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

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Summary

The goal of this project is to characterize the dissolved organic carbon (DOC) pathways within two first-order watersheds in contrasting climates of coastal California in order to quantify: (1) the DOC redistribution of C within the soil profile (and storage at depths/locations subject to lower decomposition rates); (2) the magnitude of DOC losses relative to respiratory CO₂ losses; and (3) seasonal changes in DOC export (both in magnitude and composition) from these upland soils to the local stream network.

Rain water percolating through the upper soil horizons is effective at mobilizing significant quantities of DOC. Most of this DOC is rapidly adsorbed as water passes through the mineral horizons, resulting in small net losses of DOC from the soil. 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. We have found distinct and consistent chemical shifts in the DOC as it passed through the soil column at both sites. These trends are consistent with the hypothesis that DOC is progressively altered through continual exchange with native soil organic matter. Additionally, the size and composition of a potential DOC source pool appears to shift throughout the rainy season as shown by dropping DOC concentrations and changing δ¹³C values. DOC concentration and composition emerging at the channel head appear to be controlled by dominant hydrologic flow paths. High concentrations of fresher DOC are found during periods of saturated subsurface and saturated overland flow.

Objectives

This study addresses the role of dissolved organic carbon (DOC) in both translocating carbon within soils and in exporting carbon from terrestrial 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?
2. How do DOC fluxes determine the vertical carbon distribution within a soil?
3. How much soil carbon is lost annually in aqueous fluxes (DOC, DIC and POC) from a small source area?

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Figure 1. Vegetation, climate, parent material, average slope and dominant soil type of study sites.

Approach and Procedures

Two contrasting zero-order watersheds in Northern California have been selected for this study (fig. 1): 1) a second-growth redwood-Douglas fir dominated watershed (1.4 ha) in the Caspar 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 CO$_2$ concentrations and surface efflux rates are also being measured to contrast DOC versus respiratory losses.

Results

As communicated to the Kearney Foundation on July 11, 2003, we modified the scope of this project from its original form focusing on DOC fluxes along the Mendocino “ecological staircase” to these two watersheds. The primary reason for this shift in field sites was the wealth of previous hydrologic research and infrastructure at these two watersheds and the opportunity to link upland soil processes directly to stream losses.

Sampling began with the onset of rain in 2003 at the redwood site in Caspar Creek, but was delayed until February 2004 at Tennessee Valley due to delays in the National Park Service
permitting process. Laboratory work is nearly complete for samples from the 03/04 California water year (October – September).

![Graph](image)

**Figure 2.** Seasonal trends in DOC concentration and $\delta^{13}C$ values for selected samples from the Caspar Creek watershed. Stream flow data courtesy of the USFS Redwood Sciences Laboratory.

At the redwood-Douglas fir site (fig. 2), the forest canopy is a large source of DOC with average throughfall concentrations of 12 mgC L$^{-1}$. This throughfall picks up additional DOC as it percolates through the litter layer (O horizon leachate = 40 mgC L$^{-1}$). DOC concentrations quickly drop as this water moves through the mineral soil. Concentrations of DOC in water flowing out of the study watershed were only slightly elevated relative to rainfall (1.8 mgC L$^{-1}$). There is also a pronounced seasonal trend in this data, in which DOC concentrations seem to steadily drop as the rainy season progresses. Soil solution collected in the zero-tension lysimeters had significantly higher DOC concentrations than solution collected in the tension lysimeters, pointing to the importance of preferential flow paths rapidly transmitting DOC rich water deep into the mineral soil (fig. 3).
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Figure 3. Seasonally averaged DOC concentration at Caspar Creek (error bars = 1 s.e. \( n = 9 \)) showing the importance of macropore flow in transmitting water high in DOC deep into the mineral soil.

Using these data on DOC concentration coupled with rainfall, throughfall and soil moisture data, rough DOC fluxes can be calculated (fig. 4a). Water fluxes were calculated using a multilayer water balance model that solved for drainage from any given layer, \( D_i \):

\[
D_i = P_i - \Delta S_i - ET_i;
\]

where \( P_i \) is throughfall or drainage from an overlying layer, \( \Delta S_i \) is the change in storage based on soil texture, organic matter content and the continuous soil moisture record for that layer; and \( ET_i \) is the evapotranspiration from a given layer (\( ET \) measured at a nearby weather station was partitioned among soil horizons, after accounting for evaporation at the surface, by root distribution). This simple model yielded fluxes in magnitude and timing similar to what was observed at the stream weir (fig. 2). These preliminary data seem to indicate that the soils in Caspar Creek are fairly conservative in regards to dissolved organic C losses. However, leaching does play a significant role in translocating C deeper into the soil profile.

Soil solution DOC concentrations and fluxes were surprisingly high at the coastal prairie site (fig. 4b). Zero-tension lysimeter solution collected immediately below the main rooting zone (10 cm) averaged 9.8 mg C L\(^{-1}\) for samples collected in February and March 2004. Concentrations only dropped to 4.1 mg C L\(^{-1}\) in Prenart samples collected in the C horizon at 100 cm, similar to the concentration that was found in stream water samples. With the absence of a distinct litter layer, this large pool of DOC is likely a product of root exudates and high microbial turnover. This is a hypothesis that will be readily testable with the \( ^{13} \)C NMR data.

The stable carbon isotope data seems to support the hypothesis that DOC is progressively altered with depth. Figure 5a compares the \( ^{13} \)C value of the soil organic C and the DOC at both field sites site. At any given depth, DOC is isotopically more similar to slightly less processed soil organic matter closer to the surface than to the soil organic matter at the same depth. UV spectroscopic data (specific UV absorption (SUVA); the absorption at 254 nm normalized to the DOC concentration) for Caspar Creek is shown in figure 6. SUVA values increase through the
litter layer and then decrease with increasing depth in the mineral soil. This drop in SUVA is consistent with our hypothesis that DOC becomes more degraded and less like fresh plant material as water percolates through the soil profile.

The Δ\(^{14}\)C value of DOC follows a similar trend to that of the stable C isotope (fig. 5b) down through the A horizon at Caspar Creek (increasingly different with depth) but then appears to reach a consistent 14C age through the B horizon. A critical point in this data is that DOC at depth is significantly aged (Δ\(^{14}\)C ≈ 0 ‰); it is not simply young plant-derived material that has been transported as water percolates through the soil profile. Data from Tennessee Valley also support this conclusion – the DOC throughout the profile looks more like A horizon soil organic matter (Δ\(^{14}\)C ≈ 14 ‰) than fresh plant material (Δ\(^{14}\)C ≈ 70 ‰). The observation that there is less vertical differentiation in the Tennessee Valley data can perhaps be explained by the fact that during these mid-winter sampling times there was significant converging downslope flow instead of primarily vertically infiltrating fluxes as observed at Caspar Creek.

At the watershed scale, Tennessee Valley Stream exported 24 kgC ha\(^{-1}\) as DOC while Caspar Creek only exported about 8 kgC ha\(^{-1}\) as DOC. This figure is striking given that the DOC production at the prairie site was only about 25% as much in the redwoods (fig. 4). Two factors which help explain this trend are that 1) the soil is generally thinner at Tennessee Valley and 2) the slope gradient is much gentler leading to higher water tables and near surface saturated flow.
In fact, tensiometric and peizometric data indicate exfiltrating flow for the lower third of the hillslope transect at Tennessee Valley (data not shown). This is in contrast to Caspar Creek, where flow is predominately vertically infiltrating everywhere except the immediate toeslope and hollow axis.

**Figure 5.** (A) $\delta^{13}$C trends for mean mid-winter DOC samples (error bars = 1 s.d. (n=3)) and (B) $\Delta^{14}$C trends with depth for mid-winter composite DOC samples (analytical error ~ 4‰). Percolate is free flowing water collected in zero-tension lysimeters, while pore water samples were collected using Prenart tension lysimeters.

Based on isotopic and UV spectroscopic data, DOC exported from Tennessee Valley appears less altered than stream water DOC at Caspar Creek. Mean SUVA values for TV stream water was $5.43 \pm 0.53$ (s.d.) while at Caspar Creek mean SUVA = $3.42 \pm 0.72$. Stream water at Tennessee Valley had a $\delta^{13}$C range of -27 to -28‰ (fig. 5a), which corresponds closely with the isotopic values measured at the depth of saturated subsurface storm flow that was inferred from piezometric measurements at this measurement date. During low flow conditions at Caspar Creek, the $\delta^{13}$C value of stream water DOC was -24.0 to -24.5‰, similar to that of water in the
deep subsoil. During a large storm event with highly elevated pore pressures, the $\delta^{13}C$ value of stream water DOC dropped to -27‰, similar to litter and surface soil samples (fig. 2).

![SUVA (L-m/mgC) Trends with Depth in Soils at Caspar Creek](image)

**Figure 6.** Seasonally averaged specific UV adsorption (SUVA) trends with depth in soils at Caspar Creek. Error bars represent 1 standard error (n = 8-20).

**Discussion**

Over the course of the last two years, this project has matured into a thorough examination of the biogeochemistry of dissolved organic carbon bridging the fields of soil biogeochemistry and watershed hydrology. The above results can be summarized into three main categories: 1) the chemistry of soil and dissolved organic matter; 2) the role of DOC fluxes in the soil C cycle; and 3) hydrologic controls on C export in small mountainous catchments.

**Soil-DOC Chemistry**

As a start to a discussion of DOC chemistry, we must first determine what the main sources of DOC are for these ecosystems. The answer to this question is not entirely straightforward, especially in the coastal chaparral ecosystem. Even in coniferous forests with significant aboveground litter inputs and a distinct O horizon, the source of DOC entering the mineral horizon has been the subject of much debate (Currie and Aber 1997; Froberg et al. 2003; McDowell and Likens 1988; Qualls and Haines 1991). The two main candidates are leaching of freshly fallen litter or more microbially processed organic matter deeper within the O horizon. Laboratory leaching experiments indicate that the litter (mix of redwood and Douglas fir) rapidly loses 12% of its initial mass, 5% of initial C and 40% of its initial N (data not shown). Based on this result and litterfall rates, leaching of freshly fallen litter may contribute upwards of 50%
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of the total O horizon DOC flux. However, isotopic and spectroscopic data from leachate leaving the litter layer does not resemble fresh litter leachate.

DOC fluxes in grassland and chaparral ecosystems have rarely been studied, and there is no obvious source pool like the O horizon in coniferous systems. Throughfall beneath the dominant shrub, *Bacaras* sp., can be a significant source to the soils directly beneath these plants. However, the aerial coverage by *Bacaras* is less than 50% of the watershed and sampling locations were purposely located in open grassy patches, so the high DOC concentrations found at 10-cm depth could not be a result of throughfall. The rhizosphere (both root exudates and microbial products) seems to be an excellent candidate as the main site of DOC production in these soils. This is a hypothesis that we will try to test through an experiment analogous to the litter leaching experiment mentioned above.

As water percolates through the mineral soil, we found significant and consistent shifts in isotopic and spectroscopic properties of DOC. A comparison of SUVA versus $\delta^{13}$C of DOC (fig. 7) indicates that as the number of UV-adsorbing functional groups (aromatics, carboxylic and carboxylic) relative to DOC concentration decreases, the $\delta^{13}$C value of DOC increases. Interestingly, there are distinctly different relationships for the two field sites. Kalbitz et al. (2004) also found that greater SUVA values are associated with more negative $\delta^{13}$C values. However, these authors concluded that this drop in $\delta^{13}$C was due to a release of more decomposed organic material. In general, $\delta^{13}$C of soil organic C increases with increasing depth which is most often interpreted as being related to degree of decomposition/humification (Baisden et al. 2002; Brenner et al. 2001). Following this line of reasoning, we interpret the stable isotope and UV adsorption trends shown in figures 5 and 6 to represent an increase in the degree of decomposition of DOC as water moves through the soil.

![Figure 7](image_url)  
*Figure 7.* Seasonally averaged specific UV adsorption (SUVA) v. $\delta^{13}$C for Caspar Creek (blue diamonds) and Tennessee Valley (red circles) soil and stream water samples.

Are these depth trends in DOC chemical properties a result of exchange processes with native soil organic matter or a result of the biodegradation of the DOC in solution? If the latter process
was dominant, then it is unlikely that we would find $\Delta^{14}C$ values of DOC much older than that of fresh plant litter given that the mean residence time of water in the soil of similar mountainous catchments is on the order of days to months (Asano et al. 2002). In this scenario, the DOC would have to stay in the soil on the order of 10-150 years to account for the $\Delta^{14}C$ values at depth. To further investigate this question, we are preparing to conduct incubations to assess the biodegradability of DOC coupled with some simple tracer studies to quantify soil water residence times at our field sites.

The continual exchange with native soil organic matter appears to impart the distinct depth trends in $\delta^{13}C$, $\Delta^{14}C$ and SUVA that are highlighted in figures 5 and 6. Laboratory sorption experiments interpreted with the initial mass isotherm model (Nodvin et al. 1986; Neff and Asner 2001) support the concept of rapid exchange. The sorption results indicate that these soils have a high capacity to both adsorb (high clay content) and release organic carbon (high organic C content) from and into solution (data not shown).

Figure 2 highlights the distinct seasonal trends in selected samples from Caspar Creek. These results suggest that a pool of readily leachable organic compounds builds up in the litter layer during the dry summer months due to steady litterfall. This pool is then rapidly leached with the onset of winter rains with DOC concentrations dropping to quasi-steady state values by the middle of the rainy season. The seasonal trend in $\delta^{13}C$ values may indicate a shift in the composition of a DOC source pool towards more recalcitrant (higher $\delta^{13}C$ values) organic material. The drop in $\delta^{13}C$ values (towards more “fresh” looking organic material) and the slight rise in DOC concentrations in early spring coincide with the annual pulse of redwood cones falling to the forest floor.

New data from this fall/early winter at Tennessee Valley indicate that DOC concentrations and composition undergo a similar marked seasonal shift. DOC concentrations from early storm samples were found to be as high as 100 mgC L$^{-1}$ at 10-cm depth. This value can be compared to data from March and April storms of 2004 in which the concentrations were only 5-10 mgC L$^{-1}$. Although the seasonal pattern at both sites seems similar, the mechanisms are likely to differ. There is little productivity during the summer months at Tennessee Valley – most of the grasses are dormant and the soils are extremely dry. The new grasses emerge shortly after the first significant rain storm. It is this period of intense productivity that is likely the cause of the elevated DOC concentrations.

**Soil C Cycle**

For soil C to be effectively sequestered beyond a timescale of a few decades, this C must become incorporated into the subsurface mineral horizons. Leaching of DOC represents a direct mechanism that holds the potential of moving significant quantities deep into the soil. Neff and Asner (2001) found that when DOC fluxes were incorporated into a terrestrial biogeochemical model, total soil C storage increased 25% for a temperate forest soil.

In the redwood forest with distinct soil horizonation, we found that significant quantities of organic C are translocated down the soil profile in the dissolved phase (fig. 4a). Leaching from the litter layer represented nearly 20% of annual litter inputs. If we make the assumption that all DOC loss as it percolates through the soil is due to adsorption to mineral and organic matter
surfaces, then incorporating DOC fluxes alone into a simple steady-state soil C turnover model can nearly explain the apparent turnover times of the A and B horizons shown in figure 4:

$$\tau = \frac{C_{\text{stock}}}{(\text{DOC}_{\text{add}} - \text{DOC}_{\text{loss}})}$$

For example, 450 kgC ha\(^{-1}\) yr\(^{-1}\) entered the A horizon as DOC while only 80 kgC ha\(^{-1}\) yr\(^{-1}\) leached out of the A horizon leading to a net input of 370 kgC ha\(^{-1}\) yr\(^{-1}\). Dividing this value into the C content of the A horizon (63 tC ha\(^{-1}\)) yields a turnover time of 170 years. This value is remarkably similar to the value of 150 years derived using a multi-pool model based on the incorporation of the “bomb spike” of \(^{14}\)C into the soil (Trumbore et al. 1996). If we conduct this exercise for the B horizon, we find that DOC flux alone can more than explain the \(^{14}\)C-derived turnover time of 5,000 years. While this is an admittedly simplistic view of soil C dynamics, it does highlight the importance of DOC as a potential mechanism for regulating long-term C sequestration.

This model is not quite as applicable to the coastal chaparral site because, as discussed above, the source pool for DOC is not straightforward. It may be that the upper A horizon is a net source of DOC and the lower horizons are the dominant sink given the lack any overlying litter layer. Regardless of the interpretation, what is most striking about figure 4b is the quantity of DOC moving in this predominately grassland soil. In fact, these presented fluxes are likely a large underestimate of the annual fluxes given that we were lacking early season DOC measurements, which now appear to be much greater than the values from later in the rainy season.

In terms of an annual input/output budget for the entire soil, DOC losses are minor relative to respiratory CO\(_2\) losses. DOC flux out of the B horizon is less than 1% of estimated soil CO\(_2\) efflux. We have been calculating soil respiration using a CO\(_2\) gradient-diffusion modeling approach outlined by Davidson and Trumbore (1995) that is appropriate for the highly aggregated clay-rich soils at our field sites. These authors presented a model that partitions soil air-filled porosity into inter- and intra-aggregate porosity, each with distinct diffusivities, by making the assumption that all intra-aggregate pores are water filled when soil moisture is at or above field capacity. By utilizing the CO\(_2\) gradient approach, we take the view that although CO\(_2\) is produced biotically within the soil, it is physical processes (i.e. diffusion or leaching) that remove the CO\(_2\). This is in contrast to the typically held views that soil efflux is only controlled by controls on root respiration and microbial activity (e.g., temperature, moisture, substrate availability). Over the course of the year, CO\(_2\) gradients varied by a factor of about three, but the diffusivity (which is controlled by soil water content) varied by twice this number (data not shown), therefore exerting a much greater control on soil respiration rates.

Utilizing this approach to calculate soil respiration, we are finding that respiration is severely diminished during the mid-winter months when the soils are mostly saturated with water. This is especially true in the converging hollows. Periodic direct soil respiration chamber measurements seem to support these findings. At times of saturated conditions, we might expect the short-term dissolved C losses (both organic and especially inorganic) to make up a much greater percentage of overall C loss. When the soil is nearly saturated, soil CO\(_2\) concentrations often build up to greater than 2% due to the reduction in diffusivity with corresponding dissolved inorganic carbon (DIC) values between 5 and 10 mgC L\(^{-1}\). It is exactly during the periods that gaseous
losses are retarded that dissolved losses are expected to be the greatest. DIC losses can equal or even exceed respiratory losses on shorter time scales (days to weeks). This is an interesting avenue of research that we are currently pursuing in more detail.

**Soil-Stream Connections**

In the previous two sections, we’ve pretty much assumed vertical infiltration of water through the soil. Tensiometric and peizometric data for soils on the ridges and sideslopes support this notion, and we limited the above data analysis to those plots that conform to this pattern. However, as we travel down slope into the convergent hollows, pore water pressure rapidly increases and more and more water flow becomes slope parallel or even upward (i.e., exfiltrating). The upslope contributing area (i.e., the region of saturated soil where flow is predominately slope parallel) to the channel head will vary greatly over the course of the winter season depending on storm intensity, duration and antecedent soil moisture conditions. The flow path that water takes on its way to the stream network is hypothesized to have a large impact upon the concentration and composition of stream DOC. By focusing on these two small catchments, this study truly affords a great opportunity to directly address the role of upland soils in controlling stream chemistry in the small mountainous watersheds of coastal California.

At Caspar Creek, the hillslope soils are thick and the hydraulic conductivity is great enough that water flow is predominantly vertical throughout the soil horizons well into the saprolite. Even during the largest storms, pore pressures do not rise significantly, except in the immediate vicinity of the main hollow axis. The majority of water entering the stream network is through a series of macropores (or pipes) in the saprolite (Albright 1995) that are extremely effective in rapidly transmitting large volumes of water into the channel. In fact for the 03/04 winter, the area-weighted discharge through the main gauged soil pipe (drainage area = 1.14 ha) and the nearest downstream weir (area = 16 ha) were nearly equal at 525 mm. These soil pipes effectively limit the build up of soil pore pressure and shallow soil flow paths. These hydrologic conditions are reflected in the consistently low DOC concentrations found flowing out the soil pipes and in the stream. Despite the low DOC concentrations, DOC composition does seem to vary between low and high flow conditions. This is particularly apparent with the samples collected during the Feb. 18, 2004, storm – the δ13C value dropped by nearly 2‰ from baseflow to stormflow with a concurrent increase in the specific UV adsorption from 3 to nearly 10.

A very different picture is emerging at Tennessee Valley. Here, due to the thinner, denser soils and gentler slope, pore water pressures build up significantly in a much larger upslope contributing area leading to significant saturated subsurface flow and even saturated overland flow during storms (Montgomery and Dietrich 1995). Tensiometric data indicate that exfiltrating gradients are found along most of the lower half of a hillslope transect from ridge to channel head (data not shown). Consistent with our hypothesis that near-surface flow paths bypass most DOC removal mechanisms, we find that DOC concentrations in the stream are as high as 13 mgC L⁻¹ during peak flow dropping to about 4 mgC L⁻¹ during baseflow.

**Conclusions**

While much progress has been made, this project is very much still a work in progress. Thanks to the continued support of the Kearney Foundation (Grant #2004.215 to RGA) we have the
resources to fully develop the concepts highlighted in the preceding discussion. We have also received a Doctoral Dissertation Improvement Grant from the NSF to collaborate with Dr. Jeffrey Baldock at the CSIRO, Land and Water Division in Australia, to conduct $^{13}$C-NMR spectroscopic analyses which will really complement the isotopic data that we have been collecting on soil-DOC interactions.

An unexpected benefit of this project is that the field instrumentation lends itself to any number of geochemical studies. Dr. Kyungsoo Yoo, a post-doctoral fellow in our lab group, compared soil profile derived chemical weathering rates to those obtained from soil solution samples. This weathering work was an extension of a study in Australia (NSF Ecosystems grant to RGA). We also conducted a second major collaboration with Dr. Kathleen Lohse detailing the biogeochemistry of nitrogen at these two sites.

**References**


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