Biogeochemistry (2008) 89:181–198
DOI 10.1007/s10533-008-9211-x

ORIGINAL PAPER

Dissolved organic carbon chemistry and dynamics in contrasting forest and grassland soils

Jonathan Sanderman · Jeffrey A. Baldock · Ronald Amundson

Received: 24 October 2007 / Accepted: 9 May 2008 / Published online: 10 July 2008

Abstract In this study, we examined changes in isotopic (^{13}C and ^{14}C) and spectroscopic (UV and ^{13}C NMR) properties of dissolved organic carbon (DOC) in relation to soil organic matter (SOM) to elucidate the sources and sinks of DOC as water percolates through the soils of two contrasting upland coastal California ecosystems—a redwood forest and a coastal prairie. Despite differences in the distribution of C stocks and litter chemistry at these two sites, we found similar shifts in DOC chemistry with soil depth. DOC concentrations dropped rapidly with increasing depth, with an accompanying decrease in the C:N ratio, an increase in the δ^{13}C value and an decrease in specific UV adsorption. In the grassland soil, Δ^{14}C values declined from current atmospheric values (+70‰) in the surface horizon to −75‰ at 100 cm. In the redwood soil, the Δ^{14}C value of 111‰ in O horizon leachates was indicative of OM with a residence time of 8–10 yrs, with a decrease in Δ^{14}C values to −80‰ at 100 cm. Solid-state CP/MAS ^{13}C NMR spectra were generally most similar to highly humified OM, with a general decrease in the relative abundance of aromatic compounds and an increase in the alkyl C/O-alkyl C ratio with increasing depth. All of these trends are consistent with the shifts in SOM properties with increasing depth, which are interpreted to mean a shift from fresh plant material to older, highly altered OM. In this Mediterranean climate, we found distinct seasonal shifts in the quantity and composition of DOC found in soil solution during the winter rainy period that was also consistent with a shift from recent labile substrates to older, highly altered OM. These results fit in with a growing body of literature suggesting that the source of much of the DOC within mineral soils is the local soil OM, and the ^{14}C data, in particular, indicate that DOC at depth is not simply the fraction of surficial leachates that have not been adsorbed or decomposed. Rather, exchange reactions with a portion of the more stabilized SOM pool exert the strongest control on both the concentration and composition of DOC found in these soils.

Keywords Carbon-14 · Carbon-13 · Dissolved organic carbon · Dissolved organic matter · NMR spectroscopy · Soil organic matter · Specific UV adsorption

Abbreviations

A/O-A	Alkyl C to O-alkyl C ratio
Ar/O-A	Aromatic C to O-alkyl C ratio
CEC	Cation exchange capacity
CC	Caspar Creek

J. Sanderman (✉) · R. Amundson
Division of Ecosystem Sciences, University of California,
137 Mulford Hall – MC3114, Berkeley, CA 94720, USA
e-mail: jsandman@nature.berkeley.edu

J. A. Baldock
CSIRO Land and Water, Glen Osmond, SA, Australia

CP/MAS ^{13}C NMR	Cross polarization/magic angle spinning carbon-13 nuclear magnetic resonance
DOC	Dissolved organic carbon
RSD	Relative standard deviation
RSP	Reactive soil pool
SOM	Soil organic matter
SUVA	Specific ultraviolet adsorption
TF	Through fall
TV	Tennessee Valley
UV	Ultraviolet
WEOM	Water-extractable organic matter

Introduction

The flux of dissolved organic carbon (DOC) from continents to marine reservoirs is a significant component of the C cycle and the concentration of DOC in stream water has been increasing in recent decades in northern latitudes (Evans et al. 2006; Freeman et al. 2001; Roulet and Moore 2006). However, the mechanisms that produce this DOC and the controls on these mechanisms are not well understood, but they must reside in processes that occur in soils. Despite typically high fluxes of DOC into soils from surficial organic horizons (Currie et al. 1996; Guggenberger and Zech 1993; Kaiser et al. 2001a; Michalzik and Matzner 1999), there is a growing body of literature suggesting that DOC found at lower depths is derived primarily from within the mineral soil itself, and that this DOC most resembles highly altered soil organic matter (SOM) rather than fresh plant leachates. Based on ^{14}C measurements, Karltun et al. (2005) found that a large portion of soil DOC at ~20 cm depth is derived from older, pre-bomb carbon rather than from C recently fixed by vegetation. Froberg et al. (2006) found similar results for DOC leaving the B horizon of a podzol soil. Gregorich et al. (2000) found that the δ^{13}C values of water-extractable organic matter (WEOM) in agricultural soils were closest to that of the average SOM rather than fresh maize residues or the microbial biomass growing on the maize residues. By utilizing the shift in δ^{13}C values when a C_3 forest is converted to a C_4 crop, John et al. (2003) found that only 5–30% of DOC within the mineral soil was C_4-derived after 40 years of continuous maize cropping. Using analytical pyrolysis, Huang et al. (1998) found that DOC was the most oxidized and microbially processed fraction of SOM. Kaiser and Guggenberger (2000) showed that the carbohydrate and lignin profiles of DOC most resembled that of C found in the clay fraction of the mineral soil, which is generally considered to be a highly altered biological reaction product. Thus, DOC released from fresh plant material and litter would seem to undergo transformations, transport reactions and lag times prior to exiting mineral soil profiles and being released to streams.

While these studies point to the significance of highly altered OM found within the mineral soil as a major source of DOC, other investigations (e.g. Aufdenkampe et al. 2001; Hernes et al. 2007; Kaiser et al. 2001b) have stressed the importance of preferential or selective adsorption of surficially derived DOC in controlling the DOC composition in mineral soils. For example, Hernes et al. (2007) found that the physical processes of leaching and sorption can fractionate fresh litter-derived DOC in ways that would appear to “age” the lignin phenol composition of that fresh DOC. Unfortunately in most circumstances, without direct measurement of the ^{14}C activity, researchers are left to speculate as to whether or not DOC is derived from recent litter or a more aged SOM source.

Soil organic matter exists as a continuum from fresh plant residues to highly microbially-processed and stable reaction products, and there exists a wide variety of individual compounds in both the solid and dissolved phases in the soil. In this paper, we are interested in comparing the chemistry of DOC to that of the organic carbon in the solid phase of soil to determine whether DOC originates from OM with short or long turnover times and to develop a framework by which DOC chemistry is altered as it passes through various soil compartments, and ultimately the watershed. Here we present results from a multi-year study that tracked the changes in soil pore water DOC chemistry at two sites with greatly contrasting vegetation and potential DOC sources. We have employed isotopic (^{13}C and ^{14}C) and spectroscopic (UV and ^{13}C NMR) analytical techniques to assess the age and character of the dissolved and solid phases of OC, and using these observations have developed a hypothesis regarding the evolution of soluble C as it passes from the surface litter through the soil and into stream waters.

Methods

Site descriptions

This research has been conducted at two contrasting coastal northern California ecosystems. These field sites are part of a larger study of DOC fluxes on multiple scales including the soil profile scale, hillslope scale and watershed scale (Sanderman 2007). These two sites were chosen primarily for flora differences, and because of the previous hydrologic research and existing infrastructure (i.e. Brown 1995; Montgomery and Dietrich 1995; Ziemer 1998).

Tennessee Valley

This watershed is located in the rolling soil-mantled hills of coastal Marin County, California. The area was used for cattle grazing since the late nineteenth century, with active fire suppression until its incorporation into the Golden Gate National Recreation Area in 1972, when large scale grazing ceased. Current vegetation is a mixture of northern coastal scrub, coastal prairie associations and both native and European grasses. Woody shrubs, dominated by *Baccharas sp.*, have only recently become a significant component of the vegetative community, likely as a direct result of the cessation of grazing and fire suppression. Despite the recent *Baccharas* invasion and its aerial extent (40–50% by area based on multiple transect surveys), we decided to locate all of our soil sampling pits at least 2 m away from the nearest *Baccharas* individual so that our sampling best represents C cycling under the grassland communities.

Soils are classified as Typic Haplustolls. Profiles have a series of prominent dark A horizons, approximately 40 cm thick, that appear to be well-mixed by burrowing gophers and other animals. This resides on top of a clayey, organic-poor, relatively unmixed horizon that consists of highly weathered sandstone that still retains some evidence of rock structure (Table 1). Pocket gopher (*Thomomys bottae*) and, to a lesser extent, earthworm burrowing are responsible for the mixing of this clayey material with the A horizons, and for downslope transport within what has been referred to as a biomantle (Gabet 2000; Yoo et al. 2005).

Caspar Creek

The Caspar Creek Experimental Watershed in Mendocino County, CA, is a long-term experiment revealing the effects of logging on the hydrologic cycle. The experimental site is operated by the Redwood Science Laboratory of the US Forest Service, and Ziemer (1998) provides an overview of the research at this site over the last 40 years. We have focused our investigation in a small headwater catchment that has been used as a control for the other experiments since the inception of the experimental watershed. This control site, typical of the coastal Redwood region, was clearcut and burned around 1900 (Tilley and Rice 1977) with little human disturbance since then. Currently, a nearly 100-year old even mix of second growth Redwood (*Sequoia sempervirens* (D. Don) Endl.) and Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco) dominates the site, with small amounts (~1% by biomass) of tan oak (*Lithocarpus densiflorus*) in the understory. Standing biomass was estimated by Dahlgren (1998) to be 644 MgC ha^{-1} with less than 7% in below-ground root biomass.

The soils in this region are dominated by Typic Haplohumults (U.S. Soil Conservation Service 1972). However, on the steeper slopes there appears to have been significant loss of topsoil due to destructive logging practices of the late 1800 s. This appears to have removed a significant portion of the former A horizons, eliminating textural differences between the A and B horizons, and thus changing the apparent classification from an Ultisol to an Inceptisol (Table 1). Regardless of classification, the soils in the watershed typically have a thin O horizon with an 80–100 cm thick well-weathered, clay-rich mineral soil profile that rests on top of several meters of saprolite derived from greywacke sandstone.

Climate

Both sites have a Mediterranean climate with warm dry summers and cool wet winters derived from Pacific storms. The more northern Caspar Creek typically receives greater precipitation amounts. During this study, mean annual precipitation was 1,450 mm at Caspar Creek and 1,300 mm at Tennessee Valley, which was approximately 200 mm above the 30 year mean at both sites (NCDC 2007;

Table 1 Select properties of the two soils examined in this study

	Horizon	Depth (cm)	Bulk density (mg/m^3)	Structure[a]	Sand (%)	Clay[b] (%)	Gravel (%)	pH (1:1 H_2O)	CEC[c] (cmol+/kg)	Base Sat.[d] (%)	Dith-citrate[e]		NH$_4$ oxalate[f]		Na pyrophosphate[g]		
											Al (g/kg)	Fe (g/kg)	Al (g/kg)	Fe (g/kg)	Al (g/kg)	Fe (g/kg)	OC (g/kg)
Caspar Creek	Oi	6–3	0.04														
	Oe	3–0	0.18														
	A1	0–7	0.75	3f-vfgr	32.4	41.7	25	6.1	30.8	46.6	2.06	10.9	2.82	3.36	1.19	0.89	5.52
	A2	7–15	1.07	3fsbk-gr	31.9	46.0	15	6.0	20.6	44.3	2.17	11.8	3.19	3.73	1.36	1.00	5.23
	AB	15–21	1.27	3fsbk	32.3	50.1	15	5.9	19.7	36.8	2.15	12.7	2.86	3.51	1.19	0.91	2.67
	Bt1	21–37	1.40	2msbk->3fsbk	35.7	47.6	20	5.8	21.8	29.3	1.94	12.4	1.93	2.27	0.82	0.62	1.09
	Bt2	37–68	1.55	2m-cosbk->2fsbk	44.2	42.4	20	5.8	15.4	32.3	1.55	12.5	1.83	3.11	0.67	0.49	2.08
	BC	68–120	1.63	m	50.5	39.3	30	5.7	18.2	23.5	1.60	13.7	1.34	1.81	0.88	0.60	1.23
	Cr	120+	1.41	m	60.4	27.0	70	5.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tennessee Valley	A1	0–10	0.86	2fsbk->3m-fgr	41.1	36.5	50	6.2	33.5	50.3	2.63	21.0	1.25	1.98	0.92	0.71	6.86
	A2	10–27	1.12	3co-msbk->2m-fgr	40.2	34.6	40	6.2	26.8	56.2	2.65	21.5	1.24	1.83	1.00	0.70	5.84
	A3	27–40	1.15	3cosbk->2fsbk	40.2	34.7	20	6.4	26.6	62.1	2.58	22.5	1.53	2.33	0.83	0.59	4.39
	AC	40–60	1.21	2co-msbk	38.2	39.9	50	6.7	26.9	74.4	3.04	27.2	1.33	2.06	0.39	0.37	2.85
	Cr	60+	1.39	m	21.5	54.4	75	7.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

[a] Structure refers to the grade (0–3, structureless to strong), size (vf, very fine; f, fine; m, medium; co, coarse) and type (gr, granular; sbk, subangular blocky; m, massive). Arrow refers to smaller structural units remaining after lightly breaking apart dominant units in hand (Schoeneberger et al. 2002)

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

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

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

[e] Dithionite-citrate extractable metals following methods of McKeague and Day (1966)

[f] Ammonium oxalate extractable metals following methods of McKeague and Day (1966)

[g] Sodium pyrophosphate extractable Al, Fe and organic C following methods of McKeague et al. (1971)

Ziemer 1981). The coastal location of these sites moderates the 5 cm soil temperature range to 6–16°C at Caspar Creek and 8–20°C at Tennessee Valley.

Field sampling and monitoring

At both field sites, seven soil pits along a hillslope gradient from ridge to hollow were excavated, sampled by genetic horizon and described using standard NRCS methods (Schoenberger et al. 2002). Each excavation was instrumented for hydrometric monitoring and water collection before carefully backfilling (see Sanderman 2007) for more details on spatial arrangement of sites). For this paper, we focus on soils along the upper part of the hillslope transects where vertically infiltrating water flow dominates the soil hydrological pathways.

Soil water sampling

In each soil excavation, Prenart super-quartz tension lysimeters were installed at multiple depths corresponding to the dominant genetic horizons in the mineral soil. A steel rod of similar diameter to the lysimeters was hammered ~20 cm into the upslope soil pit face at a slight downward angle. The lysimeter was then inserted into the hole in a silica flour slurry to ensure good contact with soil matrix. After a 3 month equilibration period, these lysimeters were sampled every few weeks throughout the rainy season by applying 60 cbar vacuum to 2L glass vacuum bottles.

To sample macropore flow during storms, zero-tension lysimeters were built similar to those of Driscoll et al. (1988). Briefly, 10 × 15 cm PVC pans with 2 cm high walls were filled with 4 mm diameter acid-washed HDPE beads and capped with a fine mesh screen. These lysimeters were installed in the soil at depths of 10, 20, 35 and 50 cm at Tennessee Valley and at depths of 0, 7, 15, 30 and 50 cm at Caspar Creek by inserting the pan into an excavated hole of similar size in the soil pit face below desired sampling depth to minimize disturbance to soil structure. The pan sampler was pushed against the roof of the excavated hole by backfilling underneath the sampler to ensure good contact with the soil. These pans were then plumbed to 4L HDPE collection bottles that were buried within the mineral soil. To allow easy collection of water samples, two access tubes for each collector protruded up through the ground. A portable vacuum pump was used to empty the collection bottles following most major storms throughout the study period.

Analytical procedures

In this study, we are assessing the character of C in both the dissolved and solid phases using several macromolecular methods. The C:N ratio and the δ^{13}C value of OM have been used as an indicators of the degree of microbial alteration of fresh OM (e.g. Baisden et al. 2002; Wynn et al. 2005), while ^{14}C measurements yield more direct information the material's age or mean residence time (Trumbore 2000).

While the above methods yield an overall assessment of the degree of processing, spectroscopic methods can yield more specific information on the relative abundances of different classes of chemical species present in a sample. Specific UV adsorption (SUVA, L mgC^{-1} m^{-1}), adsorption at 254 nm normalized to DOC concentration, has been shown to be a good indicator of the aromaticity of dissolved humic substances (Chin et al. 1994; Weishaar et al. 2003). A much more direct and quantitative assessment of the overall character of organic matter can be obtained from ^{13}C NMR spectroscopy (Baldock et al. 1992; Kogel-Knabner 1997). In particular, Baldock et al. (1997) has shown that the relative abundance of alkyl C to O-alkyl C is a sensitive index of the degree of decomposition of organic materials with the ratio increasing with increasing stage of decomposition.

While these methods yield detailed information on the chemical composition and degree of microbial alteration of OM, they only provide an indirect assessment of the recalcitrance of the sample. We attempt to reserve the use of the term recalcitrance only to refer to the ease or difficulty in which microorganisms can degrade a substrate. Recalcitrance is due to both physical and chemical processes, and chemically labile C may be physically protected from biological processes (Ewing et al. 2006; Kleber et al. 2005; Six et al. 2004).

Soil organic carbon analyses

Total organic C, total N and stable isotope ratios of C were determined on the <2 mm fraction of bulk soil samples using a Leico autoanalyzer interfaced with a Finnegan Mat IRMS. Isotope results are reported relative to the Pee Dee Belemite standard (Craig 1957):

$$\delta^{13}\mathrm{C} = \frac{R_{\mathrm{sample}}}{R_{\mathrm{standard}}},\ \text{where}\, R = \frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}.$$

For Δ^{14}C analysis, 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). The purified CO_2 was converted to graphite using a H_2 reduction method (Vogel et al. 1984) and loaded into targets for Δ^{14}C analysis (in October, 2004) at the Keck Center for Carbon Accelerator Mass Spectrometry, University of California, Irvine. Δ^{14}C was calculated as:

$$\Delta^{14}\mathrm{C} = \left(\frac{A_{\mathrm{sample}}}{A_{\mathrm{abs}}} - 1\right) \times 1000,$$

where A_{sample} is the activity of the sample normalized to its δ^{13}C value and A_{abs} is the activity of the standard (0‰), which represents approximately the ^{14}C/^{12}C ratio of the pre-industrial atmosphere. Positive Δ^{14}C values indicate incorporation of recent atmospheric CO_2 enriched in ^{14}C produced by nuclear weapons testing. The long-term accuracy and precision (1σ) of this technique on modern C is better than 5‰ (Southon et al. 2004).

Solid-state cross-polarization magic-angle spinning ^{13}C nuclear magnetic resonance (CP/MAS ^{13}C-NMR) spectra were obtained on selected intact litter and demineralized soil samples. Demineralization was accomplished by sequential treatment with 2% HF as described by Skjemstad et al. (1994). All NMR spectra were acquired on a Varian Unity 200 spectrometer operating at a ^{13}C frequency of 50.3 MHz located at the Waite NMR Center at the University of Adelaide, Australia. A standard cross polarization pulse sequence (Wilson 1987) was used with a contact time of 1 ms. The duration of the recycle delay was defined by a preliminary inversion recovery experiment (Wilson 1987) and set to a value $>10\times$ the inversion recovery time when the intensity of all spectral resonances had become positive. For each analysis, a measured mass of litter or soil (200–300 mg) was packed into a 7 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 5,000 ± 100 Hz in a Doty Scientific magic angle spinning probe. Each free induction decay was acquired using a sweep width of 40 kHz. Over an acquisition time of 15 ms, 1,216 data points were collected. All spectra were zero filled to 8,192 data points. Data were processed with both Lorentzian and Gaussian functions of widths 50 Hz and 0.005 s respectively. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm. The signal intensity associated with four broad spectral regions (Alkyl C—0–45 ppm; O-alkyl C—45–110 ppm; aromatic C—110–165 ppm; carbonyl C—165–210 ppm) corresponding to the dominant forms of C present in the samples was determined by integration using algorithms associated with the Varian NMR software. In addition, variable spin lock NMR experiments were performed using a 1 ms contact time and 5–7 spin lock times to calculate values for the spin lattice relaxation in the rotating frame, $T_1\rho H$. The value of $T_1\rho H$ was combined with the mass of the sample and its carbon content to define the relative observability of organic C in the samples relative to that of glycine (Baldock and Smernik 2002; Smernik and Oades 2000a, b).

Dissolved organic carbon analyses

Field samples were filtered to <0.7 µm using Whatman GF/F glass fiber filters within 24 hrs of collection and stored at 4°C in opaque acid-washed HDPE bottles. While some fine colloidal organic C in addition to truly dissolved organic C may reside in this fraction, the 0.7 µm size was chosen instead of 0.45 µm because of the far superior particle loading abilities of the glass fiber filters. We filtered multiple samples using both filter sizes and found no significant differences in DOC concentration, δ^{13}C or Δ^{14}C values between the two filters.

DOC concentration in aqueous samples was measured on an OI Analytical model 1,010 analyzer (OI Analytical, College Station, TX) by persulfate oxidation following acidification with phosphoric acid. The δ^{13}C value of DOC was determined by isotope ratio mass spectrometry at the UC Davis Center for Stable Isotope Biogeochemistry where CO_2 generated by OI Analytical model 1,010 analyzer is carried by a He stream to an infra-red gas analyzer (IRGA) and a PDZ Europa 20–20 IRMS (PDZ Europa, Northwich, UK). The $^{13}C/^{12}C$ ratios of unknowns are measured and compared to ratios of standard samples (ANU Sucrose dissolved in milliQ water in concentrations ranging from 1 to 20 mgC l^{-1}, $\delta^{13}C = 26.5‰$).

DOC samples for $\Delta^{14}C$ analysis and solid-state ^{13}C-NMR analysis 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, between 50 and 250 mg dry weight, were then prepared for analysis in the same manner as the solid OM samples. Due to sample size requirements, NMR spectra were obtained only on DOC collected in zero-tension lysimeters. Radiocarbon analyses on DOC samples were performed in the fall of 2005.

Ultraviolet (UV) absorption at 254 nm (a_{254}) was determined on a Shimadzu 1601 UV/Vis Spectrophotometer using a 1 cm quartz cell and milliQ water (Millipore, Inc.) as the reference blank. These data are reported as specific UV adsorption ($SUVA = a_{254}/[DOC], 1\ mgC^{-1}\ m^{-1}$), which has been shown to have a strong positive correlation with the percent of aromatic compounds in the sample (Chin et al. 1994; Weishaar et al. 2003). When measuring natural water samples, other dissolved constituents can potentially contribute to the absorbance in the same wavelengths of interest. Iron (as either Fe^{2+} or Fe^{3+}) is found in high concentrations in soil water and stream water samples at Tennessee Valley. At this site, we corrected for this interference due to Fe by subtracting the theoretical absorption due to Fe alone based on published molar extinction coefficients and the additive nature of absorption (Weishaar et al. 2003).

Batch adsorption experiment

Given the hypothesized significance of adsorption and exchange reactions in controlling DOC concentrations and composition, the field measurements were supplemented with a controlled batch adsorption experiment (e.g. Nodvin et al. 1986). Briefly, triplicate 3 g dried surface (A1 horizon) and subsurface (A3 or Bt1 for TV and CC, respectively) mineral soil samples were equilibrated with 30 ml DOC solutions, derived from freshly collected litter (CC) or surface soil contain live grass and roots (TV), 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. Both stock solution and equilibrated soil solutions were immediately analyzed for DOC concentration and ^{13}C content. Here we focus on the isotopic results from this experiment (see Sanderman and Amundson 2008) for more details).

Results

Soil profile DOC trends

At the forested site, DOC concentrations were highest in O horizon leachates and were rapidly attenuated with increasing depth (Fig. 1). At the coastal prairie site, concentrations were highest immediately below the main rooting zone and were attenuated at a somewhat more gradual rate with depth than in the forest. At both sites, macropore flow collected in zero-tension lysimeters contained significantly more DOC than matrix water samples collected with tension lysimeters at the same depth.

Overall trends in DOC chemical characteristics were very similar between these two sites despite greatly contrasting vegetation and C distribution patterns (Fig. 2). For all analyses we found a general shift from fresher, more plant-like, OM near the surface (i.e. high C:N ratio and low $\delta^{13}C$ value) to more humified OM (i.e. low C:N ratio and high $\delta^{13}C$ value) with increasing depth. At the forested site, C:N ratios of DOM decrease from 45 in O horizon leachates to <10 below 50 cm (Fig. 2), with a concurrent shift in $\delta^{13}C$ values from −27.5 to −23‰ and SUVA values from 4 to <2 with increasing depth (Figs. 3 and 4). These shifts in C:N ratios and $\delta^{13}C$ values of DOC closely follow the depth trends in bulk SOM. At the coastal prairie site, the same trends in decreasing C:N ratios, increasing $\delta^{13}C$ values and decreasing SUVA values with increasing depth were found, but the DOC differed more from bulk SOM values than in the forest soil. For both sites, one-way analysis of variance indicated that the depth trends in DOC concentration, $\delta^{13}C$, SUVA and C:N ratio were significant at $P < 0.05$. Additionally, at similar depths, macropore water had higher DOC concentrations, higher C:N ratios, lower $\delta^{13}C$ values and higher SUVA values than comparable matrix water samples (see Figs. 1 and 2 for statistical summary).

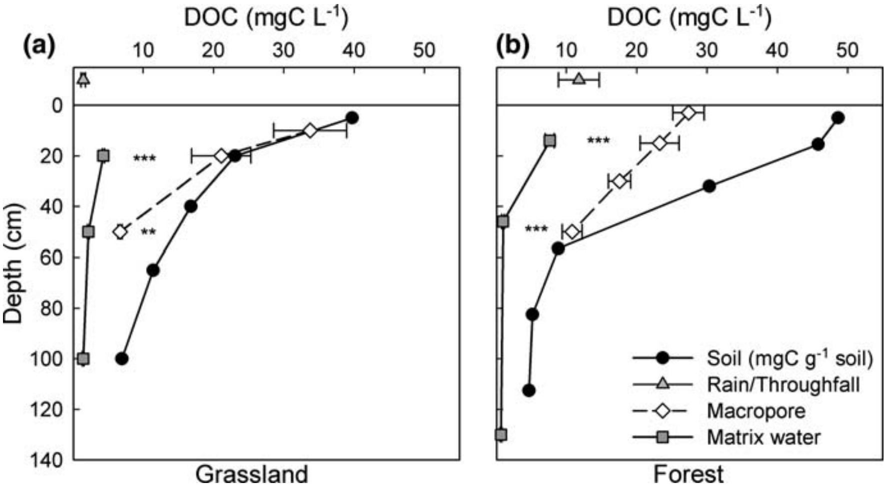

Fig. 1 Seasonal mean DOC concentrations at Tennessee Valley (**a**) and Caspar Creek (**b**). Macropore samples are soil water samples collected in zero-tension lysimeters and the matrix water refers to samples collected in Prenart tension lysimeters. Soil organic C content (mgC g soil^{-1}) is shown for reference. Error bars = 1 s.e. ($n = 16$). Significant differences between macropore and matrix water samples at similar depths are shown (ns, not significant; $*P < 0.05$; $**P < 0.001$; $***P < 0.0001$)

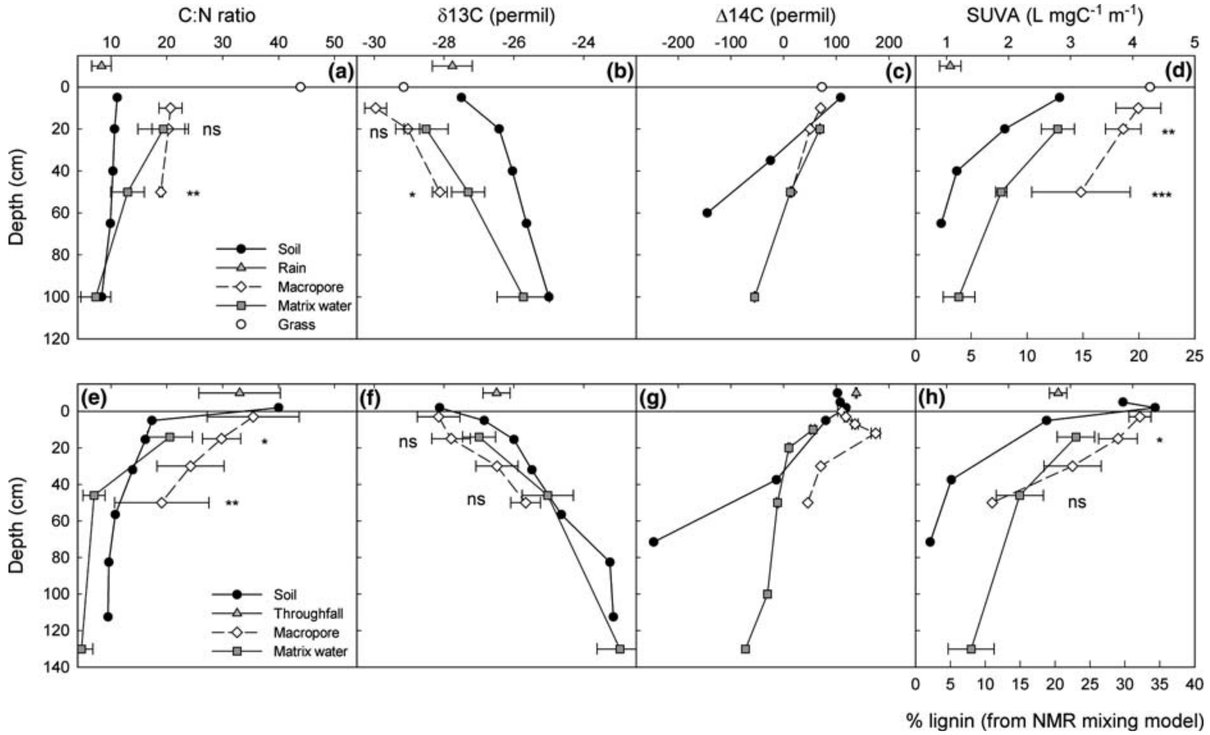

Fig. 2 Seasonal mean C:N ratio (**a** and **e**), δ^{13}C values (**b** and **f**), Δ^{14}C values (**c** and **g**) and SUVA (**d** and **h**) of soil and dissolved organic matter at Tennessee Valley (top) and Caspar Creek (bottom). Symbols the same as in Fig. 1. Error bars = 1 s.e. ($n = 16$). Significant differences between macropore and matrix water samples at similar depths are shown (ns, not significant; $*P < 0.05$; $**P < 0.001$; $***P < 0.0001$). In the SUVA plots (**d** and **h**), the % lignin in the solid phase samples determined by a bimolecular mixing model (Nelson and Baldock 2005) using the ^{13}C NMR spectra is also shown for comparison

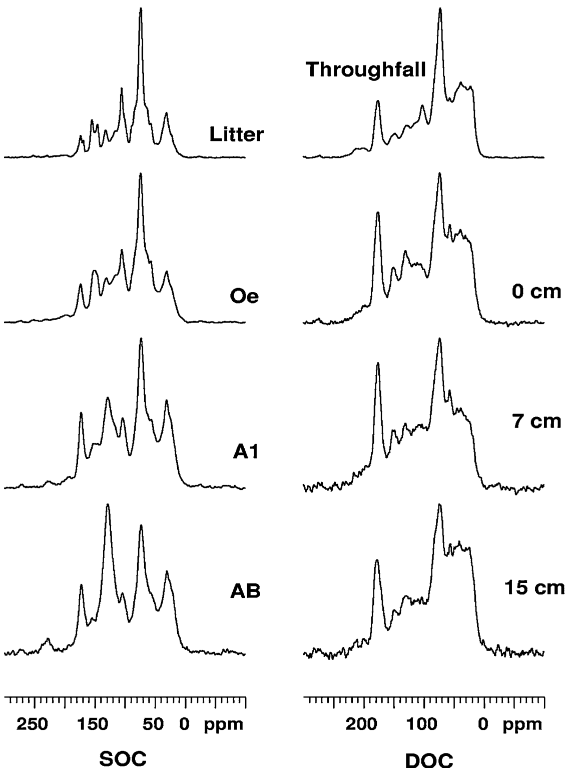

Fig. 3 Solid-state CP/MAS ^{13}C NMR spectra for soil and macropore DOC collected at same depths at Caspar Creek

Carbon-14

At the forested site, the Δ^{14}C value of fresh litter was 102‰, while the Oi and Oe horizons were 107 and 118‰, respectively. When considered in combination with changes in Δ^{14}C values of atmospheric CO_2 since the 1950's (Levin and Kromer 2004), the changes in Δ^{14}C values indicate an increasing mean residence time of carbon with depth within the litter layer assuming that the C stocks in these horizons are in approximate steady state (Gaudinski et al. 2000; Trumbore 2000). The O horizon leachates had a value of 111‰, suggesting that the major source of this DOC was not fresh litter but rather slightly older organic components of the lower portion of the litter layer (e.g. more enriched in bomb C than existed within the past decade) that have been present and cycling in the O horizon for a few years. With increasing depth, the macropore Δ^{14}C values increased to a maximum of 180‰ and then decreased to −80‰ at 100 cm (Fig. 2). Due to the movement of the 'bomb spike' of atmospheric $^{14}CO_2$ into the terrestrial biosphere, the increase and subsequent decrease in the macropore Δ^{14}C values with depth may indicate that this DOC is coming from progressively older OM sources with increasing depth. At the coastal prairie site where the sampling density is lower in the upper soil horizons, we found a steady shift from recent photosynthates near the surface (annual grasses are indicative of that year's atmospheric value of 70‰) to more ^{14}C-depleted OM at greater depths (−75‰ at 100 cm). Overall, we found a similar trend of increasing DOC age with depth in both soils.

Solid-state CP/MAS ^{13}C-NMR spectroscopy

Well resolved solid-state CP/MAS ^{13}C-NMR spectra were obtained for zero-tension DOC samples from

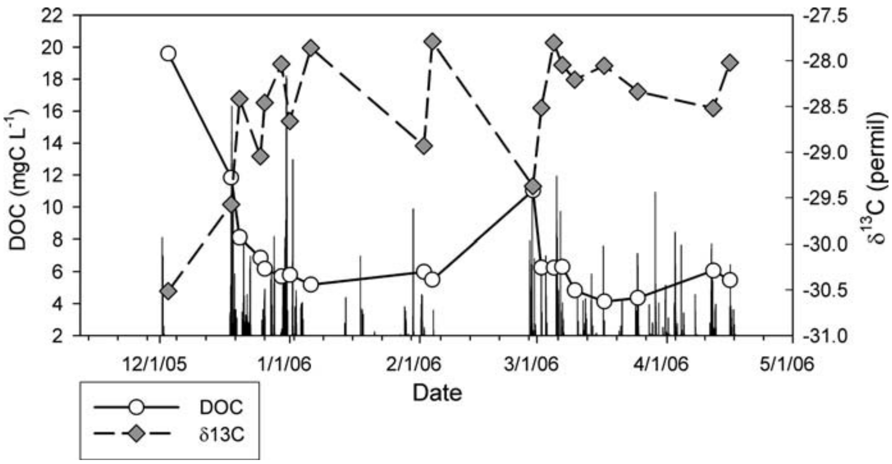

Fig. 4 Seasonal shifts in DOC concentration and δ^{13}C values of macropore water samples collected at 10 cm at Tennessee Valley. Hourly rainfall (mm, left axis) at 10 cm plotted in background

Caspar Creek, with an average observability of C relative to a gylcine standard of 75 ± 10% (mean ± 1 s.d.). Unfortunately at Tennessee Valley, high Fe concentrations in the soil solution, even after passing samples through a cation exchange resin, reduced the C observability to only 50 ± 13% and as such the relative signal intensities listed in Table 2 should be only considered semi-quantitative. Additionally, we found that the precipitation of carbonate salts in some DOC samples at Tennessee Valley created a distinct peak at 168 ppm. The inorganic C peaks were successfully removed from these spectra by subtracting an idealized carbonate-only spectra identified by a spectra separation technique called proton spin relaxation editing (Smernik 2005) from the original spectra (see Sanderman 2007).

The NMR spectra (Fig. 3) reveal that DOC resembles highly-altered and chemically recalcitrant OM rather than fresh plant residues. For all DOC samples, we found a large and broad resonance in the alkyl-C region (0–45 ppm) indicative of numerous aliphatic compounds of varying chain length and branching (Kogel-Knabner 2002). There was greater resonance in the carbonyl-C region (165–210 ppm), a major functional group of organic acids, in DOC than in the bulk soil samples. Overall, these DOC spectra are most similar to NMR spectra of more humified fractions of OM such as those found in silt- and clay-sized soil fractions (e.g. Baldock et al. 1992) and mineral-associated density fractions separated from soils (e.g. Golchin et al. 1994, 1995).

With increasing depth at Tennessee Valley, the DOC samples showed decreasing abundances of aromatic and carbonyl C and a relative enrichment in alkyl C relative to O-alkyl C (Table 2). This drop in aromatic C corroborates the decrease in SUVA values presented in Fig. 2. At Caspar Creek, there were no consistent trends in the abundance of aromatic or carbonyl C, only a large increase in the proportion of alkyl C to O-alkyl C. The relative enrichment in aromatic C in the soil samples in Fig. 3 is due primarily to the abundance of char and not lignin in these soils (Sanderman 2007). In fact, using the biomolecular mixing model of Nelson and Baldock (2005), we found that the lignin content in the bulk soil samples dropped from 20–30% in litter to <5% at a depths below 60 cm in both soils (Fig. 2d, h). In contrast to the soil samples, results

Table 2 Percentages of total CP/MAS ^{13}C NMR spectral intensity associated with each major chemical shift region and the calculated alkyl to O-alkyl C (A/O-A) and aromatic to O-alkyl C (Ar/O-A) ratios for DOC collected from zero-tension lysimeters and associated soil samples from the Tennessee Valley and Caspar Creek sites

	Tennessee Valley							
	DOC				SOM			
Major shift regions	10 cm	20 cm	35 cm	50 cm	Litter	A1 horizon	A3 horizon	Bt2 horizon
Alkyl (0–45)	14.0	18.3	21.2	24.5	7.3	18.9	14.9	16.3
O-Alkyl (45–110)	39.2	42.1	43.9	44.9	74.2	43.1	34.9	37.2
Aromatic (110–165)	29.8	25.3	22.1	20.0	13.8	26.9	37.7	34.6
Carbonyl (165–210)	16.9	14.3	12.8	10.6	4.7	11.1	12.5	12.0
A/O-A ratio	0.36	0.44	0.48	0.55	0.10	0.44	0.43	0.44
Ar/O-A ratio	0.76	0.60	0.50	0.45	0.19	0.62	1.08	0.93
	Caspar Creek							
	DOC				SOM			
Major shift regions	TF	0 cm	7 cm	15 cm	Fresh litter	Oe horizon	A1 horizon	AB horizon
Alkyl (0–45)	23.1	19.1	22.0	24.3	14.1	13.0	14.5	15.3
O-Alkyl (45–110)	48.9	42.2	42.1	39.7	57.5	51.1	42.2	36.0
Aromatic (110–165)	17.4	23.4	20.4	24.6	23.5	28.2	32.7	39.6
Carbonyl (165–210)	10.6	15.3	15.5	11.4	5.0	7.6	10.6	9.1
A/O-A ratio	0.47	0.45	0.52	0.61	0.24	0.25	0.34	0.43
Ar/O-A ratio	0.35	0.55	0.49	0.62	0.41	0.55	0.78	1.10

from this mixing model indicated that the aromatic signal in all of the analyzed DOC samples was dominated by lignin-derived compounds (data not shown).

Seasonal DOC trends

At the more seasonal coastal prairie site, a pool of readily leachable material builds up during the dry season and is rapidly flushed with the onset of rains (Fig. 4). After this initial flushing, the δ^{13}C values of DOC shift from low plant-like values to more enriched soil OM-like values. This temporal trend also shows that this potential DOC pool can be replenished with a mixture of fresh and older OM sources after a several weeks without appreciable precipitation (see Jan–Feb period in Fig. 4).

Radiocarbon results also show that there is a shift in DOC sources toward older soil OM pools later in the rainy season (Fig. 5). NMR results indicate a decreasing contribution from the O-alkyl region (fresh easily decomposed carbohydrates), and a subsequent increase in the A/O-A ratio, as the season progresses.

A similar flush of DOC from the surface horizons during the first few storms was also observed at the forested site. Here, DOC concentrations in excess of 80 mgC l^{-1} were found at 3 cm, but dropped to values fluctuating around 20 mgC l^{-1} (data not shown) by January. However, the chemical characteristics of the DOC did not seem to be quite as variable as those found at the coastal prairie site, with a mean δ^{13}C value of -27.7 ± 0.5 (s.e., $n = 13$) and mean SUVA value of 3.5 ± 0.2. No significant seasonal trends in these two parameters were found.

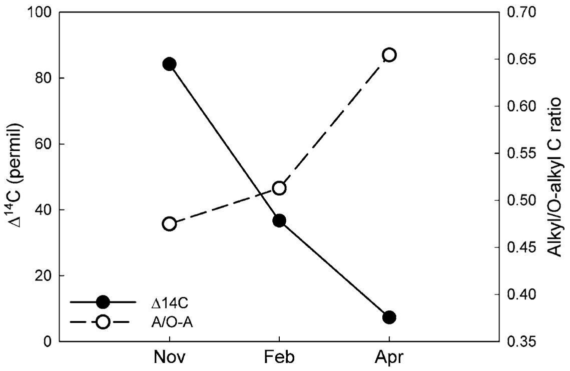

Fig. 5 Seasonal changes in Δ^{14}C values and the alkyl/O-alkyl C ratio as determined by solid-state CP/MAS ^{13}C NMR spectroscopy in soil DOC samples collected at 10 cm depth from Tennessee Valley

In general, the surface horizons showed the greatest seasonal chemical variability, with much smaller fluctuations with increasing depth at both field sites. Relative standard deviations (RSD) decreased from >100% in surface macropore water samples to <20% in matrix water samples below 50 cm depth.

Batch adsorption results

All 4 soils had a high propensity to adsorb DOC, while the surface horizons also had a propensity to desorb C into solution, which for the range of starting DOC concentrations used in this experiment were described well by the initial mass isotherm (Sanderman and Amundson 2008). Equilibrated solutions were consistently enriched in ^{13}C relative to the initial DOC following equilibration regardless of net adsorption or desorption (Fig. 6). The difference between initial and final DOC δ^{13}C values increased with increasing degree of desorption.

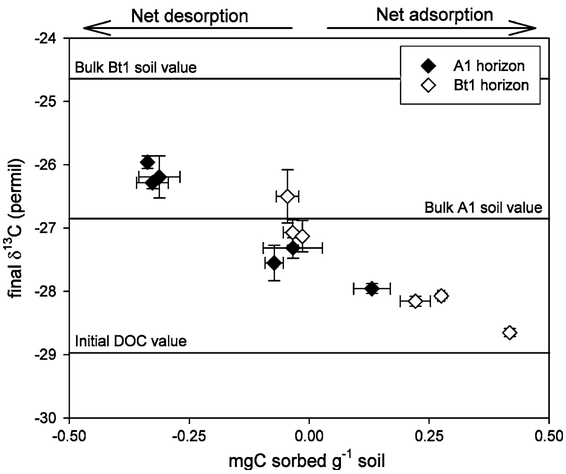

Fig. 6 The δ^{13}C value of DOC after batch adsorption for all starting concentrations plotted against amount of C adsorbed or desorbed for A1 and Bt1 horizon soils at Caspar Creek. Low initial DOC concentrations tended to show strong net desorption, while high initial DOC concentrations tended to show strong net adsorption. Initial DOC δ^{13}C value for all starting concentrations, as well as the A1 and Bt1 horizon bulk soil values are show in the background for reference

Discussion

Soil profile DOC

As water percolates downward through the mineral soil, the isotopic and spectroscopic properties of DOC changed from those similar to fresh plant residues to that more consistent with humified soil OM. There were strong correlations between all of these characteristics of soil DOC at both sites (Table 3). Kalbitz et al. (2004) also found that greater SUVA values were associated with more negative δ^{13}C values. However, those authors concluded that the decrease in δ^{13}C was due to additions of decomposed organic material. At our sites, the δ^{13}C of soil organic C increases with increasing depth, which is most consistent with increasingly altered material (Baisden et al. 2002; Wynn et al. 2005). Additionally, lignin, which is the predominant non-charcoal aromatic compound in SOM, does not persist long in most well-drained soils (Baldock et al. 1992) and lignin is depleted in ^{13}C relative to bulk plant material (Benner et al. 1987). Thus, the stable isotope and UV adsorption trends in Fig. 2 represent a shift from relatively fresh to more altered sources for DOC as water moves through the soil.

In a companion study, we conducted a bioavailability experiment (Sanderman and Amundson 2008) that provides direct support for the hypothesis that DOC becomes progressively more chemically recalcitrant with increasing depth. The %C mineralized over a 2 month period decreased sharply with increasing sampling depth (36% for throughfall, 27% for O horizon leachates and only 20% for A1 horizon leachates) and was positively correlated with initial δ^{13}C and SUVA values ($r > 0.99$ for both measures, $P < 0.05$, $n = 3$).

The cause of these depth trends in DOC is likely complex, and could be due to selective absorption of a chemically distinct fraction of DOC, the biodegradation of the DOC in solution, exchange processes with native SOM, or any combination thereof. Several researchers have interpreted observations of δ^{13}C enrichment in DOC (Kaiser et al. 2001b) and soil C (Cleveland et al. 2004) with depth to be due to the retention of ^{13}C-depeleted hydrophobic compounds in the upper soil horizons and the preferential movement of ^{13}C-enriched hydrophilic compounds deeper into the mineral soil. Laboratory leaching and sorption experiments have also shown an apparent "aging" of fresh lignin phenols (Hernes et al. 2007) and amino acids (Aufdenkampe et al. 2001) due to selective adsorption. While the profile trends in δ^{13}C, C:N and SUVA (Fig. 2) could be explained by selective adsorption, the ^{14}C results can only be explained by exchange reactions with older soil OM because Δ^{14}C measurements are corrected for any fractionation by normalizing to a standard δ^{13}C value. If selective absorption and/or degradation were dominant, then the Δ^{14}C values of DOC should be similar to fresh plant litter given that the mean residence time of water in the upper meter of soil is on the order of days to months. Additionally, using ^{14}C measurements, Froberg et al. (2007) demonstrated that fresh litter leachates are almost completely retained within the O horizon and that DOC leaching into the mineral soil originated from older C within the Oe and Oa horizons themselves. Results from our redwood site substantiate these findings. Thus, despite laboratory evidence for

Table 3 Correlation matrix for soil DOC chemistry at Tennessee Valley ($n = 11$ except for δ^{15}N where $n = 5$). A/O-A is the alkyl C/O-alkyl C ratio, Ar/O-A is the aromatic C/O-alkyl C ratio and %Ar is the % aromatic C as determined by ^{13}C NMR spectroscopy

	δ^{13}C	δ^{15}N	C:N	SUVA	A/O-A	Ar/O-A	%Ar
δ^{13}C		.89*	−.91***	.63*	.76**	−.85**	.67*
δ^{15}N	.89*		−.89*	.68*	.94*	−.98**	$.71^{ns}$
C:N	−.91***	−.89*		.70**	−.84**	−.86***	$-.32^{ns}$
SUVA	.63*	.68*	.70**		−.74*	−.80*	.92**
A/O-A	.76**	.94*	−.84**	−.74*		−.90***	−.97***
Ar/O-A	−.85**	−.98**	−.86***	−.80*	−.90***		.99***
%Ar	.67*	$.71^{ns}$	$-.32^{ns}$	.92**	−.97***	.99***	

ns, Not significant, *$P < 0.05$, **$P < 0.01$, ***$P < 0.001$

selective adsorption (i.e. Aufdenkampe et al. 2001; Hernes et al. 2007), in these natural systems, a continuous exchange between downward migrating DOC with solid phase organic matter best accounts for the distinct depth trends in C:N, δ^{13}C, Δ^{14}C and SUVA.

Exchange processes with the soil C pool can also explain the batch absorption experiment result (Fig. 6) that regardless of whether net absorption or desorption of OC occurred, the DOC in solution became enriched in ^{13}C relative to the starting δ^{13}C value of the DOC in solution. Kaiser et al. (2001b) explained similar findings as the selective adsorption of a ^{13}C-depleted hydrophobic fraction (based on sorption to XAD-8 resin) and the preferential release of a ^{13}C-enriched hydrophilic fraction. Because we did not attempt to fractionate the DOC using resin-exchange columns, we cannot directly support or refute the interpretation of Kaiser et al. (2001b). However, if the released hydrophilic fraction was derived primarily from older OM sources, then their explanation would fit well with our field observations and interpretation.

Sources of DOC

The Δ^{14}C (Fig. 2) and ^{13}C NMR spectroscopy (Fig. 3 and Table 2) results indicate that fresh plant residues comprise only a small fraction of field collected DOC. While the ^{13}C NMR spectra of DOC do not resemble fresh plant residues, they also are not representative of the bulk SOM pool, and are more similar to spectra of the humified silt- and clay-associated OM fractions found in a cultivated mollisol (e.g. Baldock et al. 1992) and heavier mineral-associated density fractions found in alfisols, entisols and oxisols (e.g. Golchin et al. 1994, 1995). Thus, the field and laboratory results suggest that most field-collected DOC within the mineral soil is derived from humified SOM, and microbial processing of SOM and aqueous/solid exchange likely contributes to the majority of this potential DOC pool (Currie et al. 1996).

The portion of this potentially exchangeable C pool that is accessible to the soil solution is likely spatially limited to the linings of pores and aggregate surfaces. These preferential flowpaths are often “hot spots” for biological activity (Bundt et al. 2001). Based on ^{14}C measurements, Ewing et al. (2006) found that C on aggregate surfaces was younger than the bulk C pool and that these differences became more pronounced with increasing depth. The ^{14}C measurements (Fig. 2) indicate that most soil DOC, while significantly older than fresh litter, was younger than the bulk C pool, and that these differences were most pronounced in the macropore water and with increasing depth. In contrast, water-extractable organic matter, derived from disaggregated soil, at all depths in both soils had a similar Δ^{14}C value to that of the bulk soil (Table 4). These results are consistent with the hypothesis that the soil solution is interacting with a spatially limited C pool that is smaller, but more dynamic, that the bulk C at any given depth within the mineral soil.

Despite the more dynamic nature of the potential DOC pool relative to bulk SOM, the field-collected DOC, even within the O horizon, is rarely dominated by the low molecular weight, hydrophilic and highly labile organic compounds which are suggested by studies that examine water-extractable OM from fresh litter material (e.g. Kalbitz et al. 2003). This apparent paradox is easily rectified by considering the spatial and temporal pattern of DOC production, consumption and collection. In the laboratory, collecting DOC via a water-extraction yields a suite of compounds that are immediately dissolved based solely on their respective solubility characteristics. These extractions are then either immediately analyzed or, if stored, kept in a state that minimizes any microbial activity. However, in the field, the equivalent of a pure water-extraction occurs within micropores or within a thin film of water surrounding the organic material. In near surface horizons, there

Table 4 A comparison of water-extractable organic matter (WEOM) and bulk soil Δ^{14}C values (‰). WEOM was obtained by shaking 10 g of oven dried <2 mm soil with 500 ml of DDI water overnight and then centrifuging and filtering solution to <0.45 μm

	Horizon	Bulk soil	WEOM
Tennessee Valley	A1	21.4	42.5
	A3	−110.7	−52.5
	Bt1	−285.7	−276.8
Caspar Creek	O	107.3	111.0
	A1	52.6	28.4
	AB	−142.3	−152.0
	Bt	−442.9	−488.0

are highly active communities of microorganisms that can metabolize many of these compounds within hours of being released into solution (Fierer and Schimel 2002, 2003). These “hot spot” regions are connected to our sampling devices via slow mass flow across a potential gradient (tension lysimeters) or when the soil saturates and these regions become connected to the macropore network (zero-tension lysimeters). This delay between the actual production and collection can result in an effective ‘microbial filter’ of the most labile material (Wickland et al. 2007), which can represent a large fraction of total DOC production (van Hees et al. 2005), creating a situation where our field-collected DOC is in fact the residue of this initial decomposition step.

The size of this potential DOC source pool is clearly finite. We found that the 6 month rainy period led to a pronounced decline in DOC concentrations and a shift in isotopic and spectroscopic properties towards more chemically recalcitrant OM (Figs. 4 and 5). The initial flush of DOC early in the season is composed of both the byproducts of decomposition of recent litter that built up in the soil during the long dry season and that of a more stabilized SOM fraction. The slow continued processing and release of a more stabilized and chemically recalcitrant OM fraction then sustains DOC production later in the winter.

Differences between the forest and grassland sites

Despite similarities between these sites, we found that in the grassland soil there were consistently greater differences in the C:N ratio, δ^{13}C and SUVA values between the dissolved and solid phases than in the forest soil. In the grassland, the majority of fresh C substrate enters the soil as fine root turnover and root exudates throughout the growing season, which begins shortly after the arrival of winter rains and peaks in early spring. This small but steady supply of fresh leachable substrate within the soil contributes to an overall DOC chemistry somewhat more intermediate between fresh plant-residues and humified SOM. Support for this idea comes from the results of Yano et al. (2000), who hypothesized that roots were a large source of DOC within the soil based on correlations between DOC and fine root biomass. However, in the forest soil, C inputs are dominated by litterfall at the soil surface and are distributed throughout the year. Here, most of the processing of fresh C substrate (and DOC production) occurs within the litter layer. This fresh DOC produced within the litter layer makes only a small direct contribution to DOC collected within the mineral soil leading to a more rapid shift in soil DOC chemistry towards humified SOM with increasing depth in the mineral soil.

Conceptual model

Based on our observations, large quantities of DOC are produced from the decomposition of fresh plant debris, either surface litter (forests) or roots/surface litter (grasslands). This DOC is then advectively transported downward with soil water. During transport, the most labile fraction of an initially large DOC pool undergoes microbial decay, partially decreasing the total DOC concentrations (van Hees et al. 2005; Wickland et al. 2007). In addition, the DOC undergoes rapid exchange with soil exchange sites, further reducing the total concentrations, but greatly changing the chemical nature through gross exchange mechanisms. The result is that soil DOC concentrations rapidly decline with depth to values close to incoming rainwater, and the DOC that remains is chemically mature and bears little resemblance to the large influxes of DOC immediately above it in the profile (Fig. 7).

There are two likely sources of OM for the initial DOC pool: (1) the leaching of organic acids from roots and fresh plant residues; and (2) the microbial production of solubilizable organic compounds during the breakdown of less-soluble material. The leaching of fresh residues plays a significant role only in the surface horizons and following long dry periods. A portion of these fresh leachates are likely metabolized so rapidly by microorganisms (van Hees et al. 2005) that only a fraction of this DOC source is actually collected in our lysimeters. Our work and that in other studies (e.g. Currie et al. 1996) suggest that the dominant process maintaining the DOC pool, especially within the mineral soil, is microbial release of smaller, more soluble compounds with a high percentage of active functional groups (^{13}C NMR results suggest carboxyl and methyl groups are particularly important) from the bulk SOM.

In these soils, the dominant mechanisms controlling the observed compositional shifts in DOC with depth are exchange reactions with a potentially

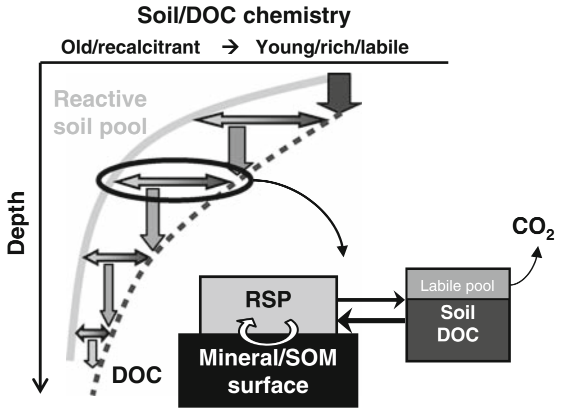

Fig. 7 Conceptual model of shifts in DOC chemistry in mineral soils. Rapid exchange with a potentially exchangeable or reactive soil C pool (RSP) is primarily responsible for the composition of DOC in soil solution. Secondarily, microbial degradation of a small labile fraction and selective adsorption of hydrophobic compounds will tend to enhance the recalcitrant nature of the soil DOC. Exchange (horizontal arrows) and decomposition likely occurs in smaller pores with downward transport (vertical arrows) being dominated by macropore flow during storms. The RSP is likely dominated by lower molecular weight OM surfically-bound to fine mineral and other OM surfaces. This pool is replenished by both sorption of organic compounds leached from above and by microbial processing of less soluble material (white circular arrow). With increasing depth, the later process comes to dominant resulting in the RSP being composed primarily of highly altered microbial metabolites. See text for more details

exchangeable or reactive soil pool (RSP) which may be akin to the “kinetic zone” of organo-mineral associations recently proposed by Kleber et al. (2007). While significant exchange occurs, there is a net trend towards adsorption that is primarily responsible for the observed drop in DOC concentration with depth. Additionally, microbial degradation of a small labile fraction of the DOC and the potential for selective adsorption (e.g. Hernes et al. 2007; Kaiser et al. 2001b) combined with net downward transport will tend to enhance both the recalcitrant nature of DOC and the drop in concentration with depth.

Our model, emphasizing transport, exchange and decomposition, is likely most applicable in fine-textured mineral soils. Organic and sandy soils with little adsorption capacity are known to be large exporters of DOC (Aitkenhead and McDowell 2000; Aitkenhead-Peterson et al. 2007; Meyer 1986) and that the DOC from these soils is commonly chemically similar to fresh plant leachates (Nelson et al. 1993). In these cases, microbial degradation of DOC might be expected to be the dominant in situ loss mechanism, with minimal exchange and greater export to the aquatic ecosystem.

Conclusions

By utilizing both isotopic and spectroscopic analytical techniques on the dissolved and soil phases of organic matter, we were able to develop a conceptual model of the nature and dynamics of DOC in some California soils. In these fine textured soils, fresh C substrates do not contribute significantly to the observed soil DOC pool because they are most likely rapidly utilized by microorganisms. Rather it is a more humified fraction of the soil OM pool and its exchange with the aqueous phase that determine the DOC composition. At sites with greatly contrasting vegetation and C distribution patterns, we found similar shifts in DOC chemistry with increasing depth that also paralleled those of soil OM. Despite a trend towards strong net absorption with depth, we found that DOC chemistry is altered primarily through gross exchange reactions with a potentially exchangeable C pool that is likely being replenished through microbial processing of less soluble organic matter. In these ecosystems, the mineral soil acts as a physical and biological filter for surficially derived DOC with the result being that most of the DOC entering the mineral soil is either quickly utilized by soil microorganisms or retained as stabilized mineral-bound organic matter.

Acknowledgments We thank K. Lohse for providing N data; E. Keppeler and the USFS Redwood Sciences Laboratory for access to and logistical support at Caspar Creek; the National Park Service for access to Tennessee Valley; M. Mangahas for assistance in the field; D. Harris and the UC Davis Stable Isotope facility for automated ^{13}C measurements of DOC; and J. Southon and G. dos Santos at the Keck Center for Carbon Accelerator Mass Spectrometry for help with radiocarbon analyses. This work was funded with a grant to R. Amundson by the Kearney Foundation of Soil Science and by a National Science Foundation Doctoral Dissertation Improvement Grant to J. Sanderman.

References

Aitkenhead JA, McDowell WH (2000) Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scales. Global Biogeochem Cycles 14:127–138. doi: 10.1029/1999GB900083

Aitkenhead-Peterson JA, Smart RP, Aitkenhead MJ, Cresser MS, McDowell WH (2007) Spatial and temporal variation of dissolved organic carbon export from gauged and ungauged watersheds of Dee Valley, Scotland: Effect of land cover and C:N. Water Resour Res 43:W05442. doi: 10.1029/2006WR004999

Aufdenkampe AK, Hedges JI, Richey JE, Krusche AV, Llerena CA (2001) Sorptive fractionation of dissolved organic nitrogen and amino acids onto fine sediments within the Amazon Basin. Limnol Oceanogr 46:1921–1935

Baisden WT, Amundson R, Brenner DL, Cook AC, Kendall C, Harden JW (2002) A multiisotope C and N modeling analysis of soil organic matter turnover and transport as a function of soil depth in a California annual grassland soil chronosequence. Global Biogeochem Cycles 16:1135. doi:10.1029/2001GB001823

Baldock JA, Smernik RJ (2002) Chemical composition and bioavailability of thermally, altered pinus resinosa (red pine) wood. Org Geochem 33:1093–1109. doi:10.1016/S0146-6380(02)00062-1

Baldock JA, Oades JM, Waters AG, Peng X, Vassallo AM, Wilson MA (1992) Aspects of the chemical-structure of soil organic materials as revealed by solid-state C-13 NMR-spectroscopy. Biogeochemistry 16:1–42

Baldock JA, Oades JM, Nelson PN, Skene TM, Golchin A, Clarke P (1997) Assessing the extent of decomposition of natural organic materials using solid-state C-13 NMR spectroscopy. Aust J Soil Res 35:1061–1083. doi:10.1071/S97004

Benner R, Fogel ML, Sprague EK, Hodson RE (1987) Depletion of C-13 in lignin and its implications for stable carbon isotope studies. Nature 329(6141):708–710. doi: 10.1038/329708a0

Brown DL (1995) An analysis of transient flow in upland watersheds: interactions between structure and process. Dissertation, University of California, Berkeley

Bundt M, Widmer F, Pesaro M, Zeyer J, Blaser P (2001) Preferential flow paths: Biological ‘hot spots’ in soils. Soil Biol Biochem 33:729–738. doi:10.1016/S0038-0717(00)00218-2

Chapman HD (1965) Cation-exchange capacity. In: Black CA, Evans DD, White JL, Ensminger LE, Clark FE (eds) Methods of soil analysis. Part 2. American Society of Agronomy, Madison, WI, pp 899–904

Chin YP, Aiken G, Oloughlin E (1994) Molecular-weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environ Sci Technol 28:1853–1858. doi:10.1021/es00060a015

Clevel CC, Neff JC, Townsend AR, Hood E (2004) Composition, dynamics, and fate of leached dissolved organic matter in terrestrial ecosystems: results from a decomposition experiment. Ecosystems (NY, Print) 7:275–285. doi:10.1007/s10021-003-0236-7

Craig H (1957) Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analyses of carbon dioxide. Geochim Cosmochim Acta 12:133–149. doi:10.1016/0016-7037(57)90024-8

Currie WS, Aber JD, McDowell WH, Boone RD, Magill AH (1996) Vertical transport of dissolved organic C and N under long-term N amendments in pine and hardwood forests. Biogeochemistry 35:471–505. doi:10.1007/BF02183037

Dahlgren RA (1998) Effects of forest harvest on biogeochemical processes in the Caspar Creek watershed. Final report to California Department of Forestry and Fire Protection. Agreement Number 8CA17039

Driscoll CT, Johnson NM, Likens GE, Feller MC (1988) Effects of acidic deposition on the chemistry of headwater streams—a comparison between Hubbard Brook, New Hampshire, and Jamieson creek, British Columbia. Water Resour Res 24:195–200. doi:10.1029/WR024i002p00195

Evans CD, Chapman PJ, Clark JM, Monteith DT, Cresser MS (2006) Alternative explanations for rising dissolved organic carbon export from organic soils. Glob Change Biol 12:2044–2053. doi:10.1111/j.1365-2486.2006.01241.x

Ewing SA, Serman J, Baisden WT, Wang Y, Amundson R (2006) Role of large-scale soil structure in organic carbon turnover: evidence from California grassland soils. J Geophys Res Biogeosci 111:G03012. doi:10.1029/2006JG000174

Fierer N, Schimel JP (2002) Effects of drying-rewetting frequency on soil carbon and nitrogen transformations. Soil Biol Biochem 34(6):777–787. doi:10.1016/S0038-0717(02)00007-X

Fierer N, Schimel JP (2003) A proposed mechanism for the pulse in carbon dioxide production commonly observed following the rapid rewetting of a dry soil. Soil Sci Soc Am J 67(3):798–805

Freeman C, Evans CD, Monteith DT, Reynolds B, Fenner N (2001) Export of organic carbon from peat soils. Nature 412:785–785. doi:10.1038/35090628

Froberg M, Berggren D, Bergkvist B, Bryant C, Mulder J (2006) Concentration and fluxes of dissolved organic carbon (DOC) in three Norway spruce stands along a climatic gradient in Sweden. Biogeochemistry 77:1–23. doi:10.1007/s10533-004-0564-5

Froberg M, Kleja DB, Hagedorn F (2007) The contribution of fresh litter to dissolved organic carbon leached from a coniferous forest floor. Eur J Soil Sci 58:108–114. doi: 10.1111/j.1365-2389.2006.00812.x

Gabet EJ (2000) Gopher bioturbation: Field evidence for nonlinear hillslope diffusion. Earth Surf Process Landf 25:1419–1428. doi:10.1002/1096-9837(200012)25:13<1419::AID-ESP148>3.0.CO;2-1

Gaudinski JB, Trumbore SE, Davidson EA, Zheng SH (2000) Soil carbon cycling in a temperate forest: radiocarbon-based estimates of residence times, sequestration rates and partitioning of fluxes. Biogeochemistry 51:33–69. doi: 10.1023/A:1006301010014

Gee GW, Bauder JW (1986) Particle-size analysis. In: Black WC (ed) Methods of soil analysis. Part 1. American Society of Agronomy, Madison, WI, pp 398–406

Golchin A, Oades JM, Skjemstad JO, Clarke P (1994) Study of free and occluded particulate organic-matter in soils by solid-state C-13 NMR spectroscopy. Aust J Soil Res 32:285–309. doi:10.1071/SR9940285

Golchin A, Oades JM, Skjemstad JO, Clarke P (1995) Structural and dynamic properties of soil organic-matter as reflected by C-13 natural-abundance, pyrolysis mass-spectrometry and solid-state C-13 NMR spectroscopy in density fractions of an oxisol under forest and pasture. Aust J Soil Res 33:59–76. doi:10.1071/SR9950059

Gregorich EG, Liang BC, Drury CF, Mackenzie AF, McGill WB (2000) Elucidation of the source and turnover of water soluble and microbial biomass carbon in agricultural soils. Soil Biol Biochem 32:581–587. doi:10.1016/S0038-0717(99)00146-7

Guggenberger G, Zech W (1993) Dissolved organic-carbon control in acid forest soils of the Fichtelgebirge (Germany) as revealed by distribution patterns and structural composition analyses. Geoderma 59:109–129. doi:10.1016/0016-7061(93)90065-S

Hernes PJ, Robinson AC, Aufdenkampe AK (2007) Fractionation of lignin during leaching and sorption and implications for organic matter “freshness”. Geophys Res Lett 34:L17401. doi:10.1029/2007GL031017

Huang Y, Eglinton G, Van der Hage ERE, Boon JJ, Bol R, Ineson P (1998) Dissolved organic matter and its parent organic matter in grass upland soil horizons studied by analytical pyrolysis techniques. Eur J Soil Sci 49:1–15. doi:10.1046/j.1365-2389.1998.00141.x

John B, Ludwig B, Flessa H (2003) Carbon dynamics determined by natural C-13 abundance in microcosm experiments with soils from long-term maize and rye monocultures. Soil Biol Biochem 35:1193–1202. doi:10.1016/S0038-0717(03)00180-9

Kaiser K, Guggenberger G (2000) The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. Org Geochem 31:711–725. doi:10.1016/S0146-6380(00)00046-2

Kaiser K, Guggenberger G, Haumaier L, Zech W (2001a) Seasonal variations in the chemical composition of dissolved organic matter in organic forest floor layer leachates of old-growth Scots pine (*Pinus sylvestris* L.) and European beech (*Fagus sylvatica* L.) stands in northeastern Bavaria, Germany. Biogeochemistry 55:103–143. doi:10.1023/A:1010694032121

Kaiser K, Guggenberger G, Zech W (2001b) Isotopic fractionation of dissolved organic carbon in shallow forest soils as affected by sorption. Eur J Soil Sci 52:585–597. doi:10.1046/j.1365-2389.2001.00407.x

Kalbitz K, Schmerwitz J, Schwesig D, Matzner E (2003) Biodegradation of soil-derived dissolved organic matter as related to its properties. Geoderm 113:273–291. doi:10.1016/S0016-7061(02)00365-8

Kalbitz K, Glaser B, Bol R (2004) Clear-cutting of a Norway spruce stand: Implications for controls on the dynamics of dissolved organic matter in the forest floor. Eur J Soil Sci 55:401–413. doi:10.1111/j.1351-0754.2004.00609.x

Karltun E, Harrison AF, Alriksson A, Bryant C, Garnett MH, Olsson MT (2005) Old organic carbon in soil solution DOC after afforestation—evidence from C-14 analysis. Geoderma 127:188–195. doi:10.1016/j.geoderma.2004.12.008

Kleber M, Mikutta R, Torn MS, Jahn R (2005) Poorly crystalline mineral phases protect organic matter in acid subsoil horizons. Eur J Soil Sci 56:717–725

Kleber M, Sollins P, Sutton R (2007) A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces. Biogeochemistry 85:9–24. doi:10.1007/s10533-007-9103-5

Kogel-Knabner I (1997) C-13 and N-15 NMR spectroscopy as a tool in soil organic matter studies. Geoderma 80:243–270. doi:10.1016/S0016-7061(97)00055-4

Kogel-Knabner I (2002) The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. Soil Biol Biochem 34:139–162. doi:10.1016/S0038-0717(01)00158-4

Levin I, Kromer B (2004) The tropospheric (CO2)-C-14 level in mid-latitudes of the northern hemisphere (1959–2003). Radiocarbon 46:1261–1272

McKeague JA, Day DH (1966) Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Can J Soil Sci 46:13–16

McKeague JA, Brydon JE, Miles NM (1971) Differentiation of forms of extractable iron and aluminum in soils. Soil Sci Soc Am Proc 35:33–37

Meyer JL (1986) Dissolved organic-carbon dynamics in 2 subtropical blackwater rivers. Arch Hydrobiol 108:119–134

Michalzik B, Matzner E (1999) Dynamics of dissolved organic nitrogen and carbon in a central European Norway spruce ecosystem. Eur J Soil Sci 50:579–590. doi:10.1046/j.1365-2389.1999.00267.x

Minagawa M, Winter DA, Kaplan IR (1984) Comparison of Kjeldahl and combustion methods for measurement of nitrogen isotope ratios in organic matter. Anal Chem 56:1859–1961. doi:10.1021/ac00275a023

Montgomery DR, Dietrich WE (1995) Hydrologic processes in a low-gradient source area. Water Resour Res 31:1–10. doi:10.1029/94WR02270

NCDC (2007) Climatic data summary for station #4500 Kentfield, CA. http://www.ncdc.noaa.gov/oa/ncdc.html. Cited 15 April 2007

Nelson PN, Baldock JA (2005) Estimating the molecular composition of a diverse range of natural organic materials from solid-state C-13 NMR and elemental analyses. Biogeochemistry 72:1–34

Nelson PN, Baldock JA, Oades JM (1993) Concentration and composition of dissolved organic-carbon in streams in relation to catchment soil properties. Biogeochemistry 19:27–50. doi:10.1007/BF00000573

Nodvin SC, Driscoll CT, Likens GE (1986) Simple partitioning of anions and dissolved organic-carbon in a forest soil. Soil Sci 142:27–35

Roulet N, Moore TR (2006) Environmental chemistry—browning the waters. Nature 444:283–284. doi:10.1038/444283a

Sanderman J (2007) The role of dissolved organic carbon in the terrestrial carbon cycle. Dissertation, University of California, Berkeley

Sanderman J, Amundson R (2008) A comparative study of dissolved organic carbon transport and stabilization in California forest and grassland soils. Biogeochemistry (in press)

Schoenberger PJ, Wysocki DA, Benham EC, Broderosn WD (2002) Field book for describing and sampling soils. version 2.0. National Soil Survey Center, Lincoln, NE

Six J, Bossuyt H, Degryze S, Denef K (2004) A history of research on the link between (micro) aggregates, soil biota, and soil organic matter dynamics. Soil Tillage Res 79:7–31. doi:10.1016/j.still.2004.03.008

Skjemstad JO, Clarke P, Taylor JA, Oades JM, Newman RH (1994) The removal of magnetic materials from surface soils—a solid-state C-13 CP/MAS NMR study. Aust J Soil Res 32:1215–1229. doi:10.1071/SR9941215

Smernik RJ (2005) A New Way to Use Solid-State Carbon-13 Nuclear Magnetic Resonance Spectroscopy to Study the Sorption of Organic Compounds to Soil Organic Matter. J Environ Qual 34:1194–1204. doi:10.2134/jeq2004.0371

Smernik RJ, Oades JM (2000a) The use of spin counting for determining quantitation in solid state 13-C NMR spectra of natural organic matter. 1. Model systems and the effects of paramagnetic impurities. Geoderma 96:101–129. doi:10.1016/S0016-7061(00)00006-9

Smernik RJ, Oades JM (2000b) The use of spin counting for determining quantitation in solid state 13-C NMR spectra of natural organic matter. 2. HF-treated soil fractions. Geoderma 96:159–171. doi:10.1016/S0016-7061(00)00007-0

Southon J, Santos G, Druffel-Rodriguez K, Druffel E, Trumbore S, Xu XM et al (2004) The Keck carbon cycle AMS laboratory, University of California, Irvine: Initial operation and a background surprise. Radiocarbon 46:41–49

Tilley FB, Rice RM (1977) Caspar Creek watershed study–a current status report. State Forest Notes No. 66. State of California, Department of Forestry, Sacramento, CA

Trumbore S (2000) Age of soil organic matter and soil respiration: Radiocarbon constraints on belowground C dynamics. Ecol Appl 10:399–411. doi:10.1890/1051-0761(2000)010[0399:AOSOMA]2.0.CO;2

U.S. Soil Conservation Service (1972) Soil survey of Mendocino County. U.S. Forest Service and U.C. Agricultural Experiment Station. G.P.O, Washington, DC

van Hees PAW, Jones DL, Finlay R, Godbold DL, Lunstomd US (2005) The carbon we do not see—the impact of low molecular weight compounds on carbon dynamics and respiration in forest soils: a review. Soil Biol Biochem 37:1–13. doi:10.1016/j.soilbio.2004.06.010

Vogel JS, Southon JR, Nelson DE, Brown TA (1984) Performance of catalytically condensed carbon for use in accelerator mass-spectrometry. Nucl Instrum Methods Phys Res B 233:289–293. doi:10.1016/0168-583X(84)90529-9

Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol 37:4702–4708. doi:10.1021/es030360x

Wickland KP, Neff JC, Aiken GR (2007) Chemistry and biodegradability of terrestrially-derived DOC in Boreal black spruce forests, Alaska (in review)

Wilson MA (1987) NMR Techniques and Applications in Geochemistry and Soil Chemistry. Pergamon Press, Oxford, UK

Wynn JG, Bird MI, Wong VNL (2005) Rayleigh distillation and the depth profile of C-13. Geochim Cosmochim Acta 69:1961–1973. doi:10.1016/j.gca.2004.09.003

Yano Y, McDowell WH, Aber JD (2000) Biodegradable dissolved organic carbon in forest soil solution and effects of chronic nitrogen deposition. Soil Biol Biochem 32:1743–1751. doi:10.1016/S0038-0717(00)00092-4

Yoo K, Amundson R, Heimsath AM, Dietrich WE (2005) Process-based model linking pocket gopher (*Thomomys bottae*) activity to sediment transport and soil thickness. Geology 33:917–920. doi:10.1130/G21831.1

Ziemer RR (1981) Stormflow response to roadbuilding and partial cutting in small streams of northern California. Water Resour Res 17:907–917

Ziemer RR (1998) Proceedings of the conference on coastal watersheds: the Caspar Creek story. 1998 May 6; Ukiah, CA. General Tech. Rep. PSW GTR-168. Pacific Southwest Research Station, Forest Service, U.S. Department of Agriculture, Albany, CA