The relationship between soil heterotrophic activity, soil dissolved organic carbon (DOC) leachate, and catchment-scale DOC export in headwater catchments

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Abstract. Dissolved organic carbon (DOC) from terrestrial sources forms the major component of the annual carbon budget in many headwater streams. In high-elevation catchments in the Rocky Mountains, DOC originates in the upper soil horizons and is flushed to the stream primarily during spring snowmelt. To identify controls on the size of the mobile soil DOC pool available to be transported during the annual melt event, we measured soil DOC production across a range of vegetation communities and soil types together with catchment DOC export in paired watersheds in Summit County, Colorado. Both surface water DOC concentrations and watershed DOC export were lower in areas where pyrite weathering resulted in lower soil pH. Similarly, the amount of DOC leached from organic soils was significantly smaller (p < 0.01) at sites having low soil pH. Scaling point source measurements of DOC production and leaching to the two basins and assuming only vegetated areas contribute to DOC production, we calculated that the amount of mobile DOC available to be leached to surface water during melt was 20.3 g C m⁻² in the circumneutral basin and 17.8 g C m⁻² in the catchment characterized by pyrite weathering. The significant (r² = 0.91 and p < 0.05), linear relationship between over-winter CO₂ flux and the amount of DOC leached from upper soil horizons during snowmelt suggests that the mechanism for the difference in production of mobile DOC was heterotrophic processing of soil carbon in snow-covered soil. Furthermore, this strong relationship between over-winter heterotrophic activity and the size of the mobile DOC pool present in a range of soil and vegetation types provides a likely mechanism for explaining the interannual variability of DOC export observed in high-elevation catchments.

1. Introduction

Organic carbon in the aquatic environment of headwater catchments primarily is derived from the upper organic soil horizons in most temperate and boreal ecosystems. A significant component of this carbon is in the form of dissolved organic carbon (DOC) [Schiff et al., 1990], the vast majority of which is transported to the aquatic environment during spring snowmelt [Hornberger et al., 1994; Boyer et al., 1997]. This carbon not only provides the major source of energy for non-photosynthetic biological activity [Webster and Meyer, 1997; Wetzel, 1992] but also is a major control on the mobility of in-stream metal concentrations in systems impacted by point source contaminants [McKnight and Bencala, 1990]. While a qualitative understanding of DOC transport from terrestrial to aquatic environments has been forged [Lewis and Grant, 1979; Baron, 1991; Denning et al., 1991; Mulholland and Hill, 1997], a quantitative description of the processes controlling the quantity, composition, and timing of carbon available to be transported to the stream is important for understanding the aquatic ecology and surface water chemistry in these catchments [McKnight and Bencala, 1990; McKnight et al., 1992; Boyer et al., 1997].

A simple conceptual model describing the delivery of allochthonous DOC to surface water can be constructed by considering three processes: (1) partial decomposition of terrestrial fixed carbon producing soluble DOC, (2) hydrologic transport of DOC from the terrestrial environment to surface water, and (3) modification of both quantity and composition of DOC during transport. Complicating this model are the multiple and non-independent effects that climatic and environmental variability have on the production of organic carbon in the terrestrial environment, the decomposition of fixed carbon in the soil environment, and the transport of carbon to surface waters. Substantial progress has been made in quantifying both hydrologic transport of DOC and in-stream reactions of DOC in the naturally acidic Snake River and the circumneutral Deer Creek watersheds in Summit County, Colorado. This work provides a context for evaluating the controls on the size of the mobile soil DOC pool.

Recently, Hornberger et al. [1994] and Boyer et al. [1996] developed a quantitative model describing the hydrologic transport of terrestrial DOC from soil to the aquatic environment in these catchments. Using mass balance constraints of both water and soil water DOC amounts, they demonstrated...
that a significant fraction of catchment soils must contribute to measured annual surface water export of DOC. While mineral soil horizons retain a large portion of DOC leached from organic soils [McDowell and Wood, 1984], DOC sorption on metal oxides on the stream bed, and possibly in the subsurface, of the naturally acidic Snake River catchment is responsible for a further decrease in surface water DOC concentrations when compared to Deer Creek [McKnight et al., 1992]. DOC concentrations in the Snake River remain roughly half those measured in Deer Creek throughout the snowmelt period, while discharge increases several orders of magnitude. Sorption processes would not be expected to remove a consistent percentage (~50%) of in-stream DOC over the range of discharge observed in these systems, suggesting the possibility of a difference in the size of the mobile DOC pool. Furthermore, the long-term surface water chemistry record from both of these catchments identifies significant interannual variability in DOC concentrations and mass flux [McKnight and Bencala, 1990; Homberger et al., 1994; Boyer et al., 1997, 1998], suggesting that surface water DOC concentrations may be affected by controls on the production of the mobile soil DOC before melt.

The annual cycle of snowpack accumulation and snowmelt provides a unique opportunity for separating the controls on DOC production in soil from DOC transport by consistently flushing the soil of accumulated DOC each spring. Preceding this snowmelt-induced flush of soil DOC pools, there is a long period of snow cover where DOC accumulates in the soil following the input of fixed carbon to the soil during plant senescence and litter fall. Recent work has identified high levels of soil heterotrophic activity and litter decomposition in the soil organic horizons under snow cover [Sommersfeld et al., 1993; Hobbie and Chapin, 1996, Brooks et al., 1996, 1997, 1998], suggesting the potential for significant heterotrophic processing of soil carbon under snow. The majority of nonliving organic carbon within these environments is contained in the organic layer, which serves as the major source of DOC in soil water [Boyer et al., 1997]. Soil water DOC concentrations are high at the initiation of snowmelt and decrease dramatically as spring snowmelt flushes soil DOC to surface water early in the snowmelt period [Boyer et al., 1997].

In this work we use paired catchments having similar climate and vegetation but different bedrock geology to evaluate process-level controls on the size of the mobile DOC pool available to be leached to surface water during melt. Within the context provided by in-stream DOC concentrations and catchment-scale DOC export we examined the first process in our conceptual model, i.e., the partial decomposition of terrestrially fixed carbon-producing soluble DOC. Our working hypotheses were that DOC production within the soil would be related to overwinter soil heterotrophic activity and that overwinter heterotrophic activity and mobile DOC production would be lower in the acidified Snake River catchment.

2. Study Site

The upper Snake River and Deer Creek catchments have areas of 11.8 and 10.5 km², respectively, in Summit County, Colorado (Figure 1). Elevation ranges from 3200 to 4000 m in each catchment. The catchments drain to the north and form the larger Snake River at the confluence [Theobald et al., 1963]. The catchments contain a similar mixture of slope, aspect, and vegetation, with approximately half of their area above the treeline. The highest elevations are characterized by alpine meadows that are a mixture of grass, sedge, forb, and dwarf willow communities interspersed with exposed bedrock and talus. Lower elevations are characterized by subalpine forests containing a mixture of pine-spruce-fir forest and subalpine meadow dominated by grass, sedge, willow, and birch communities. The majority of the area adjacent to the stream in both catchments is subalpine meadow. Discharge is similar for the two streams with baseflow ranging from 0.1 to 0.2 m³ s⁻¹ and peak discharge during snowmelt between 1.0 and 2.0 m³ s⁻¹ [Boyer et al., 1998].

Bedrock geology results in one major difference between the two catchments. The Deer Creek catchment is underlain by Swandyke hornblende gneiss resulting in circumneutral weathering products, while a large portion of the Snake River is underlain by granitic rocks of the Idaho Springs formation containing large amounts of disseminated pyrite, resulting in acidic weathering products [Theobald et al., 1963]. The majority of both the forest and subalpine meadow environments in the Snake River is located in areas with acid-generating parent materials (Figure 2 and Table 1).

Soils are classified as mixed typic Cryochrepts and vary in depth from ~0.3 to 1.0 m (National Resource Conservation Service, Summit County, Colorado, personal communication, 1980). Organic carbon below the A horizon is typically <1% by weight. The O horizon ranges from 0 to 10 mm, and the A horizon ranges from 80 to 100 mm in depth. The pH of this layer in a 1:1 (weight:volume) deionized water (DI) slurry ranges between 4.5 and 5.6 in the Snake River catchment and from 5.8 to 6.5 in the Deer Creek catchment. The bulk density of the upper 80–100 mm (A horizon) averaged 0.55 g cm⁻³, with no significant difference among the sites.

Surface water pH in the Snake River ranges from 3.2 to 4.5, while pH in Deer Creek ranges from 6.8 to 7.7. Surface water DOC concentrations in Snake River are less than half of those in Deer Creek, at least partially because of sorption of DOC by metal oxides [McKnight et al., 1992].
3. Methods

Stream water samples during the 1996 water year were collected weekly during snowmelt and biweekly to monthly during the rest of the year. Sampling sites were located just above the confluence in each of the two streams. Additional stream water chemistry samples were collected during two synoptic sampling periods performed during snowmelt, one on 17 May during the ascending limb of the snowmelt hydrograph and one on 8 July during the descending limb of the snowmelt hydrograph. These synoptic sampling events were designed to identify spatial patterns in DOC delivery to the stream along an elevational gradient from the alpine meadows to the confluence and from above and below areas subject to pyrite weathering in the Snake River catchment. During each synoptic, water samples were collected at 10 sites located at ~400 m intervals in the main channel of each stream and at 5 to 12 major, discrete inflows from above the treeline down to the confluence.

All water samples were filtered immediately after collection through Whatman glass fiber (GF-F) filters and stored at 4°C in pre-combusted amber glass bottles until analysis on a Dornan carbon analyzer. (The use of brand names does not constitute an endorsement by the USGS.) Discharge measurements were made weekly to monthly intervals and used to create a stage-discharge relationship for the gages located above the confluence. Gages consisted of a bubbler gas purge system connected to a pressure sensor. Pressure was recorded hourly and converted to stage readings on a data logger. The stage-discharge relationship was used to calculate mean daily discharge for the two catchments by averaging these hourly data.

Soil production of mobile DOC was measured at six experimental plots established in January 1996, one in each of the three major vegetated landscape types of each catchment: alpine meadow, subalpine forest, and subalpine meadow. The paired landscape sites in each basin were chosen to be as similar in vegetation, elevation, aspect, and snowpack regime as possible. Extreme avalanche danger precluded establishment of sites in the nonacidic portions of the Snake River catchment subalpine meadow or forest soils. Snowpits were dug to the soil surface and three soil cores, of 50-mm diameter, were collected from the O and A horizons (~80–100 mm deep) for initial site characterization. Concurrently, three intact blocks of soil measuring ~200 by 300 by 80 mm deep were removed and two resin collectors designed to capture DOC leached from soil were placed in the underlying soil, and the soil blocks were immediately replaced. This yielded a total of 6 collectors in each of the six plots. Resin collectors were retrieved immediately after the sites became snow free in late June and early July. A late-season avalanche moved the site marker at the Snake River alpine soils, and the collectors could not be located.

Resin collectors consisted of mixed-bed ion exchange resin bags contained in acid-washed, 35-mm diameter radiator hose open at both top and bottom to collect leachate from the overlying O and A horizons. Each collector contained 20 mL (wet volume) of mixed cation and anion exchange resins (15–50 mesh) and are similar to those used to measure N export from surficial soil in other systems [Hart and Binkley, 1984; DiStefano and Gholz, 1986; Hart and Gunther, 1989; Fisk and Schmidt, 1995; Brooks et al., 1996]. Immediately after retrieval, resins were removed from the collectors, air dried overnight in the laboratory, and extracted with 2N KCl (1:5, weight:volume) by shaking at 250 rpm for 60 min. Extracts were filtered through Whatman GF-F filter paper and stored at 4°C until analyzed.

On April 18 and 19, shortly before snowmelt, snowpits were dug to the soil surface adjacent to each of the experimental plots, and soil samples were collected from the upper 80 mm of soil for extractable DOC. Immediately upon return from the field, soils were homogenized using a 2-mm sieve, and subsamples were extracted with deionized water (1:5, weight:volume) by shaking at 250 rpm for 60 min. Extracts were filtered through Whatman GF-F filters and stored at 4°C until analyzed. Additional soil subsamples were dried at 60°C for percent soil C and N analyses on a Carlo Erba CHN analyzer.

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**Table 1. Physical Characteristics of the Snake River and Deer Creek Catchments, Summit County, Colorado**

<table>
<thead>
<tr>
<th></th>
<th>Snake River</th>
<th>Deer Creek</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area</td>
<td>11.76 km²</td>
<td>10.50 km²</td>
</tr>
<tr>
<td>Elevation</td>
<td>3350–4150 m</td>
<td>3350–4150 m</td>
</tr>
<tr>
<td>Discharge Baseflow</td>
<td>0.1–0.3 m³ s⁻¹</td>
<td>0.1–0.3 m³ s⁻¹</td>
</tr>
<tr>
<td>Discharge Peak</td>
<td>1.0–2.0 m³ s⁻¹</td>
<td>1.0–2.0 m³ s⁻¹</td>
</tr>
<tr>
<td>Surface water pH</td>
<td>3.2–4.5</td>
<td>6.7–7.7</td>
</tr>
<tr>
<td>Soil pH</td>
<td>4.5–5.6</td>
<td>5.8–6.3</td>
</tr>
<tr>
<td>Landscape Type</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpine meadow</td>
<td>38%</td>
<td>46%</td>
</tr>
<tr>
<td>Subalpine forest</td>
<td>15%</td>
<td>NA</td>
</tr>
<tr>
<td>Acidified</td>
<td>15%</td>
<td>NA</td>
</tr>
<tr>
<td>Nonacidified</td>
<td>5%</td>
<td>34%</td>
</tr>
<tr>
<td>Subalpine meadow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acidified</td>
<td>5%</td>
<td>NA</td>
</tr>
<tr>
<td>Nonacidified</td>
<td>2%</td>
<td>5%</td>
</tr>
<tr>
<td>Exposed rock/talus</td>
<td>35%</td>
<td>15%</td>
</tr>
</tbody>
</table>
Soil pH was measured in a 1:1 (weight:volume) soil:deionized water slurry. All DOC samples were analyzed on a Dohrmann carbon analyzer.

Soil heterotrophic activity under the snowpack was estimated by measuring CO₂ flux through the snow at weekly intervals throughout the winter. Ten flux measurements were made on each date in each landscape type. Three measurements were made within each experimental plot, and seven others were made within the same landscape type at other locations within the catchment. On any date there were no statistically significant differences between the three flux measurements made at each soil sampling site and the seven flux measurements at the corresponding landscape type, so all ten measurements were averaged into the values presented. Fluxes were calculated using a steady state diffusional model based on vertical CO₂ concentrations through the snowpack and depth, porosity, tortuosity, temperature, and pressure [Sommerfeld et al., 1993; Brooks et al., 1996, 1997].

The potential volume of infiltrating meltwater to each site was measured at maximum snow accumulation. Snowmelt was dug to the soil surface adjacent to each plot during the last week in April, and snow density was measured in 10-cm increments using a 1 L stainless steel cutter [Elder et al., 1991; Williams et al., 1996]. Snow water equivalence (SWE) at each site was calculated as snow depth times density measurement from the adjacent pit. Differences in pH, DOC leachate, DOC concentrations, and discharge between paired sites were determined using protected two-tailed t tests.

4. Results

Spring snowmelt in 1996 resulted in two distinct peaks in discharge, a sharp, early peak in mid-May and a second, broader peak in June and July (Figure 3). Stream water DOC concentrations increased during the ascending hydrograph in each basin, reaching maxima several days before the two peaks in discharge. Maximum discharge in the Snake River was higher than in Deer Creek, but the duration of high discharge was 10 days shorter. DOC concentrations at the gage in Deer Creek (mean 3.8, standard deviation 1.2, and range 2.5-6.9) were significantly (p < 0.05) higher than at the Snake River gauge (mean 1.1, SD 0.4, and range 0.4-1.8). Discharge during baseflow ranged between 0.02 and 0.10 m³ s⁻¹ for both streams, and DOC concentrations ranged from 0.5 to 1.0 ppm in the Snake River and from 2.4 to 2.7 ppm in Deer Creek. Annual DOC export calculated using weekly to monthly stream water samples and daily discharge and assuming only vegetated area contributed to DOC production was 0.9 g C m⁻² yr⁻¹ for the Snake River and 2.2 g C m⁻² yr⁻¹ for Deer Creek. The majority of this export, 70% for the Snake River and 80% for Deer Creek, occurred between April 15 and July 15.

DOC concentrations in both catchments were higher during the first synoptics than during the second, consistent with patterns observed at the confluence (Table 2). Inflow DOC concentrations during both synoptics in the Snake River catchment were higher at the sites above the area of pyrite weathering than at lower elevations, suggesting that alpine areas were a larger source of DOC to the stream than forest and subalpine meadows (Table 2). In contrast, there was no clear pattern to DOC concentrations in Deer Creek inflows, suggesting a relatively constant source above and below the treeline. During the second synoptics both inflow and in-stream DOC concentrations above the area of pyrite weathering in Snake River were similar to concentrations at the higher elevations of Deer Creek.

SWE at the end of April ranged from 53.7 cm of water at the Snake River forest sites to 74.6 cm of water at the Deer Creek alpine sites (Table 3). While the amount of water potentially available to infiltrate through the upper soil horizon at melt increased along an elevational gradient with more water present in the snowpack at alpine sites than at either forest or meadow sites, there was no significant difference in corresponding forest, meadow, and alpine sites between the two catchments.

The initial characterization of soil at the six sampling sites revealed several differences between the two catchments (Table 3). Mean soil pH ranged from a low of 4.5 at the Snake River meadow to a high of 6.5 at the Deer Creek meadow sites. Soil pH was significantly lower at the forest (p < 0.05) and meadow (p < 0.001) Snake River sites affected by pyrite weathering when compared to corresponding sites in Deer Creek. There was no significant difference in pH between the alpine soils of the two catchments (Table 3). Bulk soil C in the A horizon ranged from 3.9 to 11.2 kg C m⁻² with no clear pattern based on landscape type (Table 3). While alpine soils in both catchments had a similar carbon content, the lower pH soils from the Snake River forest contained more carbon than Deer Creek forest soils. There was not a consistent difference between the catchments based on pH, as Snake River meadow
soils had lower soil carbon content than Deer Creek meadow soils.

DI-extractable soil DOC immediately before melt was quite variable with no significant differences between the catchments. In general, meadow soils had the highest concentrations of DI-extractable DOC, but there was no relationship between extractable DOC and soil pH or soil carbon content. The amount of DOC leached from the A horizon during melt (Table 3) was related to the amount of DOC extracted from soil collected immediately before melt using deionized water ($r^2 = 0.56$) and $p < 0.05$ (Figure 4). Measurements of DOC leachate were much lower than the amount of extractable DOC at all sites, but there was no relationship between snow water equivalence available to infiltrate soil at a site and the amount of DOC leached. However, there were differences in DOC leachate between the paired landscapes in the two basins (Table 3). The 10.8 ($\pm 0.3$) g C m$^{-2}$ leached from the upper soil horizon at Snake River forest sites was significantly ($p < 0.05$) less than the 19.0 ($\pm 2.6$) g C m$^{-2}$ leached from Deer Creek forest soils. Similarly, the 22.1 ($\pm 2.0$) g C m$^{-2}$ leached from the upper soil horizon at Snake River meadow sites was significantly ($p < 0.05$; protected t test) smaller than the 28.5 ($\pm 2.2$) g C m$^{-2}$ leached from Deer Creek meadow soils. Total DOC leachate from soils in the Snake River catchment of $134.1 \times 10^6$ g C was less than the $182.1 \times 10^6$ g C from Deer Creek soils (Table 3). Assuming only vegetated areas contribute to DOC production, catchment-scale DOC leachate amounts were 178 g C m$^{-2}$ for Snake River soils and 203 g C m$^{-2}$ for Deer Creek soils.

Mean daily CO$_2$ flux ranged from 125 ($\pm 10$) mg C m$^{-2}$ d$^{-1}$ to 386 ($\pm 40$) mg C m$^{-2}$ d$^{-1}$ (Figure 5). Throughout the winter, mean daily fluxes within each catchment were smaller at the forest sites than either alpine or subalpine meadow sites. Fluxes at both forest and meadow sites in the Snake River catchment were significantly lower than from corresponding Deer Creek mountainous, but there was no significant difference between flux at the alpine sites in the two catchments (Figure 5). This pattern is similar to the DOC leachate data obtained from the buried resin collectors, and comparing these data sets identifies a strong linear relationship ($r^2 = 0.91$ and $p < 0.01$) between CO$_2$ flux and DOC leached from organic soils during melt (Figure 6).

5. Discussion

Surface water DOC concentrations throughout snowmelt, both at the confluence and during the two synoptic sampling events, were consistent with the soil flush of DOC during the ascending hydrograph that characterizes DOC export in these catchments [Hornberger et al., 1994; Boyer et al., 1997]. The 70–80% of annual export that occurred from April 15 to July 15 also is consistent with the long-term record from these catchments [Boyer et al., 1998]. While the time constant for catchment-scale flux is ~3 months, individual locations are flushed of accumulated DOC in 10–30 days [Boyer et al., 1997]. The rapid flush of soil DOC early during melt and similar amounts of water in the snowpack in the two catchments are consistent with soil-based controls on the size of the mobile DOC pool as a possible explanation for the lower DOC concentrations and export in the Snake River. The timing of this export indicates that soil processes occurring during the pre-

### Table 2. Stream Water Dissolved Organic Carbon (DOC) Concentrations in Snake River and Deer Creek, Summit County, Colorado

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>DOC at Confluence</th>
<th>Early Snowmelt (May 17)</th>
<th>Late Snowmelt (July 8)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Instream</td>
<td>Inflows</td>
<td>Instream</td>
</tr>
<tr>
<td>Snake River</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Above pyrite weathering (alpine)</td>
<td>1.1 (0.4)</td>
<td>1.3 (0.1)</td>
<td>1.2 (0.2)</td>
</tr>
<tr>
<td>Below pyrite weathering (below treeline)</td>
<td>1.0 (0.5)</td>
<td>1.0 (0.5)</td>
<td>0.6 (0.4)</td>
</tr>
<tr>
<td>Dear Creek</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpine</td>
<td>3.8 (1.2)</td>
<td>3.1 (0.1)</td>
<td>1.4 (0.3)</td>
</tr>
<tr>
<td>Below treeline</td>
<td></td>
<td>3.1 (0.3)</td>
<td>1.7 (0.4)</td>
</tr>
</tbody>
</table>

Concentrations are in ppm. Values are mean, Standard Deviations (SD) are given in parentheses.

### Table 3. Selected Physical and Chemical Properties of the Organic Soil Horizon in the Six Study Plots in the Snake River and Deer Creek Catchments, Summit County, Colorado

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>pH</th>
<th>C, kg m$^{-2}$</th>
<th>N, kg m$^{-2}$</th>
<th>Snow Water Equivalents (SWE), cm H$_2$O$^\circ$</th>
<th>Extractable DOC, g C m$^{-2}$</th>
<th>Leachate DOC, g C m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Snake River</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpine</td>
<td>5.6 (0.3)</td>
<td>6.5 (2.5)</td>
<td>0.47 (0.12)</td>
<td>68.9</td>
<td>95 (12)</td>
<td>10.8 (0.7)</td>
</tr>
<tr>
<td>Forest</td>
<td>5.2 (0.3)</td>
<td>11.2 (4.6)</td>
<td>0.52 (0.18)</td>
<td>53.7</td>
<td>178 (72)</td>
<td>22.1 (4.9)</td>
</tr>
<tr>
<td>Meadow</td>
<td>4.5 (0.2)</td>
<td>4.5 (1.3)</td>
<td>0.31 (0.10)</td>
<td>56.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deer Creek</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpine</td>
<td>6.3 (0.2)</td>
<td>5.9 (0.8)</td>
<td>0.36 (0.05)</td>
<td>74.6</td>
<td>124 (45)</td>
<td>20.5 (6.6)</td>
</tr>
<tr>
<td>Forest</td>
<td>5.8 (0.1)</td>
<td>3.9 (0.8)</td>
<td>0.32 (0.07)</td>
<td>55.1</td>
<td>132 (28)</td>
<td>19.0 (6.4)</td>
</tr>
<tr>
<td>Meadow</td>
<td>6.5 (0.1)</td>
<td>11.0 (2.5)</td>
<td>0.35 (0.07)</td>
<td>57.1</td>
<td>152 (68)</td>
<td>28.5 (2.9)</td>
</tr>
</tbody>
</table>

Values represent the mean (±1 SD) of three to nine measurements.

$^a$There is only one SWE estimate for each site.

$^b$The bottles containing the soil extracts from the Snake River alpine sites were broken in transit.

$^c$Collectors from the Snake River alpine sites could not be located after snowmelt.
ceding 6–8-month snow-covered season are important in controlling the size of this mobile soil DOC pool.

There was no relationship between overlying soil carbon content and either extractable or leached DOC at the plot scale. In contrast, a strong relationship between soil carbon pools and DOC export has been found at the catchment scale over a broad range of soil carbon pools [Hope et al., 1997]. This relationship may be due either to the carbon content of the soil directly or to longer hydraulic residence time and flowpaths in low slope, high carbon environments [Mulholland, 1997]. The absence of a relationship between soil organic matter and plot-scale DOC leachate in this study may be due to the smaller range in soil DOC, the short residence time for infiltrating meltwater in soil, or most likely, the difference in spatial scale (catchment versus plot) of the measurements.

The relationship between extractable DOC immediately before melt and DOC leachate measured in resin bags suggests that the actively cycling carbon pool is a better predictor for mobile DOC production than total soil carbon in the organic soil layer in these catchments. This is supported by the significant relationship between CO₂ flux and DOC leachate and indicates that the amount of heterotrophic processing of labile soil carbon is a primary control on the production of mobile DOC pools in these catchments. The highest CO₂ fluxes and DOC leachate were measured in meadow soils with large, labile carbon inputs in litter from grasses and forbs, while the lowest fluxes were measured from forest soils characterized by more recalcitrant carbon inputs [Schlesinger, 1991; Aber and Melillo, 1991]. Slightly lower values at the alpine meadow sites compared to subalpine meadow are probably due to lower carbon inputs during the shorter growing season at the temperature- and moisture-stressed higher elevations [May and Webber, 1982; Walker et al., 1994]. While comparative data on plot-scale DOC leachate during snowmelt are generally lacking, the differences in CO₂ fluxes between landscape types are

Figure 5. Mean CO₂ flux from alpine, meadow, and forest sites in (left) Deer Creek and (right) Snake River. Values are mean plus or minus standard error (SE) of 100–120 measurements.

Figure 4. Relationship between the amount of deionized water (DI) extractable dissolved organic carbon (DOC) in soil before melt and DOC leachate from the organic soil horizon during snowmelt from the five sites where collectors were retrieved.

Figure 6. Relationship between DOC leached from the organic soil horizon and mean daily CO₂ flux from the five sites where resin collectors were retrieved.
consistent with previous research that indicates that overwinter heterotrophic activity is controlled primarily by the availability of labile soil carbon [Schimel and Clein, 1996; Brooks et al., 1996, 1997; Fahrenstock et al., 1998]. This also is consistent with results from catchment-scale DOC research [Hope et al., 1997; Mutholland, 1997] because soils having a high bulk carbon content and a long hydraulic residence time are likely to have higher amounts of heterotrophic processing.

The large differences in both heterotrophic activity and DOC leachate between the Snake River and Deer Creek soil types also are consistent with known controls on soil heterotrophic activity. The smaller CO₂ fluxes and DOC leachate amounts from the soils subject to pyrite weathering may be due to pH-decreasing heterotrophic activity directly [Wardle, 1992], or indirectly through reduced nutrient availability to plants decreasing primary production and labile carbon inputs to the soil [Aber et al., 1989]. The smaller mobile DOC pools in the Snake River soils subject to pyrite weathering are primarily responsible for the lower total mobile DOC production between the two catchments.

While heterotrophic processing of labile soil carbon controls the size of the mobile DOC pool, surface water export of DOC is controlled both by the size of the mobile DOC and hydrologic transport. Because soil at any site is flushed of DOC within a 10–30-day period [Boyer et al., 1997], the two synoptic sampling events provide an opportunity to evaluate the importance of the measured differences in soil DOC production to surface water DOC export. During the first synoptic, when primarily forest and meadow soils at the lower elevation were being flushed, the differences in DOC concentrations between the two catchments were the greatest. DOC concentrations in inflows entering the stream within the area of pyrite weathering below 1.0 ppm are consistent both with smaller DOC pools and greater immobilization in Snake River soils affected by pyrite weathering. DOC concentrations were lower in both basins during the second synoptic, but there was no difference between concentrations in the Snake River above the area of pyrite weathering and concentrations in upper Deer Creek.

The decrease in DOC concentrations within the area of pyrite weathering probably was due to a combination of lower DOC production identified in this study and to the sorption of DOC to metal oxides on the streambed previously identified in these catchments [McKnight and Bencala, 1990; McKnight et al., 1992].

The importance of physicochemical removal on the mobile/leached DOC pool is apparent in the measurements of DOC in soil extracts, leachate, and catchment-scale export. While plot-scale extractable DOC measurements from the organic soil horizon indicated that potentially mobile carbon pools in soils were 95–178 g C m⁻² before melt, the 10.8–28.5 g C m⁻² captured as leachate in the buried resin collectors indicated that only 10–20% of this potentially mobile C pool moved with infiltrating meltwater. At the catchment scale, DOC export at the confluence of 0.9 g C m⁻² yr⁻¹ for the Snake River and 2.2 g C m⁻² yr⁻¹ for Deer Creek were 5% and 11%, respectively, of the 17.8 and 20.3 g C m⁻² yr⁻¹ DOC leachate from the organic soil horizon for each catchment. These decreases are consistent with the adsorption of DOC in mineral soil horizons as a major control on DOC transport to surface water [McDowell and Wood, 1984; Thurman, 1985]. Similarly, the lower percentage of DOC leachate subsequently exported from the Snake River catchment compared to Deer Creek is consistent with DOC removed by metal oxides on the streambed of the Snake River [McKnight et al., 1992; McKnight and Bencala, 1990]. Furthermore, inflow concentrations suggest that the geochemical environment that results in DOC sorption on the streambed also enhances DOC retention in the mineral soils of the Snake River catchment.

6. Summary

The delivery of allochthonous DOC to the aquatic ecosystem in these high-elevation catchments is controlled by the snowmelt flush of a variable soil DOC pool and by differential removal of leached DOC as it moves through the catchment. The size of the mobile DOC pool in these catchments appears to be related to the amount of heterotrophic processing of labile carbon sources in snow-covered soils. Patterns in both the mass of DOC in leachate from the organic soil horizon during snowmelt and overwinter CO₂ flux suggest that the size of the actively cycling carbon pool is a major control on both of these carbon fluxes. Because overwinter heterotrophic activity is sensitive to small changes in the annual snowpack, these findings provide a mechanism for evaluating interannual variability in catchment-scale DOC export.

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