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# Snowmelt dominance of dissolved organic carbon in high-latitude watersheds: Implications for characterization and flux of river DOC

Jacques Finlay,[1] Jason Neff,[2] Sergei Zimov,[3] Anna Davydova,[3] and Sergei Davydov[3]

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[1] Transport of dissolved organic carbon (DOC) from land to water is an important but poorly known component of northern carbon cycles. We examined seasonal patterns of arctic river DOC flux, focusing on the largely uncharacterized snowmelt period. High-intensity sampling of the Kolyma River showed rapid increases in DOC concentration during peak discharge, yielding unique DOC-water flux relationships compared to summer, fall and winter. Our annual DOC flux estimates were 31% higher than previous estimates for the basin based on few or no snowmelt samples. Synthesis of the sparse literature show that 55% of arctic river DOC flux occurs during snowmelt. Biogeochemical characterizations of DOC in large rivers are usually done after snowmelt runoff, and are thus unrepresentative of most DOC transported to the Arctic Ocean. Finally, the proportion of annual DOC flux at snowmelt is considerably higher than for water, suggesting that cold season production is an important but little known process regulating arctic DOC transport.

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## 1. Introduction

[2] High-latitude ecosystems will play a pivotal role in determining the response of the terrestrial carbon cycle to a rapidly changing climate. The arctic and boreal regions hold between 20–60% of global terrestrial organic carbon (C) in cold or permanently frozen soils [*Gorham*, 1991; *Post et al.*, 1982]. Arctic and boreal regions warmed significantly during the last half of the 20th century [*Serreze et al.*, 2000; *Chapin et al.*, 2005], and current warming is altering vegetation, decreasing permafrost, increasing soil temperatures, and changing fire and hydrologic regimes in the pan-arctic [*Hinzman et al.*, 2005]. These changes are likely to influence the role of high-latitude ecosystems as sources or sinks of atmospheric $CO_2$.

[3] Lateral fluxes of dissolved organic carbon (DOC) from land to water are an especially important and sensitive component of high-latitude carbon cycles. Large northern rivers have the highest average concentrations of DOC of any region, and riverine transport to the Arctic Ocean is 11% of the global DOC flux [*Köhler et al.*, 2003], representing a significant fraction of terrestrial NEP. The dynamics of boreal and arctic ecosystems and their connections to aquatic systems are thus an important facet of the contemporary carbon cycle and are crucial for projecting impacts of future change.

[4] Climate change at high latitudes has the potential to greatly affect river DOC fluxes because factors affecting both DOC production and transport are climate sensitive. Production in soils is positively affected by temperature and $CO_2$ [*Hobbie et al.*, 2002; *Neff and Hooper*, 2002; *Freeman et al.*, 2004; *Prokushkin et al.*, 2005], and thus it is widely expected that arctic DOC fluxes will increase in the future. This hypothesis is supported by stream flux studies in north-temperate watersheds [*Freeman et al.*, 2001; *Tranvik and Jansson*, 2002] and a study of 96 Siberian peatland watersheds where temperature was correlated with summertime stream DOC concentration [*Frey and Smith*, 2005]. This study suggests that expected warming of permafrost soils would significantly increase stream DOC export and reduce storage of soil organic carbon. Another recent study, however, suggests an alternate hypothesis that warming could increase summer active layer thickness in permafrost soils, thus deepening water flow paths below organic-rich soils and reducing summertime DOC fluxes from high-latitude watersheds [*Striegl et al.*, 2005].

[5] The contrasting results of these and other recent studies demonstrate that current understanding of DOC dynamics are insufficient to predict responses to warming and hydrologic change at high latitudes. A major limitation is that flux estimates for arctic rivers are largely based on a very small number of studies from the middle of last century. These estimates were made with very small sample sizes, with especially limited data for springtime conditions [*Köhler et al.*, 2003]. In addition, lab and field process studies focus primarily summertime conditions. However, runoff, an important factor controlling DOC flux, is dominated by snowmelt at high latitudes [*Lammers et al.*, 2001]. Moreover, warming and hydrologic change (e.g., increasing river discharge) are most intense during fall and winter [*Symon et al.*, 2005]. However, despite the well-known runoff patterns of northern watersheds, and evidence for intensified climate change during winter, DOC sources and transport during spring have received little study. For example, we know of no detailed time series of DOC in large arctic rivers during this period [*Köhler et al.*, 2003]. Thus the spring period is a critical period for improving estimates of contemporary fluxes to the Arctic Ocean and for understanding effects of warming and hydrologic change on carbon transport. Here we examine river DOC

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[1] Department of Ecology, Evolution and Behavior, University of Minnesota, St. Paul, Minnesota, USA.

[2] Geological Sciences and Environmental Studies, University of Colorado at Boulder, Boulder, Colorado, USA.

[3] North-East Scientific Station, Pacific Institute of Geography, Far East Branch, Russian Academy of Sciences, Cherskii, Russia.

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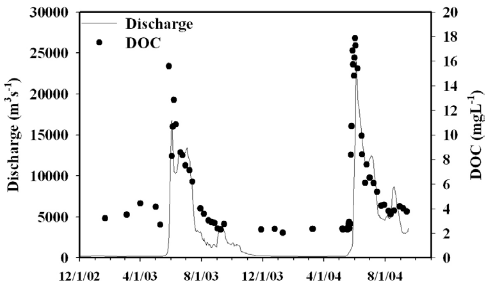

**Figure 1.** Discharge and DOC time series for the Kolyma River, 2003–2004.

concentration and flux from a large watershed completely underlain by permafrost in northeast Siberia. We then synthesize existing high-resolution flux data from arctic and boreal rivers to assess the importance of hydrologic and landscape controls on the timing of river DOC flux, and their importance to understanding of DOC transport in high latitude watersheds.

## 2. Methods

### 2.1. Kolyma River

[6] The Kolyma River is the sixth largest river entering the Arctic Ocean with a watershed area of 650,000 km$^2$ and an average annual water flux of 132 km$^3$. The watershed is the largest underlain by continuous permafrost and has extremely low mean annual temperatures (e.g., −12.4°C at Cherskii, Siberia). We used high-frequency sampling to examine DOC dynamics during the major annual hydrologic event and to estimate annual fluxes from the watershed. The river was sampled ~2 km upriver from the town of Cherskii, 160 km below the discharge station at Kolymskoye [*Welp et al.*, 2005]. Samples were collected at 1 or 2 mid channel points through ice in winter, via hovercraft and from a municipal water system intake during spring melt, and by boat from 2002 to 2004. Comparisons of DOC concentration in samples collected via the municipal intake compared to direct sampling on three dates were in close agreement, with a mean difference of 0.5 mgL. DOC samples were filtered immediately through glass fiber filters, preserved with HCL to pH 2, and stored in glass vials until analyses via high temperature combustion (Shimadzu TOCvcpn).

[7] Hydrological data was accessed through http://rims.unh.edu/. Flux estimates for 2004 were made based on discharge data and 35 measurements of DOC concentration including 14 during snowmelt. Linear interpolation was used to estimate DOC concentration between measurement dates. Flow data were unavailable for several winter low flow periods, so discharge was estimated from long-term mean daily discharge. Since water flux during these periods is very low, annual DOC flux estimates are robust to our discharge estimates.

[8] DOC and water export occurring during snowmelt was calculated at the beginning of the rapid rise in discharge and DOC concentration and ending at a brief leveling off in discharge 28d later. A small discharge peak followed due to continued snowmelt or rain. This period was not considered in the snowmelt water and DOC flux calculations (Figures 1, 2, and 3), yielding conservative estimates of springtime contributions to annual fluxes.

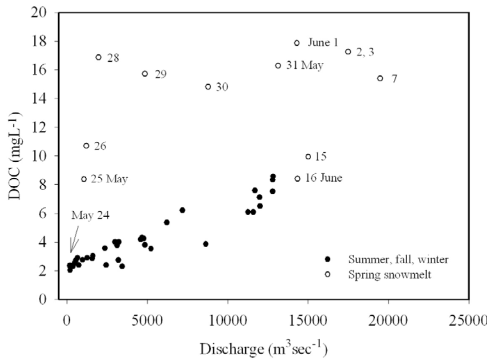

**Figure 2.** Discharge versus DOC concentration for the Kolyma River late 2003–2004. Dates of sampling during spring melt are listed next to data points.

### 2.2. Literature Synthesis

[9] To broaden our analysis of seasonality of DOC transport by northern rivers, we examined other high-resolution time series (i.e., at least five data points over peak discharge conditions, and sufficient data to calculate annual water and DOC flux) for watersheds north of 60° latitude. This search yielded 12 estimates (Table 1). We used these data to explore the causes of variation in the proportion of annual DOC flux during snowmelt.

## 3. Results and Discussion

### 3.1. Kolyma River

[10] The Kolyma River showed a rapid increase in DOC concentration during snowmelt (Figure 1) and much higher DOC loads than would have been predicted from DOC-water flux relationships observed at other times of year (Figure 3). DOC increased from 3 to 18 mgL$^{-1}$ over 4d and remained elevated during peak discharge before decreasing rapidly as flows dropped (Figures 1 and 2). DOC flux estimated with this high-resolution time series (1830 kg km$^{-2}$ yr$^{-1}$) were 31% higher than the average of previous estimates using samples collected during summer only or for uncharacterized flow conditions [*Dittmar and Kattner*, 2003; *Gordeev et al.*, 1996]. Our 2004 DOC flux estimates

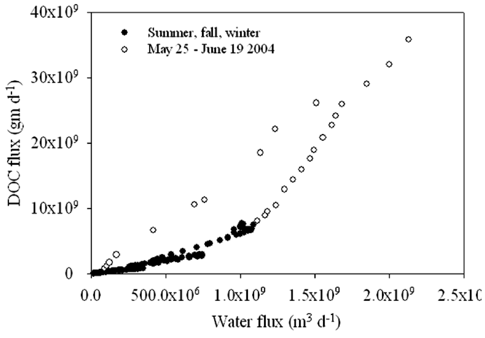

**Figure 3.** Relationship between daily water and DOC flux in the Kolyma River.

**Table 1.** Site Characteristics for DOC Flux Analyses[a]

| Site | Location | Watershed Area, km$^2$ | Permafrost, % | Runoff, mm | DOC Flux, kg km$^{-2}$ y$^{-1}$ | Wetland Cover, % | Spring Runoff, % | Spring DOC Flux, % |
|---|---|---|---|---|---|---|---|---|
| Vastrabacken | N Sweden[b] | 0.1 | 0 | 204 | 3600 | 5 | 59 | 68 |
| Kallkalstmyrn | N Sweden[b] | 0.2 | 0 | 228 | 7600 | 43 | 66 | 50 |
| Kallkalsbacken | N Sweden[b] | 0.5 | 0 | 230 | 6100 | 17 | 61 | 61 |
| C2 | Alaska[c] | 5.2 | 3 | 164 | 434 | 0 | 7 | 25 |
| C3 | Alaska[c] | 5.7 | 53 | 104 | 834 | 0 | 25 | 45 |
| Granger Basin | Yukon Territory[d] | 6 |  | 383 | 1640 | 0 | 34 | 67 |
| Stridbacken | N Sweden[b] | 9 | 0 | 192 | 3500 | 40 | 64 | 57 |
| C4 | Alaska[c] | 10 | 18 | 228 | 532 | 0 | 9 | 25 |
| Lillan | N Sweden[b] | 21.0 | 0 | 219 | 6400 | 23 | 52 | 53 |
| Mellansjobacken | N Sweden[b] | 26.0 | 0 | 223 | 5100 | 32 | 59 | 55 |
| Sorbacken | N Sweden[b] | 62.0 | 0 | 248 | 4800 | 14 | 58 | 64 |
| Kiiminkijoki | N Finland[e] | 3660 | 0 |  | 6455 |  |  | 69 |
| Kolyma | NE Siberia[f] | 526000 | ~100 | 175 | 1830 |  | 38 | 48 |
| Lena | Siberia[g] | 2420000 | >78 | 217 | 1811 | <5 | 40 | 73 |

[a] The authors' estimates of the duration of the snowmelt period were used in all cases.
[b] *Laudon et al.* [2004].
[c] *Petrone* [2005].
[d] *Carey* [2003].
[e] *Heikkinen* [1989].
[f] This study.
[g] *Cauwet and Sidorov* [1996].

are conservative because runoff (175 mm) was lower than the long-term average (192 mm). Conservatively assessed snowmelt water and DOC fluxes represented 38% and 45%, respectively, of the annual flux.

### 3.2. Literature Synthesis

[11] A review of the literature and the Kolyma River data suggests that flux of DOC to the Arctic Ocean is dominated by the period of spring runoff (1–2 weeks in streams, 4–6 weeks in large rivers). On average, 55% of annual DOC flux occurs during the brief spring melt, with a range from 25% to 70% (Table 1).

[12] The large flux of DOC to aquatic ecosystems in the spring is related in part to runoff patterns (Table 1). Snowmelt dominates runoff from many high-latitude watersheds via combined effects of long winters, little groundwater storage, and high summer evapotranspiration. However, DOC flux cannot be directly estimated from water flux during snowmelt (Table 1) because of complex relationships between land cover and flux. For upland catchments (wetland cover <5%), the percentage of annual DOC export during snowmelt exceeds that of water by up to 33% (Figure 4). In these watersheds, maximum DOC concentration occurs at or near peak discharge during snowmelt, and is typically 10–25 mgL$^{-1}$ higher than baseflow. In contrast, watersheds with extensive wetlands show a similar or greater percentage of water compared to DOC flux (Figure 4). DOC concentration is diluted by up to 29 mgL$^{-1}$ below baseflow conditions during snowmelt. This suggests limited soil DOC available for transport in wetlands compared to uplands perhaps due to less overwinter DOC production or differences in flowpaths [*Laudon et al.*, 2004]. The consequence of these poorly understood contrasts is that the proportion of annual DOC flux from upland watersheds during spring is far greater than that of water, but these differences decrease with wetland coverage (Figure 4). The hydrologic responses of DOC transport during snowmelt thus vary with watershed morphology, and these differences determine DOC fluxes observed in larger rivers that integrate both landscape types.

[13] The hysteresis in DOC-discharge relationships and seasonally pulsed DOC flux observed in this study have been studied elsewhere [e.g., *Boyer et al.*, 1997; *Hornberger et al.*, 1994; *Laudon et al.*, 2004; *Moeller et al.*, 1979]. Such relationships are indicative of a large soil pool of DOC available for leaching and transport during high runoff periods. Several important contrasts to temperate and tropical watersheds are evident, however. First, the lack of significant groundwater contribution to streamflow in many arctic watersheds suggests that river DOC dynamics are driven largely by processes occurring at the soil surface. In addition, surface soils are frozen during much of the long arctic winter period antecedent to spring runoff. The sustained, high concentrations of DOC at snowmelt imply production of a large DOC pool under very cold conditions. Finally, while our data set is somewhat biased toward studies in Sweden and Alaska, it suggests dominance of spring DOC flux across an extremely large geographic range in the pan-arctic and boreal zone.

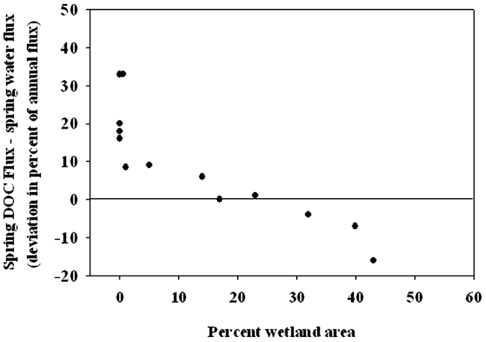

**Figure 4.** Relationship between the difference in percent annual DOC and water flux during spring and percent wetland cover in the watershed.

[14] The most common approach to estimating annual DOC flux from large arctic rivers is from the product of annual water discharge and mean DOC concentration, the latter calculated using average values of a small number of samples most often collected quarterly or during the summer [*Dittmar and Kattner*, 2003, and references therein; *Lobbes et al.*, 2000]. Such methods show large snowmelt fluxes because water discharge is high during spring, but rarely consider the substantial increase in DOC concentration occurring at peak discharge that is prevalent in northern rivers. Even river flux studies that have used more extensive sampling usually collect a very small number of samples (1–2) during snowmelt [e.g., *Cauwet and Sidorov*, 1996]. Our analyses indicate that undersampling of DOC in large rivers during spring could significantly underestimate DOC flux. Rapid changes in DOC concentration with discharge require higher-intensity sampling for accurate flux measurements than other times of the year. Sampling during snowmelt is hampered by dangerous ice conditions, but the relationships observed in this study (Figures 2 and 3) indicate that accurate estimates are possible with modest sampling effort during peak discharge.

[15] DOC transported by rivers in spring is likely of very different composition and bioavailability compared to summer. During spring melt, permafrost soils are frozen so runoff leaches the upper litter layers rather than deeper horizons. DOC and organic nitrogen leached from upper soil layers during spring appear to be highly bioavailable to aquatic heterotrophs, while DOC in rivers during summer is not [*Köhler et al.*, 2003; *Michaelson et al.*, 1998; *Stepanaukas et al.*, 2000]. This suggests that spring-transported DOC is of distinct composition compared to winter and summer, yet all detailed chemical and isotopic characterizations of DOC in large arctic rivers have been performed on samples collected during summer and fall.

[16] Arctic climate change is influencing a number of drivers of DOC production and transport that will affect spring fluxes. For example, warming is increasing soil temperatures, deepening active layer depth in permafrost soils, and lengthening its thawed period, [*Hinzman et al.*, 2005; *Sturm et al.*, 2005]. These effects may provide a longer season for winter DOC production to occur before soils freeze [e.g., *Park et al.*, 2005]. Further, warming is increasing terrestrial productivity [*Sturm et al.*, 2001] leading to increased litter inputs to soils with greater potential for leaching of soluble organic compounds during overland flow conditions at snowmelt. Finally, precipitation is projected to increase substantially in winter [*Symon et al.*, 2005] and there is evidence of increased runoff in northern basins [e.g., *McClelland et al.*, 2004]. This suggests that arctic river DOC composition and transport will be sensitive to conditions during winter, a period that is poorly known relative to summertime where most current research is focused.

## 4. Conclusion

[17] A majority of DOC transport from terrestrial to aquatic ecosystems at high latitudes occurs during the short snowmelt period but previous flux estimates and chemical characterizations for large rivers are largely based on summer sampling. This study shows that DOC concentration in most high-latitude rivers peaks during snowmelt, accounting for an average of 55% of the annual flux from land to water. The limited available literature suggests DOC released at snowmelt is highly bioavailable and that snowmelt accounts for a larger proportion of annual DOC loss from upland watersheds than from wetlands. Although snowmelt DOC generation and transport are least known, they are likely to be important and climate-sensitive components of carbon fluxes in high latitude watersheds.

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S. Davydov, A. Davydova, and S. Zimov, North-East Scientific Station, Pacific Institute of Geography, Far East Branch, Russian Academy of Sciences, P.O. Box 18, Cherskii, Russia. (sazimov@cher.sakha.ru; davydoffs@mail.ru)

J. Finlay, Department of Ecology, Evolution and Behavior, University of Minnesota, St. Paul, MN 55108, USA. (jfinlay@umn.edu)

J. Neff, Geological Sciences and Environmental Studies, University of Colorado at Boulder, 2200 Colorado Avenue, Boulder, CO 80309, USA. (jason.c.neff@colorado.edu)