



## Lability of DOC transported by Alaskan rivers to the Arctic Ocean

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[1] Arctic rivers transport huge quantities of dissolved organic carbon (DOC) to the Arctic Ocean. The prevailing paradigm is that DOC in arctic rivers is refractory and therefore of little significance for the biogeochemistry of the Arctic Ocean. We show that there is substantial seasonal variability in the lability of DOC transported by Alaskan rivers to the Arctic Ocean: little DOC is lost during incubations of samples collected during summer, but substantial losses (20–40%) occur during incubations of samples collected during the spring freshet when the majority of the annual DOC flux occurs. We speculate that restricting sampling to summer may have biased past studies. If so, then fluvial inputs of DOC to the Arctic Ocean may have a much larger influence on coastal ocean biogeochemistry than previously realized, and reconsideration of the role of terrigenous DOC on carbon, microbial, and food-web dynamics on the arctic shelf will be warranted. **Citation:** Holmes, R. M., J. W. McClelland, P. A. Raymond, B. B. Frazer, B. J. Peterson, and M. Stieglitz (2008), Lability of DOC transported by Alaskan rivers to the Arctic Ocean, *Geophys. Res. Lett.*, 35, L03402, doi:10.1029/2007GL032837.

### 1. Introduction

[2] Arctic rivers transport large quantities of organic carbon to the Arctic Ocean, most in the form of dissolved organic carbon (DOC) [Gordeev *et al.*, 1996; Dittmar and Kattner, 2003; Rachold *et al.*, 2004; Raymond *et al.*, 2007]. The degree to which the DOC in arctic rivers is available for microbial decomposition (its lability) determines its significance for the biogeochemistry of the Arctic Ocean, particularly in the shallow shelf region where river influence is greatest. At one extreme, highly refractory DOC would pass through the Arctic Ocean unaltered, with little significance for microbial processes and the food-web in the Arctic Ocean. At the other extreme, DOC that was highly labile would be an important resource for near-shore and shelf microbial communities, with cascading impacts for primary producers and higher trophic levels.

[3] One view, developed mainly through the analysis of samples collected during mid to late summer months, is that arctic river DOC is refractory. Two lines of evidence support this conclusion. First, mixing diagrams (plots of DOC concentration vs salinity) from oceanographic research cruises have shown apparently conservative mixing of relatively high DOC concentration river water and lower DOC concentration ocean water, with little or no evidence of loss of DOC as it traverses the continental shelf [Cauwet and Sidorov, 1996; Dittmar and Kattner, 2003; Köhler *et al.*, 2003; Amon, 2004; Amon and Meon, 2004]. Second, experiments have demonstrated extremely low consumption of arctic river DOC during extended incubations in the laboratory [Köhler *et al.*, 2003; Amon, 2004]. Taken together, these results have strongly suggested that little processing of terrigenous DOC occurs in the Arctic Ocean, at least during timescales relevant to its residence time on the continental shelf.

[4] Counter to this view, Cooper *et al.* [2005] suggest that ~30% of the DOC in arctic rivers may be reactive during transport across the ocean shelf. This tentative conclusion is based on a reassessment of mixing diagrams, taking into consideration newer (higher) estimates of annual DOC inputs by rivers to the Arctic Ocean. Over much longer time scales, Hansell *et al.* [2004] calculate that only 21–34% of terrestrially-derived DOC in the Beaufort Gyre is exported to the North Atlantic Ocean prior to decomposition. These studies, coupled with the young nature of DOC exported during ice-out [Neff *et al.*, 2006; Raymond *et al.*, 2007], cast doubt on the assumption that riverine DOC is refractory in the Arctic Ocean.

[5] Here we investigate whether seasonal changes in the lability of arctic river DOC may account for the apparent discrepancy concerning its lability, particularly over the relatively short timescales relevant to its residence time on the arctic shelf. Past sampling of arctic shelf waters from oceanographic research vessels has largely focused on mid-late summer because this is the period when sea ice retreats sufficiently to allow easy access to the river plumes. However, this period is well past the time of peak discharge on arctic rivers, when much of the annual DOC flux to the Arctic Ocean occurs [Gordeev *et al.*, 1996; Carey, 2003; Rember and Trefry, 2004; Finlay *et al.*, 2006; Raymond *et al.*, 2007]. Thus, if arctic river DOC is relatively labile during the spring freshet, mixing models and incubation experiments conducted during mid-late summer would not have detected it, yet mass balance approaches using new annual flux estimates that account for seasonal variations in the concentrations of inputs would. Specifically, we use incubation experiments to assess DOC lability during the spring freshet and into the summer low flow period for the

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three largest rivers on the North Slope of Alaska: the Kuparuk, Sagavanirktok, and Colville rivers.

## 2. Data and Methods

[6] Samples were collected from the Kuparuk, Sagavanirktok, and Colville rivers between late May and the end of July, 2006, capturing the spring freshet and the much lower flow conditions thereafter. The Sagavanirktok was sampled near Deadhorse (70°14.924'N, 148°18.180'W). The Kuparuk was also sampled near Deadhorse (70°19.722'N, 148°56.964'W), and was sampled far upstream near the Toolik Field Station (68°38.583'N, 149°24.250'W). The Colville was sampled near Nuiqsut (70°13.502'N, 150°59.653'W). Water was drawn from the main flow, ~0.5 m below the surface and stored in polycarbonate bottles. On each sampling date, water was filtered through pre-combusted 47-mm GF/F filters and then apportioned into thirty separate 60-mL polycarbonate containers in preparation for incubation experiments to determine relative lability of DOC. As these and other arctic rivers have notably low nutrient levels [Peterson *et al.*, 1992; Holmes *et al.*, 2000; McClelland *et al.*, 2007], half of the bottles were amended with NO<sub>3</sub>, NH<sub>4</sub>, and PO<sub>4</sub> to assess DOC lability under nutrient replete conditions, whereas the other half were unamended to assess lability under conditions at the time of sampling. Amended bottles received NO<sub>3</sub> and NH<sub>4</sub> to increase ambient concentrations by 80 μM, and PO<sub>4</sub> to increase ambient concentrations by 10 μM.

[7] Samples for all experiments were stored in the dark at 4°C for ~1 week between the time of collection and initiation of 20°C dark incubations in the laboratory. Reference samples were also frozen upon the day of collection. Comparison of reference samples to experimental samples showed that the amount of DOC lost during this pre-incubation period was never more than 30 μM and was less than 10 μM in most cases. To characterize DOC disappearance, four distinct time points were taken for each experimental incubation. At each time point, six samples (three unamended and three with added nutrients) were frozen. The first time point was taken upon arrival at the laboratory. Subsequent time points were taken 7, 30, and 90 days after initiation of the 20°C incubations in the laboratory. Incubations were conducted at a standard temperature (20°C) to allow determination of relative lability changes seasonally (independent of temperature changes) and to facilitate comparisons with other systems [del Giorgio and Davis, 2003]. River water and ocean shelf temperatures in the Arctic are typically lower than this so actual DOC loss rates in situ are likely lower. DOC concentrations were measured with a Shimadzu TOC-5000A analyzer. In addition to using triplicate samples, the instrument ran 3–5 injections per sample, injecting each sample until the coefficient of variation was less than 2%, or five injections, whichever came first. Means and standard errors among replicate samples are reported in Table S1 (see auxiliary materials)<sup>1</sup>. Values are reported for time zero, 1 month, and 3 months. Coefficients of variation among replicates were typically less than 5%.

[8] Discharge values for the Kuparuk River near Deadhorse were acquired from the US Geological Survey (site #15896000), whereas discharge values for the other two rivers were modeled using a version of the NASA Seasonal to Inter-annual Prediction Project (NSIPP) Catchment Based Land Surface Model [Koster *et al.*, 2000; Ducharme *et al.*, 2001; Déry *et al.*, 2005]. A detailed description of the model as recently applied to the Kuparuk River is given by McClelland *et al.* [2007]. While the model provides daily output, it does not account for ice damming that can alter the arrival of flood waters at a specific location during the spring freshet. Thus, we anchored the model output to the observed timing of peak flow at each sampling site. The model also does not account for input from springs and net melting of glaciers. We therefore imposed monthly minimum flow values on the model output as determined from USGS gauges at upstream locations on the Colville (site #15875000) and Sagavanirktok (site #15908000) rivers.

## 3. Results and Discussion

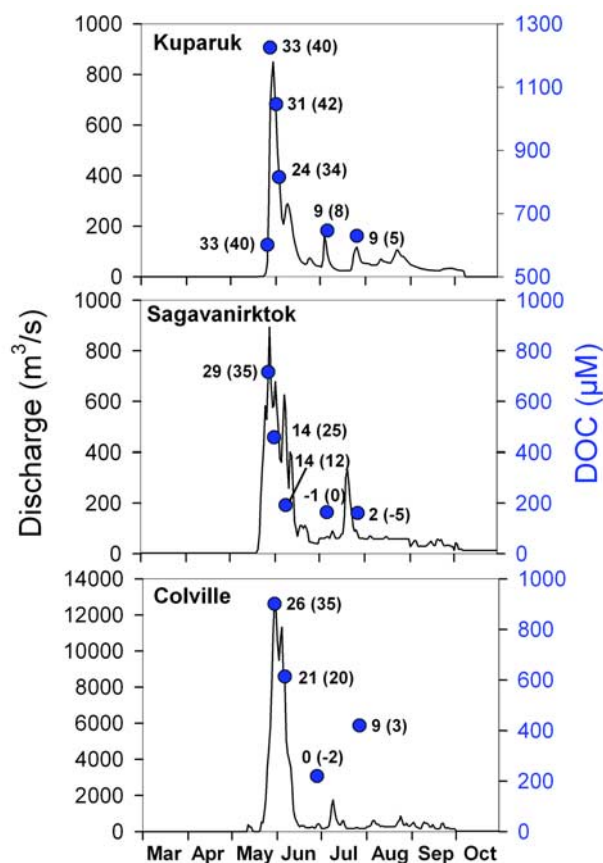
[9] A striking feature of the rivers investigated here is the extremely rapid progression from low flow conditions during winter to peak discharge in late May or early June. In each river it took only a few days to go from little or no discharge to peak flow (Figure 1). DOC concentrations were positively correlated with discharge (Figure 1), further accentuating the importance of the spring freshet for annual DOC fluxes. As a consequence, the majority of the annual DOC flux in these rivers occurred during the spring freshet period.

[10] Sharp discharge and DOC flux peaks are not unique to arctic rivers in Alaska but are characteristic of arctic rivers in general [Finlay *et al.*, 2006; Raymond *et al.*, 2007]. Given the unpredictability of the timing of breakup on these rivers, obtaining DOC samples during the freshet is challenging, requiring long stays at the field sites or luck. Furthermore, sea ice severely limits the ability to sample the river plume on the ocean shelf during this dynamic period, so samples used to generate published DOC mixing diagrams all come from later in the summer or fall after sea ice had retreated [Cauwet and Sidorov, 1996; Dittmar and Kattner, 2003; Köhler *et al.*, 2003; Amon, 2004; Amon and Meon, 2004]. Consequently, the most important period of the year with respect to DOC flux in arctic rivers and terrigenous DOC input to the Arctic Ocean has received remarkably little attention.

[11] In agreement with previous incubation experiments done on other arctic rivers, DOC losses during incubations were negligible for samples collected during summer low flow conditions on the Kuparuk, Sagavanirktok, and Colville rivers (Figure 1; and see Table S1 in the auxiliary material for additional data). For the samples collected after the spring freshet, DOC losses during three-month incubations were always <10%, and given the lower DOC concentrations during summer this translates to very little DOC loss compared to the annual DOC flux. Taken alone, these results would reinforce the view that DOC in arctic rivers is largely refractory.

[12] In contrast to incubation of samples collected during summer, DOC losses were substantial for samples collected

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2007GL032837.



**Figure 1.** DOC concentration and % loss of DOC after three months of incubation at 20°C in the dark. Parenthetical values show loss with nutrient amendment. In general DOC lability was high (20–40%) during the freshet period and declined greatly during summer low flow conditions.

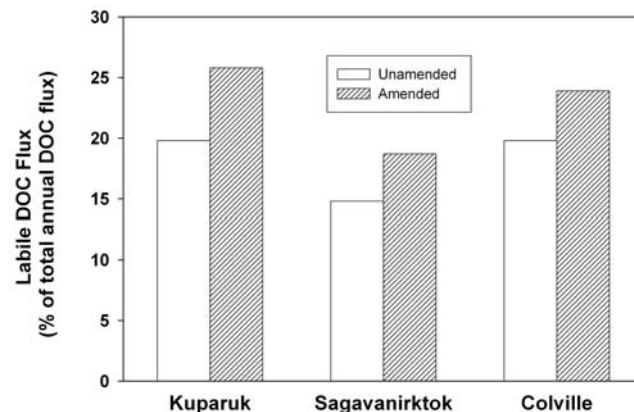
during the spring freshet, with 20–40% of DOC being degraded within three months (Figure 1; Table S1). Decreased lability of DOC as opposed to nutrient limitation of microbial processing is the explanation for reduced losses following the freshet, because the transition from high to low percentage losses of DOC occurs in both nutrient amended and unamended samples (Figure 1). Because the majority of the annual discharge of the Kuparuk, Sagavanirktok, and Colville rivers occurs during the three-week freshet period when lability is high, even if we assume that there is no labile DOC during other times, on an annual basis a relatively high fraction of the DOC entering the Arctic Ocean from these rivers is labile (Figure 2).

[13] Overall changes in DOC lability between the spring freshet and later in the summer were accompanied by a change in nutrient amendment effects. Addition of nutrients to samples collected during the spring freshet stimulated greater DOC consumption in almost all cases (Figure 1, Table S1). In contrast, nutrient additions did not stimulate greater DOC consumption in samples collected after the spring freshet. It is possible that the apparent partial nutrient limitation of DOC consumption observed during incubation of samples collected during the freshet would not be a factor in situ: in nature, the river water would have soon entered

the Beaufort Sea where nutrient concentrations during the time of the spring freshet are considerably higher than in the river water [Dunton *et al.*, 1982; Walsh *et al.*, 2005]. Thus, low nutrient levels may limit DOC consumption in these rivers during the spring freshet, resulting in a pulse of activity once the riverine DOC enters the relatively nutrient-rich coastal ocean.

[14] Why are DOC concentrations highest during the spring freshet, and why is DOC lability greatest at that time? The likely explanation is that before and during the spring freshet, the ground is mostly frozen so water flows across the surface or along shallow flowpaths on its way to the river channel. These surface or near-surface flowpaths intersect organic-rich soils and surface organic horizons, picking up organic matter along the way [Finlay *et al.*, 2006]. Short residence times and cold temperatures limit microbial processing which otherwise might remove the most labile components of the DOC prior to reaching the river channel. In contrast, over the course of the summer soils thaw and active layers deepen, so hydrologic flowpaths interact less with the organic rich surface horizons. This also slows the movement of water to the river channel, allowing for more processing of groundwater DOC along the way [Striegl *et al.*, 2005]. This explanation is supported by recent assessments of the age of DOC in arctic rivers over the seasonal cycle. Most DOC in the arctic rivers studied so far is young (<5–10 years), but there is a trend of increasing age of the bulk DOC pool from spring through summer as the active layer deepens [Neff *et al.*, 2006; Raymond *et al.*, 2007]. The assumption is that DOC of more recent origin is likely to have undergone less degradation and therefore be more labile.

[15] Given the time-consuming and labor-intensive nature of incubation experiments to assess DOC lability,



**Figure 2.** Labile DOC flux as a percentage of total annual DOC flux. To derive these estimates, we assumed that labile DOC was present only during the three-week period of maximum river discharge encompassing the spring freshet, with DOC during the remainder of the year being 100% refractory. Within the freshet period, we derived a flow-weighted estimate of DOC lability and applied that value to the total DOC flux during the high-flow period. Estimates were based on results of three-month incubations for both nutrient amended and unamended treatments.

ideally proxy measurements could be found. Several recent studies have reported compositional changes in the DOC pool of high latitude rivers over the seasonal cycle [Neff *et al.*, 2006; Guo *et al.*, 2007; Striegl *et al.*, 2007]. For example, Striegl *et al.* [2007] and Neff *et al.* [2006] show that specific UV absorbance of DOC (SUVA) peaks during the spring in the Yukon (Alaska) and Kolyma (Siberia) rivers, respectively. Neff *et al.* [2006] also show that the high DOC concentrations during the spring flood in the Kolyma River are correlated with high concentrations of terrestrial lignin monomers. The direct relationship between DOC lability and these and other compositional measurements of DOC in arctic rivers requires further investigation, but it seems likely that relatively simple proxy measurements will be found that are tightly coupled to DOC lability.

#### 4. Conclusions

[16] DOC concentrations and lability changed dramatically between the spring freshet and later in the summer for the Kuparuk, Sagavanirktok, and Colville rivers, with maximum lability occurring during the relatively understudied freshet period when most of the annual DOC flux occurs. This seemingly simple story has potentially profound implications. If the Alaskan arctic rivers studied here are characteristic of arctic rivers as a whole, then fluvial inputs of DOC to the Arctic Ocean will have a much larger influence on coastal biogeochemistry than previously realized, and reconsideration of the role of terrigenous DOC on carbon, microbial, and food-web dynamics on the arctic shelf will be warranted. Not only will the relatively labile fluvial DOC discharged during the spring freshet fuel heterotrophic microbial metabolism on the shelf, but inorganic nutrients regenerated during the decomposition of the dissolved organic matter may stimulate marine primary production. Moreover, though the magnitude and even the sign of future changes are uncertain, there is widespread agreement that climate change will substantially impact land-to-ocean carbon flux in the Arctic [Striegl *et al.*, 2005; Frey and Smith, 2005]. This amplifies the importance of understanding the current functioning of the system – a necessity for detecting and then understanding future changes.

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