

Dissolved Organic Matter Controls on Terrestrial Carbon Sequestration and Export in Contrasting California Ecosystems

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Summary

Dissolved organic carbon (DOC) plays an important role in the upland soil carbon cycle while simultaneously, via the hydrologic cycle, providing a direct link between the terrestrial and aquatic ecosystems. We have monitored changes in DOC fluxes and chemistry as rainwater percolates through the soil and reemerges at the channel head in two contrasting upland watersheds in coastal California: a redwood-Douglas fir forest and a coastal prairie ecosystem.

At the soil profile scale when vertically infiltrating flow dominates, significant quantities of C move as DOC into the mineral soil. These fluxes are rapidly attenuated with increasing depth in the mineral soil, primarily due to sorption reactions with these fine-textured soils. This movement and subsequent adsorption of DOC seems to be a critical mechanism in accumulating large stores of organic C in deep soil horizons. Isotopic and spectroscopic data indicate that soil DOC is not composed simply of fresh plant leachates; rather DOC appears to be a mixture of plant-derived compounds and more humified material. Radiocarbon data, in particular, point to the fact that soil DOC is not just fresh litter leachate, but rather it is a mixture of more aged organic constituents.

In terms of an input-output budget, DOC losses are minor relative to respiratory CO₂ losses. However, DOC plays a significant role in translocating surficial C to the deeper mineral soil. In support of this notion, we found that DOC flux rates are very similar to model-derived vertical transport velocities. Additionally, DOC-based mean residence times in the mineral soil are of similar magnitude to those derived from carbon-14 measurements of the soil organic C pool.

Differences in hydrologic flowpaths impart distinct stream chemical patterns at these two sites. When vertically infiltrating throughflow dominates, DOC and other reactive solutes appear to be governed by exchange reactions in the regolith, resulting in little temporal variation in stream chemistry. However, when shallow saturated flow paths are triggered, large quantities of DOC can be exported from these systems. As discharge increases, we generally find an increase in DOC concentration and a shift in composition towards fresher, less processed organic material.

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Objectives

This study addresses the role of dissolved organic carbon (DOC) in both translocating carbon within soils and in exporting carbon from terrestrial to aquatic ecosystems via the hydrologic cycle. Our main objective is to monitor DOC fluxes from “rain to river” in relation to soil/sediment C concentration, composition and turnover in two contrasting ecosystems.

- 1) How do the concentration, composition and age of DOC change as it moves through the soil and out into the stream network? How do these parameters change seasonally?

The O horizon is believed to be the source of most DOC in temperate forests, while the mineral horizons act as the dominant sinks (Kalbitz et al. 2000). As DOC percolates through the soil profile, it is continually interacting with mineral surfaces and being degraded by microorganisms. Following this logic, we can hypothesize that DOC will become progressively more recalcitrant and have a progressively older radiocarbon signature with increasing soil depth, yet will likely be much younger than the native SOC at any given depth.

- 2) How do DOC fluxes determine the vertical carbon distribution within a soil and how do DOC losses compare to gaseous C losses as CO₂?

For soil C to be effectively sequestered beyond a timescale of a few decades, this C must become incorporated into the subsurface mineral horizons, yet the actual mechanisms by which this occurs is at best poorly known. 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 (CEC, soil structure/texture, nutrient status and pH), and vegetation type (root distribution and litter quality).

Most of our current understanding of C fluxes comes from studies conducted on relatively flat terrain, yet the majority of the landscape is dissected by rivers and streams forming discrete sloping watersheds. Schimel et al. (2001) found that these upland ecosystems hold the greatest potential as C sinks in the continental USA based on net ecosystem CO₂ exchange (NEE) measurements. However, eddy covariance-derived estimates of NEE are often only a few percent of annual net primary productivity (Sanderman et al. 2003); a figure which is of similar magnitude to the estimated global annual DOC export to oceans (Schlesinger 1991). Better estimates of soil DOC losses are clearly needed to adequately address this issue.

- 3) How do the concentration, composition and age of stream DOC vary seasonally with hydrological flow paths?

The majority of stream and riverine DOC is hypothesized to originate from rainfall percolating through the soil of small upland watersheds. The flow path that this water takes on its way to the stream network will have a large impact upon the concentration and composition of stream DOC.

Approach and Procedures

Two contrasting zero-order watersheds in Northern California have been selected for this study: 1) a second-growth redwood-Douglas fir dominated watershed (1.4 ha) in the Caspar

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Creek Experimental Watershed in the Jackson Demonstration State Forest, Mendocino County; and 2) a coastal shrub-grass-dominated watershed (2.6 ha) at Tennessee Valley, in the Golden Gate National Recreation Area, Marin County. These field sites were carefully selected because they have been the focus of previous hydrologic research on the rates and mechanisms of runoff and soil water flow paths (Albright 1991; Brown 1995; Montgomery and Dietrich 1995).

These sites were instrumented with a series of tension and zero-tension lysimeters, along with equipment to monitor soil hydrologic conditions. For the 03/04 and 04/05 water years, water fluxes from rain to river are being monitored more or less continuously. Aqueous samples are being collected on a periodic basis to determine the DOC concentration, and isotopic and chemical composition of these water fluxes. Detailed carbon inventories have been made in order to establish the magnitude of the DOC fluxes within the larger C cycle of these sites. Soil CO₂ concentrations and surface efflux rates are also being measured to contrast DOC versus respiratory losses.

Results and Discussion

The following sections are organized around the three themes outlined in the project objectives section. For each of these sections, a manuscript is currently under preparation.

Soil-DOC chemistry and soil profile trends

When vertically infiltrating throughflow dominates, soil DOC is progressively altered as water percolates vertically through the soil profile. This appears to hold at both of these sites. Despite greatly contrasting vegetation and C allocation patterns, these coupled trends in soil and DOC properties are remarkably consistent between sites. Figure 1 only highlights these trends for the forested site at Caspar Creek, but very similar trends are found at Tennessee Valley. The available isotopic and spectroscopic data indicate that soil DOC is not composed simply of fresh plant leachates; rather DOC appears to be a mixture of plant-derived compounds and more humified material. Despite the trend towards net adsorption of DOC with depth, there appears to be significant exchange with a potentially-exchangeable pool of soil OC that controls the overall composition of DOC as water moves through the soil.

Results from solid-state CPMAS ¹³C NMR spectroscopic analyses support the conclusions introduced earlier that soil DOC does not look like fresh plant leachates and that the DOC is progressively altered towards more humified/recalcitrant material with depth (*fig. 2 and 3*). The relative proportion of alkyl-C (0-45 ppm chemical shift region) to O-alkyl C (45-110 ppm) in the DOC samples increases with depth, which generally indicates a greater contribution of more recalcitrant microbially-processed organic materials (Baldock et al. 1997). Figure 3 also highlights the general similarity in DOC between these contrasting ecosystems. The only major difference between the spectra shown in figure 3 is the additional peak at 55 ppm indicative of a greater abundance of N-containing organic compounds.

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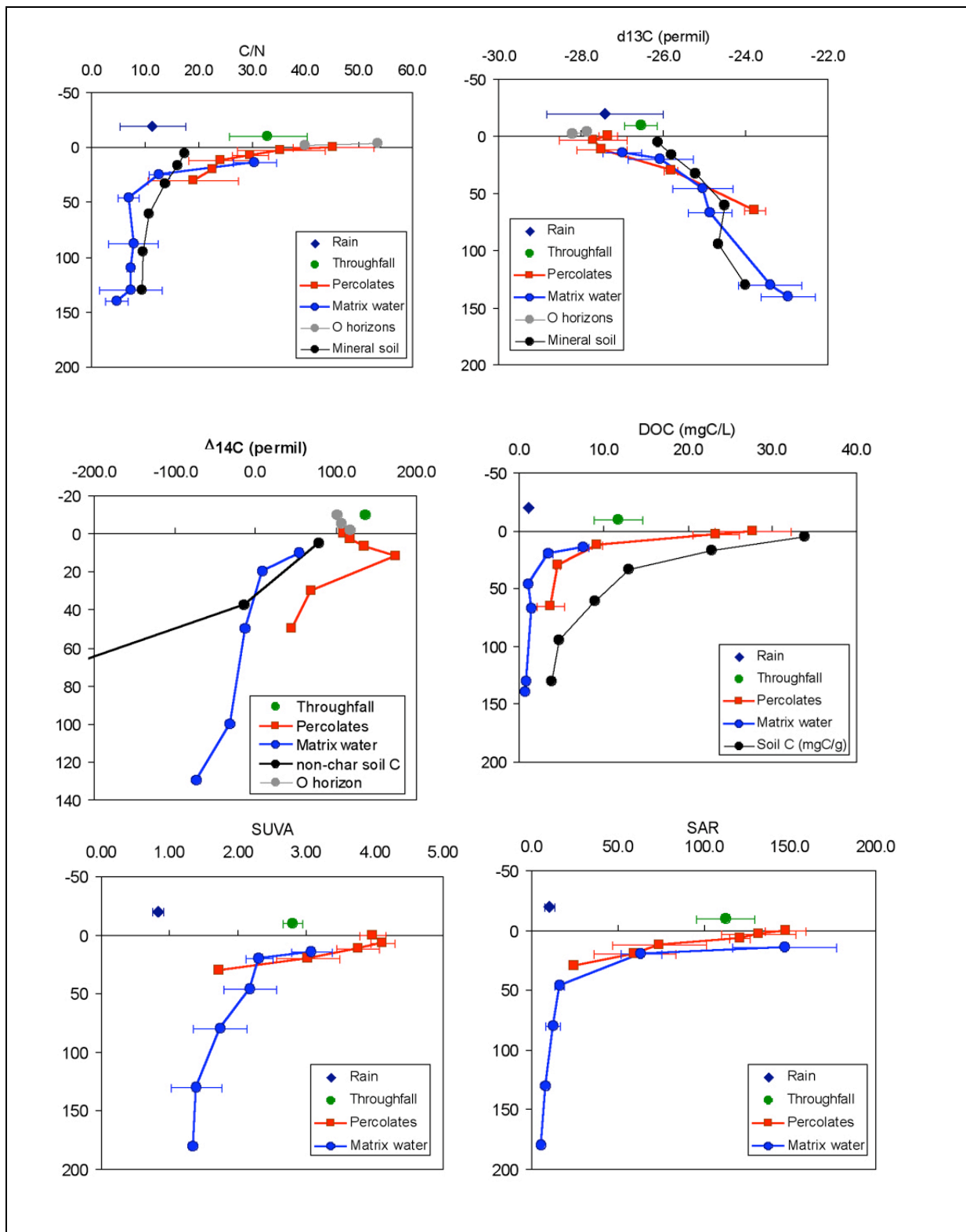


Figure 1. Caspar Creek seasonal mean soil profile trends: (a) DOC concentrations, (b) C/N ratio, (c) $\delta^{13}\text{C}$ values, (d) $\Delta^{14}\text{C}$, (e) specific uv adsorption (SUVA) and (f) specific adsorption ratio (SAR).

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A two-month laboratory incubation of field-collected DOC also supports the notion that DOC becomes progressively more recalcitrant with depth (data not shown). The proportion of DOC mineralized slowed by nearly a factor of 2 as DOC moved from the litter layer through the A horizon in the forested ecosystem. Similar trends were found at the non-forested site. A two-pool first-order decay model (Townsend et al. 1997) that divides the C into fast and slow cycling pools was fit to the incubation data. Using this model, it is interesting to note that the decay rates did not change appreciably between samples ($k_f \approx 0.04 \text{ days}^{-1}$) but the proportion of the DOC in a fast cycling pool dropped from 40 to 30 to 15% for the throughfall, O horizon leachate and A horizon leachate, respectively.

While mineralization proceeds slowly on only a select proportion of the DOC, sorption to mineral surfaces and exchange with soil organic matter bound to these surfaces occurs rapidly. Batch adsorption experiments (data not shown) when interpreted using the initial mass isotherm approach of Nodvin et al. (1986) indicate that the soils from both of these sites (fine textured with an abundance of 2:1 phyllosilicate clays) have a large capacity to adsorb DOC from solution while the C-rich surface horizons also have a large capacity to desorb C into solution. This equilibrium exchange creates a pattern of significant exchange between the solid and liquid phases regardless of net sorption or desorption.

Seasonal soil DOC trends

In addition to the vertical profile trends highlighted above, there is also a significant seasonal shift in DOC concentration and composition in these Mediterranean ecosystems (*fig. 4*). There is a build-up of readably-soluble organic material during the dry season that is rapidly depleted following the onset of the rainy season. DOC concentrations at 10 cm rapidly fall from nearly 100 mgC L^{-1} to less than 10 mgC L^{-1} by mid-winter with a concurrent increase in $\delta^{13}\text{C}$ values from about -30 to -28‰. Specific uv adsorption (SUVA) values ($a_{254}/[\text{DOC}]$) and the specific adsorption ratio (SAR, a_{254}/a_{600}) show steady shifts towards more humified material throughout the season. Radiocarbon results (data not shown) from 10cm soil DOC samples at Tennessee Valley indicate a drop in $\Delta^{14}\text{C}$ from 75‰ to 7‰ between late December and mid April.

A more detailed examination of figure 4 shows a slightly more dynamic pattern in which DOC is depleted through continued flushing but is rapidly replenished during periods of minimal water flux. For example, DOC concentrations are low in early January but, following an extended four-week dry period, the next rain event produced high concentrations of more labile C. In aggregate, the seasonal trends in DOC concentration and composition indicate that this potentially soluble pool of organic C is finite and highly dynamic.

DOC and the soil C cycle and annual carbon budgets

Figure 5 summarizes the annual fluxes of DOC and CO_2 relative to standing stocks of organic C at both sites. At Caspar Creek, both the forest canopy and the litter layer are large sources of DOC. In fact, >15% of the annual litterfall is from the O horizon as DOC each year. These fluxes are attenuated as DOC moves through the mineral soil, and at 120 cm, DOC fluxes are actually less than that entering in rainwater. At the non-forested site, there is no obvious DOC source pool analogous to the O horizon of a forest soil, yet we still found large amounts of DOC moving through the mineral soil. Here, the organic-rich, biologically active

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rooting zone is likely the dominant source of DOC. As water percolates deeper into the soils at Tennessee Valley, we find that most of the DOC is retained at deeper depths.

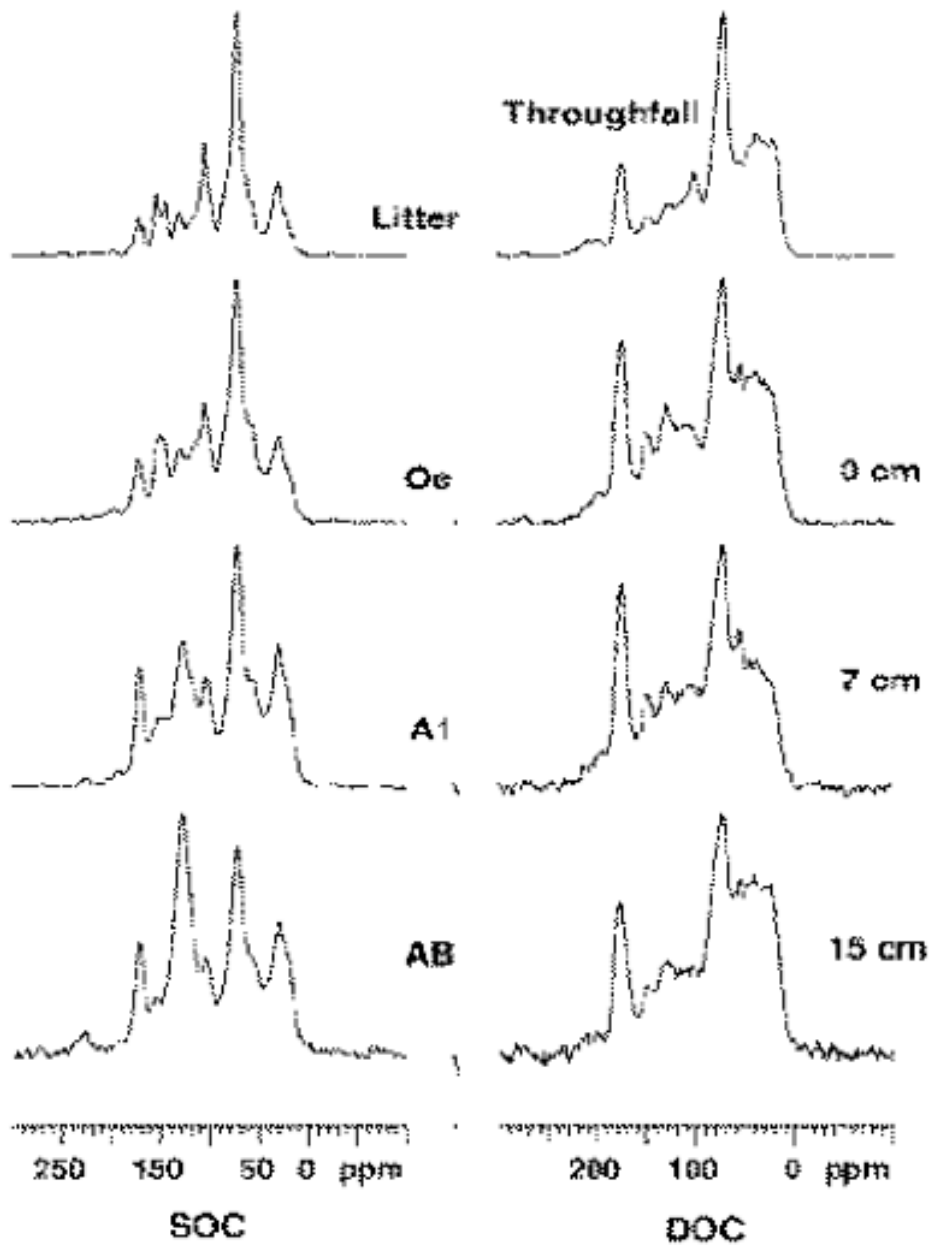


Figure 2. Solid-state CPMAS ^{13}C NMR spectra of SOM and the DOC collected flowing through that horizon in a Redwood forest soil. Soil samples were demineralized using 2% HF. DOC samples were concentrated on a rotary evaporator and then lyophilized to a powder.

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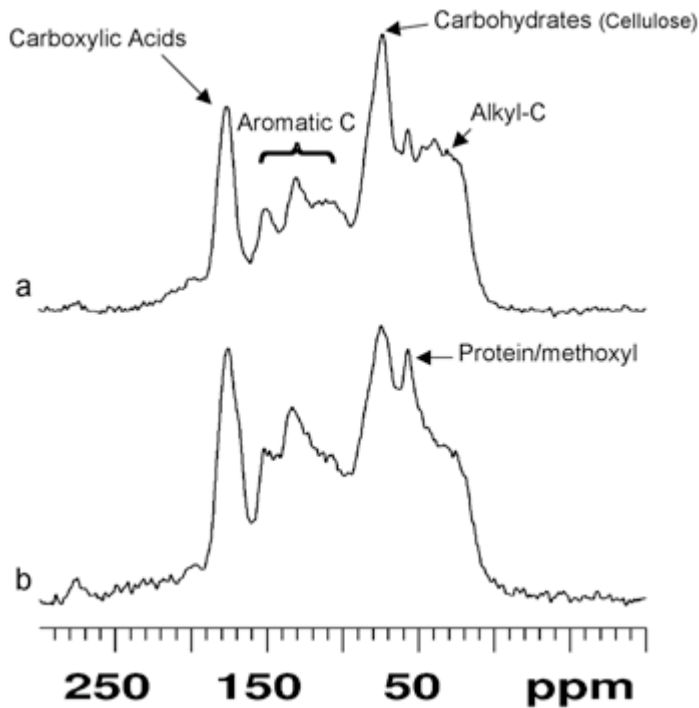


Figure 3. Comparison of solid-state CPMAS ^{13}C NMR spectra of soil DOC samples from (a) Caspar Creek and (b) Tennessee Valley.

CO₂ versus DOC fluxes

When considering a 1-m thick soil pedon with vertically infiltrating flow, CO_2 efflux at the soil surface is nearly three orders of magnitude greater than DOC losses (*fig. 5*). However, if we look into the daily and weekly patterns, we find that DOC leaching becomes a significant flux component over these shorter timescales. At the wetter and cooler forested site, we compared the CO_2 production in the upper 20 cm to the DOC production or loss from this same horizon ($\text{DOC}_{\text{out}} - \text{DOC}_{\text{in}}$) and found that the DOC/ CO_2 production ratio is 3.8% on an annual basis. The ratio rises to 6.5% if we only consider fluxes during months with measurable precipitation (October-May). However, the daily DOC/ CO_2 ratio exceeds 50% on 16 days with a maximum value of 185% (*fig. 6a*). At Tennessee Valley, on an annual basis the DOC/ CO_2 production ratio is only 1.6% and 2.1% if we limit the summation to months with measurable precipitation (November-April). Here, lower precipitation and warmer temperatures combine to allow the soils to dry more between winter storms, resulting in lower DOC production and greater CO_2 production relative to Caspar Creek.

Due to these microclimatic differences between sites, we find distinct patterns when comparing the daily DOC/ CO_2 production ratio to precipitation (*fig. 6b*). Because the soil at Caspar Creek is at or near field saturation all winter, this site responds rapidly to rainfall, creating the strong linear correlation seen in figure 6b. Whereas, at Tennessee Valley, due to a combination of lower antecedent soil moisture and a lower hydraulic conductivity, creating a tendency for water flux to persist for longer periods after the cessation of rainfall, the three-day prior cumulative rainfall total produced a significantly improved relationship.

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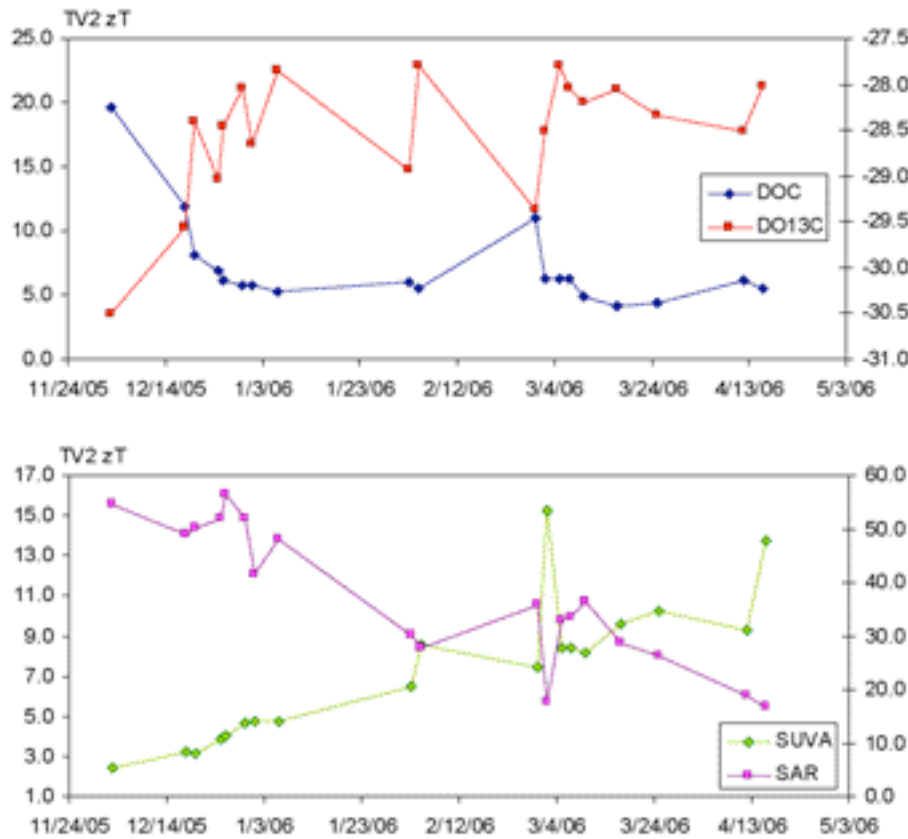


Figure 4. Seasonal shifts in 10 cm soil DOC concentration and chemistry as indicated by $\delta^{13}\text{C}$ (top panel), SUVA and SAR (bottom panel) at Tennessee Valley.

DOC flux/retention/turnover time

DOC transport and retention in deeper fine-textured soil horizons in which decomposition proceeds at much reduced rates, represents a potential mechanism to effectively sequester large quantities of C for significant periods of time. In order to make a comparison between DOC fluxes and soil C storage, we must transform the measured DOC fluxes (*fig. 2*) at any particular depth into a net loss or gain of DOC for a given thickness of soil by examining the difference between the DOC entering and leaving a given soil horizon. The potential role of downward DOC fluxes in deep soil C storage can then be estimated by making the simplifying assumption that all C inputs to a given horizon are due to downward transport and retention of DOC, so that at steady state the mean residence time (τ) of soil C (OC) in any given soil horizon (i) is given as: $\tau_i = OC_i / (\text{DOC}_{\text{in}} - \text{DOC}_{\text{out}})$. Mean residence times as calculated from this equation can then be compared to τ values derived from $\Delta^{14}\text{C}$ measurements.

A second approach to assess the role of DOC in the soil C cycle is to fit an advection-diffusion model (e.g., Elzein and Balesdent 1995) to the C content and $\Delta^{14}\text{C}$ data to calculate downward transport velocities (v , mm s^{-1}). Transport velocities can also be calculated from the DOC flux data as the DOC flux out of a soil horizon divided by C content per-unit depth. Using this approach at Caspar Creek, we calculate transport velocities of 1.2 mm s^{-1} in upper

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soil horizons dropping to 0.1 at depth. At Tennessee Valley, transport velocities range from 0.25 to 0.1 mm s⁻¹. These values compare favorably to published v values across a range of ecosystems (Baisden et al. 2002).

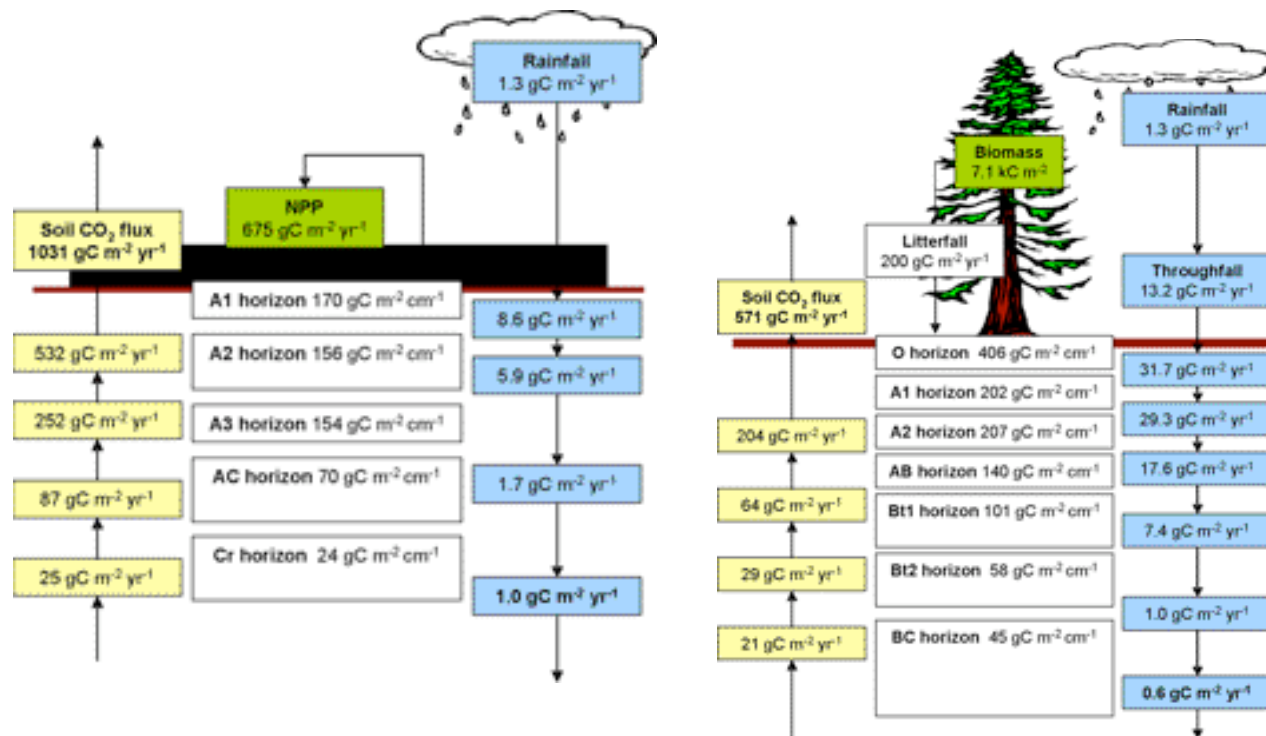


Figure 5. Carbon budgets, annual CO₂ fluxes (yellow) and DOC fluxes (blue) at Tennessee Valley (left) and Caspar Creek (right). NPP estimates at TV include aboveground and belowground inputs, whereas at CC, only litterfall was measured. Soil organic C stocks are reported on a per cm basis. Total C to 1m depth at TV is 8.7 kgC m⁻²; and at CC, 8.8 kgC m⁻² in the mineral soil and an additional 2.4 kgC m⁻² in the O horizon. CO₂ fluxes have been calculated at the soil surface and at depths of 18, 38, 63 and 88 cm from soil CO₂ concentration data using the Millington and Shearer (1971) gaseous diffusion model appropriate for aggregated soils (details of CO₂ and DOC flux models will be presented in a forthcoming manuscript). 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.

Soil-stream connections

The majority of stream and riverine DOC is hypothesized to originate from rainfall percolating through the soil of small upland watersheds. The dissolved solute load in a particular system is often thought to be controlled by a combination of source and/or transport limitations (Inamdar and Mitchell 2006). Stream DOC concentrations are source limited if production of DOC (either through leaching, desorption or microbial production) cannot keep pace with the rate of removal via soil water flow. The flow path that this water takes on its way to the stream network will also likely have a large impact upon the concentration of stream DOC. Differing flow paths also have implications for the chemical recalcitrance and age of the DOC that is entering the channel network. During throughflow conditions, the water takes a slow tortuous path through the clay-rich B horizon, in which there is ample

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opportunity for exchange on mineral surfaces. Fitting with our progressive alteration hypothesis, the DOC emerging at the channel head would be older and composed of more resistant and more degraded organic compounds. During times of macropore and saturation overland flow, we would expect the DOC entering the channel network to be composed of younger and more labile organic compounds because the water is flowing along a pathway that avoids most of the removal mechanisms.

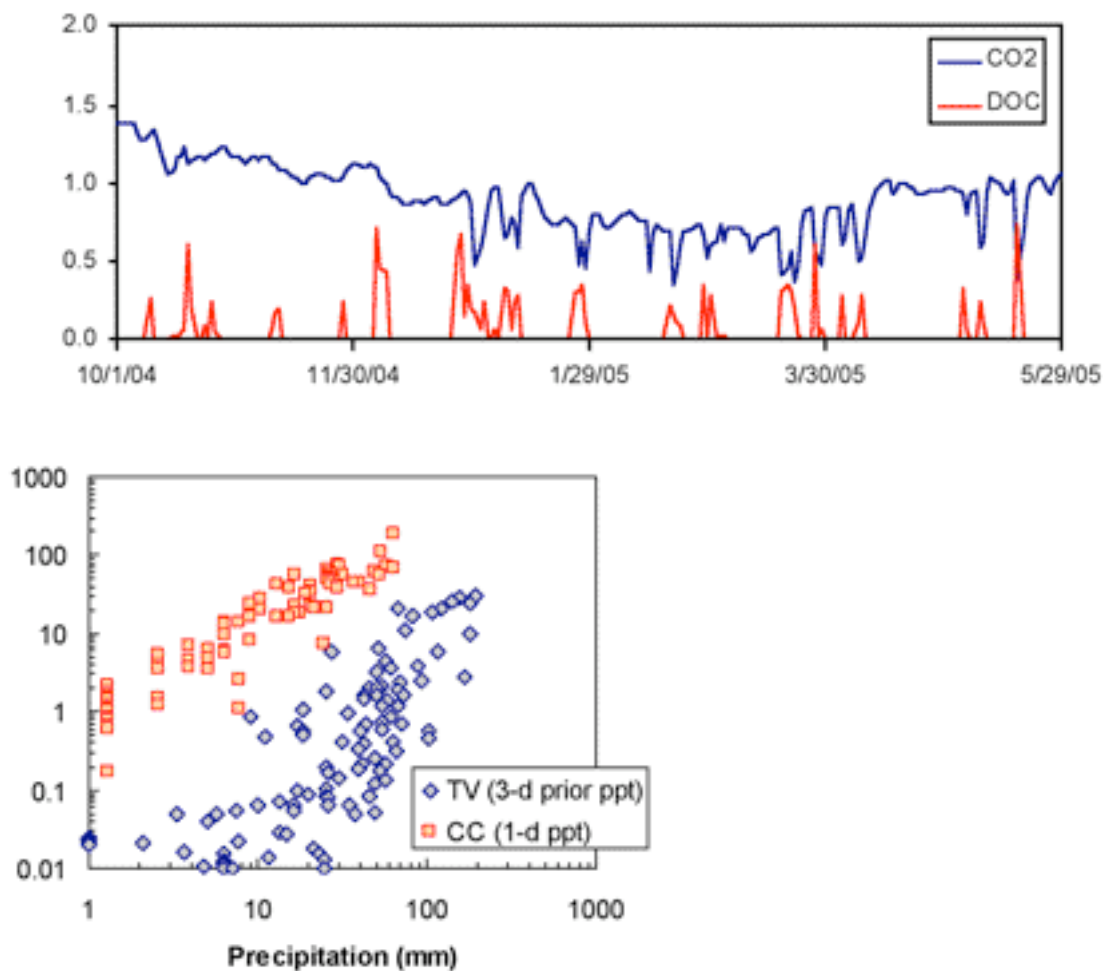


Figure 6. Comparison of daily CO₂ and DOC production (gC m⁻² d⁻¹) from the top 20 cm of soil at Caspar Creek (top panel). In the bottom panel, we have plotted the ratio of daily DOC production to CO₂ production (%) in the top 20 cm regressed against daily precipitation at Caspar Creek (red squares; R² = 0.87 with power fit) and plotted against 3-day prior cumulative precipitation at Tennessee Valley (blue diamonds; R² = 0.62 with exponential fit). For the water year (10/1/04 – 9/30/05), there were 102 days with measurable precipitation at CC and 91 days at TV.

At Caspar Creek, vertically infiltrating throughflow dominates in this deeply weathered catchment. Storm flow is rapidly transmitted to the channel via a series of macropores, effectively limiting the build-up in pore water pressure and thus shallow flow paths. Here, DOC concentrations are rapidly attenuated, due to adsorption reactions in the fine-textured

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soil. Given that the majority of water takes this tortuous path through the regolith, we do indeed find low concentrations of well-altered, chemically recalcitrant DOC in Caspar Creek with small fluctuations during storms. For the entire study period, DOC concentrations of water entering the stream network only ranged from 0.4 to 1.6 mgC L⁻¹ with $\delta^{13}\text{C}$ values between -23.3 and -25.2‰.

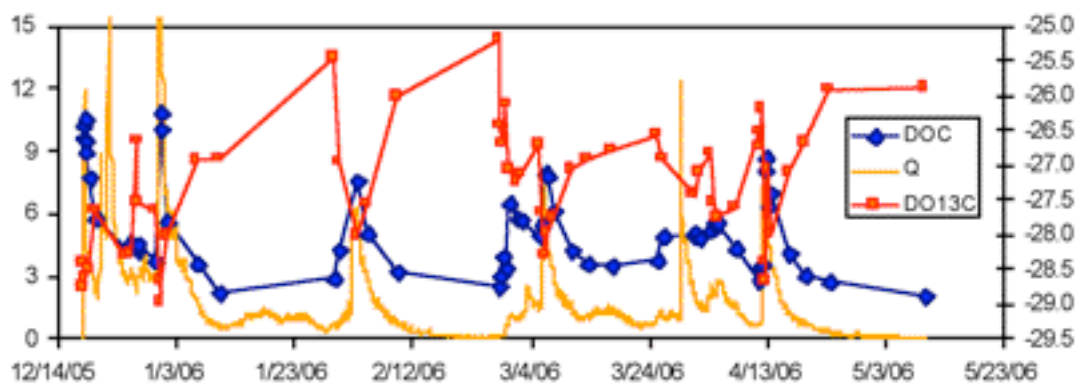


Figure 7. DOC concentrations and isotopic composition in stream water at Tennessee Valley plotted with discharge (L s⁻¹) in background.

At Tennessee Valley, the hydrology is much more dynamic, due to a combination of thinner regolith over more competent bedrock and a gentler slope. These factors act to produce exfiltrating pore water pressure gradients, resulting in lateral subsurface and saturated overland flow during storms. In line with previous work by Montgomery and Dietrich (1998), hydrometric readings (tensiometers and piezometers) and physical observations of extent of saturated overland flow indicate that nearly the entire colluvial hollow and a significant proportion of the upland area can be connected to the channel via shallow saturated flow paths during large storm events.

There are two major trends operating to produce the observed patterns in Tennessee Valley stream water chemistry observed in figure 7. There is a background trend showing the same seasonal depletion and/or shift in DOC source pool that we see in the soil water samples indicating a role for source limitations in controlling stream DOC chemistry here. However, superimposed over this is a highly dynamic response to storm events in which DOC concentrations can more than double with a concurrent shift in $\delta^{13}\text{C}$ and SUVA values, indicating “fresher” organic material. $\Delta^{14}\text{C}$ values range from about +100‰ during the first flush to less than -200‰ during base flow late in the season. Figure 8 highlights the strong correlation between DOC concentration and chemistry and discharge, indicating the dominance of hydrologic routing in controlling stream DOC chemistry.

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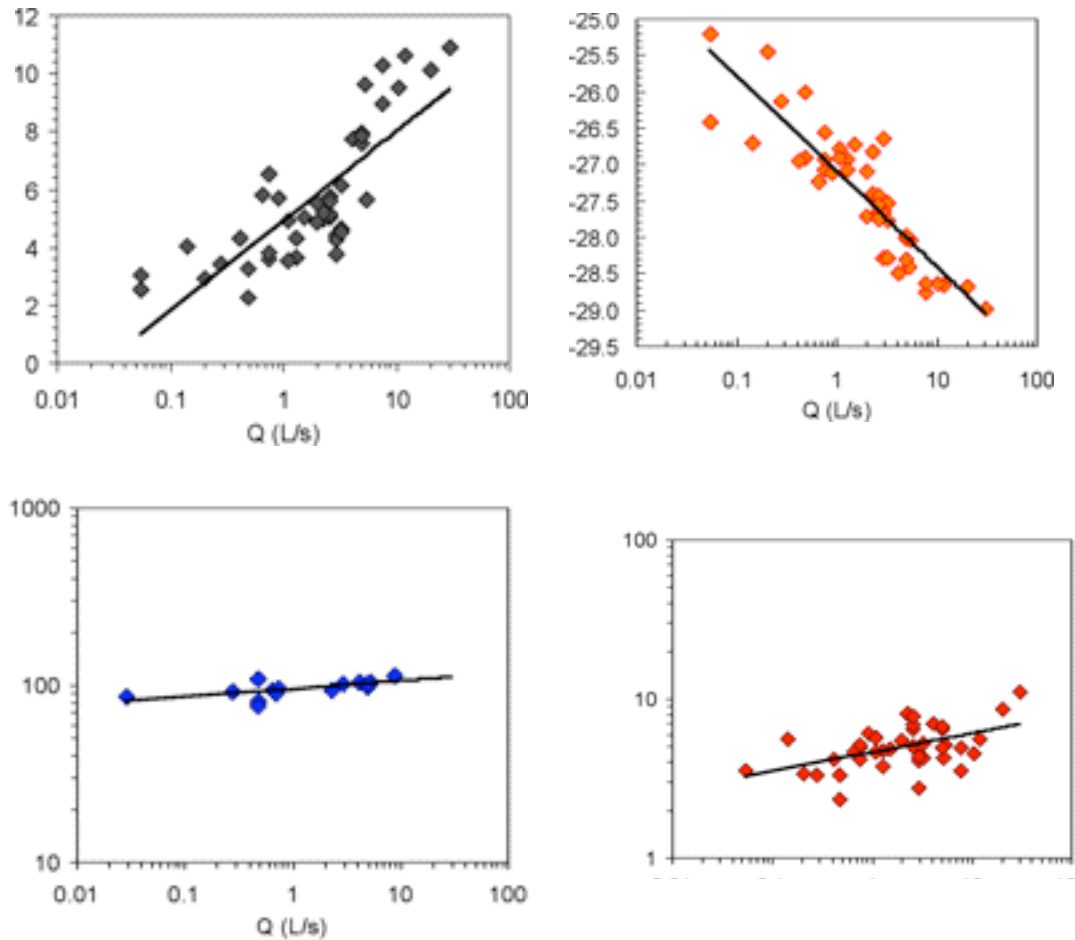


Figure 8. DOC concentration and chemistry vs. discharge relationships at Tennessee Valley: (a) concentration; (b) $\delta^{13}C$ values; (c) % modern C; and (d) DOC/DON ratio.

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