50 cm and that was best explained by the addition of a deep decadally-reactive SOM pool to a 3-pool turnover model (e.g. Baisden et al. 2002a). This pool, which the authors attribute primarily to DOC movement and retention, was found to comprise 10–40% of the C below 50 cm in three different grassland soils.

DOC-based advective transport rates

Rates of soil particle or matter transport have been notoriously difficult to constrain, yet are essential to quantitatively understand soil C (and other) processes. The DOC fluxes can be used to calculate downward advective transport rates (v, mm year^{-1}) by dividing the average DOC flux through a soil layer (gC m^{-2} year^{-1}) by the C content of that layer per unit thickness (i.e. gC m^{-2} mm^{-1}). Flux-weighted mean values (±1 s.e.) of v were 1.05 ± 0.20 and 0.45 ± 0.07 mm year^{-1} at the forested and prairie sites, respectively (Fig. 7). The differences between these rates reflect the relative effectiveness of aqueous transport (forest) versus biological mixing (grassland) in moving mass downward in the soil. These transport rates are similar to those estimated using carbon simulation models (Baisden et al. 2002b; Elzein and Balesdent 1995) and distributions of radionuclides in soil profiles (Kaste et al. 2007). In modeling the distribution and turnover of ^{12}C and ^{14}C in a soil profile, Elzein and Balesdent (1995) calculated $v = 0.42$ mm year^{-1} for an Alfisol broadly similar to our prairie site. Kaste et al. (2007), using the distribution of short-lived weapons-derived nuclides (^{137}Cs and ^{241}Am) within the top 20 cm of the soil, found that $v = 0.6$ mm year^{-1} at Tennessee Valley and between 1.0 and 2.0 mm year^{-1} at a coniferous forest in New Hampshire. In summary, our estimates of advection velocities are reasonable relative to other independent estimates of this flux rate, and add much insight into how downward transport varies between ecosystems.

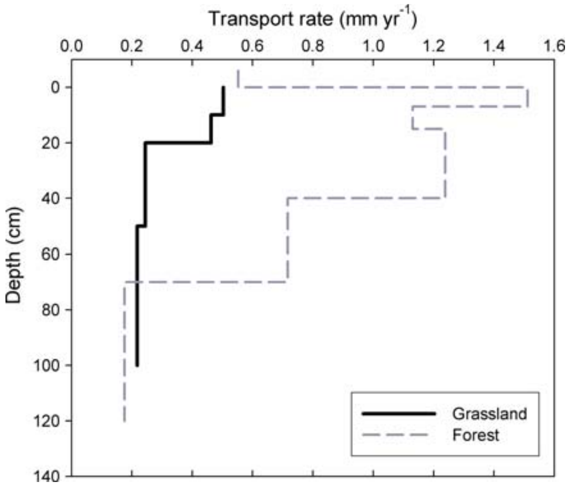

Fig. 8 Advective transport rates (v, mm year^{-1}) calculated from DOC fluxes

While uniform advective and diffusive transport rates are usually adopted when modeling soil transport processes (Baisden et al. 2002b; Dorr and Munnich 1989; Elzein and Balesdent 1995; Kaste et al. 2007; O'Brien and Stout 1978), we find that a decreasing v with increasing depth at both sites (Fig. 7) is likely more realistic of both abiotic and biotic processing occurring within the soil. With increasing depth, bulk density and structure change drastically resulting in significantly reduced hydraulic conductivities, restrictions on root growth and limitations on faunal burrowing. Additionally, for reactive solutes such as DOC, the sorptive capacities of mineral surfaces will vary with mineralogy (Kahle et al. 2003; Kleber et al. 2005) and degree of saturation (Guggenberger and Kaiser 2003); two properties which vary significantly throughout most soil profiles (Fig. 8).

Conclusions

Despite small annual losses of DOC relative to respiratory CO$_2$ losses, DOC leaching plays a significant role as a C input, transport and stabilization mechanism in mineral soil. Here, we have shown that DOC movement and retention in the mineral soil contributes 22% of the annual C inputs below 40 cm in a coniferous forest, whereas only 2% of the C inputs below 20 cm in a prairie soil could be accounted for by this process. In line with these C input estimates; we calculated advective transport velocities of 1.05 and 0.45 mm year^{-1} for the forested and prairie sites, respectively. Radiocarbon measurements of field-collected DOC interpreted with a simple transport-turnover model indicated that this transported and sorbed C has a mean residence time of 90–150 years. Given these mean residence times, the process of DOC movement and retention is responsible for 20% of the total mineral soil C stock in the forest soil and 9% in the prairie soil.

These results support long standing assumptions about differences between forests and grasslands, provide numerical data for the magnitude of the C cycling differences between these two ecosystems, and point to large changes in C cycling with changes in flora driven by land use or climate change. The soils examined in this study are relatively clay-rich, thus they likely more rapidly attenuate downward-moving DOC than that which would occur in sandier soils. Thus, it may be hypothesized that in sandier soils, downward moving C is transported to greater depths, and this DOC may not be stabilized against decomposition as effectively as in fine textured soils. These results suggest the need for further interdisciplinary studies that combine DOC flux measurements with root turnover and diffusive mixing rates and quantify these rates in a wider array of climatic and geological regimes, in order to be able to incorporate a better mechanistic understanding of soil C transport, storage and turnover processes into both local and regional C cycle models.

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Appendix: soil water flux models

Water balance model

A 6-layer soil water balance model, similar to models employed by Lohse and Matson (2005) and Spittlehouse and Black (1981), was solved for drainage (D, mm h^{-1}):

$$D_{t,z} = D_{t,z-1} - ET_{t,z} - \Delta S_{t,z},$$

where ET is evapotranspiration (mm h^{-1}), ΔS is change in storage over time (mm h^{-1}), t = time (h) and z = model layer ($D_{z=0}$ is rainfall). Hourly rainfall or throughfall (for forested site) was recorded with a series of four recording tipping buckets (Spectrum Technologies, Plainfield, IL) at each site. We used the hourly ET record scaled to site vegetation from the nearest California Irrigation Management Information System (CIMIS 2007) station which uses a modified version of the Penman-Monteith equation (Allen et al. 1998). ET was divided among soil layers using an exponential drop with depth. Storage capacity or the maximum water holding capacity (WHC, mm) for each layer was calculated as the product of porosity (mm^3 mm^{-3}) and layer thickness (mm). We adopted the following simplifying rules: (1) water only drains down; and (2) there is no drainage from a layer until $\theta_z > WHC_z$ and then excess water drains into the next layer. The model was run using the hourly rainfall and ET records from the first rain of the each rainy season until drainage ceased following the last storm of the season.

Soil hydrology model

We also utilized soil water content and tension measurements, and applied Richard's equation to calculate vertical fluxes (Cassel and Klute 1986; Harr 1977):

$$J_w = K(h)\frac{\partial H}{\partial z},$$

where J_w is water flux (mm h^{-1}), $K(h)$ is the unsaturated hydraulic conductivity (mm h^{-1}) as a function of pressure head (h), and dH/dz is the change in total head (gravity + pressure head) over the measurement interval. $K(h)$ was estimated from the SPAW hydrologic model (Saxton and Rawls 2006; Saxton et al. 1986) using the volumetric water content (θ) record and measured soil physical properties, and dH/dz was calculated directly from soil water tension sensor data (Spectrum Watermark sensors, Spectrum Technologies, Plainfield, IL).

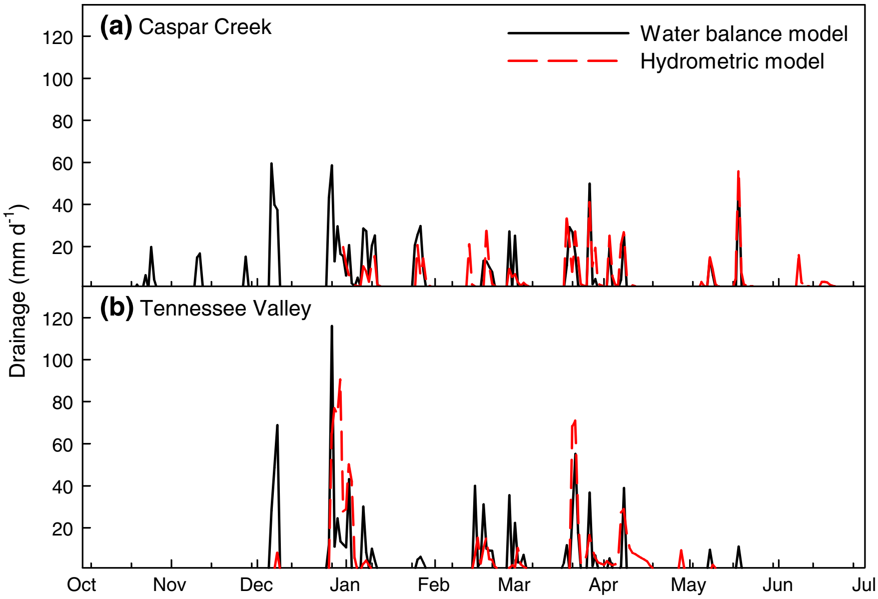

Fig. 9 Modeled vertical soil water fluxes at (**a**) 20 cm at Caspar Creek and (**b**) 10 cm at Tennessee Valley. Hydrometric data is missing prior to December 29, 2004 for Caspar Creek

Goodness of fit was assessed by calculating the root mean square error (RMSE) and bias between the two models:

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n} d_1^2}$$

and

$$bias = \frac{1}{n}\sum_{i=1}^{n} d_i,$$

where d_i is the difference between model outputs for time interval i.

Model evaluation

Overall, we found a very good agreement between seasonal totals for the two methods. At Tennessee Valley, the water balance model estimated 870 and 590 mm of drainage at 10 and 50 cm, respectively, while the hydrometric model estimated 930 and 640 mm at the same depths. At Caspar Creek, for the period of overlapping measurements drainage at 20 cm was estimated to be 660 and 700 mm by the water balance and hydrometric models, respectively.

The calculated daily water fluxes were a bit more variable between methods and between sites (Fig. 9). For depths where we can compare the two methods, the mean relative standard deviation of daily flux at Tennessee Valley is 12.4 ± 5.5% and at Caspar Creek, the mean RSD is 8.7 ± 5.7%. At Caspar Creek, where soils saturate and drain very rapidly, the two methods agreed very well (at 20 cm, $RMSE = 5.02$ and $bias = -0.38$ (towards hydrometric model)). However, at Tennessee Valley, the water balance approach was likely moving water through the soils at too rapid of a rate ($RMSE = 11.75$ and 9.35, and $bias = -0.26$ and -0.20 (towards hydrometric model), for 10 and 50 cm depths, respectively). The hydrometric results here (Fig. 9b) show slower but more sustained drainage pattern which was in line with field data and observations that significant saturated flow continued for a few days following large storms. This pattern was especially pronounced at greater depths (data not shown).

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