

Linkages among runoff, dissolved organic carbon, and the stable oxygen isotope composition of seawater and other water mass indicators in the Arctic Ocean

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[1] Flow-weighted dissolved organic carbon (DOC) concentrations and $\delta^{18}\text{O}$ values were determined from major arctic rivers, specifically the Ob, Yenisey, Lena, Kolyma, Mackenzie, and Yukon during 2003–2004. These data were considered in conjunction with marine data for DOC, $\delta^{18}\text{O}$ values, nutrients, salinity, and fluorometric indicators of DOC obtained during sampling at the shelf-basin boundary of the Chukchi and Beaufort seas. On the basis of these data, freshwater in the sampled marine waters is likely derived from regional sources, such as the Mackenzie, the Bering Strait inflow, and possibly eastern Siberian rivers, including the Kolyma, or the Lena, but not rivers farther west in the Eurasian arctic. Freshwater from melted sea ice is insignificant over annual cycles, although melted sea ice was a locally dominant freshwater component following summer sea-ice retreat in 2002. DOC concentrations were correlated with the runoff fraction, with an apparent meteoric water DOC concentration of $174 \pm 1 \mu\text{M}$. This is lower than the flow-weighted concentrations measured at river mouths of the five largest Arctic rivers (358 to $917 \mu\text{M}$), indicating removal of DOC during transport through estuaries, shelves and in the deep basin. Flow-weighted DOC concentrations in the two largest North American arctic rivers, the Yukon ($625 \mu\text{M}$) and the Mackenzie ($358 \mu\text{M}$), are lower than in the three largest Eurasian arctic rivers, the Ob ($825 \mu\text{M}$), the Yenisey ($858 \mu\text{M}$), and the Lena ($917 \mu\text{M}$). A fluorometer responding to chromophoric dissolved organic matter (CDOM) was not correlated with DOC concentrations in Pacific-influenced surface waters unlike previous observations in the Atlantic layer. Nutrient distributions, concentrations, and derived ratios suggest the CDOM fluorometer may be responding to the release of chromophoric materials from shelf sediments. Shipboard incubations of undisturbed sediment cores indicate that sediments on the Bering and Chukchi Sea shelves are a net source of DOC to the Arctic Ocean.

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1. Introduction

[2] A number of previous studies in the Arctic Ocean have documented strong linear correlations between salinity and marine dissolved organic carbon (DOC) concentrations [Dittmar and Kattner, 2003, and references therein]. These apparently conservative relationships suggest that terrestrial allochthonous DOC entering the Arctic marine environment is resistant to degradation. Labile, autochthonous DOC by contrast is rapidly recycled in the upper water column [e.g., Wheeler *et al.*, 1996]. Much of the work leading to the conclusion that allochthonous DOC is conserved during transport through the Arctic Ocean, however, has focused on the Eurasian side of the basin. In this study we examined new North American marine data from the Shelf-Basin Interactions (SBI) program and pan-Arctic river data from

the Pan-Arctic River Transport of Nutrients, Organic Matter and Suspended Sediments (PARTNERS) efforts. Our study included fluorometric indicators of DOC, DOC directly determined from bottle samples, and indicators of runoff and water masses such as oxygen isotope ratios, salinity, and inorganic nutrient ratios, to gain an enhanced understanding of the transport and fate of DOC introduced into the Arctic marine environment. For the purposes of this study, we define runoff broadly as all freshwater of meteoric origin including direct precipitation to the sea surface and the freshwater component of marine waters transported north from lower latitudes. The SBI program that provided marine water samples is a ship-based effort focused on the shelf-basin boundary of the Chukchi and Beaufort seas, and has sampled seasonally as shelf waters are advected into the Canada basin. Likewise, a large volume of seasonally distributed runoff chemistry data are being generated by regular sampling of major arctic rivers by the PARTNERS project.

[3] The transport and fate of dissolved organic carbon delivered into the Arctic Ocean is a potentially important carbon system component that could have a significant impact on global carbon cycling in the context of environmental change [Shaver *et al.*, 1992; Neff and Hooper, 2002]. The rivers draining into the Arctic Ocean encompass catchments that contain about half of the organic carbon stored globally [Opsahl *et al.*, 1999; Dittmar and Kattner, 2003; Smith *et al.*, 2004]. Ten percent of global runoff flows into the Arctic Ocean, and many Arctic rivers carry high concentrations of DOC (up to 1000 μM). Concentrations of DOC are on average 8 times higher than particulate organic carbon (POC) in 12 Russian rivers draining into the Arctic [Lobbis *et al.*, 2000], which is consistent with worldwide patterns of higher DOC relative to POC in lowland river discharge [Meybeck, 1982] and the high lateral export of DOC from wetland and peat-dominated watersheds [Mulholland and Watts, 1982; Raymond and Hopkinson, 2003]. In addition to runoff, much of the Arctic coastline consists of unconsolidated sediments and peat that is dynamically contributing organic materials to the coastal zone as a result of shoreline erosion [Are, 1999]. The POC load contributed to marine systems in some Arctic continental shelf seas approaches or exceeds that contributed through runoff [Rachold *et al.*, 2000], and DOC contributions from peat directly eroded into coastal zones must also be significant. Although initial studies have not been entirely in agreement [e.g., Pastor *et al.*, 2003; Neff and Hooper, 2002; Hobbie *et al.*, 2002], climate warming is likely to have a significant impact on organic carbon decomposition on land and ultimately transport of DOC into the ocean [Freeman *et al.*, 2004; Frey and Smith, 2005]. The retreat of seasonal sea ice coverage is also likely to increase wave-based shoreline erosion [Serreze *et al.*, 2000; Proshutinsky *et al.*, 1999] thereby increasing organic contributions to coastal areas of the Arctic.

[4] Ultimately, the linkages among DOC processes are central to northern carbon cycling studies, particularly as permafrost thaws, vegetation changes occur on land, and coastal erosion accelerates [Benner *et al.*, 2004]. For instance, the sources of DOC from terrestrial and aquatic ecosystems can vary temporally and spatially due to the nature of arctic and boreal vegetation and soil attributes in

specific watersheds [Waddington and Roulet, 1997; Neff and Hooper, 2002]. Thus a complete understanding of DOC in the coastal zone not only requires marine studies but also linked process studies of terrestrial DOC dynamics as well as the mechanisms controlling DOC production and consumption, inputs and coastal zone erosion processes.

[5] Among the recent technological introductions to increase information on DOC distributions in arctic marine waters have been the development of high-resolution fluorescence measurement devices that respond to humic substances and other components of terrigenous DOC [e.g., Guay *et al.*, 1999; Amon *et al.*, 2003]. Although calibrations of these devices with bottle DOC measurements have been initially successful in the Eurasian Arctic [Amon *et al.*, 2003], high-resolution measurements of DOC fluorescence made during the submarine based SCICEX program [Guay *et al.*, 1999] indicated that the apparent relationship between fluorometrically measured DOC and salinity observed off Russian rivers might not be as applicable in the North American basin. A distinctly different freshwater DOC concentration (extrapolating to zero salinity from 30 psu, the least saline water accessible from the submarine that was used as a sampling platform) was observed in the portions of the submarine track most influenced by North American river discharge. Hansell *et al.* [2004] have further expanded understanding of this difference by using samples collected as part of the ship-based SBI program in the Chukchi and Beaufort seas. They interpreted the apparent DOC end-member in runoff in the North American Arctic to be a result of a longer residence time for DOC in the Beaufort gyre, using radium isotopes as an indicator of time since contact with the continental shelf. Their findings indicate that a substantial proportion of terrigenous DOC can be oxidized in the gyre, which may not be the case for DOC that is more quickly exported within the Transpolar Drift from the Russian shelves.

[6] Oxygen isotope ratios of runoff and marine water masses may be of particular value in tracing DOC as it moves from estuaries into Arctic marine waters. The $\delta^{18}\text{O}$ values have been successfully used as large-scale tracers of runoff and sea ice melt in the Arctic [e.g., Macdonald *et al.*, 1989, 1995; Cooper *et al.*, 1997, 1999a; Ekwurzel *et al.*, 2001]. The oxygen isotope composition of the ocean is little changed by sea ice formation and melt, but sea ice formation and dissolution are processes that alter salinities significantly and complicate the use of salinity as a water mass tracer in ice-covered seas. Seawater becomes enriched in ^{18}O as it freezes, but the isotopic fractionation observed in sea ice is typically small, ranging from 1.6‰ to 2.5‰ for multiyear floes with a 2 m thickness [Eicken, 1998]. Arctic field observations also suggest that an isotopic fractionation of $\sim 2\%$ is reasonable as a bulk estimate of the average enrichment of sea ice in ^{18}O relative to surface seawater [Melling and Moore, 1995; Macdonald *et al.*, 2002; Eicken *et al.*, 2002; Pfirman *et al.*, 2004]. Thus the volume of water converted into ice during the formation of a 2-m-thick ice floe in a well-mixed 100-m surface layer undergoing brine rejection would decrease $\delta^{18}\text{O}$ values by ~ 2 percent of the apparent 2‰ ice-liquid isotopic fractionation (2 m of 100 m converted to ice), or less than the analytical error of the mass spectrometric measurement (0.05 to 0.10‰). During sea ice melt, under stratified conditions, it is possible that

the slightly elevated ^{18}O content of melted sea ice could be measured relative to surface waters that had never been frozen, but the large difference from the oxygen isotope composition of meteoric runoff allows separation of this freshwater derived from melted sea ice.

[7] In addition to broadly distinguishing between freshwater from continental runoff and sea-ice melt, oxygen isotopes may help us to identify freshwater from individual rivers well into offshore regions. Growing data on major arctic rivers indicate that they differ substantially in oxygen isotopic composition. In coastal ecosystems, variation in $\delta^{18}\text{O}$ values for freshwater will be larger than the relatively fixed end-member that is assumed for offshore studies. The scale of variation will depend upon the rivers contributing to the localized coastal zone. For example, rivers draining higher altitude portions of the Brooks Range in Alaska with continental climate (e.g., Kuparuk, Sagavanirktok, and Colville) are likely to be more depleted in ^{18}O than rivers draining lowland tundra on the North Slope (e.g., Meade River). The geographical variation can be significant, even during snowmelt runoff in a single river watershed, such as the Kuparuk [Cooper, 1998]. These complexities in the stable isotope composition of runoff hold great promise for improving understanding of coastal physical oceanographic processes in the Arctic, but also emphasize the need for adequate temporal and spatial coverage that is difficult to achieve.

[8] Over the past several years, new data sources contributed through both marine and river sampling have begun to enhance our understanding of the transport and fate of DOC introduced into the Arctic marine environment [Dittmar and Kattner, 2003; Amon and Meon, 2004; Benner et al., 2004; Hansell et al., 2004; Shin and Tanaka, 2004; Benner et al., 2005; Mathis et al., 2005]. Our goal in this study is to examine new data from SBI in combination with data from PARTNERS, including fluorometric indicators of DOC, DOC directly determined from bottle samples, and indicators of runoff and water masses such as oxygen isotope ratios, salinity, and inorganic nutrient ratios in order to advance the larger objective of understanding DOC transport and fate.

2. Methods

[9] River data presented here were collected as part of the PARTNERS program (<http://ecosystems.mbl.edu/partners/>) in 2003–2004 from sampling points near the mouths of the Mackenzie, Yukon, Kolyma, Lena, Yenisey, and Ob rivers. The sampling protocol includes use of a United States Geological Survey D-96 sampler to acquire flow-weighted, depth-integrated samples across the river channel, a Teflon churn to homogenize the samples, and clean sampling techniques to assure high-quality data. Following collection, samples for DOC were filtered with QMA quartz filters, immediately frozen in 125-mL polycarbonate bottles and kept frozen until analysis. The polycarbonate bottles used had been soaked in 1% sulfuric acid overnight and then rinsed with milli-Q water; each bottle was stored and shipped inside individual plastic bags. Blank tests with these bottles indicate that there is no measurable leaching associated with this protocol. DOC analysis used standard high temperature

oxidation protocols following acidification to release inorganic carbon at the Yale School of Forestry and Environmental Studies, Yale University. River samples for stable oxygen isotope analyses were collected in 30-mL high-density polyethylene bottles and stored sealed under refrigerated conditions. Mass spectrometric analyses were accomplished at the University of Waterloo with a precision of $<\pm 0.1\%$.

[10] Marine data presented here were generated during two SBI (<http://sbi.utk.edu>) cruises of the USCGC Healy in May–June and July–August 2002. A conductivity-temperature-depth profiling system was used to determine temperature and salinity and two of the other units on the instrument package also measured fluorescence associated with terrestrial humics and fluorescence associated with chlorophyll. The electronic fluorescence associated with terrestrial humics was measured using a chromophoric dissolved organic matter (CDOM) fluorometer (Haardt Optic and Mikroelektronik, Hamburg) and the instrumental response was compared with several other parameters. This device incorporates fixed excitation at 350 to 460 nm with measurement of emissions at 550 nm. These wavelengths were chosen based upon an empirical response to concentrations of humic substances with terrestrial origins [Amon et al., 2003].

[11] Seawater samples were collected from a rosette of 30-L bottles. Inorganic nutrients were determined shipboard using an autoanalyzer; sampling and analyses used JGOFS and WOCE protocols to assure high-quality data. Other water samples from the rosette of bottles were returned to the laboratory for determinations of stable oxygen isotopes and DOC. The oxygen isotope composition of the seawater samples was measured using an automated equilibration unit linked to a Finnigan Delta Plus dual inlet mass spectrometer at the University of Tennessee. Precision, based upon repeated measurements of an internal standard, was $<0.05\%$. DOC data used here have been presented elsewhere [Hansell et al., 2004; Mathis et al., 2005]. These analyses were accomplished following filtration with 42-mm GF/F filters mounted within polycarbonate filter holders. Samples were stored frozen in high-density polyethylene bottles and were analyzed using standard high temperature oxidation protocols following acidification to release inorganic carbon at the Rosenstiel School of Marine and Atmospheric Science, University of Miami. The detection limit for DOC was approximately $2\ \mu\text{M}$.

[12] Replicate sediment cores were collected using a $133\ \text{cm}^2$ HAPS sediment corer for shipboard incubations, which were maintained in the dark at in situ bottom temperatures in a low temperature incubator for 12–24 hours. Motorized paddles were used to prevent water gradient formation [Grebmeier and McRoy, 1989; Cooper et al., 2002]. Under optimal conditions, the cores recovered with our HAPS corer system have very low degrees of disturbance; we have also established criteria to identify disturbed cores [Cooper et al., 2002]. Subsamples from the overlying water in these cores were filtered, acidified, frozen and returned to the University of South Carolina for analysis of DOC concentrations. Other data from these sediment incubations, including fluxes of dissolved oxygen, nutrients, alkalinity, pH, total CO_2 , and taxonomic

Table 1. DOC, Stable Oxygen Isotope Composition, and Runoff Estimates for Six Rivers and the Runoff Incorporated Into the Bering Strait Inflow to the Arctic Ocean^a

River	Mean DOC, μM	Standard Deviation	Flow-Weighted DOC, μM	N	$\delta^{18}\text{O}_{\text{V-SMOW}}$ Mean	Standard Deviation	N	$\delta^{18}\text{O}_{\text{V-SMOW}}$ Flow Weighted	Runoff, $\text{km}^3 \text{yr}^{-1}$
Lena	724	283	917	8	-20.8	1.8	26	-20.6	524–533
Mackenzie	375	100	358	6	-19.4	0.6	6	-19.0	249–333
Ob	733	167	825	7	-15.7	0.9	4	-15.3	404–419
Yenisey	733	316	858	8	-19.2	2.1	4	-18.8	562–577
Yukon	533	242	625	14	-20.4	0.4	9	-20.2	195
Kolyma	500	167	-	7	-	-	34	-22.2	71–98
Bering Strait runoff end-member (includes Yukon)					-21.1				1670

^aDischarge data are from *Dittmar and Katmer* [2003], except for the Yukon, which is from *Meybeck* [1982]. The Bering Sea runoff end-member estimate is based upon regression of 102 oxygen isotope and salinity measurements made of bottom seawater from the Bering continental shelf (<150 m [*Cooper et al.*, 1997]). DOC data for the Yukon River are from USGS, 2002–2004, and $\delta^{18}\text{O}$ data for the Kolyma River are from *Welp et al.* [2004], 2003–2004. All others are PARTNERS data from 2003–2004. Mean values of $\delta^{18}\text{O}$ and DOC for the rivers are simple averages from separate temporal samplings. Flow weighted data are based upon averaging samples from a given month, and flow weighting these monthly averages using long-term average monthly discharge data. Missing months have been interpolated for the flow-weighted $\delta^{18}\text{O}$ estimates. Monthly flow rates were obtained from the R-ArcticNet data archive at the University of New Hampshire (<http://www.r-arcticnet.sr.unh.edu/v3.0/>). Flow-weighted DOC values are generally higher than straight averages because of higher DOC concentrations during high flow.

identifications of macrofaunal organisms in the cores will be reported elsewhere.

3. Results

[13] The oxygen isotope composition and DOC concentrations of the river waters sampled are shown in Table 1. Values are expressed as both simple averages from seasonal sampling at points of confluence near the mouths of each river during 2003 and 2004, as well as flow-weighted averages based upon historical monthly flow records. In addition to core PARTNERS sampling, higher resolution temporal and spatial sampling was accomplished at the Lena and Yukon rivers for $\delta^{18}\text{O}$ analysis.

[14] The $\delta^{18}\text{O}$ values of Arctic Ocean seawater are normally well correlated with salinity particularly in areas with significant runoff. In our SBI sampling, we found better correlations between salinity and $\delta^{18}\text{O}$ values during the May–June 2002 cruise (Figure 1) than during the follow-on cruise in July–August 2002 that occupied the same general station grid. An analysis of the estimated contributions of freshwater derived from melted sea ice and from direct runoff is also shown (Figure 1). It was prepared by assuming that these two freshwater sources mixed conservatively with Atlantic water and the mixing could be described as part of two three-component mixing equations. An analysis of the estimated runoff component for each water sample was made by solving three simultaneous equations for a simplified Arctic surface water mixing system with components including Atlantic water, runoff and melted sea ice.

[15] The core oxygen isotope composition of each of these three components was designated as follows: sea ice $\delta^{18}\text{O}$ value = -1.9‰ (based upon sea ice sampling [*Eicken et al.*, 2002; H. Eicken, unpublished data, 2004]; Atlantic water: $\delta^{18}\text{O}$ = $+0.3\text{‰}$ [*Bauch et al.*, 1995] and Arctic basin runoff: $\delta^{18}\text{O}$ = -21.0‰ [*Östlund and Hut*, 1984]):

$$\delta^{18}\text{O} = (-1.9\text{‰} \times \text{SIM}) + (+0.3\text{‰} \times \text{AW}) + (-21\text{‰} \times \text{MW}),$$

where SIM is fraction sea ice, AW is fraction Atlantic seawater, and MW is fraction runoff. The core salinity of each component was assumed to be as follows: sea ice = ~ 4 [*Östlund and Hut*, 1984; *Bauch et al.*, 1995; *Ekwurzel et al.*, 2001]; Atlantic water = 34.8; runoff = 0:

$$S = (\text{SIM} \times 4) + (\text{AW} \times 34.8) + (\text{MW} \times 0),$$

where S is salinity of sample. The third equation was

$$\text{SIM} + \text{AW} + \text{MW} = 1.$$

[16] These simultaneous equations were solved to provide an estimate of the runoff fraction present relative to DOC concentrations (Figure 2) during the May–June 2002 SBI cruise that was prior to sea ice retreat when runoff was the dominant freshwater source. As expected, DOC concentrations were significantly correlated with the estimated runoff fraction, although there were indications that DOC concentrations in many of the Atlantic layer (salinity >33.5) samples were influenced by factors other than runoff fraction. For example, many of the Atlantic layer sample points fall below the apparent mixing line and may reflect long-term degradation of DOC (Figure 2). However, small, but unrealistic negative runoff fractions were also observed (Figure 2) and probably reflect uncertainties in the end-member $\delta^{18}\text{O}$ values. These uncertainties limit our capability to evaluate long-term degradation of DOC in the Atlantic layer. Therefore, excluding Atlantic layer samples, the regression equation relating the estimated runoff fraction to DOC concentration ($\text{DOC} = 115 \times \text{runoff fraction} + 58.96$) indicates that the estimated DOC concentration in meteoric water (the apparent DOC concentration in all freshwater of meteoric origin) should be approximately $174 \mu\text{M}$ (Figure 2). Using this method, any deviations of this value from the actual river end-member sampling (Table 1) are presumed to be due to within-system processing.

[17] Another means to estimate the apparent meteoric DOC concentration is to simply regress DOC concentrations against salinity [*Hansell et al.*, 2004] or to use stable

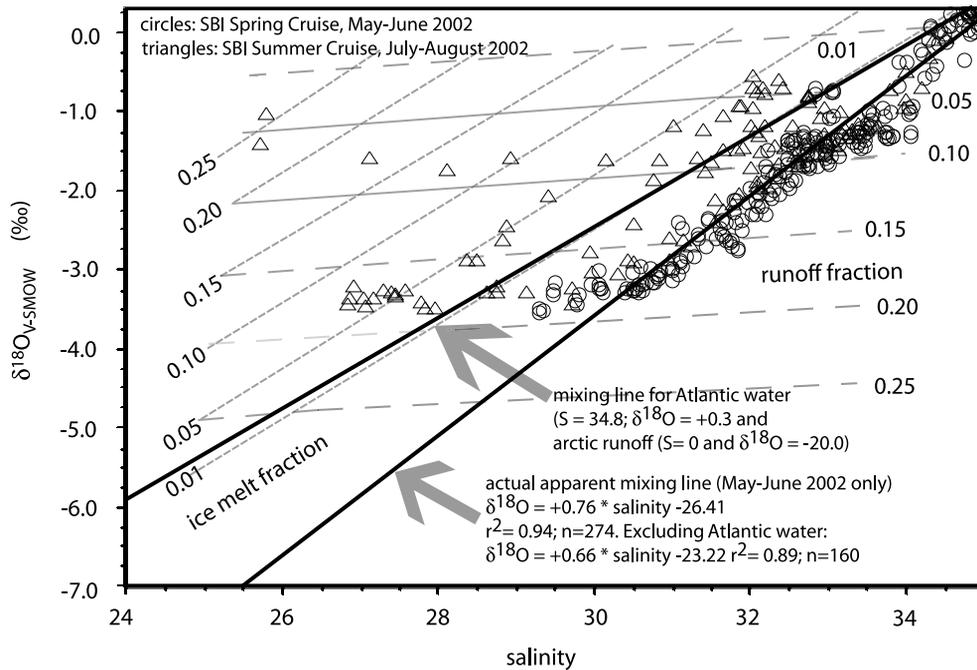


Figure 1. Relationship between $\delta^{18}\text{O}$ values and salinity in SBI water samples collected in the Chukchi and Beaufort seas, May–June 2002 and July–August 2002. Mixing lines shown are actual best-fit regression for all May–June 2002 samples (right line), and the expected mixing line between Atlantic water and freshwater runoff with a $\delta^{18}\text{O}$ value of -20 per mil (left line). Dashed lines show the estimated proportions of freshwater in samples derived from runoff and melted sea ice. When Atlantic water (salinity >33.5) is included, the estimated $\delta^{18}\text{O}$ value of the freshwater end-member is $-26.39 \pm 0.77\text{‰}$ (95% confidence interval). When Atlantic water is excluded, the estimated $\delta^{18}\text{O}$ value of the freshwater end-member increases to $-23.22 \pm 1.17\text{‰}$ (95% confidence interval).

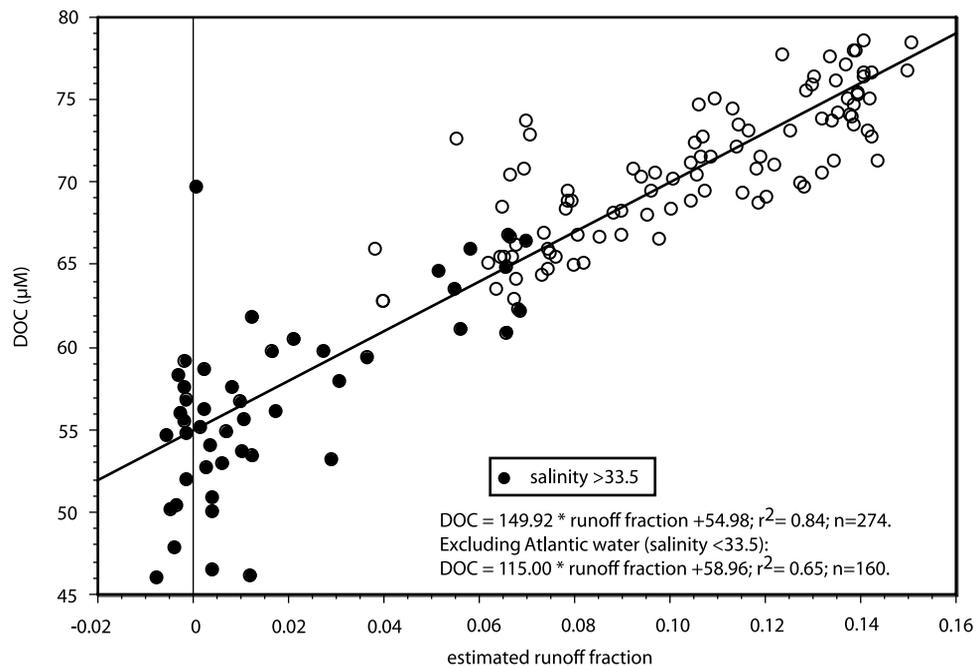


Figure 2. Estimated runoff fraction, calculated from algebraic solutions of three-member mixing equations for melted sea ice, runoff, and Atlantic water relative to DOC concentrations.

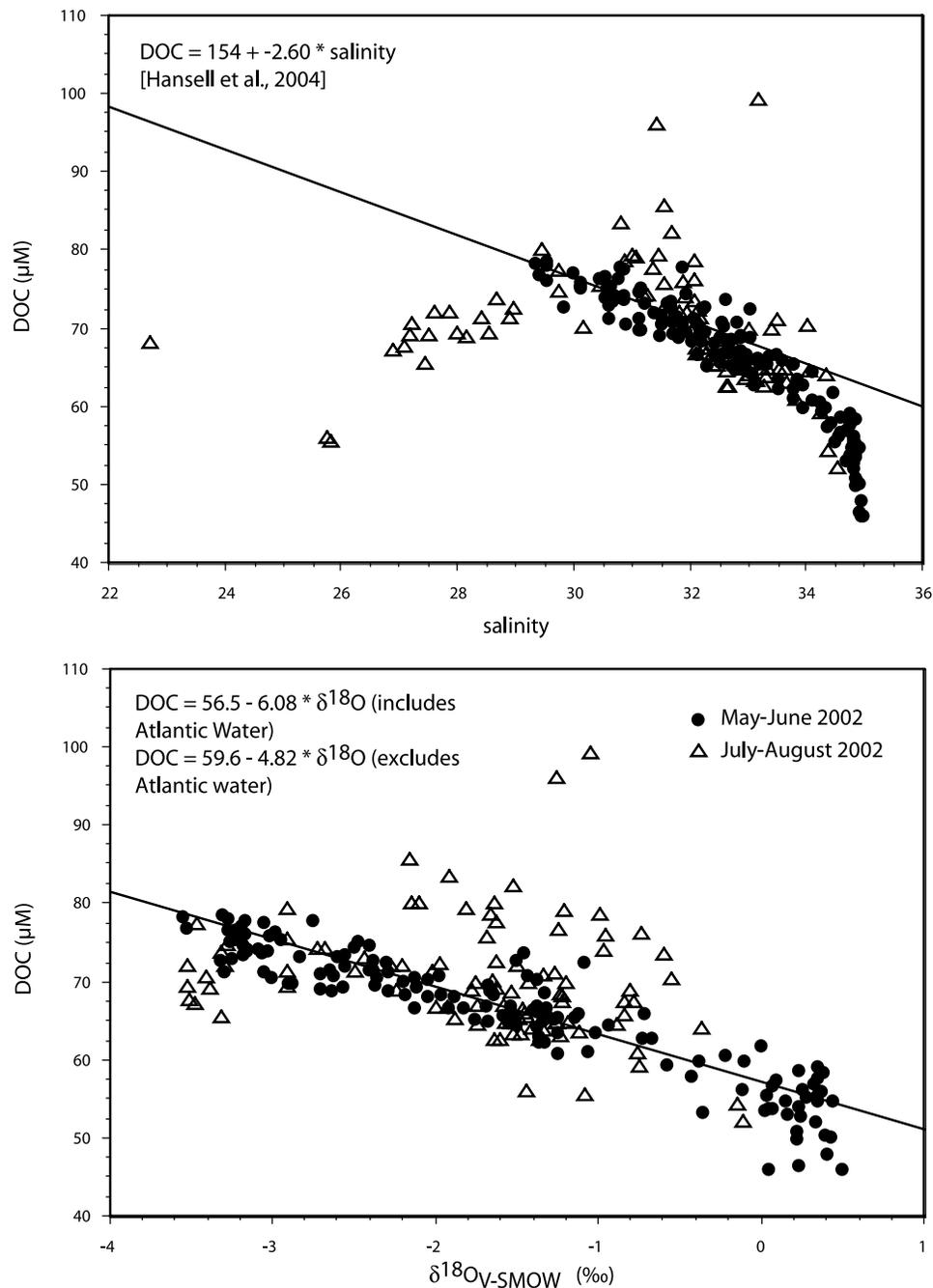


Figure 3. Relationship between DOC and (top) salinity and (bottom) $\delta^{18}O$ values for marine samples collected in the Chukchi and Beaufort seas, May–June 2002 and July–August 2002. Least squares fit lines (spring samples only) exclude salinities >33.5 that are below the upper halocline and correspond to Atlantic layer. A runoff $\delta^{18}O$ value of -20‰ was used to extrapolate to the DOC concentrations for runoff discussed in the text. Salinity-DOC regression data are from *Hansell et al.* [2004].

oxygen isotopes. In these analyses, we used the same DOC data as *Hansell et al.* [2004] from May to June 2002, and we found that DOC was correlated with $\delta^{18}O$ values for the late winter period (solid symbols, Figure 3). The results indicate a similar apparent meteoric DOC concentration ($\sim 156 \pm 7 \mu\text{M}$ standard error) at a presumed runoff end-member that has a $\delta^{18}O$ value of $\sim -20\text{‰}$ (i.e., zero salinity). In the *Hansell et al.* [2004] analysis, they also excluded salinities greater than 33.5 with the reasoning that

these waters correspond to the Atlantic layer that are below the halocline and do not readily mix with surface waters. Assuming that there may be circumstances when surface waters can mix to the depth of Atlantic water as a result of ventilation events, we included all $\delta^{18}O$ value measurements from samples collected in May–June 2002. In this alternative analysis, the apparent meteoric DOC concentration for freshwater with a $\delta^{18}O$ value of $\sim -20\text{‰}$ was $178 \pm 3 \mu\text{M}$ (standard error). If the appropriate runoff end-member for

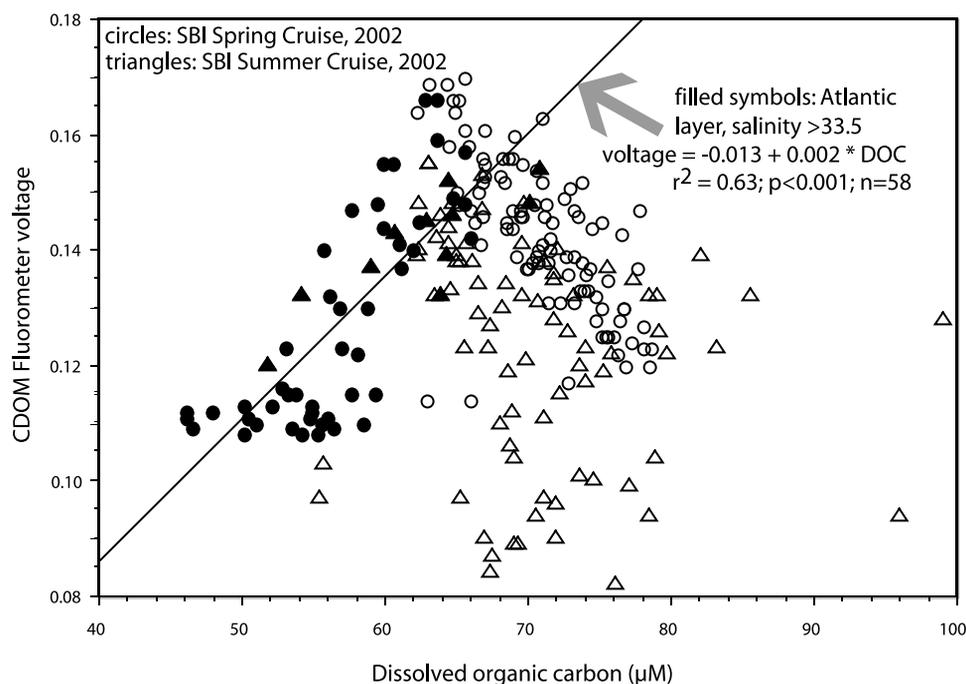


Figure 4. Relationship between DOC measured from bottle samples and fluorescence measured by the CDOM fluorometer for marine samples collected in the Chukchi and Beaufort seas, May–June 2002 and July–August 2002. Regression line shown is the least squares fit for all data with salinities >33.5 (Atlantic layer).

$\delta^{18}\text{O}$ is $\sim -21\text{‰}$, which is within the range observed in some of the flow-weighted river sampling (Table 1), then the apparent meteoric DOC concentration increases further to $184 \pm 3 \mu\text{M}$ (standard error). Our analysis also shows seasonal differences in apparent meteoric DOC concentrations; during the summer sampling (open symbols, Figure 3) the two highest concentrations of DOC were observed in Bering Strait, indicating DOC associated with “fresh” runoff. In other cases (other open symbols, Figure 3), dilution by melted sea ice reduced DOC concentrations [Shin and Tanaka, 2004; Mathis et al., 2005].

[18] The CDOM fluorescence was only strongly correlated with DOC in Atlantic water with salinity greater than 33.5 (Figure 4). In waters we sampled that were above the upper halocline (lower salinities), CDOM fluorescence was not correlated to DOC concentrations as measured in bottle samples (Figure 4). With the exception of two Bering Strait samples collected in July 2002, maximum voltages on both cruises were observed at waters close to the salinity (33.1) and $\delta^{18}\text{O}$ value (-1.1‰) associated with the upper halocline that is derived from high-nutrient Bering Sea water that has had brine added to it over the winter (Figure 5). Because waters in the upper halocline in the Amerasian Arctic are associated with nutrient maxima, we chose to further evaluate the CDOM fluorometer voltage data with several nutrient parameters to see if some additional information could be elucidated. By and large, for waters above the halocline (salinity <33.5) on the May–June 2002 cruise when diluting sea ice melt was negligible, CDOM fluorometer voltages were positively correlated with nutrients such as nitrate (data not shown), phosphate (data not shown), and silicate (Figure 6). However, despite the generally positive

correlation with silicate, which is probably the best nutrient indicator of the Bering Strait inflow, the highest silicate concentrations ($\sim 45 \mu\text{M}$) were not associated with the highest CDOM fluorometer voltages (Figure 6). We evaluated another derived nutrient tracer, N^* [Gruber and Sarmiento, 1997], which has been primarily used as an indicator of denitrification or of nitrogen fixation depending upon the system, and is based upon observed variances from Redfield nitrate/phosphate ratios in seawater. In the Gruber and Sarmiento [1997] formulation, $\text{N}^* = (\text{N} - 16\text{P} + 2.90 \mu\text{mol kg}^{-1}) \times 0.87$, with N and P representing the inorganic nitrate and nitrite (N) and phosphate pools (P).

[19] Ammonium was not explicitly included in the original N term defined by Gruber and Sarmiento [1997], but this ion can be a significant component of inorganic nitrogen available on shelves in the region sampled during SBI [Codispoti et al., 2005]. Consequently for the SBI samples, to avoid confusion, we use a modified N^* variable, N^{**} , that explicitly also includes concentrations of ammonium in addition to nitrate and nitrite. We found a pattern of increasing impacts of denitrification (more negative N^{**} values) in water samples that had higher CDOM fluorescence, although again, the water samples that had been subject to the highest degree of denitrification impacts on nitrate/phosphate ratios did not exhibit the highest CDOM fluorescence (Figure 5).

[20] Results from the shipboard incubation experiments indicate that some Chukchi shelf (<200 m) sediments are a net source of DOC to overlying waters with mean DOC release rates of up to $0.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Figure 7), which coincides with higher sediment oxygen uptake and nutrient effluxes that were observed in shelf sediments (J. Grebmeier,

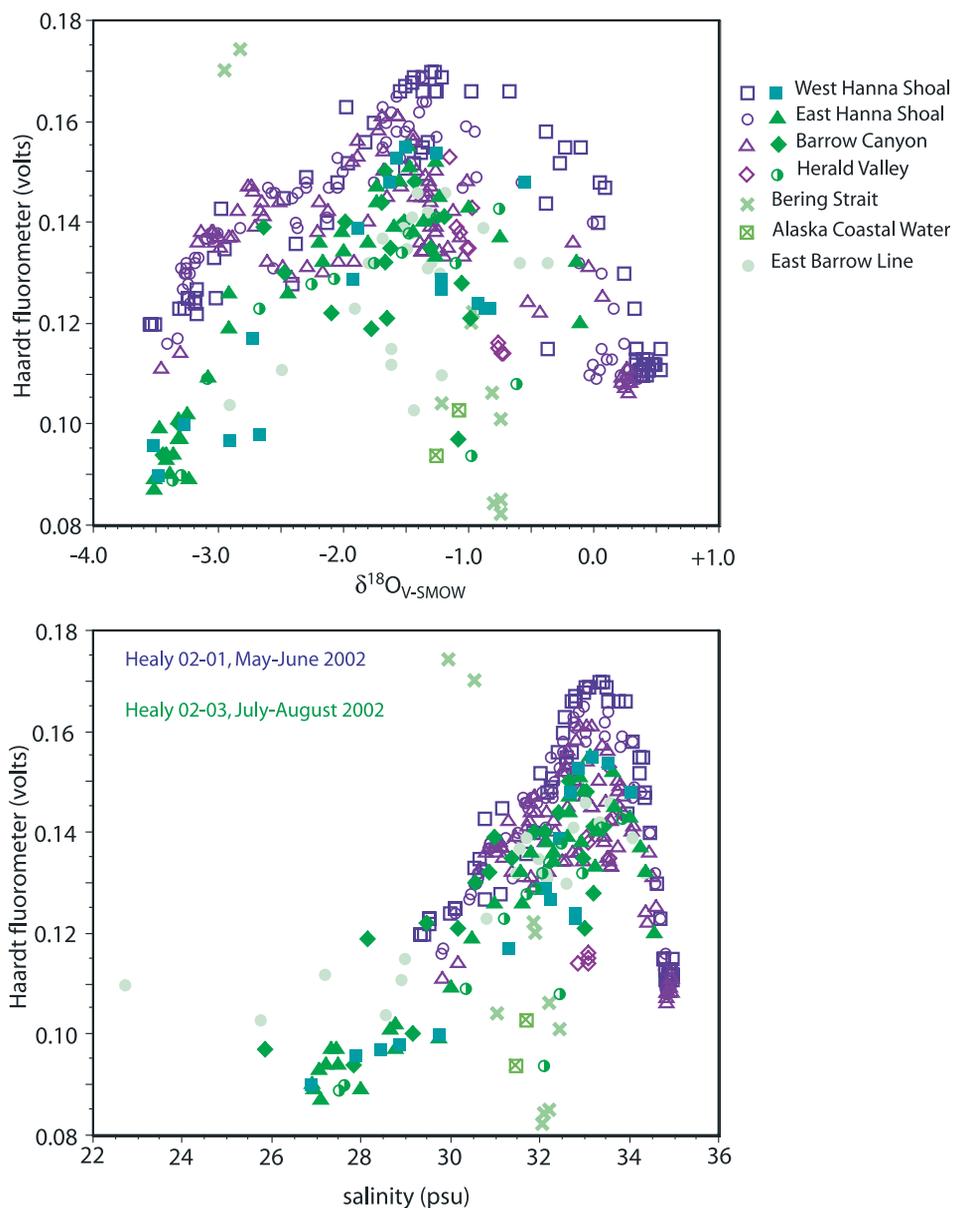


Figure 5. Relationship between (bottom) salinity and (top) $\delta^{18}\text{O}$ values in relationship to voltages recorded by the CDOM fluorometer for marine samples collected in the Chukchi and Beaufort seas, May–June 2002 (purple) and July–August 2002 (green). Symbols differentiate transects used during the SBI field program (see <http://sbi.utk.edu> for geographical locations).

unpublished data, 2005). Fluxes of DOC into the water column from slope stations and one basin sediment station were much less apparent, and in several instances, sediments were net sinks for DOC (Figure 7).

4. Discussion

[21] The regression line relating salinity and $\delta^{18}\text{O}$ data is influenced by contributions of melted sea ice and brine. We assume the endpoints are Atlantic water with a salinity of 34.8 and $\delta^{18}\text{O}$ value of +0.3‰ and runoff with a $\delta^{18}\text{O}$ value of approximately -20‰ and salinity of zero (Figure 1). Data falling to the left of this presumed conservative mixing line in Figure 1 indicate the influence of freshwater inputs from melting sea ice, whereas values falling to the right of

the conservative mixing line indicate the influence of brine generated during sea-ice formation. If mixing is based upon these two end-members, the y-intercept estimates the $\delta^{18}\text{O}$ value of runoff (including precipitation upon the sea surface). Within this framework, it appears that melted sea ice was only a significant component of surface waters during the cruise in July–August 2002. It also appears that brine generated from sea ice formation was present in almost all samples collected on the May–June 2002 cruise and in many samples in July–August 2002 because almost all samples (in May–June 2002) fall to the right of the simple presumed mixing line between runoff and Atlantic water. This deflection of data to the right of the simple mixing line illustrates one of the limitations of using these regression analyses to identify runoff sources.

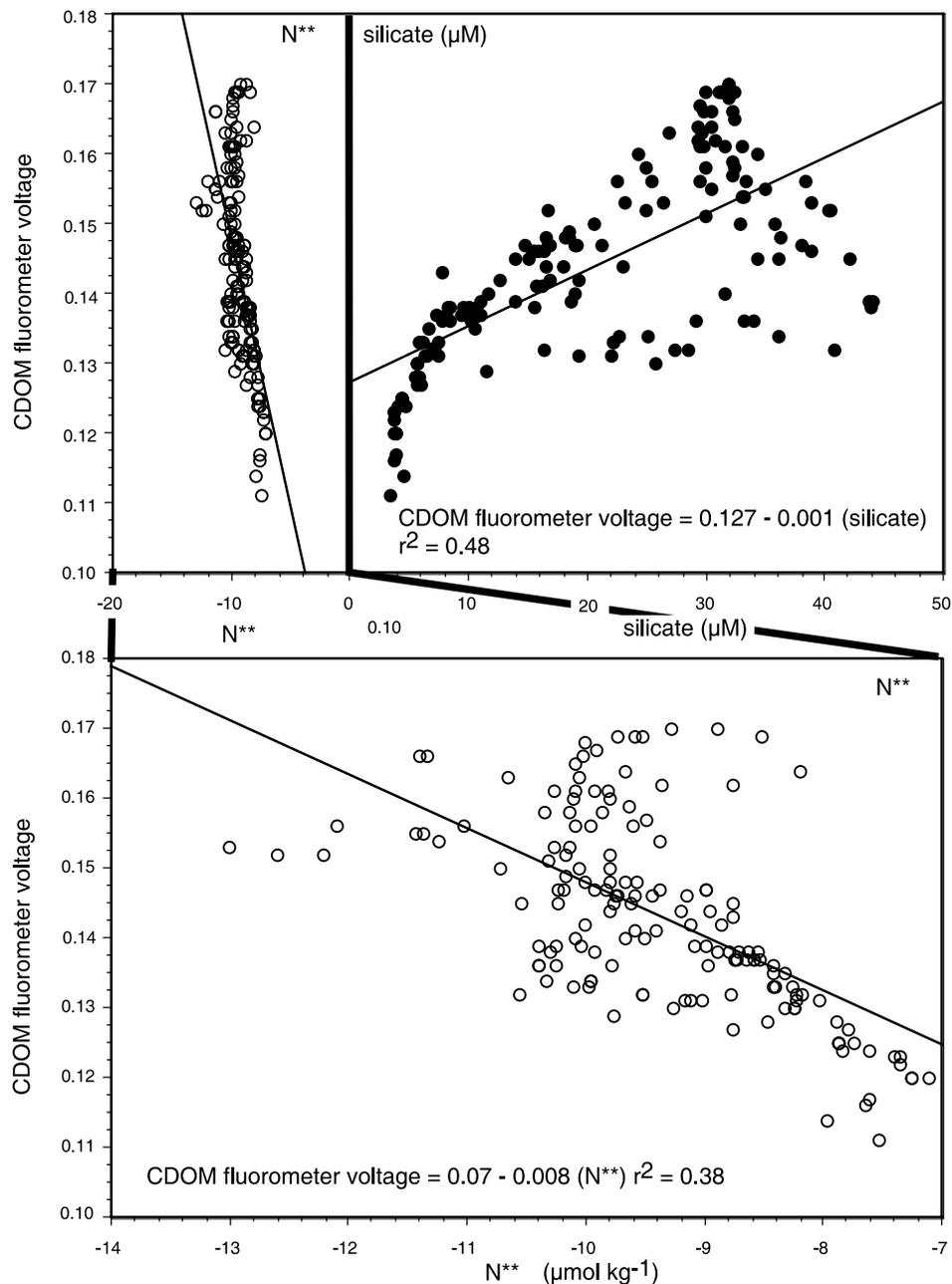


Figure 6. (top left and bottom) Relationship between the denitrification indicator N^{**} [Gruber and Sarmiento, 1997] and CDOM fluorescence for marine samples collected in the Chukchi and Beaufort seas, May–June 2002 and July–August 2002. (top right) Relationship between silicate concentration and CDOM fluorescence. Regression lines shown are all least squares best fit with associated equations.

[22] Another approach we used was to solve simultaneous equations for a simple three mixing model system (runoff, melted sea ice, and Atlantic water) in order to estimate runoff fractions in samples on the May–June 2002 cruise during which sources of melted ice were negligible (Figure 3). Many of the Atlantic layer samples (salinity >33.5) appeared to naturally separate from water samples above the halocline on the basis of DOC concentrations; many Atlantic layer DOC concentrations fell below the regression line relating DOC concentrations and estimated

runoff fraction (Figure 2). These data below the mixing line probably reflect long-term degradation of DOC in the Atlantic layer, which has a much longer residence time than surface layers of the Arctic Ocean. The small, but unrealistic negative runoff fractions observed in some Atlantic layer samples (Figure 2) also suggest that it is prudent to consider Atlantic layer DOC concentrations separately from surface waters. The regression equation used to estimate the apparent meteoric DOC concentration ($\text{DOC} = 115 \times \text{MW} + 58.96$) indicates that the DOC concentration in arctic river

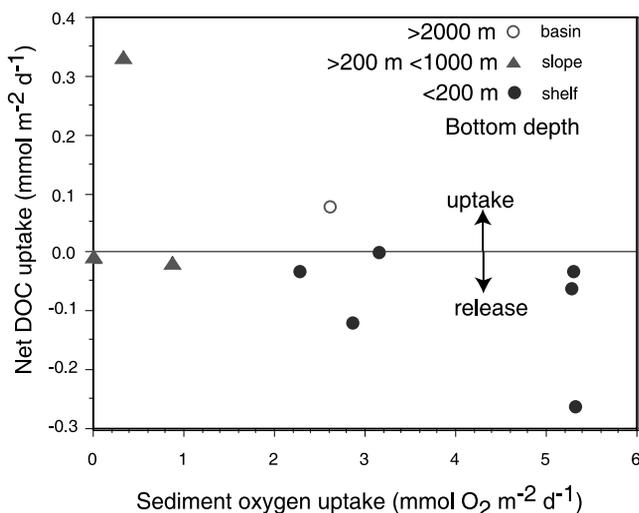


Figure 7. DOC exchange rates for sediment incubation experiments undertaken on shipboard at in situ temperatures in July–August 2002 using undisturbed HAPS cores from shelf, slope, and basin sediments. Negative uptake rates reflect release of DOC into the overlying water column.

water is somewhat higher (174 μM) than estimated from y-intercepts in simple regression analyses of salinity and $\delta^{18}\text{O}$ versus DOC concentration ($\sim 156 \mu\text{M} \pm 7$ standard error). Regardless, all estimates are much lower than actual measured values in rivers (Table 1).

[23] It is possible that the arctic-wide estimate of river water $\delta^{18}\text{O}$, -20‰ [Östlund and Hut, 1984] used in our calculations of conservative mixing is not representative of the river waters contributing to the study area. Dominant inputs from the Lena River, Kolyma River, and Bering Strait inflow (includes Yukon) would result in a regional runoff end-member closer to -21‰ (Table 1). Contributions from rivers draining the North Slope of Alaska such as the Meade, Colville, Kuparuk, and Sagavanirktok are also likely to contribute a more depleted $\delta^{18}\text{O}$ end-member value, although the Mackenzie is somewhat less depleted due to its lower latitude origin. Even considering these sources of variation, the best-fit regression line for the May–June data suggests a $\delta^{18}\text{O}$ value for freshwater of $\sim -26.39 \pm 0.77\text{‰}$ (95% confidence interval). Although runoff could have this isotopic composition, it is also possible that consistent brine injection in almost all water samples shifted the apparent mixing line to the right and downward, resulting in a more negative y-intercept that is essentially an artifact (Figure 1). In particular, if we exclude all samples below the upper halocline (salinity >33.5) to remove the Atlantic waters that may not effectively mix with surface waters, the apparent runoff intercept for $\delta^{18}\text{O}$ increases to $-23.22 \pm 1.17\text{‰}$ (95% confidence interval, Figure 1) which is probably more reasonable as a regional runoff end-member. Nevertheless, the presence of brine in almost all samples collected on the May–June 2002 cruise indicates that the runoff end-member $\delta^{18}\text{O}$ value should be cautiously interpreted, and may be too negative. If this is the case, runoff in the SBI sampling region would likely reflect a slightly less negative runoff intercept, ~ -20 to -21‰ , for contributions to surface ocean waters.

[24] Regardless of the uncertainty associated with choosing an appropriate regional $\delta^{18}\text{O}$ value for runoff in our conservative mixing calculations, it is clear that melted sea ice was only a significant component of surface waters during the July–August 2002 cruise. Because sea ice coverage was continuous and nearly 100% in May–June, and largely absent by the time of the July–August cruise in the same region, we assume that much of the ice cover melted and dissipated in place to generate a freshwater lens. Surface water had a freshwater component from melted sea ice that was as high as one-quarter of surface waters during July–August (Figure 1), and in some cases exceeded the fraction of freshwater derived from runoff. However, the absence of freshwater contributions from sea-ice melt in May–June along with radium isotope dating of these surface waters in the spring by Hansell *et al.* [2004] indicate that the freshwater contributed by melted sea ice is almost completely overwhelmed by runoff contributions on an annual basis. This is a significant observation because the volume of freshwater exported in the form of sea ice that ultimately melts in the North Atlantic after it transits Fram Strait ($2790 \text{ km}^3 \text{ yr}^{-1}$) is on the same scale as Arctic Ocean runoff ($3300 \text{ km}^3 \text{ yr}^{-1}$ [Aagaard and Carmack, 1989]). However, at least in this portion of the Arctic, it does not appear that the large retreat of sea ice that seasonally occurs in the Chukchi Sea has more than short-term seasonal impacts on regional surface salinities.

[25] Using the mean discharge data from the rivers shown in Table 1 that directly discharge into the Arctic Ocean (i.e., excluding the Yukon), total discharge is approximately $1884 \text{ km}^3 \text{ yr}^{-1}$. This discharge accounts for a significant fraction of the $\sim 3300 \text{ km}^3 \text{ yr}^{-1}$ of direct runoff into the Arctic basin (i.e., excluding freshwater entrained in the Bering Strait; [Aagaard and Carmack, 1989]). After incorporating the proportional contribution of each river's flow-weighted $\delta^{18}\text{O}$ value (Table 1), an Arctic Ocean $\delta^{18}\text{O}$ value for runoff is calculated to be -18.7‰ . A similar calculation using Aagaard and Carmack's [1989] generally higher discharge volumes for these same rivers was little different, -18.5‰ . These values are significantly more positive than the value commonly ascribed to Arctic Ocean runoff, -20 to -21 [Östlund and Hut, 1984]. One major reason for the significant difference is that sampling only the largest rivers (Table 1) biases the precipitation sources to include comparatively low latitudes that have less heavy isotope-depleted precipitation. The watersheds of several of the large rivers draining into the Arctic Ocean including the Ob, Yenisey and Mackenzie extend well south into the middle latitudes of the Northern Hemisphere. In addition, freshwater entrained in Bering Strait, ($\sim 1670 \text{ km}^3 \text{ yr}^{-1}$ [Aagaard and Carmack, 1989] and now thought to be probably higher [Woodgate and Aagaard, 2005]), has a $\delta^{18}\text{O}$ freshwater end-member value during peak summer flow of -21.1‰ [Cooper *et al.*, 1997; Clement *et al.*, 2004]. When this stable oxygen isotope composition for runoff in the Bering Strait inflow ($\sim 1670 \text{ km}^3 \text{ yr}^{-1}$ or more) is added to the total discharge of the five rivers (excluding the Yukon) monitored for $\delta^{18}\text{O}$ values (Table 1, $1884 \text{ km}^3 \text{ yr}^{-1}$), total runoff for the Bering Strait (assumed to include the Yukon) and the five other rivers in Table 1 is at least $3554 \text{ km}^3 \text{ yr}^{-1}$. The proportional contribution of each of these freshwater sources to an integrated $\delta^{18}\text{O}$ value

for runoff is -19.8% , and would be even more negative if we take into account the higher proportion of freshwater projected to be present in the Bering Strait inflow [Woodgate and Aagaard, 2005]. Total freshwater input to the Arctic marine system, including runoff from rivers and through Bering Strait and the excess of local precipitation over evaporation is therefore at least $\sim 5870 \text{ km}^3 \text{ yr}^{-1}$. Consequently, $\sim 60\%$ of that freshwater is supplied by the five largest rivers that discharge directly into the Arctic Ocean (Table 1) plus the freshwater entrained in the Bering Strait inflow. The remaining 40% of Arctic runoff, which includes smaller rivers that do not drain subpolar or temperate latitudes as well as local precipitation on sea ice, would have an integrated $\delta^{18}\text{O}$ value of -21.5% if the overall end-member for the $\delta^{18}\text{O}$ value of runoff in the Arctic Ocean is -20.5% .

[26] The end-member $\delta^{18}\text{O}$ values (i.e., y-intercepts for salinity (x) and $\delta^{18}\text{O}$ (y) regressions) around -23% , such as we observe in the SBI sampling, can be explained by inputs from rivers of eastern Siberia and the North Slope of Alaska, and freshwater delivered through the Bering Strait. Nonetheless, the runoff end-member for the marine data set collected on the Chukchi and Beaufort margins is also reasonably consistent with a Bering Strait origin with contributions from the Mackenzie River (somewhat less depleted in ^{18}O), from the eastern Siberian rivers such as the Kolyma and Lena (somewhat more depleted in ^{18}O), and from rivers draining the North Slope of Alaska (even more depleted in ^{18}O). Contributions of freshwater from the large Eurasian rivers farther to the west do not seem as likely, either on the basis of the $\delta^{18}\text{O}$ values of those rivers or prevailing surface water currents that tend to route surface waters out of the Eurasian Arctic via the Transpolar Drift.

[27] One other means to address the North American versus Eurasian origins of runoff on the Chukchi and Beaufort shelf and slope region is to examine distributions for tracers that are specific to the North American Arctic or Eurasian Arctic. For example, barium concentrations in major North American rivers such as the Mackenzie have been observed to be higher ($138\text{--}574 \text{ nmol L}^{-1}$) than in a number of Eurasian rivers ($12\text{--}175 \text{ nmol L}^{-1}$) [Guay and Falkner, 1997, 1998]. Although there are complexities with the use of barium as a runoff tracer because it is biologically scavenged, in sampling accomplished in 1993 in the same shelf-basin boundary region as the 2002 SBI sampling, Guay and Falkner [1997] observed high concentrations of barium that they identified as having Mackenzie River origins. In contemporaneous sampling also conducted in 1993–1994, Beasley *et al.* [1998] and Cooper *et al.* [1999a] found that $^{237}\text{Np}/^{129}\text{I}$ ratios were significantly different in the Canada basin and shelf from that observed on the Amundsen basin and shelf that are highly influenced by the Ob and Yenesei River outflow. Specifically, in waters influenced by Ob and Yenesei runoff in the Amundsen shelf and basin, $^{237}\text{Np}/^{129}\text{I}$ ratios are significantly lower (~ 0.1 to 0.2 atom/atom) than in the Beaufort Sea (>0.3 to 0.5 atom/atom) [Cooper *et al.*, 1999a]. In summary, in the 1993 sampling on the Beaufort and Chukchi shelf and Canada Basin, not only was a North American river tracer (barium) present, no evidence was found for a significant presence of an Ob and Yenesei river tracer (low $^{237}\text{Np}/^{129}\text{I}$ ratios). The salinity and stable oxygen data from the August

1993 sampling on the Beaufort and Chukchi Sea shelf and basin [Cooper *et al.*, 1999b] (and unpublished data cited therein) are similarly distributed in sea ice melt and runoff fields to that observed in July–August 2002 (Figure 1). As a result it seems reasonable to conclude that the DOC and water carrying it that was sampled in 2002 is likely to be of primarily North American (via direct inputs and transport through Bering Strait), rather than Eurasian origin regardless of the evidence for a lengthy transit in the Beaufort Gyre [Hansell *et al.*, 2004].

[28] The spring sampling in May–June 2002 shows that water column DOC concentrations are correlated with both salinity and $\delta^{18}\text{O}$ values (Figure 3). Although brine injection in these samples could have some impact on the apparent DOC concentration in the runoff (meteoric water) end-member estimated from DOC versus salinity (Figure 3, zero salinity), the relationship between DOC concentrations and $\delta^{18}\text{O}$ values provides a runoff end-member estimate that is much less responsive to brine injection. In addition to longer residence times of terrigenous DOC in the Beaufort Gyre relative to the Transpolar Drift [Hansell *et al.*, 2004], the lower DOC concentrations we report here for North American rivers such as the Yukon and Mackenzie (Table 1) may play a role in the difference in the relationship between salinity and DOC between the North American and Eurasian Arctic basins. For the three largest Eurasian rivers, the Ob, Yenisey and Lena, the flow-weighted DOC concentrations in freshwater near river mouths during PARTNERS sampling in 2003–2004 were ~ 800 to $1000 \text{ }\mu\text{M}$, relative to the apparent meteoric water DOC concentration of ~ 500 to $700 \text{ }\mu\text{M}$ observed in the Eurasian Arctic basin [Dittmar and Kattner, 2003]. This implies that $\sim 30\%$ of runoff DOC is initially reactive and is lost during transport to the Arctic Ocean. If the flow-weighted DOC concentrations reported here for the Mackenzie ($358 \text{ }\mu\text{M}$) and Yukon ($625 \text{ }\mu\text{M}$) are representative of the North American Arctic, and if a similar $\sim 30\%$ of DOC is reactive over shelves, then the apparent DOC concentration for meteoric waters influenced predominantly by North American rivers would be approximately $250\text{--}450 \text{ }\mu\text{M}$. Significantly relatively high DOC was observed in July 2002 sampling in Bering Strait (Figure 4), which suggests that even if some of the shelf-basin boundary waters sampled were ultimately from Bering Strait sources, significant loss of DOC had occurred by the time we sampled those offshore waters.

[29] There is a significant difference between the expected apparent intercept that is arrived at by subtracting $\sim 30\%$ from measured river concentrations ($250\text{--}450 \text{ }\mu\text{M}$) and the intercept ($154 \text{ }\mu\text{M}$) reported by Hansell *et al.* [2004], which we also corroborated here independently using oxygen isotope measurements and solution of three end-member mixing equations. This presumably reflects a loss of DOC while surface waters circulate in the Beaufort Gyre over a time period estimated from radium isotope measurements to be 12 ± 1 years [Hansell *et al.*, 2004]. Much of this loss would be due to bacterial decay and photo-oxidation in the upper water column; small fractions of terrigenous dissolved organic materials can also be transported into the deep Arctic from shelf waters as a result of brine injection [Dittmar, 2004]. However our PARTNERS data and the associated rapid decay projections suggest a lower rate of DOC decay than Hansell *et al.*

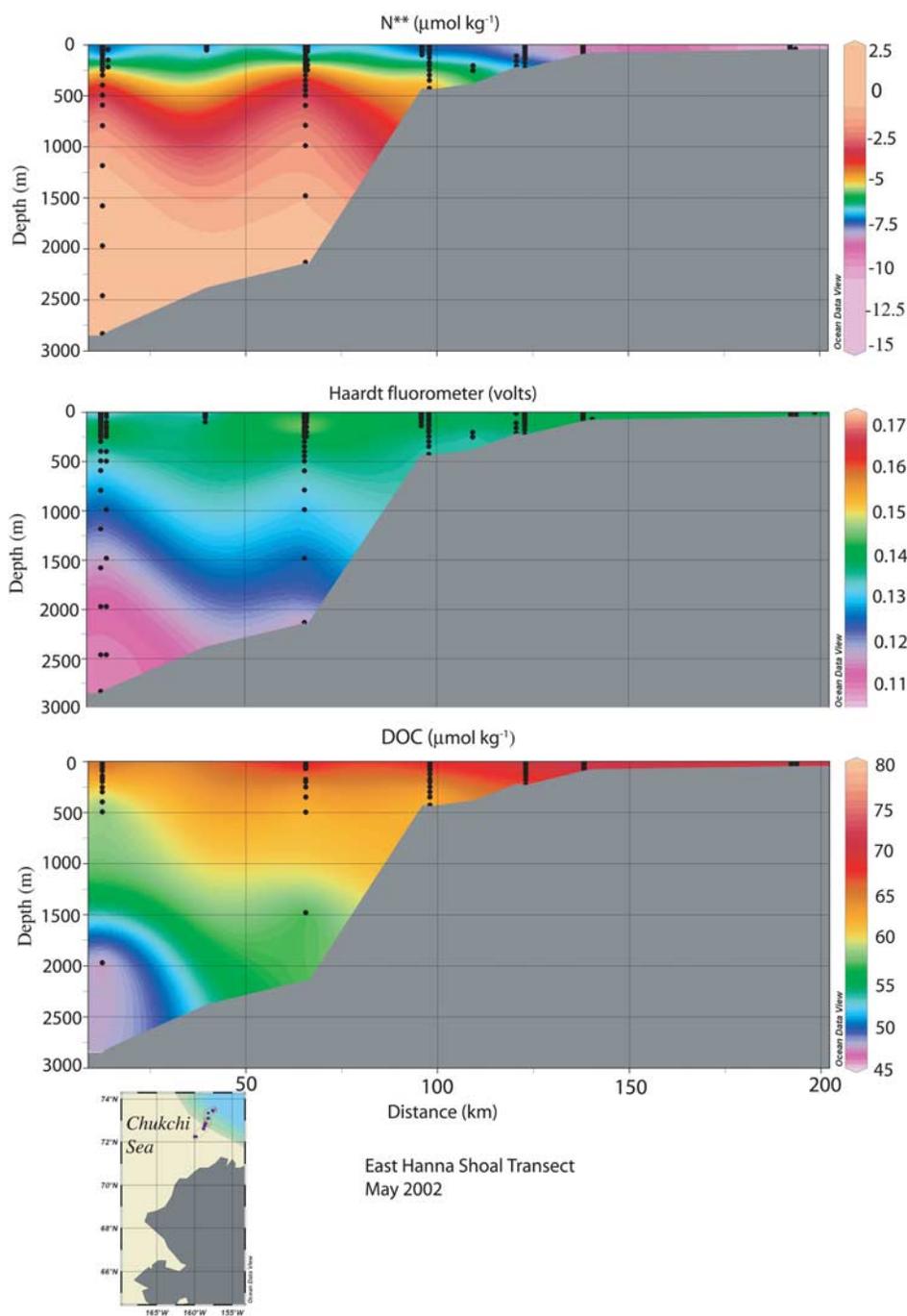


Figure 8. Section transect along East Hanna Shoal Line from shelf to deep Arctic basin, May 2002 showing property distributions of N^{**} , CDOM fluorometer voltage response, and DOC. Figure was generated using Ocean Data View software (R. Schlitzer, Ocean Data View, <http://www.awi-bremerhaven.de/GEO/ODV>, 2005).

[2004] estimated. They projected a loss of $396 \pm 50 \mu\text{M}$ of DOC over a ~ 12 -year period in the Beaufort Gyre, while these calculations project a loss of as little as $\sim 100 \mu\text{M}$ over the same 12-year period, using the Mackenzie River flow-weighted DOC concentrations. The major uncertainties that are the basis for this difference are the degree of accuracy for estimates of the concentrations of DOC in major rivers such as the Mackenzie and Yukon. *Hansell et al.* [2004] use

higher concentration estimates from other data sources. It is not clear to what extent DOC is rapidly mineralized, photo-oxidized, or flocculated at river mouths and therefore not measured in the offshore Arctic Ocean such as our SBI sampling. Another complication is that DOC concentrations in Arctic rivers are highly variable, with extreme maxima over a few days at peak runoff [*Rember and Trefry*, 2004]. The only way to adequately address these uncertainties, as

well as to understand initial processing of DOC in coastal waters will be through more detailed sampling of seasonal variation in runoff, along with measurements of concentrations of DOC and appropriate tracers in coastal waters. Presumably regular well-coordinated river sampling programs such as PARTNERS will help continue to reconcile these apparent differences for the largest Arctic rivers.

[30] DOC measurements show that the instrumental (CDOM) fluorometer response is correlated with DOC in the Atlantic layer (salinity >33.5) as might be expected since this fluorometer has been used to produce empirical estimates of DOC in the Eurasian Arctic [Amon *et al.*, 2003] where Atlantic waters dominate. However, we did not observe such correlations in the waters above the Atlantic layer. Higher voltages were observed in the upper halocline (salinity = 33.1; $\delta^{18}\text{O} = -1.1$; Figure 5), which is characterized by nutrient maxima and N^{**} minima. Therefore it is not surprising that nutrients in waters above the halocline were generally correlated with instrumental fluorescence during the May–June 2002 cruise when melted sea ice contributions were negligible (Figure 5). However within the upper halocline, nutrient maxima were strongest near the shelf/slope and the CDOM fluorometer voltages were higher offshore (Figure 8). It is outside of the scope of this study to determine the actual materials that are contributing to the fluorometer voltage response while not appearing to significantly influence DOC concentrations measured in bottle samples, but we speculate that materials released from the sediments are involved. Our sediment incubation experiments (Figure 7) indicate that DOC can be actively released from continental shelf sediments, and perhaps this DOC fraction gives a relatively high instrumental fluorometer signal. But why is the CDOM fluorometer response in the upper halocline larger offshore than near the slope? We do know that turbidity within the halocline increases toward the shore [Codispoti *et al.*, 2005] and perhaps this turbidity depresses the CDOM signal giving an apparent decrease in “CDOM DOC” toward the shelf/slope (Figure 8). We speculate, therefore, that as the signals generated over the shelf/slope proceed toward the interior of the Arctic Ocean, turbidity will decrease the fastest producing an increase in the CDOM fluorometer voltage response while the strength of the observed nutrient signals decrease more or less as expected. While we cannot specify the particulate or dissolved materials that the CDOM fluorometer is responding to, it is clear that further investigation is required before the CDOM fluorometer can be routinely used to estimate DOC concentrations in Arctic waters, despite its apparently consistent performance in the Eurasian Arctic [Amon *et al.*, 2003].

[31] In sediment incubation experiments conducted during SBI field studies, DOC effluxes from incubated sediment cores were largest from shelf sediments (Figure 7). Relative to the full water column, these fluxes do not appear large, up to $0.3 \text{ mmol m}^{-2} \text{ d}^{-1}$, but nevertheless additional work is probably necessary to evaluate the importance of this flux, which could possibly be detectable on the scale of individual ship transects (Figure 8). Concentrations of water column DOC at the depth ($\sim 120 \text{ m}$) of the halocline (salinity = 33.1) are approximately $70 \mu\text{M}$ (Figure 3), so a cubic meter of bottom water in contact with the sediments at this stratified depth would already contain $\sim 70 \text{ mmol}$ of DOC. Observations from the SBI field program indicate that

ubiquitous plumes of brine injected shelf waters with high concentrations of silicate, ammonium and other nutrients flow into the deeper Arctic basin after coming into contact with shelf sediments [Codispoti *et al.*, 2005]. The DOC concentrations from sediments probably are also entrained in these plumes, including DOC from sediment pore waters that originate from the breakdown of organic matter, both marine and terrestrial, as well as the excretion products from benthic animals [Hulth *et al.*, 1996]. This suggests that the DOC flux from the sediments would likely be more labile than that already in the water column. The fact that these shelves are influenced by extremely high marine primary production and terrestrial input from coastal rivers and erosion, suggests that understanding of DOC transport in the Arctic needs to consider runoff, erosion and related DOC interactions with marine sediments, particularly over the extensive continental shelves where carbon is processed [Olsson and Anderson, 1997; Fransson *et al.*, 2001].

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