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Riverine export and the effects of circulation on dissolved organic carbon in the Hudson Bay system, Canada

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Abstract

The distribution of dissolved organic carbon (DOC) in Hudson Bay (HB), Foxe Basin (FB), and Hudson Strait (HS) was examined during 01–14 August 2003. The HB system displayed relatively high DOC concentrations with medians of 109, 90, and 100 μmol L^{-1} for measurements made in HB, FB, and HS, respectively. Waters were significantly modified as they circulated through the HB system. An influence of marine-derived DOC was inferred for waters entering the system from northern HS and FB. The presence of a cold-water layer and elevated DOC concentrations observed in HB along the western coast and at depth was explained through either brine rejection and export of surface DOC to depth during sea ice formation or the decomposition of a settling algal bloom. As waters circulated in HB, an input of terrigenous DOC was the dominant modifying factor. In particular, DOC-laden rivers in southern HB increased the DOC concentration and then displayed a conservative behavior as water exited the bay along the southern coast of HS. Additionally, the late stages of ice melt observed during this study showed a significant dilution effect on surface DOC concentrations within eastern HB. Input and export of riverine DOC in the HB system was estimated at $\sim$ 5.5 Tg C yr^{-1}, which is approximately 23% of the annual DOC input from rivers draining directly into the central Arctic Ocean and therefore represents an important contribution of terrigenous carbon to northern seas.

Dissolved organic carbon (DOC) in seawater represents a globally important pool of carbon (Hedges 2002). However, for the Arctic Ocean, Amon (2004) argued that the scarcity of spatial and seasonal observations of DOC limit our ability to derive a realistic carbon budget. River runoff is one of the largest sources of DOC in the Arctic Ocean; however, biological production also represents a significant seasonal and spatially variable source (Anderson 2002). It is likely that climate change will have an effect on the marine DOC pool, particularly in Arctic and sub-Arctic regions where changes to the sea ice cover (Serreze et al. 2007; Comiso et al. 2008), river discharge (Déry et al. 2005; McClelland et al. 2006), permafrost temperature (Taylor et al. 2006), and coastal erosion rates (Mars and Houseknech 2007) have been observed.

The Hudson Bay (HB) system, including HB, Foxe Basin (FB), and Hudson Strait (HS), represents one of the largest drainage basins on the North American continent. Riverine input into the HB system averages 717 km^3 yr^1 (McClelland et al. 2006), draining approximately one-third of Canada (Déry et al. 2005). Furthermore, there is a strong yet difficult-to-estimate contribution of freshwater from sea ice melt and local precipitation (Prinsenberg 1986; Ingram and Prinsenberg 1998).

Recent evidence suggests that waters modified in the HB system may have an important influence as far as the Newfoundland Shelf (Déry et al. 2005). More recently, Granskog et al. (2007) have described the distribution of chromophoric dissolved organic matter (DOM) in HB, solidifying the important influence of rivers on DOM in the system. Nevertheless, little information exists on the distribution of DOC in HB. Furthermore, the influence of ice melt on DOC concentrations in HB is unknown. In this study, we present the first observations on the vertical and horizontal distribution of DOC in the marine portion of the HB system and discuss how DOC concentrations are modified through terrigenous and marine-derived sources as oceanic waters circulate through the system. We also provide a focus on the input of riverine DOC, using previous studies and our own observations to derive an estimate of the annual riverine DOC contribution to the HB system.

Methods

The data for this study were collected during the MERICA-nord program from 01–14 August 2003 (Harvey et al. 2006). The 13 hydrographic sampling stations visited in HB, FB, and HS are mapped in Fig. 1. Temperature and salinity, and in vivo chlorophyll *a* (Chl *a*) fluorescence were obtained via a SBE 19 plus conductivity, temperature, and depth probe (SeaBird Electronic) and WETStar fluorometer (Wet Labs), respectively, mounted to a rosette equipped with 10-liter Niskin bottles, which were used to collect water samples at discrete depths. Depending on water depth, 6 to 10 depths were sampled at each station for a total of 127 discrete water samples. Fluorescence measurements were regionally calibrated against Chl *a* concentration estimated from water subsamples (100 mL) filtered through Whatman GF/F filters and determined fluorometrically (Turner Designs TD-700 fluorometer) in duplicate after extraction in 90% acetone in the dark at 4°C (Parsons et al. 1984). Water samples for DOC determination were collected from rosette hydrocasts (n = 88). Each sample was filtered through precombusted (450°C for 5 h) Whatman GF/F filters. The filtrate was collected in

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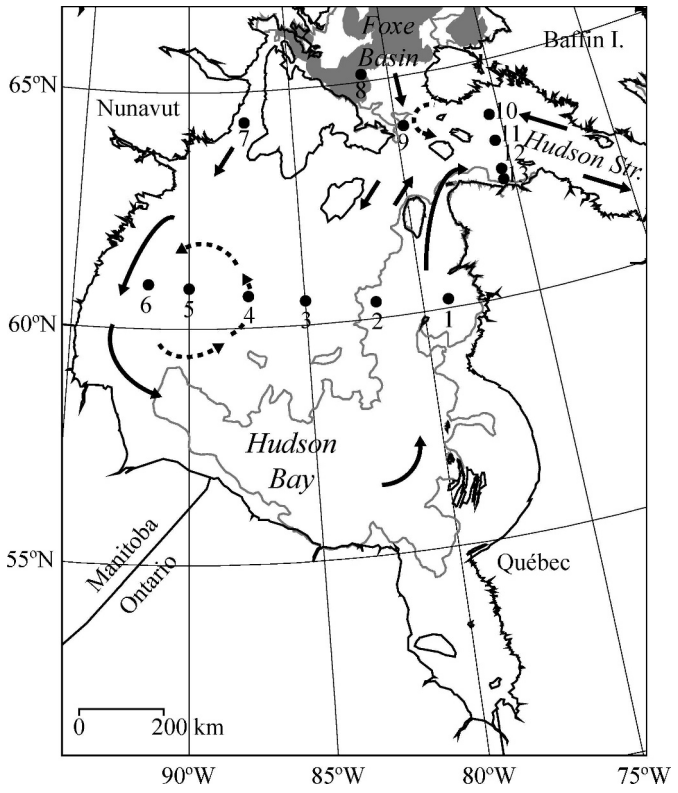

Fig. 1. Map of hydrographic sampling stations in the HB system during MERICA-nord 2003. The spatial extent of > 20% sea ice concentration on 21 July (light gray line) and 11 August (dark gray shading), 2003 is shown (reproduced from Environment Canada's Canadian Ice Service on-line archive, http://ice-glaces.ec.gc.ca/App/WsvPageDsp.cfm?ID=11391&Lang=eng). Solid arrows indicate general circulation patterns. Dashed arrows represent currents that have been modeled (western HB gyre; Saucier et al. 2004) or where low certainty exists (influence of waters entering the system through HS).

5-mL glass storage vials with Teflon-lined caps previously cleaned following the protocol of Burdige and Homstead (1994) and acidified to pH ~ 2 with 25% H_3PO_4 (10 μL mL^{-1}). The DOC samples were kept at 4°C in the dark until analysis. DOC was determined on a high-temperature combustion Shimadzu TOC-5000A autoanalyzer using the analysis procedure given in Whitehead et al. (2000). Potassium hydrogen phthalate was used to standardize DOC measurements. In addition, samples were systematically checked against low-carbon water (2 μmol L^{-1}) and deep Sargasso Sea reference water (44–47 μmol L^{-1}) every seventh sample analysis. These seawater DOC reference standards were produced by the Hansell's certified reference materials (CRM) program (http://www.rsmas.miami.edu/groups/biogeochem/CRM.html). The mean DOC of three replicate injections of each water sample showed a typical C.V. < 3%.

Results

Figure 1 shows the spatial extent of > 20% sea ice concentration on 21 July and 11 August 2003. The distribution of this melting ice reflects both the cyclonic circulation of HB (general circulation patterns are identified as arrows in Fig. 1) and the consistent residency of ice in FB during the study period. Accordingly, Stas. 1 and 2 in HB and Stas. 8 and 9 in FB show a recent input of sea ice meltwater to the surface layer as evidenced by low surface temperature and salinity relative to adjacent stations (Fig. 2a,b). A layer of cold water (< −1.4°C) in HB was observed at depth at Stas. 5 and 6 and extended east at a depth of approximately 50 m, with a slight rise approaching the eastern coast. This plume was likely a remnant of local winter mixing processes (Prinsenberg 1986). The cold waters extending to the bottom at Stas. 5 and 6 and at depths > 100 m in HB are most likely associated with sea ice formation. This statement is corroborated by $\delta^{18}O$ data that show evidence of a substantial brine component in waters at Stas. 5 and 6 and along bottom waters in HB (K. Azetsu-Scott unpubl. data). HS also showed evidence of colder waters around 100 m toward the southern coast; however, most noteworthy are the lower surface salinities observed at Stas. 12 and 13, a result of outflow from HB, and the warmer and saltier inflow from the Labrador Sea observed at Stas. 10 and 11.

HB has been previously characterized by a subsurface Chl *a* maximum (Roff and Legendre 1986). Similarly, the vertical profiles of Chl *a* fluorescence presented in our study show a subsurface Chl *a* maximum observed around 20 to 50 m throughout the HB system (Fig. 2c). In HB, the Chl *a* maximum was observed along the upper layer of cold water described above. It is interesting to note the elevated concentrations of Chl *a* observed below the subsurface Chl *a* maximum at Stas. 9 (FB) and 10 (northern HS), and within HB (Fig. 2c).

DOC concentrations measured in the oceanic portion of the HB system were within the upper range of those found in the Arctic Ocean for respective salinities (Anderson 2002; Amon 2004) with medians of 109 μmol L^{-1} (83 to 202 μmol L^{-1}), 90 μmol L^{-1} (83 to 120 μmol L^{-1}), and 100 μmol L^{-1} (67 to 180 μmol L^{-1}), and corresponding salinity ranges of 25.5 to 33.2, 29.1 to 33.5, and 29.1 to 33.0, for HB, FB, and HS, respectively. It is noted that an outlier of 91 μmol L^{-1} DOC and 10.7 salinity was removed from the medians and data ranges presented above because of the influence of ice melt (*see* Discussion). Figure 2d shows the distribution of DOC concentrations within the HB system. Elevated DOC concentrations associated with direct riverine input were observed near surface waters along the eastern and southern shores of HB and HS, respectively. However, elevated DOC concentrations were also observed at depth and along the western coast in HB and along subsurface waters in FB and northern HS, coinciding with the cold waters observed at depth in HB and the subsurface Chl *a* maxima in FB and northern HS, respectively.

Discussion

Riverine DOC input—Although limited measurements of DOC exist for the HB system, it has been shown that rivers draining into the system have a high range of DOC concentrations (Table 1; see Fig. 3 for approximate river location). Southerly rivers (rivers 1–7 in Table 1) tended to

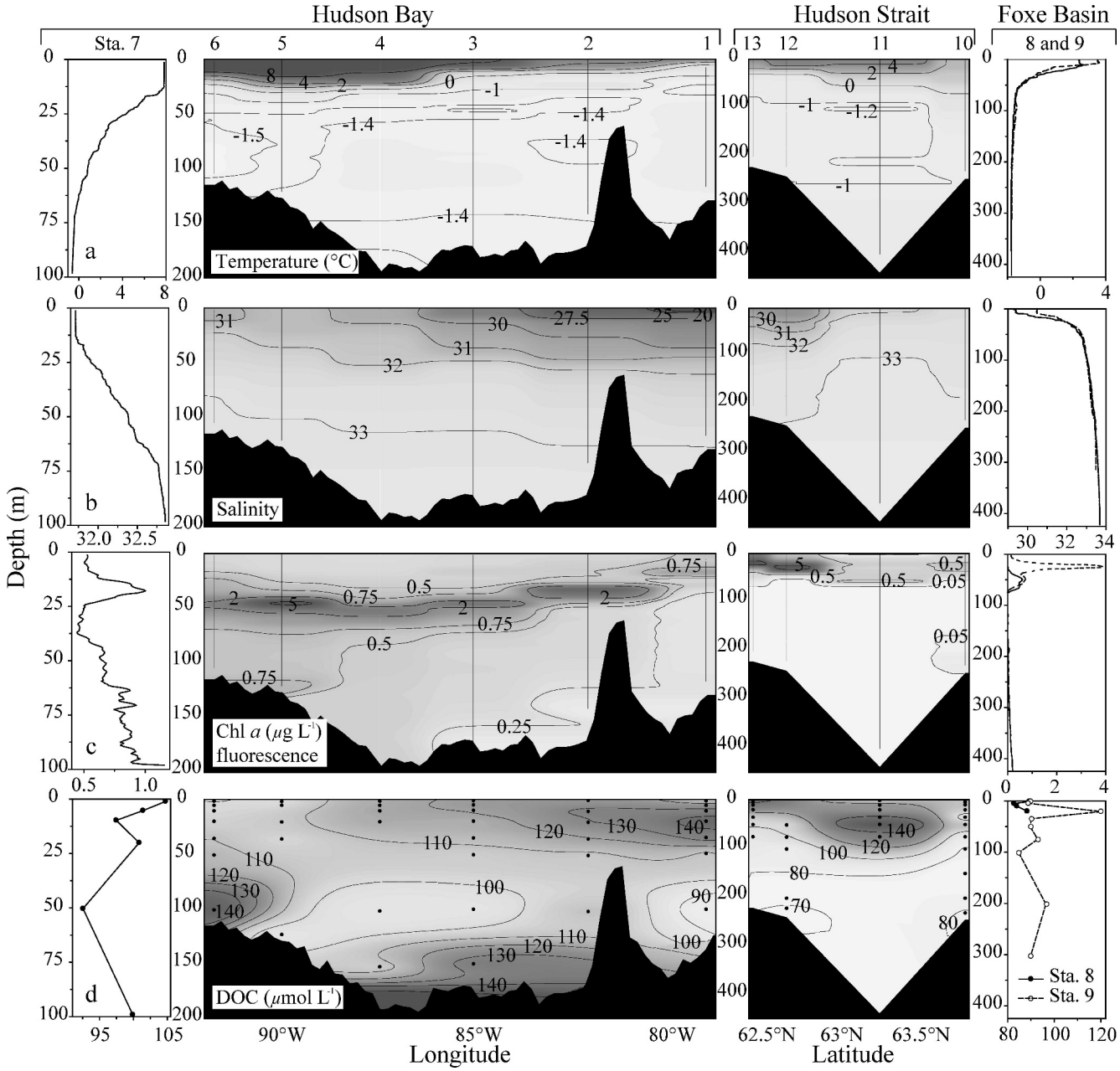

Fig. 2. Interpolated profiles of (a) temperature, (b) salinity, (c) chlorophyll *a* (Chl *a*) fluorescence, and (d) dissolved organic carbon (DOC) concentration in the Hudson Bay system. Data were interpolated and plotted using Ocean Data View v. 3.3.1 (Schlitzer 2006).

have high DOC concentrations, with an average of 702 μmol L^{-1} relative to rivers draining HB's northeastern coast and Ungava Bay that have averages of 266 and 188 μmol L^{-1}, respectively. Unfortunately, to the authors' knowledge there are no direct estimates of DOC concentrations for rivers draining into northwest HB, FB, and northern HS.

We note that southern watersheds of HB are mostly covered by Hudson Plains and Boreal Shield terrestrial ecozones, characterized by extensive peatlands and closed coniferous forest stands, respectively (Wiken 1986; Fig. 3), whereas rivers draining along the eastern HB coast, beginning from the La Grande in James Bay and north to Ungava Bay as well as north of the Churchill River along the western HB coast, drain a south-to-north progression of ecozone types from Taiga Shield to Southern Arctic to Northern Arctic and Arctic Cordillera, respectively (Fig. 3). This progression represents a transition from open coniferous forest stands to discontinuous cover of tundra vegetation, including shallow soils underlain by continuous permafrost (Wiken 1986). Therefore, on the basis of ecozone type and the DOC concentration reported in the previous paragraph, it is surmised that northerly rivers within the HB system will have a lower DOC flux than that for rivers along the southern coast, from the Churchill River east to the lower Eastmain River.

Table 1. Data summary for rivers located in Fig. 3 and plotted in Fig. 4.

		Watershed characteristics			DOC		
No.	River	Area (km^2)	Discharge ($km^3\ yr^{-1}$)	Yield ($m^3\ m^{-2}\ yr^{-1}$)	Concentration ($\mu mol\ L^{-1}$)	Yield ($g\ C\ m^{-2}\ yr^{-1}$)	Reference
1	Churchill	288,880	85.2	0.295	1180	4.16	Granskog et al. (2007)
2	Nelson	1,100,000	209	0.190	814	1.86	Granskog et al. (2007)
3	Hayes	103,000	79.5	0.772	935	8.66	Granskog et al. (2007)
4	Winisk	50,000	25.2	0.504	199	1.20	Granskog et al. (2007)
5	Nottaway	57,500	37.3	0.649	708	5.51	Hydro-Québec (2004)
6	Broadback	17,100	11.8	0.692	717	5.95	Hydro-Québec (2004)
7	Rupert	40,900	27.5	0.671	367	2.95	Hydro-Québec (2004)
8	Grande Baleine	42,735	21.0	0.492	354	2.09	Hudon et al. (1996)
8.1	Grande Baleine	42,735	21.0	0.492	279	1.65	Hudon et al. (1996)
8.2	Grande Baleine	43,200	19.8*	0.458*	191	1.05	Granskog et al. (2007)
8.3	Grande Baleine	43,200	19.8*	0.458*	248	1.37	Retamal et al. (2007)
9	Petite Baleine	15,850	5.3	0.332	254	1.01	Hudon et al. (1996)
9.1	Petite Baleine	11,700	3.7*	0.316*	354	1.34	Granskog et al. (2007)
10	du Nord	1437	1.2	0.813	275	2.68	Hudon et al. (1996)
11	Nastapoca	13,364	8.1	0.605	306	2.22	Hudon et al. (1996)
11.1	Nastapoca	12,500	8.0*	0.640*	206	1.58	Granskog et al. (2007)
12	Povungnituk	28,000	11.9*	0.425*	194	0.99	Granskog et al. (2007)
13	Arnaud	49,469	20.1	0.406	114	0.56	Hudon et al. (1996)
14	aux Feuilles	42,476	19.0	0.447	138	0.74	Hudon et al. (1996)
15	aux Mélèzes	42,735	19.6	0.458	230	1.26	Hudon et al. (1996)
16	Caniapiscau	89,610	54.1	0.603	229	1.66	Hudon et al. (1996)
17	Baleine	31,857	17.5	0.550	256	1.69	Hudon et al. (1996)
18	George	41,699	27.7	0.664	161	1.28	Hudon et al. (1996)

* Data were calculated from climate-averaged annual discharge rates presented in McClelland et al. (2006).

Raymond et al. (2007) estimated a river runoff DOC flux to the central Arctic Ocean of $\sim$ 25 Tg C yr^{-1} using a relationship between average DOC and water yields. This estimate was believed to be conservative, as it did not include smaller tributaries that may contribute much higher DOC fluxes along the Eurasian and Alaskan coastlines. Similarly, using the watershed area provided by McClelland et al. (2006) for the HB system, an estimated DOC flux for rivers draining into the system of $\sim$ 5.9 Tg C yr^{-1} was made as a first-order approximation (Raymond et al. 2007). However, the DOC–water yield relationship for eastern HB and Ungava Bay rivers reported in Hudon et al. (1996) had a much lower slope than that for the major rivers draining directly into the Arctic Ocean (Raymond et al. 2007). This difference reflects the lower concentrations of DOC in the HB and Ungava Bay rivers (Hudon et al. 1996), believed to be a function of the vegetation and soil cover of the drainage basin.

DOC and water yields were also calculated from DOC concentrations reported for additional studies made on rivers within the HB system (Table 1). River discharge data were not reported for the DOC water samples collected as part of Granskog et al. (2007) and Retamal et al. (2007). Therefore, for southern rivers reported in Granskog et al. (2007), monthly river discharge data were obtained from the Water Survey of Canada's Hydrometric Database and matched to the month of the original DOC water sample collection. However, we were unable to obtain monthly discharge data for northern HB rivers and therefore, climate-averaged annual discharge rates presented in McClelland et al. (2006) were used purely for comparative purposes (i.e., they were not added to the DOC–water yield relationship originally presented in Hudon et al. [1996]). With the exception of two outliers (Winisk and Rupert rivers), data from southern and northern rivers lay along two significantly different DOC–water yield relationships, supporting their separation on the basis of ecozone type (Fig. 4; $F_{2,15}$, $p < 0.0001$). Therefore, we estimated the DOC flux from river runoff in the HB system as a function of the predominant ecozone type(s) covering individual catchment basins and using the climate mean river discharge data presented in McClelland et al. (2006). This resulted in a total terrigenous DOC flux estimate of $\sim$ 5.5 Tg C yr^{-1} (Table 2). We note that our estimate is likely conservative as it does not include runoff from oceanic watersheds that line the coasts of the HB system and does not account for seasonal variability in DOC flux associated with peak discharge periods in northern rivers (Finlay et al. 2006). Furthermore, the low DOC concentrations observed in the Winisk and Rupert rivers highlight scale limitations of using the regional ecozone-based classification to categorize individual watersheds.

Change in DOC concentrations during circulation through the HB system—Relations between salinity, temperature, and Chl *a* and DOC concentrations were used to examine the different waters entering and exiting the HB system, and thereby identify the sources determining DOC distributions in HB, FB, and HS. Sources considered included: riverine input, sea ice melt and brine rejection, marine production, and water mass origin. On the basis of sampling location and the aforementioned relations, data

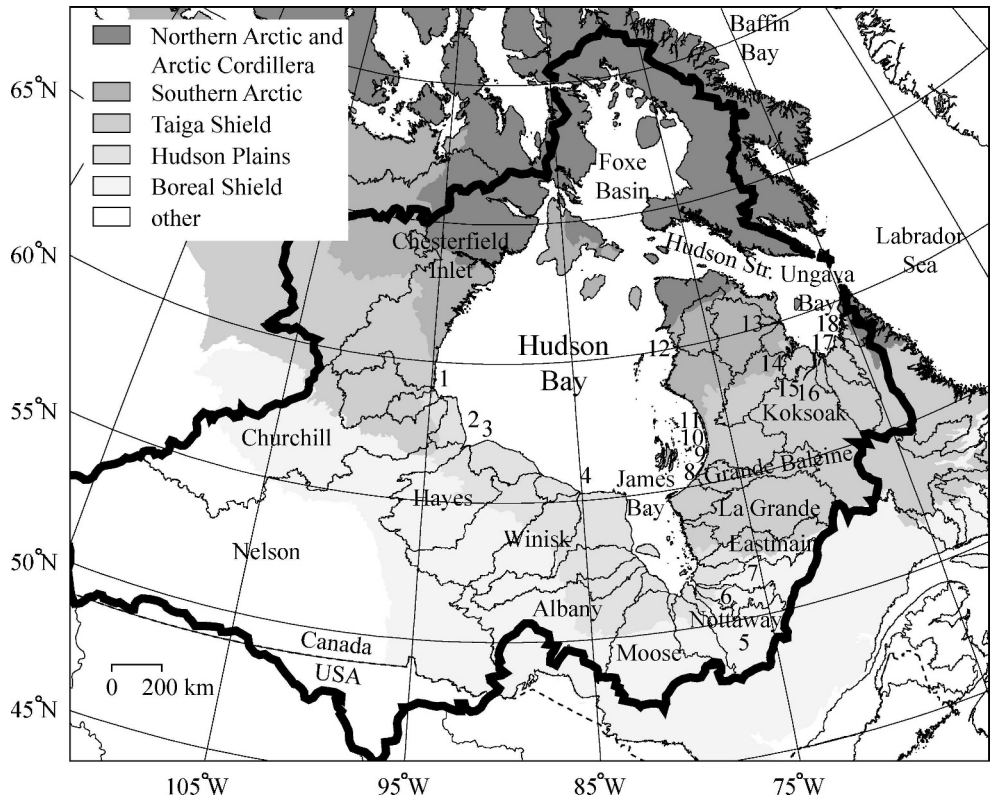

Fig. 3. Map of individual watersheds and terrestrial ecozones surrounding the Hudson Bay system (reproduced using geospatial data obtained through the Natural Resources Canada Geogratis website, http://geogratis.cgdi.gc.ca).

were split into groups for analysis. These groups and their DOC vs. salinity relationships are presented in Table 3 and plotted in Fig. 5.

Riverine input to the HB system accounted for the most notable change to DOC concentrations in the upper water column. As water moved from FB into western HB, DOC concentrations increased. The zero salinity intercept for Stas. 3–5 and 7 suggests a river DOC concentration end member of 312 μmol L^{-1} for northwestern HB (Table 3). The main source of riverine water in this region is from northern rivers draining through Chesterfield Inlet (Table 1; Fig. 3). This inferred end member fell within the range of DOC concentrations reported for rivers along the eastern HB coast (Hudon et al. 1996; Granskog et al. 2007; Retamal et al. 2007) and our estimate on the basis of the land cover type of the region. Following waters along the cyclonic circulation of HB, the influence of a higher DOC concentration end member, associated with more southerly HB and James Bay rivers, is evident (i.e., 698 μmol L^{-1} at Stas. 1 and 2 at $>$ 10 m water depth, Table 3, Fig. 5a). Furthermore, there was no significant difference between the mixing curves of Stas. 1 and 2 with Stas. 12 and 13 ($F_{2,15}$, $p = 0.51$), demonstrating the conservative behavior and stability of DOC concentrations as waters exited out of the HB system along the southern coast of HS.

The late stages of sea ice melt presented in this paper suggest a dilution effect on surface DOC concentrations as shown by the significant positive relationship observed in FB and in surface waters at Stas. 1 and 2 in HB (Table 3;

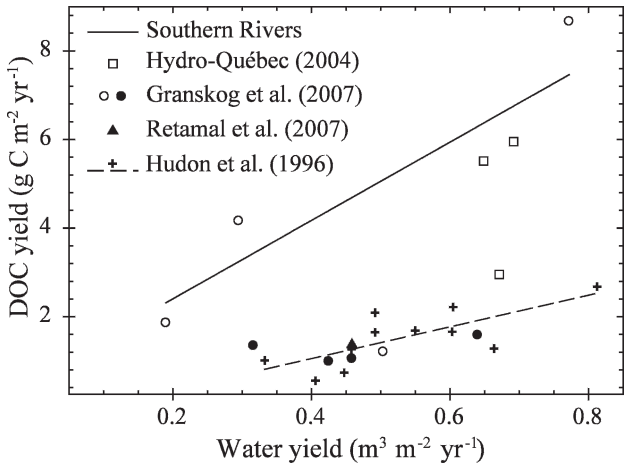

Fig. 4. DOC yield (y) vs. water yield (x) relationships for southern (open symbols; $y = 8.84x + 0.64$; $r^2 = 0.84$) and northern rivers, the latter represented by the relationship originally presented in Hudon et al. (1996; crosses; $y = 3.57x - 0.37$; $r^2 = 0.55$). The two southern river data points lying along the northern rivers relationship were considered outliers and not included in the relationship calculations. Furthermore, northern river data (solid symbols) from Granskog et al. (2007) and Retamal et al. (2007) were not included in the northern rivers relationship for reasons discussed in the text. Raw data for individual watersheds are provided in Table 1 and their locations are shown in Fig. 3.

Table 2. Watershed area, discharge (McClelland et al. 2006), and carbon flux estimates made on the basis of DOC yield vs. water yield relationships for southern and northern rivers as presented in Fig. 4.

Region	Watershed area (km^2)	Discharge ($km^3\ yr^{-1}$)	Carbon flux (Tg C yr^{-1})	
			Southern	Northern
Northwestern	394,539	80.1	—	0.1
Southern	2,120,130	372	4.6	—
Northeastern	231,420	127	—	0.4
Ungava Bay	267,856	138	—	0.4
Total	3,013,945	717	—	5.5*

* Value includes estimates for southern and northern rivers.

Table 3. Ordinary least-squares regression statistics from DOC concentration vs. salinity relationships for different groups in Hudson Bay, Foxe Basin, and Hudson Strait.

Station	n	y-Intercept ($\mu mol\ L^{-1}$)	Slope ($\mu mol\ L^{-1}$)	r^2	p
1, 2 (> 10 m)	7	698	−18.9	0.97	< 0.01
1, 2 (< 10 m)	5	60.6	2.7	0.94	< 0.01
3–5, 7 (< 100 m)	24	312	−6.6	0.67	< 0.01
6 (< 100 m)	6	−108	6.8	0.52	0.10
2–4, 6 (≥ 100 m)	4	−6950	215	0.71	0.16
8, 9	12	45.3	1.4	0.33	0.05
10, 11	17	1130	−31.5	0.12	0.17
12, 13	12	733	−20.1	0.93	< 0.01

Fig. 5a [inset], b). The zero salinity intercepts from FB and eastern HB surface water DOC–salinity relationships allowed the inference of a DOC ice melt end member that ranged between 45 and 61 $\mu mol\ L^{-1}$. This ice melt dilution effect agrees with recent studies (Shin and Tanaka 2004; Mathis et al. 2007); however, it is contrary to previous studies that suggest a potential increase of surface DOC to be associated with sea ice melt (Smith et al. 1997; Scully and Miller 2000; Anderson 2002). The opposing concentrating and diluting influence of sea ice melt in the literature can be explained through sea ice desalination processes. That is, high DOC concentrations measured in sea ice are associated with brine in sea ice where photosynthetic activity occurs and organisms reside. During melt, brine flushes from the sea ice as it is replaced by a snow- and ice-melt hydrostatic head at the surface, which has lower DOC concentrations (Belzile et al. 2002; Amon 2004) due mainly to the process of segregation during sea ice formation. Therefore, further ice melt would have a strong dilution effect on surface DOC concentrations as was observed in our study.

Marine production also appeared to be a strong source for DOC in the HB system. We note that a large range of DOC from 70 to 180 $\mu mol\ L^{-1}$ was observed in northern HS, represented by Stas. 10 and 11; however, DOC was not significantly related to salinity (Table 1; Fig. 5b). The presence of subsurface peaks in Chl *a* and DOC concentration at Stas. 10 and 11 point to an influence of primary production on DOC concentration in northern HS (Fig. 2c, d). The influence of new DOC production was also apparent at Sta. 9 (Fig. 2c, d).

Along the western coast and at depths > 100 m within HB, high DOC concentrations appeared to be associated with the deep cold-water layer described earlier. Two possible mechanisms, operating either exclusively or additively, can be used to explain these elevated DOC concentrations. Brine rejection during sea ice formation can act to export DOC from surface waters to depth (Amon 2004; Benner et al. 2005). It is noted that latent heat polynyas, such as those that form along the western HB coast and in FB (Saucier et al. 2004), act as ice factories when the insulating sea ice cover is removed because of prevailing winds and currents, directly exposing surface waters to the cold atmosphere during winter. Therefore, western HB would be a site of elevated DOC export associated with brine rejection. Sedimenting algae and detritus from the bottom ice springtime bloom could also act to elevate DOC concentrations at depth through different processes transforming and releasing organic carbon (e.g., exudation by ice algae, autolysis of algae, viral lysis, release from broken cells by sloppy feeding, hydrolysis of detritus by extracellular enzymes [solubilization]; Carlson 2002). It is noted that the location of elevated DOC concentrations along the western HB coast match with the timing and depth of a settling ice algae bloom as predicted from a detailed three-dimensional biophysical model for HB (V. Sibert pers. comm. 2008). Furthermore, the residence time of deep water in HB has been estimated at 3 to 5 yr (Roff and Legendre 1986), allowing time for the accumulation of DOC.

An additional influence would have been the origin of marine water masses. That is, Pacific-derived waters modified within the Arctic Ocean typically have DOC concentrations of ~ 70–90 $\mu mol\ L^{-1}$ (Anderson 2002), which is higher than that reported for Atlantic waters, which range from ~ 50 to 70 $\mu mol\ L^{-1}$ (Wheeler et al. 1997). The high DOC concentrations (85–97 $\mu mol\ L^{-1}$) observed at Stas. 8 and 9 at depth likely indicate an influx of Pacific-derived waters through FB, which corroborates conclusions from previous studies (Ingram and Prinsenberg 1998; Jones et al. 2003). It is also significant to note that DOC concentrations at depth within HS showed the lowest DOC concentrations in the HB system with a minimum concentration of 67 $\mu mol\ L^{-1}$ (Fig. 2d). These lower DOC concentrations within HS support the influence of Atlantic-derived waters from the northern Labrador Sea (Drinkwater 1986). However, as discussed above, once waters from either FB or HS enter the HB system, their DOC concentrations are substantially modified by riverine input, marine production, and by sea ice formation and melt processes. Combining DOC data collection with tracer data, such as $\delta^{18}O$ collection or using nitrate–phosphate relationships, will greatly increase our knowledge base on the dynamics of DOC in HB.

Riverine DOC export—The confinement of riverine-derived outflow along the southern coast of HS provides the unique opportunity to directly estimate the correspond-

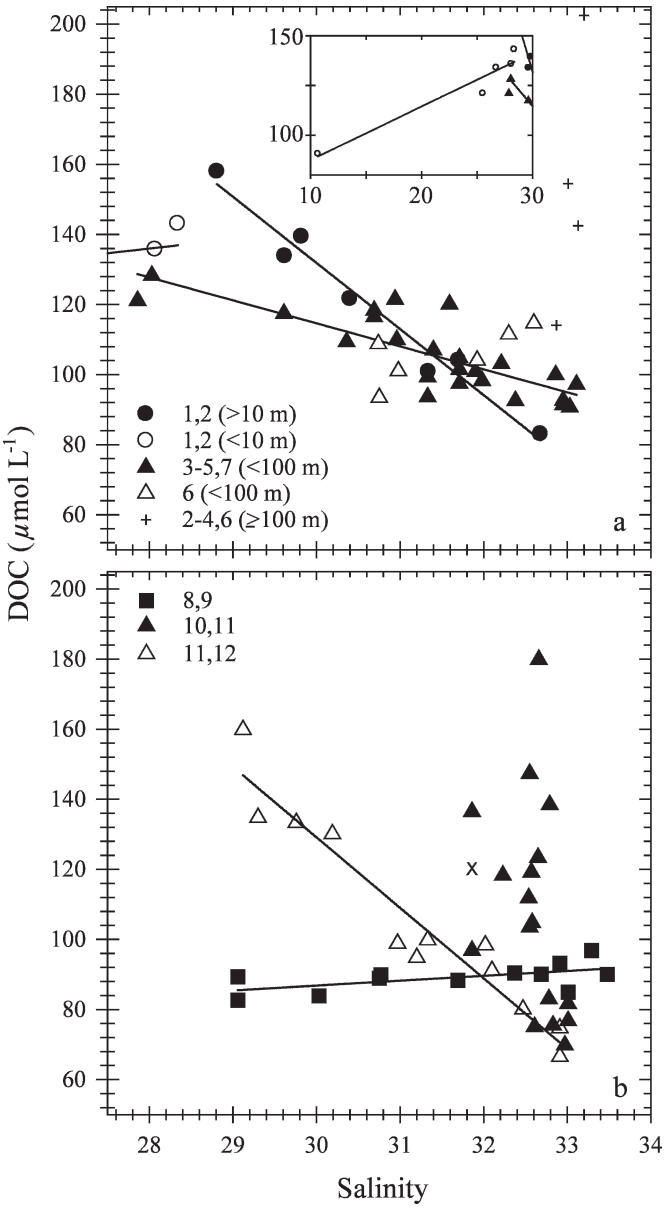

Fig. 5. DOC vs. salinity relationships for grouped data in (a) Hudson Bay and (b) Foxe Basin and Hudson Strait. The inset in (a) shows a lower salinity range encompassing observations made at Stas. 1 and 2. Lines plotted represent significant linear trends (*see* Table 3) and numbers outside of parentheses in the legend signify sampling stations. In (b), the symbol "x" represents an outlier from Sta. 9 that was associated with the subsurface Chl *a* maximum (*see* Fig. 2c,d).

ing DOC export from HB. It is noted that our estimation of a zero salinity end member from the DOC–salinity relationship has to be made with caution provided the extrapolation was made beyond a minimum salinity measurement of > 29 for observations from southern HS (Fig. 5b). That is, the slope of the DOC–salinity relationship may be higher or lower than conservative mixing of river waters due to biological and physicochemical processes affecting DOC concentrations in the ocean (Carlson 2002; present paper). However, measurements along southern HS were made shortly after the sea ice cover had melted (Fig. 1). The sea ice cover would have acted to reduce atmosphere–ocean coupling, resulting in a much more extensive influence of river plumes in HB (Ingram and Prinsenberg 1998) as well as limit photodegradation of DOC in surface waters by blocking the transmission of ultraviolet radiation (Bélanger et al. 2006). Therefore, the application of the zero salinity intercept to estimate the HB river end member was assumed appropriate for data from southern HS (Stas. 12 and 13). This assumption is further supported by the observed stability of DOC concentrations in surface waters as they circulated from northeastern HB and into HS. Using the assumed riverine end member of 733 μmol L^{-1} DOC for southern HS (Table 3) and the climate-averaged annual river discharge for the HB system of 578 km^3 yr^{-1} (i.e., not including runoff from Ungava Bay; Table 1), we estimated a riverine DOC export of $\sim$ 5.1 Tg C yr^{-1}, which, surprisingly, is equal to our previous estimate of riverine DOC input for HB made in the previous subsection. It is noted that the end member of 733 μmol L^{-1} would not have been applicable to estimate DOC export from the Ungava Bay rivers given their much lower DOC concentrations (Table 1). We conclude that during summer and early fall, the majority, if not all, of riverine DOC is exported out of the HB system through southern HS, noting that this is a time when biological and physicochemical processes affecting surface DOC concentrations would have been limited because of the recent presence of a sea ice cover. Once exported from the HB system, this significant pool of terrigenous organic carbon will flow toward the Labrador Sea and Newfoundland Shelf where it can either undergo photochemical and microbial oxidation in surface waters, providing a potential energy source to that system, or be exported to depth via brine rejection and contribute to the formation of classical Labrador Sea Water, which has high DOC concentrations (Benner et al. 2005).

The contribution of DOC from the HB system is considerable yet has been understudied in the past, even though the system is known to include a substantial river discharge that can affect waters as far as the Newfoundland Shelf. We have shown here that the HB system displays DOC concentrations within the upper range of observations at similar salinities in the Arctic Ocean. During our study period, 01–14 August 2003, the northwestern portion of the HB system appeared to be influenced by a marine production of DOC, whereas the southeastern portion was significantly modified through the addition of terrigenous DOC from the numerous DOC-rich rivers that empty into the region. Elevated DOC concentrations within HB were also observed along the western coast and at depth and were suggested to represent a potential export to depth of DOC through either a physical brine rejection mechanism or through the decomposition of previously produced particulate organic matter. Furthermore, within FB, and along the eastern side of HB where sea ice collects because of atmospheric forcing (Saucier et al. 2004), a significant ice melt dilution effect was observed on surface DOC concentrations.

In our study, we have estimated the HB system to have a riverine DOC input of $\sim$ 5.5 Tg C yr^{-1} and a near equal export. It is noted that an average of annual DOC input estimates for direct riverine contributions to the central Arctic Ocean is $\sim$ 24 Tg C yr^{-1} (23 Tg C yr^{-1} in Anderson [2002] and 25 Tg C yr^{-1} in Raymond et al. [2007]). Therefore, our results suggest that the HB system contributes a total riverine DOC export equal to $\sim$ 23% of that for the Arctic Ocean. This percentage represents an important contribution to the export of terrigenous carbon into northern seas and warrants further studies to better clarify the dynamics of DOC within the system.

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