



## Flow-weighted values of runoff tracers ( $\delta^{18}\text{O}$ , DOC, Ba, alkalinity) from the six largest Arctic rivers

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[1] We present new flow-weighted data for  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ , dissolved organic carbon (DOC), dissolved barium and total alkalinity from the six largest Arctic rivers: the Ob', Yenisey, Lena, Kolyma, Yukon and Mackenzie. These data, which can be used to trace runoff, are based upon coordinated collections between 2003 and 2006 that were temporally distributed to capture linked seasonal dynamics of river flow and tracer values. Individual samples indicate significant variation in the contributions each river makes to the Arctic Ocean. Use of these new flow-weighted estimates should reduce uncertainties in the analysis of freshwater transport and fate in the upper Arctic Ocean, including the links to North Atlantic thermohaline circulation, as well as regional water mass analysis. Additional improvements should also be possible for assessing the mineralization rate of the globally significant flux of terrigenous DOC contributed to the Arctic Ocean by these major rivers.

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### 1. Introduction

[2] The Arctic Ocean basin receives 10% of global runoff and is arguably the largest global estuarine system [Dittmar and Kattner, 2003]. The scale of the freshwater contribution produces strong vertical stratification in the Arctic marine system, separating warmer deeper Atlantic water from the surface where seasonal sea ice is as a result sustained [Aagaard and Carmack, 1989]. The outflow of freshwater from the Arctic to the North Atlantic also exerts an influence on the patterns and intensity of global thermohaline circulation. Because of the important influence runoff plays in structuring Arctic Ocean water masses, there is widespread interest in the fate and transport of runoff within the Arctic Ocean. However, at least two additional freshwater sources,

in-situ precipitation and melted sea ice are significant components of the Arctic Ocean freshwater budget, and complicate analysis of runoff transport directly from salinity alone. Pacific Ocean water transported through Bering Strait also contains a significant freshwater component, equivalent to 75% of all runoff contributed from all other Arctic sources for seawater normalized to a salinity of 34.8 [Woodgate and Aagaard, 2005].

[3] Several constituents have been used to separate and identify freshwater components in the Arctic from these specific sources. For example, the  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value of the freshwater (salinity = 0) component of melted sea ice is significantly different from the  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value of meteoric runoff, so a regression analysis of salinity versus  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  can distinguish the fractions of freshwater in a water mass that are derived from melted sea ice versus runoff and local precipitation [Östlund and Hut, 1984]. Additional conservative and semi-conservative tracers have also been used with and without  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  data in similar separations and origin analysis for Arctic runoff including Bering Sea nutrients, [Macdonald et al., 1989; Bauch et al., 1995; Ekwurzel et al., 2001], alkalinity [Anderson et al., 2004; Yamamoto-Kawai et al., 2005], dissolved organic carbon [Guay et al., 1999; Cooper et al., 2005], barium [Guay and Falkner, 1997; Macdonald et al., 1999] and nuclear fuel reprocessing tracers, specifically  $^{129}\text{I}$  and  $^{237}\text{Np}$  [Cooper et al., 1999].

[4] Despite these important on-going estuarine and oceanographic efforts to identify individual and regional sources of runoff and separate them from other sources of freshwater, a fundamental weakness is that the end-member runoff concentrations for most water column constituents used to trace runoff in the Arctic are poorly known or constrained. A primary challenge is the extreme seasonality of hydrographs for most rivers draining into the Arctic. The spring freshet releases a much larger fraction of total runoff than in temperate rivers and the concentrations of many constituents also vary to a much greater extent than in temperate rivers. Sampling during the freshet poses challenges because of ice breakup and dams, debris and flooding. There are also few data available from many arctic rivers during winter due to lack of access and logistical difficulties. Overall, arctic river chemistry data have, until recently, been most readily available for lower flow portions of the hydrograph in mid- to late-summer. Similarly oceanographic data in the Arctic are most readily available from similar periods in mid-to late-summer when seasonal sea ice has declined.

[5] Here we present data on seasonally variable  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values and concentrations of DOC, alkalinity, and dissolved barium in the six largest Arctic rivers (Ob', Yenisey, Lena,

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Kolyma, Yukon, and Mackenzie). These parameters have been widely used in studies of freshwater fate and transport in the Arctic Ocean, and we use data from the Pan-Arctic River Transport of Nutrients, Organic Matter and Suspended Sediments project (PARTNERS) [McClelland *et al.*, 2008] to derive annual flow-weighted values that can serve as improved end-members in such studies. The annualized data are specifically derived from samples collected from these six largest Arctic rivers over a four-year period from 2003–2007. The density and seasonally-explicit distribution of sample collection make the flow-weighted values presented here the most accurate available for these four constituents in the major arctic rivers. Estimates of DOC fluxes from the Ob', Yenisey, Lena, Yukon, and Mackenzie (using 2004–2005 PARTNERS data) are presented separately by Raymond *et al.* [2007].

## 2. Methods

[6] The PARTNERS sampling sites were established at Salekhard (Ob'), Dudinka (Yenisey), Zhigansk (Lena), Cherskiy (Kolyma), Pilot Station (Yukon), and Tsiigehtchic (Mackenzie). These sites are located far north on each river and thus integrate flow contributions from the vast majority of each river's watershed. Sampling was initiated in 2003 and continued into 2006 on the Ob', Yenisey, Lena, Kolyma, and Yukon. A final sample was collected from the Mackenzie in March 2007. During 2004 and 2005, sampling was conducted seven times at each river. Sampling efforts were distributed over the seasonal hydrograph including through-the-ice sampling in late winter, high flow during the spring freshet, as well as mid-summer and fall efforts. During 2006, sampling focused on peak flow and early winter. Sampling protocols followed US Geological Survey (USGS) guidelines, including the use of depth/flow integrating D-96 samplers deployed at multiple locations across each river. The D-96 samplers were equipped with Teflon nozzles and sampling bags. Details about collection and analysis of oxygen isotope and DOC samples are described by Cooper *et al.* [2005]. Water samples for barium and alkalinity determinations were filtered using a peristaltic pump equipped with pre-cleaned C-Flex tubing and inline Aquaprep 0.45- $\mu\text{m}$  filter cartridges. The barium samples were collected into HDPE sample bottles that had been previously leached at 65°C with trace-metal-clean nitric acid and rinsed copiously with ultrapure ( $\geq 18\text{ M}\Omega$ ) water [Guay and Falkner, 1998]. Following collection, the samples were immediately sealed in plastic bags and stored away from direct light and subfreezing temperatures. The alkalinity samples were collected into 250 ml HDPE bottles and refrigerated until analysis.

[7] Dissolved barium concentrations in samples collected from the Yukon River (all years) were determined by the USGS. Samples from all other rivers during 2003–2005, and from the Kolyma River during 2004 were determined at the University of Southern Mississippi Center for Trace Analysis. The remaining Ba samples were analyzed at the W. M. Keck Collaboratory for Plasma Spectrometry, Oregon State University. In all cases, concentrations were determined using inductively coupled mass spectrometry.

[8] Alkalinity was determined at the Marine Biological Laboratory by acid titration to a final pH of 2.5 using a

Hach Digital Titrator equipped with a 0.16 N  $\text{H}_2\text{SO}_4$  cartridge. The titration volumes were converted to alkalinity using the Gran Function plot method.

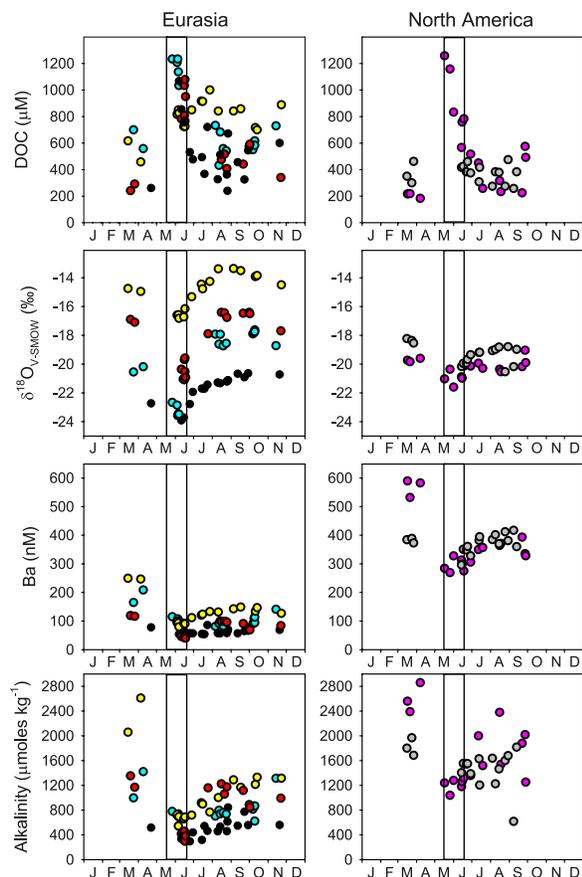
[9] Annualized flow-weighted estimates of tracer values were determined using discharge data collected by the USGS (Yukon), Water Survey of Canada (Mackenzie), and the Russian Federal Service of Hydrometeorology and Environment Monitoring (Yenisey, Ob', Lena, Kolyma). Values for missing months were interpolated linearly between measured values in surrounding months. Annual flow-weighted tracer values were then calculated using average monthly discharge from 2003–2005 for the Kolyma, and from 2003–2006 for each of the other rivers. Finally, integrated constituent values for all six rivers combined were calculated by weighting each river's individual flow-weighted values by its average annual discharge. Annual discharge values were scaled to include areas below the gauging stations on each river. Errors associated with stage-discharge relationships on the major Arctic rivers vary seasonally, with greatest percent uncertainty during low flow winter months [Shiklomanov *et al.*, 2006]. However, estimates of discharge become increasingly well constrained from daily to monthly to annual averages with errors  $\leq 3.5\%$ .

## 3. Results and Discussion

[10] Each of the four constituents measured varied significantly on a seasonal basis with changes as large as an order of magnitude for both DOC and alkalinity in individual rivers (Figure 1). River to river variation was large as were seasonal shifts. There was a significant separation among rivers for Ba (higher in North America and lower in Eurasia) and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  (least negative for the west Siberian rivers Ob' and Yenisey). During high flow, DOC reached an annual maximum and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ , alkalinity and dissolved Ba reached annual minima. The extremes during high flow have a greater proportional impact on the flow-weighted estimates for each constituent (Table 1). While water was collected during high flow at all of the rivers, sampling did not necessarily capture the peak of the spring freshet (auxiliary material).<sup>1</sup> In particular, high-flow sampling of the Ob, Yenisey, Kolyma, and Mackenzie lagged behind the peak of the freshet to varying degrees. Given the extreme values associated with peak flow, we expect that flow-weighted average will continue to be refined as more data defining the spring freshet become available.

[11] The flow-weighted data presented here nevertheless provide an improved basis for the use of  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ , alkalinity, dissolved Ba and DOC for tracing runoff contributions into the Arctic Ocean. For example, the flow-weight  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values we report here for the Ob' ( $-14.9\text{‰}$ ) and to a lesser extent the Yenisey ( $-18.4\text{‰}$ ), are significantly different from the Lena ( $-20.5\text{‰}$ ), allowing for the potential separation of Kara Sea runoff where it mixes in the Laptev Sea with runoff from the Lena after passing through the Vilkitsky Strait [Pavlov and Pfirman, 1995; Olsson and Anderson, 1997; Kattner *et al.*, 1999]. Prior published estimates of the

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2008GL035007.



**Figure 1.** Dissolved organic carbon,  $\text{H}_2\text{O}-\delta^{18}\text{O}_{\text{v-SNOW}}$ , barium, and total alkalinity variation for (left) the four largest Eurasian Arctic rivers (Lena, blue; Ob, yellow; Kolyma, black; Yenisey, red) and (right) two largest North American Arctic rivers (Mackenzie, grey; Yukon, magenta) plotted over seasonal cycles for the sampling period 2003–2007, as detailed in Table 1. The spring freshet, when discharge is disproportionately high, is outlined for the mid-May through mid-June period and corresponds to long-term hydrographic patterns, rather than the specific years sampled.

$\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value of the Lena range from  $-18.9\text{‰}$  [Létolle *et al.*, 1993] to  $-19.4\text{‰}$  [Ekwurzel *et al.*, 2001] and prior estimates for the Ob' and the Yenisey were  $-16.1\text{‰}$  and  $-17.2\text{‰}$ , respectively [Ekwurzel *et al.*, 2001]. These new estimates confirm significant river-to-river isotopic differentiation and should provide for less uncertainty in separations of runoff over the Russian shelves.

[12] Similarly the flow-weighted DOC concentration data will prove useful in assessing runoff transport and fate, as well as the likely decay rate of terrigenous DOC once within the ocean. Although allochthonous DOC in arctic runoff has been treated as a conservative or semi-conservative tracer for river discharge [e.g., Dittmar and Kattner, 2003], over uncertain time-scales this large component of the global carbon cycle is clearly subject to some oxidation [Lara *et al.*, 1994; Hansell *et al.*, 2004; Cooper *et al.*, 2005]. It is also becoming clear that younger and more labile DOC fractions are proportionally a larger component during the

spring freshet [Raymond *et al.*, 2007; Holmes *et al.*, 2008]. Another uncertainty is the potential for shifts in DOC fluxes as climate warms, including flux decreases [Striegl *et al.*, 2005]. For several of the Eurasian rivers, the flow-weighted data we present here are higher than previously reported DOC concentrations. For example, Lobbes *et al.* [2000] provided DOC concentration estimates of  $387\text{ }\mu\text{M}$  for the Kolyma (our flow-weighted estimate is 53% higher) and  $538\text{ }\mu\text{M}$  for the Lena (our flow-weighted estimate is 65% higher). Another feature that is apparent in the flow-weighted estimates is that the DOC concentration in the Mackenzie River is as little as one-half that of the four largest Eurasian arctic rivers (Table 1). This affects current estimates of the long-term oxidation of DOC in the Arctic Ocean. For example, Hansell *et al.* [2004] used  $^{228}\text{Ra}/^{226}\text{Ra}$  water mass ages to estimate decay rates of terrigenous DOC in the Beaufort Gyre, using a starting DOC concentration estimate for the Mackenzie River of  $550\text{ }\mu\text{M} \pm 100\text{ }\mu\text{M}$  to calculate the oxidation rate of DOC to an apparent freshwater end-member concentration of  $154\text{ }\mu\text{M}$  over a period of  $13 \pm 1$  years. The Yukon carries a slightly higher flow-weighted DOC concentration than the Mackenzie, but because of its intermediate discharge into the Bering Sea with oxidation potential before reaching the Arctic Ocean, the flow weighted fluxes of DOC from the two North American rivers into the Arctic Ocean are significantly lower than the four Eurasian rivers studied. These results indicate that runoff sources must be carefully evaluated in conjunction with mineralization rates of different aged DOC fractions before a better understanding of terrigenous DOC dynamics in the Arctic Ocean can be achieved.

[13] The flow-weighted Ba data we report are for the dissolved ion only and do not reflect desorption of the ion from clay particles in estuaries, which occurs in the Arctic [Guay and Falkner, 1998] as well as elsewhere at variable rates. Therefore these data represent lower limits for the effective flow-weighted contributions to the Arctic Ocean, but provide support for the use of Ba as an indicator of North American versus Eurasian fluvial inputs [Guay and Falkner, 1997]. Construction of barium input and output functions for the Arctic Ocean have been limited by lack of knowledge of seasonal variations in runoff contributions [Taylor *et al.*, 2003]. Our data show that seasonal variations in dissolved barium are most significant for the Ob' and the Yukon (Figure 1). The effective dissolved Ba concentration (dissolved plus desorbed Ba from clays) contributed to the Arctic Ocean has been estimated for four of the rivers we studied, the Mackenzie, Yenisey, Lena and Ob' [Guay and Falkner, 1998]. In all of these rivers except the Ob' the flow-weighted estimates we provide here (Table 1) are lower than the effective dissolved concentrations estimated by Guay and Falkner [1998] for the Mackenzie ( $520\text{ nM}$ ), Yenisey ( $125\text{ nM}$ ), Lena ( $130\text{ nM}$ ), and Ob' ( $100\text{ nM}$ ). The higher flow-weighted dissolved Ba concentration we report for the Ob' ( $141\text{ nM}$ ) is attributed in part to high concentrations observed in late winter, when Guay and Falkner [1998] did not collect samples. Despite this upwards estimate of the dissolved Ba concentration in runoff from the Ob' that we have developed with better seasonal sampling coverage, dissolved Ba concentrations in the North American rivers remain significantly higher than in the Eurasian rivers studied.

**Table 1.** Average  $\pm 1$  Standard Error and Flow-Weighted Average Tracer Data for Each of the Six Rivers Sampled, Corresponding to Data Shown on Figure 1<sup>a</sup>

| River (Annual Discharge, km <sup>3</sup> a <sup>-1</sup> ) | H <sub>2</sub> O- $\delta^{18}\text{O}$ (‰) V-SMOW | DOC ( $\mu\text{M}$ ) | Alkalinity ( $\mu\text{mol kg}^{-1}$ ) | Barium (nM)  |
|--|--|-----------------------|--|--------------|
| Ob' (373)  |  |                       |  |              |
| Average $\pm$ SE   | -14.6 $\pm$ 0.2                                    | 733 $\pm$ 39          | 1519 $\pm$ 160                         | 173 $\pm$ 16 |
| Flow-weighted average                                      | -14.9  | 785                   | 1181                                   | 141          |
| Yenisey (656)  |  |                       |  |              |
| Average $\pm$ SE   | -17.5 $\pm$ 0.3                                    | 454 $\pm$ 60          | 1047 $\pm$ 73                          | 92 $\pm$ 7   |
| Flow-weighted average                                      | -18.4  | 611                   | 845                                    | 76           |
| Lena (566)   |  |                       |  |              |
| Average $\pm$ SE   | -20.0 $\pm$ 0.5                                    | 762 $\pm$ 63          | 961 $\pm$ 70                           | 132 $\pm$ 11 |
| Flow-weighted average                                      | -20.5  | 841                   | 788                                    | 104          |
| Kolyma (114)   |  |                       |  |              |
| Average $\pm$ SE   | -21.9 $\pm$ 0.3                                    | 448 $\pm$ 40          | 518 $\pm$ 21                           | 70 $\pm$ 2   |
| Flow-weighted average                                      | -22.2  | 592                   | 449                                    | 63           |
| Yukon (214)  |  |                       |  |              |
| Average $\pm$ SE   | -20.0 $\pm$ 0.1                                    | 388 $\pm$ 84          | 2068 $\pm$ 149                         | 450 $\pm$ 32 |
| Flow-weighted average                                      | -20.2  | 544                   | 1707                                   | 369          |
| Mackenzie (322)  |  |                       |  |              |
| Average $\pm$ SE   | -18.9 $\pm$ 0.1                                    | 364 $\pm$ 5.6         | 1618 $\pm$ 55                          | 378 $\pm$ 5  |
| Flow-weighted average                                      | -19.2  | 368                   | 1540                                   | 371          |
| All Six Rivers (2245)                                      |  |                       |  |              |
| Flow-weighted average                                      | -18.8  | 656                   | 1048                                   | 163          |

<sup>a</sup>A flow-weighted value for the six-river ensemble is also provided. See the methods section for a description of the flow-weighting procedure. Average annual discharge over the 2003–2005 period at the Kolyma, and over the 2003–2006 period for each of the other rivers is shown in parentheses after the river names. Average discharge during these years was 93%, 101%, 103%, 90%, 102%, and 103% of discharge over the previous 25 years for the Ob', Yenisey, Lena, Kolyma, Yukon, and Mackenzie, respectively.

[14] The flow-weighted alkalinity data also shows significant variation among rivers, as well as seasonal variation, with minimum alkalinities reached during the spring freshet (Figure 1 and Table 1). *Anderson et al.* [2004] estimated that the total alkalinity of integrated arctic runoff is 1412  $\mu\text{mol kg}^{-1}$ , based on regression analysis of alkalinity to salinity in the Eurasian basin, but also reflecting re-calculated dissolved inorganic carbon concentrations of 1300, 1200, 1100, 1900, and 1700  $\mu\text{mol kg}^{-1}$  that had been measured previously for the Ob', Yenisey, Lena, Yukon, and Mackenzie, respectively. (Bicarbonate is the major component of total alkalinity, so these estimates are slightly lower than the expected total alkalinity). Although estimating the total alkalinity of all arctic runoff is beyond the scope of this study, the flow-weighted estimate of total alkalinity for all six rivers combined we provide here (1048  $\mu\text{mol kg}^{-1}$ ) is considerably lower than the *Anderson et al.* [2004] estimate for all arctic runoff. This possible discrepancy was also addressed by *Yamamoto-Kawai et al.* [2005], who applied an additional correction by treating river runoff in conjunction with the freshwater component of Pacific water and direct precipitation (negligible alkalinity) as part of a mixing line between Atlantic water and an integrated meteoric endpoint. Using multiple regressions, they estimated that total alkalinity for all of these integrated water contributions was actually 831  $\mu\text{mol kg}^{-1} \pm 100$ ; they also used the *Anderson et al.* [2004] estimated alkalinity for melted sea ice melt of 263  $\pm 65$   $\mu\text{mol kg}^{-1}$ . Use of these alkalinity end-member estimates provides for better agreement between the alkalinity freshwater separations and independent estimates of freshwater fractions obtained using  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values [*Schlosser et al.*, 2002] but our flow-weighted data indicate that further improvements in these separations may be possible because of continental scale differences. All of the Russian rivers show even lower alkalinities than these end-member estimates [*Anderson et al.*, 2004; *Yamamoto-Kawai et al.*, 2005] during peak flow (Figure 1). With the

exception of the Ob', all of the Russian rivers sampled also had much lower flow-weighted alkalinities than the two North American rivers.

#### 4. Conclusions

[15] These new flow-weighted estimates for four widely used tracers from the six largest Arctic rivers will improve the capabilities to separate freshwater components in the Arctic Ocean, including the possibilities for better regionally based analyses in the Eurasian and North American basin sectors. It should also be possible to identify individual major river signals further offshore with the better separation of individual rivers confirmed here, particularly between North American and Eurasian rivers for Ba, DOC, and alkalinity. Flow-weighted  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values show greater river-to-river variation than has been previously recognized, and it should also be possible to follow the transport and fate of the DOC pool contributed by runoff with better temporal accuracy.

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