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Key Points:
- Seventeen Hudson Bay rivers spanning a wide vegetative and permafrost range were sampled for DOC, POC, and lignin compositions
- Trends were distributed latitudinally, reflecting woody angiosperms in the south, nonwoody gymnosperms in the north
- There is evidence of release of DOC from soil permafrost based on fresh-appearing aldehyde ratios coupled with depleted $\Delta^{14}C$ activities

Supporting Information:
- Supporting Information S1

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Organic matter compositions of rivers draining into Hudson Bay: Present-day trends and potential as recorders of future climate change

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Abstract Concentrations and compositions of particulate and dissolved organic carbon (POC and DOC, respectively) and aromatic compounds including lignin were analyzed in water samples from 17 rivers flowing into Hudson Bay, northern Canada. These rivers incorporate basins to the south with no permafrost to basins in the north with continuous permafrost, and dominant vegetation systems that include Boreal Forest, the Hudson Plains, Taiga Shield, and Tundra. Major latitudinal trends in organic carbon and lignin concentrations and compositions were evident, with both DOC and dissolved lignin concentrations dominating over their particulate counterparts and exhibiting significant correlations with total dissolved and suspended solids, respectively. The composition of lignin reaction products in terms of the syringyl, cinnamyl, and vanillyl compositions indicate mixed sources of vascular land plant-derived organic carbon, with woody gymnosperms contributions dominating in the southern river basins whereas nonwoody angiosperm sources were more important in the most northerly rivers. The composition of nonlignin aromatic compounds, which provides a tracer for nonvascular plant contributions, suggests stronger contributions from Sphagnum mosses to dissolved organic matter in rivers below the tree line, including those with large peat bogs in their basins. Acid/aldehyde ratios of the lignin products together with $\Delta^{14}C$ data for DOC in selected rivers indicate that DOC has generally undergone greater alteration than POC. Interestingly, several northern rivers exhibited relatively old DOC according to the $\Delta^{14}C$ data suggesting that either old DOC is being released from permafrost or old DOC survives river transport in these rivers.

Plain Language Summary Dissolved and particulate compounds characteristic of plants have been examined at the outflows of 17 rivers entering Hudson Bay. The river basins, which occupy a wide expanse in latitude, range from no permafrost to complete permafrost, and a wide varied of vegetation types depending on the climate within the basins. The data clearly distinguish between rivers draining areas south of the treeline and those draining tundra to the north. Carbon-14 data for DOC in 8 rivers suggests that old material is being released into several rivers including the most northerly. The baseline provided by these data should help to understand the rapid change this region is going through as warming thaws permafrost and promotes vegetation changes.

1. Introduction

Warming in northern regions has the potential to set in motion a number of changes including permafrost degradation, desiccation, inundation, vegetation alteration, and wildfire incidence, each of which affects northern hydrology [e.g., see *Frey and Smith*, 2005; *Schindler and Smol*, 2006]. Given that these sorts of changes are already underway, it seems likely that the coupling between terrigenous carbon and the hydrological cycle is likewise changing with consequences for both the quality and quantity of organic components carried by northern rivers [*Guo and Macdonald*, 2006]. It is estimated that the top 3 m of circumpolar soils, alone, contain an inventory of ~1000 Pg (petagram, 10^{15} g) organic carbon [*Tarnocai et al.*, 2009] (compared to the global soil organic carbon inventory estimated at 1670 Pg [*Eglinton and Repeta*, 2006]). Thawing of permafrost, therefore, has a globally significant potential to trigger the release of old organic carbon presently preserved in frozen soil and to alter the production, storage, and release of new organic carbon through change in vegetative cover and soil permeability [*Abbott et al.*, 2016; *Guo et al.*, 2007; *Hinzman et al.*, 2005]. The mobilization of organic carbon from soils can result from aerobic processes

producing CO_2 or anaerobic processes producing CH_4 [e.g., see *McGuire et al.*, 2009]. Dissolved and particulate organic matter may also be released from the soil organic pool into streams draining affected watersheds. Note that to avoid confusion when referring to organic components carried by rivers, we will use organic carbon (OC) to refer generally to organic carbon, DOC to refer specifically to the dissolved component, POC to refer to the particulate component, and TOC to refer to the sum of DOC and POC. We use the term organic matter (OM) to refer to organic matter which, in addition to C, may contain significant amounts of O, H, S, N, and P.

The hydrological cycle provides the connection between land and sea, manifested in part by a large transfer of terrigenous OC to the global ocean, estimated at ≥350 Tg yr^{-1} (teragram; 10^{12} g) [*Eglinton and Repeta*, 2006]. For the Arctic Ocean, the TOC supplied by the northern drainage basins is presently estimated at 39 Tg yr^{-1} [*McGuire et al.*, 2009] but may be substantially larger than that [*Vonk et al.*, 2012]. Accordingly, OC carried by river runoff to northern oceans has the potential to provide integrated evidence of processes affecting the production, storage, and release of OC within northern drainage basins [e.g., *Amon et al.*, 2012; *Feng et al.*, 2013; *Hatten et al.*, 2012], partly through the quantities of TOC exported and partly through the elemental, isotopic, and molecular composition of the OM mobilized [e.g., *Feng et al.*, 2015; *Guo and Macdonald*, 2006; *Kuzyk et al.*, 2008; *Schreiner et al.*, 2013; *Vonk et al.*, 2012].

The ^{14}C activity of OC exported by rivers is an important indicator of carbon processing on land. For example, human disturbance in drainage basins tends to promote export of old DOC into rivers either by disturbing vegetation and soils (e.g., deforestation) or by intensifying the hydrological cycle (e.g., injecting wastewater) [*Butman et al.*, 2012; *Butman et al.*, 2015]. These authors found that the age of DOC tends to be greater in low-discharge rivers. In small northern drainage basins, which have low-flow rivers, widespread disturbance is presently occurring through permafrost thaw. Under these circumstances, the active layer thickness increases, releasing old carbon, which would be identifiable by low $\Delta^{14}C$ values [*Guo et al.*, 2007; *Prokushkin et al.*, 2009; *Peterson et al.*, 2002]. Using ^{14}C and other markers, *Feng et al.* [2013] estimated that ancient terrigenous OC in Eurasian Arctic rivers increased by 3 to 6% between 1985 and 2004. Clearly, more extensive regional and local studies are required to establish present baselines for riverine OC and, where possible, to determine whether changes like those observed in the Eurasian Arctic are more widespread [*Frey and McClelland*, 2009; *McGuire et al.*, 2009].

Here we present new data on POC and DOC concentrations in samples collected near the mouths of 17 Hudson Bay rivers (HBRs) with drainage basins that span a wide geographic and vegetative range (Figures 2a and 2b). Eight of the DOC samples were also measured for $\delta^{13}C$ and ^{14}C, and we use these data to evaluate carbon provenance in the different systems. We report concentrations and compositions of dissolved and particulate lignin reaction products and other nonlignin aromatic reaction products and use these biomarkers to trace contributions from different vegetation sources among the different watersheds. Specifically, we compare the lignin compositions among rivers in the context of the various permafrost and vegetative settings within the various drainage basins (Figures 1 and 2b). Nonlignin reaction products (p-hydroxybenzenes and benzoic acids) are also briefly discussed.

2. Study Area

Hudson Bay, which lies just south of the Arctic Circle in Canada, is surrounded by a large drainage basin (3.9×10^6 km^2) dominated by permafrost (Figure 1). The northern portion of the drainage basin is presently continuous permafrost, which becomes discontinuous toward the south, then isolated in patches and, finally, absent in the southernmost portion. The location of Hudson Bay to the south of the Arctic Circle places it in the vanguard of permafrost thaw, and some areas surrounding Hudson Bay have already undergone rapid thaw losing as much as 69% in extent between 1957 and 2003 [*Frey and McClelland*, 2009; *Payette et al.*, 2004]. Accordingly, Hudson Bay and its combined drainage basins provide a sentinel for Arctic warming and an opportunity to investigate interactions between drainage basin change, hydrology, and the effects on adjacent coastal marine biogeochemical cycles.

The Hudson Bay watershed has a cumulative inflow of ~714 km^3 yr^{-1} [*Déry et al.*, 2005; *Dery and Wood*, 2004] from over 40 substantial rivers draining varied combinations of plant communities, permafrost regimes, and climatic zones. The amount of riverine DOC entering Hudson Bay has been estimated at 5.5 Tg yr^{-1},

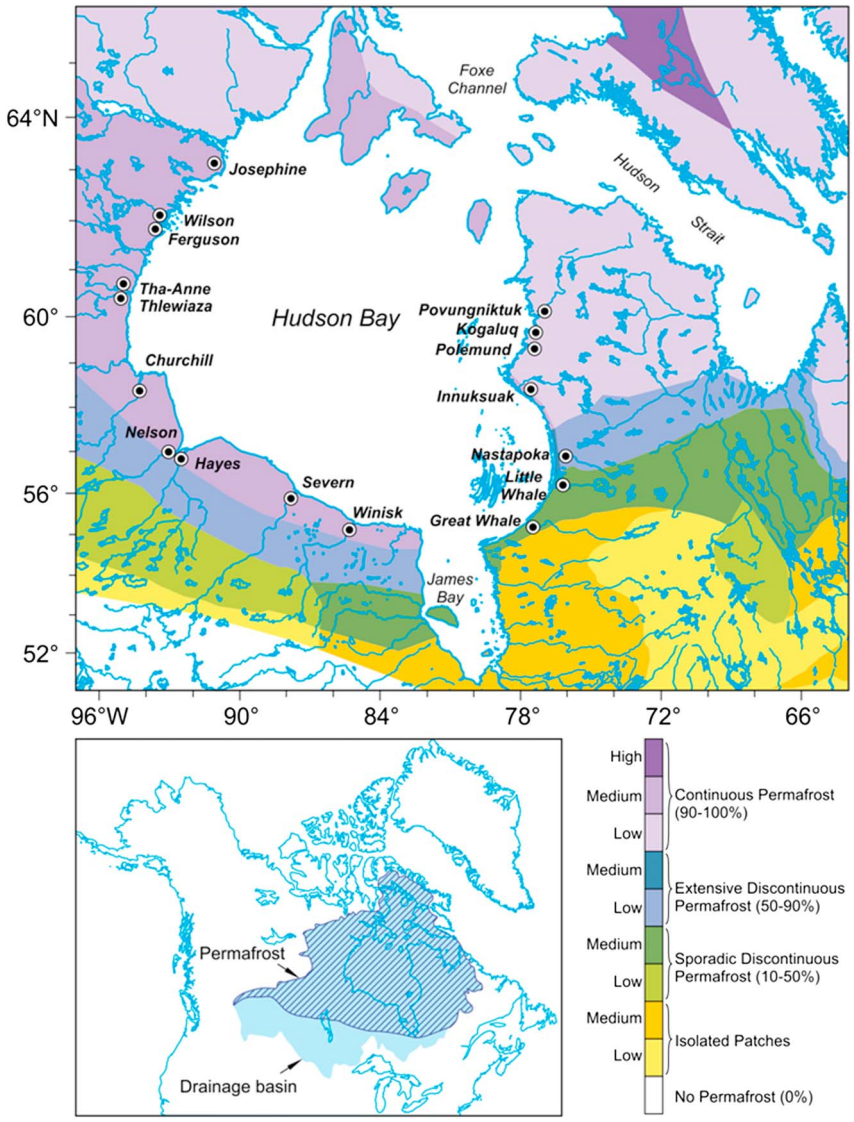

Figure 1. A map of Hudson Bay showing the locations of the 17 rivers sampled at the mouth in this study, and their dispositions within permafrost zones around the margin of the Bay (based on Natural Resources Canada Map (1995)). The inset shows the complete Hudson Bay drainage basin.

equivalent to ~23% of riverine TOC supplied to the Arctic Ocean [*Mundy et al.*, 2010]. The DOC is accompanied by a lesser amount of riverine POC, estimated at 0.46 ± 0.33 Tg yr^{-1} [*Kuzyk et al.*, 2009].

The Hudson Bay drainage basin lies predominantly within the Canadian Shield, which consists of Precambrian crystalline silicate rock and to the southwest limestone. During the Last Glacial Maximum (18 ka B.P.), this area was overlain by some of the thickest ice accumulations [see, e.g., *Stein and Macdonald*, 2004, Figure 1.2.5]. The progressive deglaciation was associated with the formation of the large proglacial Lake Agassiz-Ojibway, which drained catastrophically into the Hudson Bay precursor (Tyrrell Sea) around 8500 cal B.P. An important consequence of these large-scale features is that unlike Siberia and parts of Alaska which had no glacial ice cover, yedoma is not a dominant feature of the landscape.

The wide latitudinal range in climate and permafrost coverage spanned by the various HBR basins leads to a similarly wide range in vegetation among the various subbasins. Proceeding from south to north we find *boreal forest* (Nelson, Hayes, Severn, Winisk), *the taiga shield*—a transitioning mixed forest-tundra (Churchill, Tha-Anne, Thlewiaza, Great Whale, Little Whale, and Nastapoka) zone—which gives way to the *southern Arctic*, and ultimately the northern Arctic, a barren, sparsely vegetated, treeless tundra (Josephine,

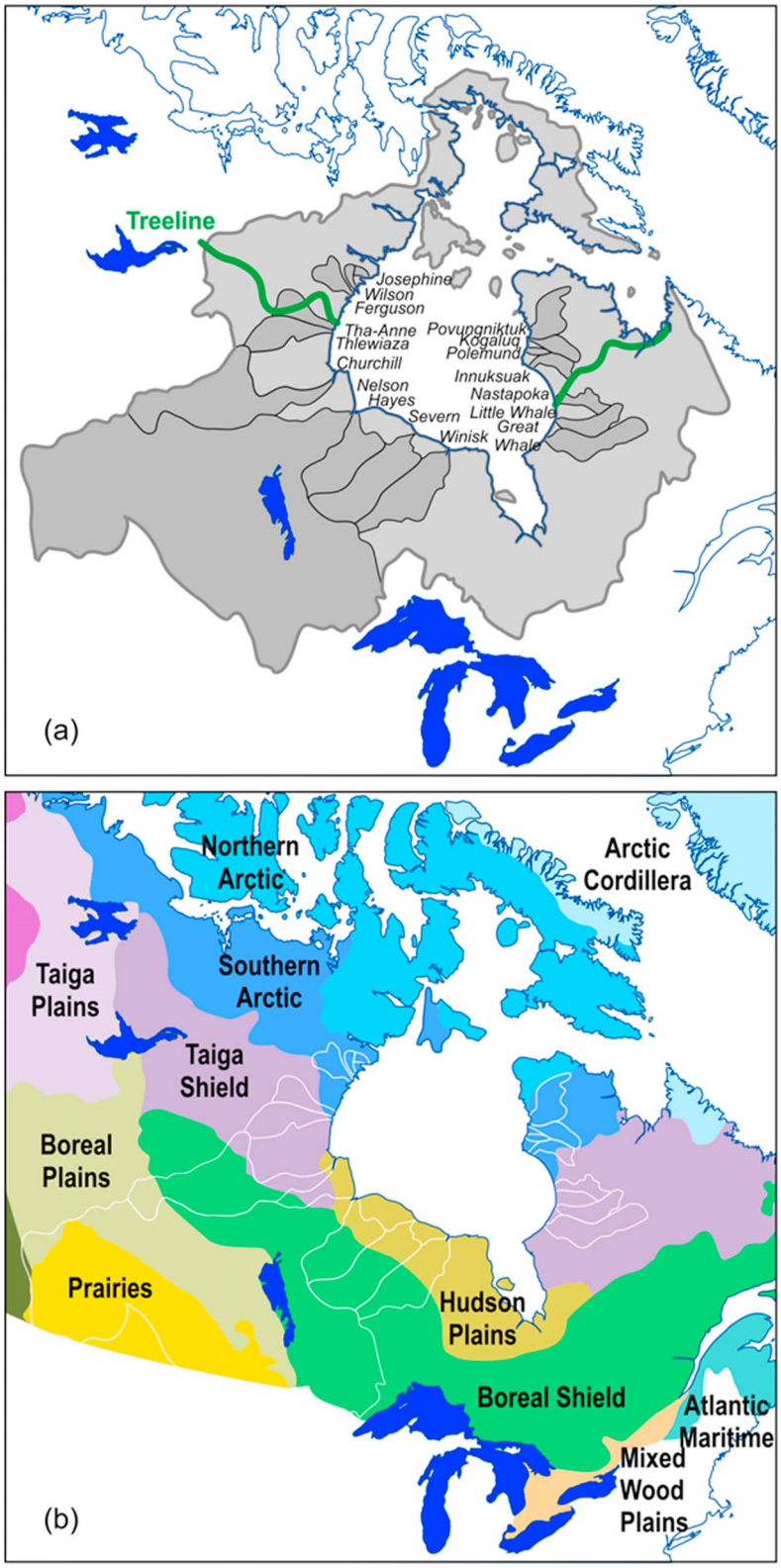

Figure 2. (a) The disposition of the drainage basin for each river sampled in this study and (b) the relationship of the drainage basins to the vegetation zones that span the Hudson Bay drainage area a list of predominant plants that populate each ecozone is given in the supporting information.

Wilson, Ferguson, Innuksuak, Polemund, Kogaluq, Povungnituk) (Figure 2b and supporting information). The tree line (Figure 2a), which provides the border between taiga shield and southern Arctic ecozones, is an especially important vegetation feature because it sets a geographical boundary for the production of lignins associated with woody gymnosperm plants.

3. Methods

3.1. Sample Collection

During an ArcticNet-funded CCGS *Amundsen* expedition in July–August 2010, dissolved and particulate samples were collected upstream from the discharge points for 15 major Hudson Bay rivers. In addition to these rivers, the Nelson and Hayes Rivers were previously sampled during a CCGS *Amundsen* cruise in August 2005 (particulate organic matter (POM)) and July 2007 (dissolved organic matter (DOM)) [*Kuzyk et al.*, 2008, 2009]. These rivers drain regions with widely varying conditions in permafrost (Figure 1 and Table 1) and vegetative cover (Figure 2 and supporting information).

3.1.1. Total Dissolved and Suspended Solids

To collect samples of total dissolved and total suspended solids (TDS and TSS, respectively), river sites near Hudson Bay but upstream of rapids or swifts were accessed by helicopter. Personnel waded in from shore and placed a simple weighted frame supporting a submersible pump on the river bottom in ~0.5–1 m water. The submersible pump was connected by Teflon-lined stainless steel tubing to a stainless steel filter holder containing two precombusted 142 cm GF/F glass fiber filters. The pump was let run (~3 L/min flow rate) for about 60–90 min to collect sufficient fines for analysis. The suspended matter in these filters represents the TSS samples used in this study. The filters were stored frozen (−20°C) on board the *Amundsen*, shipped back to the Freshwater Institute, and kept frozen until further analysis. To recover TDS samples, river water filtered through the above apparatus was collected in acid-cleaned 10 L collapsible jugs and returned to the ship. These samples were then immediately filtered again using 47 mm GF/F filters and a peristaltic pump to remove any remaining particulates. Filtrates were returned to another precleaned collapsible jug, kept in the dark at cool temperatures (~4°C), and shipped back to Winnipeg.

Once in Winnipeg, the filtered water samples (4–6 L volume) were freeze dried in order to collect the dissolved material. The weight was divided by the volume of each sample to obtain an estimate of total dissolved solids (TDS, mg/L). Filters were also freeze dried and TSS weights (mg) were determined by subtracting the average weight of 20 oven-dried 142 mm GF/F filters (0.0995 ± 0.0029 mg) from the weight of the oven-dried sample filter. Concentrations (mg/L) were determined by dividing the total sample weight by the volume of water filtered. Both TDS and TSS samples were packed and shipped to Goñi's College of Earth, Ocean and Atmospheric Sciences (CEOAS) laboratory at Oregon State University (OSU) for further analysis. Analyses at OSU were conducted approximately 4 months after the sampling date.

3.2. Laboratory Analyses

Samples (TSS and TDS) were analyzed for TOC and DOC content, respectively, using a NC2500 elemental analyzer. Subsamples were weighed out on a microscale into silver coated tin boats after which they were exposed to HCl vapor for 24 h to remove carbonates. Filter and analytical blanks, which averaged 2% of the measured sample values, were analyzed simultaneously and used to correct final TOC contents. The concentrations (mg/L) of POC and DOC were calculated as the product of TSS and TDS concentrations times the TOC content of each sample. We note that the GF/F filters used in the field and on the ship have a nominal pore size (0.7 μm) that is greater than those (0.2 to 0.45 μm) typically utilized in DOM isolation. We keep this caveat in mind when comparing our results with those of other studies that used different pore size filters.

Samples were analyzed for lignin-derived phenols and nonlignin reaction products at the CEOAS laboratory at OSU following digestion using the microwave/alkaline CuO oxidation method (full description is given in *Kuzyk et al.* [2008] and *Goñi and Montgomery* [2000]). Briefly, measured amounts of freeze dried TDS and TSS samples containing between 2 to 5 mg of OC [*Louchouarn et al.*, 2000] were reacted with CuO and NaOH in N_2-pressurized Teflon vessels for 90 min at a temperature of 150°C. Following oxidation, recovery standards of ethyl vanillin and transcinnamic acid were added and samples were centrifuged to separate out remaining solids. The aqueous hydrolysate was then acidified to a pH of 1 and extracted twice using ethyl acetate. Extracts were dried under N_2, dissolved in pyridine, and then derivatized using bistrimethylsilyl

Table 1. Sampling Locations and Permafrost Zonation With Hydrological and Ecological Site Characteristics of Hudson Bay Rivers

River	Latitude	Longitude	Sampling Date (Day of Year)	Drainage Basin (km^2)	Annual Q[a] (km^3/yr)	Peak Flow (Day of Year)[b]	Permafrost Zone[c]	Eco Zone[d]	Vegetation
				East					
Povungnituk	60.05	77.22	191	28000	11.9	184	C	S Arctic	Shrub Tundra
Kogaluq	59.61	77.48	191	11300	5.0	171	C	S Arctic	Shrub Tundra
Polemund	59.43	77.30	191	N/A	1.5[e]	170[f]	C	S Arctic	Shrub Tundra
Innuksuac	58.46	78.08	192	11200	3.3	174	C	S Arctic	Tundra
Nastapoka	56.92	76.43	193	12500	8.0	173	ED	S Arctic	Forest Tundra
Little Whale	55.97	76.67	193	11700	3.7	164	SD	Taiga Shield	Forest Tundra
Great Whale	55.27	77.57	194	43200	19.8	153	SD	Taiga Shield	Forest Tundra
				Northwest					
Josephine	63.13	90.98	199	N/A	2.5[e]	180[d]	C	S Arctic	Shrub Tundra
Wilson	62.33	93.13	199	N/A	2.6[e]	180[d]	C	S Arctic	Shrub Tundra
Ferguson	62.08	93.35	199	12400	2.6	181	C	S Arctic	Shrub Tundra
Tha-Anne	60.55	94.92	200	29400	6.3	175	C	SA/TS	Shrub Tundra
Thlewiaza	60.52	95.02	200	27000	6.9	183	C	SA/TS	Shrub Tundra
				Southwest					
Churchill	60.52	95.02	201	288880	20.6	161	C	Hudson Plains	Forest Tundra
Nelson	56.94	92.80	225/281[g]	1125520	94.1	128	C	Hudson Plains	Forest Tundra
Hayes	56.97	92.37	225/209[g]	103000	18.6	152	C	Hudson Plains	Forest Tundra
Severn	55.87	87.82	209	94300	21.3	149	C	Hudson Plains	Forest Tundra
Winisk	55.15	85.30	209	54710	14.7	148	C	Hudson Plains	Forest Tundra

[a]Annual Q discharge from HYDAT data, average from 1964 to 2000 from *McClelland* [2006] (Table S1).
[b]*Déry et al.* [2005].
[c]Permafrost zonation near the river mouth: C (continuous = 90–100%), ED (extensive discontinuous 50–90%), and SD (sporadic discontinuous 10–50%). Natural Resources Canada, 1995.
[d]*Smith et al.* [2010].
[e]Estimated from size of drainage basin and neighboring rivers.
[f]Peak flow day estimated from latitude of the river.
[g]DOM/POM; note DOM was sampled in 2007 and POM in 2005.

trifluoroacetamide and 1% trimethylchlorosilane for 30 min at 60°C. Derivatized extracts were run on the HP6890 Series GC System with DB1 column and the HP5973 mass selective detector. Selective ion monitoring provided quantitative and qualitative fractions of 100 individual CuO products [e.g., *Goñi et al.*, 2009] with detection limits of lignin-derived phenols at $<$10 ng/g sample [*Goñi et al.*, 2013b; *Kuzyk et al.*, 2008]. Typical precisions for the measurement of individual lignin phenols ranged from 5 to 12% of the measured value.

In this paper we focus on the quantification of eight reaction products derived from lignin including vanillyl (V series) phenols, (vanillin, acetovanillone, and vanillic acid), syringyl (S series) phenols (syringaldehyde, acetosyringone, syringic acid), and cinnamyl (C series) phenols (p-coumaric acid, ferulic acid). Several nonlignin derived compounds, including benzoic acid (B series) products (benzoic acid, m-hydroxy benzoic acid, 3,5-dihydroxybenzoic acid) and p-hydroxybenzene (P series) products (p-hydoxybenzaldehyde, p-hydroxyacetophenone, and p-hydroxybenzoic acid), were also quantified. Details on the molecular

precursors and mass spectra for these compounds have been discussed previously [e.g., see *Goñi et al.*, 2009, Table 1; *Tesi et al.*, 2014, Table 1]. As in previous studies [e.g., *Benner et al.*, 2005; *Goñi et al.*, 2013a], we calculated the overall concentrations of dissolved and particulate lignin by combining the yields of the eight lignin phenols ($\Sigma 8 = V + S + C$ phenols $\mu g\ L^{-1}$) and dividing them by volume of water sample collected and filtered (Table 3). In addition, as in previous studies [e.g., *Benner et al.*, 2005; *Kuzyk et al.*, 2008], lignin product yields were normalized to the organic carbon contents to evaluate the overall lignin contents (Λ_8, μg lignin/g OC) of both DOC and POC in each sample.

Finally, for each dissolved and particulate sample, we calculated several lignin compositional parameters, including syringyl to vanillyl (S/V) and cinnamyl to vanillyl (C/V) lignin ratios that have been used repeatedly as vascular plant vegetation indicators [e.g., *Goñi and Hedges*, 1992; *Goñi and Thomas*, 2000; *Hedges and Mann*, 1979; *Kuzyk et al.*, 2008; *Moingt et al.*, 2016]. We also calculated two additional parameters, specifically the ratio of p-hydroxybenzene to vanillyl products (P/V) and the ratio of p-hydroxyacetophenone to the sum of p-hydroxybenzaldehyde and p-hydroxybenzoic acid (Pn/(Pl + Pd)), which have been used recently as indicators of contributions from lower vascular and nonvascular plant sources such as Sphagnum and other mosses [e.g., *Philben et al.*, 2014; *Tesi et al.*, 2014]. It is important to note that because natural processes, including microbial and abiotic degradation, sorption/desorption, and hydrodynamic sorting, can alter these parameters from those in the original vegetation [e.g., *Goñi and Hedges*, 1992; *Hernes et al.*, 2007; *Moingt et al.*, 2016; *Opsahl and Benner*, 1995; *Tesi et al.*, 2008], we apply these parameters in a semiquantitative manner and interpret them with caution in terms of vegetation indicators.

In addition to vegetation indicators, and as in previous studies, we also calculated several parameters that have been used to evaluate the extent of lignin and vascular plant alteration. These parameters include acid to aldehyde ratios for both vanillyl ([Ad/Al]v) and syringyl ([Ad/Al]s) reaction products, which have been shown to be elevated in degraded plant materials relative to fresh vegetation due to oxidative alteration of the sidechain in the methoxylated aromatic units making up the lignin polymer [e.g., *Goñi et al.*, 1993; *Opsahl and Benner*, 1995]. In addition, we computed the ratio of 3,5-dihydroxybenzoic acid to vanillyl phenols (3,5-Bd/V), which has been shown to be elevated in soils relative to their overlying vegetation and used as a tracer of inputs from altered soil organic matter in a variety of settings [e.g., *Kuzyk et al.*, 2008; *Prahl et al.*, 1994; *Tesi et al.*, 2014]. As with the vegetation indicators introduced above, there are also important caveats in the interpretation of these degradation/alteration parameters. In particular, contrasts in solubility and particle reactivity of different lignin macromolecular components can lead to marked compositional differences in the CuO reaction products due to sorption/desorption processes [e.g., *Hernes et al.*, 2007]. Thus, as in previous studies, we use caution when interpreting parameters such as the lignin acid to aldehyde ratios, which in many cases, and especially with regard to dissolved lignin, may reflect alterations due to variable and complex hydrogeochemical cycling rather than contrasts in the extent of biological degradation [e.g., *Spencer et al.*, 2016].

Stable isotope ($\delta^{13}C$) and radiocarbon ($\Delta^{14}C$) measurements were made on eight DOC samples (Table 2) from four eastern rivers (Povungnituk, Innuksuac, Nastapoka, and Little Whale) and four western rivers (Josephine, Thlewiaza, Churchill, and Winisk) to provide representation across permafrost and vegetation zones on both sides of Hudson Bay. The samples were preacidified and analyzed at the National Ocean Science Accelerator Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution [*Goñi et al.*, 2013b; *Vogel et al.*, 1987]. Radiocarbon ages were corrected to calendar years based on NOSAMS procedures, with the "modern" designation referring to post-1950. Errors expressed as fraction of modern ranged from 0.0024 to 0.0035. These errors are equivalent to ^{14}C age errors of 20 to 40 years. Unfortunately, we did not have enough material in our particulate samples after elemental and biomarker analyses for stable and radiocarbon analyses.

4. Results

4.1. Dissolved and Particulate Concentrations

In all rivers except the Josephine, the concentrations of total dissolved solids (TDS) exceed those of total suspended solids (TSS) (Figure 3a and Table 2). Five rivers entering the south HB coast (Churchill, Nelson, Hayes, Severn, and Winisk) immediately stand out with elevated concentrations of TDS (81–241 mg L^{-1}), while the Nelson, Hayes, and Severn also have high TSS (30–60 mg L^{-1}). Similarly, all rivers except the

Table 2. Concentrations, Fluxes, and Isotopic Properties of Dissolved and Particulate Organic Carbon in Hudson Bay Rivers

River	TSS (mg/L)	POC (mg/L)	TDS (mg/L)	DOC (mg/L)	DOC[a] (mg/L)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	TOC (mg/L)
Povungnituk	3.4	0.13	20	1.95	2.3	−26.39	−91.8	2.1
Kogaluq	4.2	0.13	20	2.26		--	--	2.4
Polemund	4.9	0.15	11	0.93		--	--	1.1
Innuksuac	2.7	0.16	39	4.17	2.3	−26.1	29.2	4.3
Nastapoka	5.3	0.17	14	1.98	2.5	−27.69	−303.0	2.2
Little Whale	10	0.19	24	3.59	4.2	−27.23	−4.9	3.8
Great Whale	8.2	0.22	24	4.43	3.3, 3.0	--	--	4.7
Josephine	8.4	0.45	1.8	0.24		−26.52	−33.5	0.7
Wilson	9.0	0.67	32	3.15		--	--	3.8
Ferguson	4.7	0.34	19	2.59		--	--	2.9
Tha-Anne	3.1	0.19	8.2	1.28		--	--	1.5
Thlewiaza	10	0.23	13	2.44		−27.17	47.1	2.7
Churchill	12	0.84	241	12.3	14.1	−27.86	−303.2	13
Nelson	39*	0.56	126	8.95	9.8	--	--	9.5
Hayes	30**	0.43	134	11.9	11.2	--	--	12
Severn	60	1.41	81	8.52		--	--	9.9
Winisk	6.2	0.44	96	8.81	2.4	−27.41	35.0	9.3

[a]Values collated by *Granskog et al.* [2007] and used for budget calculations by *Kuzyk et al.* [2009].

Josephine have DOC concentrations that greatly (5 to 25 times) exceed POC concentrations (Figure 3b and Table 2) suggesting that OM exports by Hudson Bay rivers are dominated by DOM. Particulate organic carbon and DOC are weakly correlated with one another ($r^2 = 0.35$, $p = 0.013$), and rivers in the south and west appear to have higher POC concentrations than the eastern rivers.

Concentrations of both POC and DOC as well as particulate and dissolved lignins display positive and statistically significant relationships with TSS and TDS concentrations, respectively. In the case of POC versus TSS (Figure 4a), our results show two significantly distinct ($p < 0.001$) trend lines. Rivers with particles enriched in OC (5–7 wt % contents), which plot in the upper trend line, include the Churchill, Wilson, Winisk, Josephine, Ferguson, Tha-Anne, and Innuksuak Rivers (closed circles). Rivers with lower weight percent carbon contents (1.5–3%), which include the Pavungniktuk, Kogaluq, Polemund, Nastapoka, Great Whale, Little Whale, Thlewiaza, Hayes, and Nelson Rivers (open circles), plot on the lower line. The Severn River lies between the two regression lines. The TSS and POC concentrations in the HB rivers are at the low end of the range observed for other Arctic rivers (Figure 4b), but the %OC values fall within the ranges observed elsewhere.

DOC concentrations in HB rivers are significantly correlated with TDS (Figure 4c; $r^2 = 0.96$, $p \ll 0.01$), but unlike POC cocentrations, there are no differences in trends between rivers with high versus low OC contents (Figure 4b). In the samples we analyzed, DOC accounts for 5% to over 19% of the TDS (Table S1) but the contrasts in DOC are not reflected in clear separation between rivers as observed for TSS and POC. Notably, both the Churchill and Nelson Rivers fall somewhat outside the general trend, with elevated TDS concentrations relative to the DOC concentrations. Both of these river systems have undergone extensive hydroelectric development including flooding of land, alteration of seasonal hydrographs through storage and release of water, and diversion of water from the Churchill basin into the Nelson drainage basin.

Total lignin concentrations (Σ_8 lignin ($\mu g\ L^{-1}$) in Table 3 and Figure 3c) show that with the exception of the Josephine River, dissolved lignin concentration well exceeds particulate lignin concentration. Both particulate and dissolved total lignin concentrations are clearly elevated in four of the south rivers (Churchill, Nelson, Hayes, and Severn), and dissolved lignin concentrations tend to be lowest in the three northernmost rivers for both west and east sides of the Bay.

There is a statistically significant relationship between lignin and organic carbon both for the particulate component ($r^2 = 0.72$, $p < <0.01$) and the dissolved component ($r^2 = 0.77$, $p < <0.01$) (plots not shown). The ratios of lignin products to organic carbon in both the particulate and dissolved phases give an indication of the relative contributions of vascular plant-derived materials to the overall OM. In contrast to their absolute concentrations, organic carbon-normalized lignin contents (Λ_8; mg $g^{-1}C$) are more comparable between

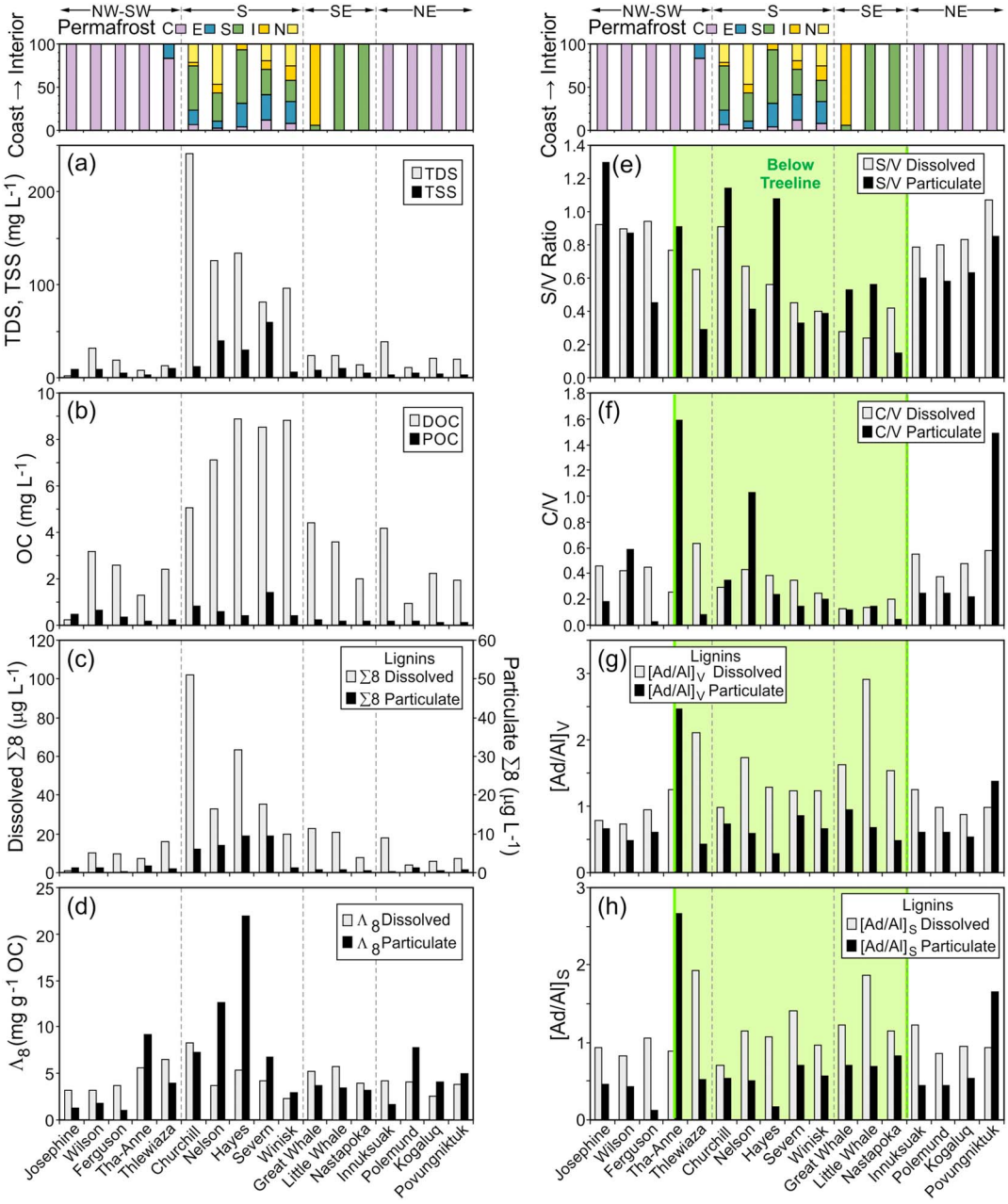

Figure 3. Data collected for particulate and dissolved components in river samples are shown for the rivers arranged in counterclockwise order commencing at the left with the Josephine River (northwest corner of the Bay). (top) The approximate disposition of permafrost along the run of the river on going from the coast (bottom) to the interior (top) for each river basin (C = continuous, E = extensive discontinuous, S = sporadic discontinuous, I = isolated patches, N = none). Data are displayed as dissolved (gray bars) and particulate (solid bars) concentrations for (a) total solids, (b) organic carbon, (c) lignins, (d) Λ_8 ($\sum_8$ normalized to OC), (e) syringyl: vanillyl phenol ratios, (f) cinnamyl:vanillyl phenol ratios, (g) acid:aldehyde ratios for vanillyl phenols, and (h) acid:aldehyde ratios for syringyl phenols. For Figures 3e–3h we have shaded in green the river basins below the tree line.

dissolved and particulate samples within any given river (Figures 3d, 5 and Table 3). These data indicate that whereas the concentrations of bulk DOC and dissolved lignin in these river systems are much higher than their particulate counterparts, the respective lignin contributions to DOC or POC are closer to each other, consistent with comparable contributions from vascular plant sources to DOM and POM in these samples. For most of the rivers, the overall contribution of lignin phenols recovered by CuO oxidation represent less than 1% of the DOC or POC. The main exceptions are samples from the Nelson and Hayes, which contain POM that is clearly enriched in lignin relative to that from other rivers.

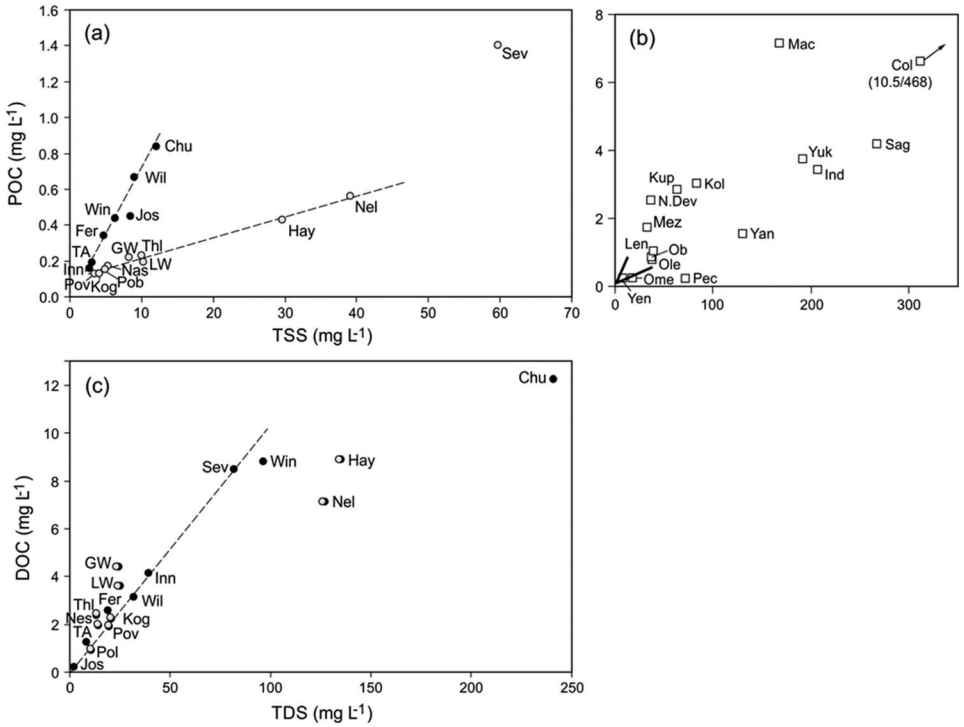

Figure 4. Relationships between (a) particulate organic carbon (POC) and total suspended solids (TSS) for the Hudson Bay rivers, (b) POC and TSS for other Arctic rivers with the Hudson Bay data indicated as lines, and (c) total dissolved solids (TDS) and dissolved organic carbon (DOC) for the 17 Hudson Bay rivers. Note differences in scale between POC and DOC.

4.2. Dissolved and Particulate Compositions

Various compositional parameters based on biomarker ratios show there are some similarities and some differences between DOM and POM compositions. For example, the ranges in lignin phenol ratios (S/V and C/V; Figure 6) indicate that there is a general similarity in the composition, and thus provenance, of vascular plant-derived lignin in both DOM and POM mobilized in the various river basins. In contrast, the acid-to-aldehyde ratios displayed by DOM samples are consistently higher than those of their POM counterparts, suggesting that the dissolved lignin and vascular plant-derived DOC has undergone greater alteration, either in soils or during river transport. Notably, several of the nonlignin ratios (e.g., 3,5-Bd/V, B/V, Pn/(Pl + Pd)) show statistically significant differences between the POM and DOM samples, with higher ranges observed in the dissolved pool (Figure S2 in the supporting information). Such contrasts indicate that while there are similarities in the provenance of lignin-derived OM in both dissolved and particulate samples, there are marked differences in the contributions from other molecular components in these two carbon pools.

4.3. Geographical Distributions

Geographical trends are also evident in the composition patterns. The clearest example is seen in the syringyl:vanillyl (S/V) and cinnamyl:vanillyl (C/V) phenol ratios (Figures 3e and 3f). Specifically, ratios are lowest for the Hayes (dissolved only), Severn, Winisk, Great Whale, Little Whale, and Nastapoka Rivers in contrast to the northernmost rivers, where the ratios tend to be higher. The latitudinal trend is most apparent in the dissolved phase S/V ($r^2 = 0.74$, $p < 0.0001$; Figure 3e). Acid to aldehyde ratios for vanillyl products ($[Ad/Al]_V$) and syringyl products ($[Ad/Al]_S$) (Figures 3g and 3h and Table 3) do not show obvious latitudinal trends for the particulate data, but the dissolved ratios are lower in the northernmost rivers, both east and west. The vanillyl and syringyl acid to aldehyde ratios were correlated for both dissolved ($r^2 = 0.74$, $p = <0.001$) and particulate ($r^2 = 0.90$, $p = <0.0001$) components suggesting that these two parameters reflect similar processes.

One way to summarize the latitudinal contrasts in our data sets is to group DOM and POM samples into two categories (above and below tree line) based on their respective watershed vegetation (Figures S1 and S2 supporting information). Statistical comparisons of these two groups (box and whisker plots and analysis

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Table 3. Lignin Product Reaction Ratios and Total Lignin Concentrations in Dissolved and Particulate Phases of HBRs

	Particulate Phase						Dissolved Phase					
Rivers	Σ8[a] μg/L	Λ_8[b] mg/g OC	S/V[c]	C/V[c]	[Ad/Al]v[d]	[Ad/Al]s[d]	Σ8[a] μg/L	Λ_8[b] mg/g OC	S/V[c]	C/V[c]	[Ad/Al]v[d]	[Ad/Al]s[d]
						East						
Povungnituk	0.64	4.9	0.85	1.49	1.38	1.65	7.46	3.8	1.07	0.58	0.98	0.93
Kogaluq	0.53	4.1	0.63	0.22	0.53	0.54	5.65	2.5	0.83	0.48	0.88	0.95
Polemund	1.17	7.8	0.58	0.25	0.60	0.45	3.83	4.1	0.80	0.38	0.98	0.85
Innuksuac	0.26	1.6	0.6	0.25	0.60	0.44	17.8	4.3	0.79	0.55	1.25	1.22
Nastapoka	0.54	3.2	0.15	0.05	0.48	0.82	7.87	4.0	0.42	0.20	1.54	1.15
Little Whale	0.66	3.5	0.56	0.15	0.67	0.69	20.7	5.8	0.24	0.14	2.91	1.87
Great Whale	0.81	3.7	0.53	0.12	0.95	0.70	22.9	5.2	0.28	0.13	1.62	1.23
						Northwest						
Josephine	1.26	2.8	1.3	0.18	0.66	0.46	0.78	3.3	0.92	0.46	0.79	0.93
Wilson	1.21	1.8	0.87	0.59	0.49	0.43	10.1	3.2	0.9	0.42	0.73	0.82
Ferguson	0.34	1.0	0.45	0.03	0.60	0.13	9.63	3.7	0.94	0.45	0.94	1.06
Tha-Anne	1.75	9.2	0.91	1.59	2.46	2.67	7.24	5.7	0.77	0.26	1.25	0.89
Thlewiaza	0.90	3.9	0.29	0.08	0.42	0.52	16.0	6.6	0.65	0.63	2.10	1.93
						Southwest						
Churchill	6.10	7.3	1.14	0.35	0.74	0.54	102	8.3	0.91	0.29	0.98	0.70
Nelson	7.05	12.6	0.41	1.03	0.59	0.50	32.7	3.7	0.67	0.43	1.73	1.15
Hayes	9.42	21.9	1.08	0.24	0.29	0.17	63.3	5.3	0.56	0.39	1.29	1.07
Severn	9.54	6.8	0.33	0.15	0.85	0.71	35.4	4.2	0.45	0.35	1.24	1.41
Winisk	1.27	2.9	0.39	0.20	0.66	0.57	19.7	2.2	0.40	0.25	1.23	0.96

[a]Σ8 μg/L = the sum of eight lignin reaction products calculated from hydrological data from Table 1; vanillyl, syringyl, and cinnamyl groups.
[b]Λ_8 = Σ8/[OC].
[c]S/V and C/V ratios are the ratios between lignin reaction product categories vanillyl (V) to cinnamyl (C) and syringyl (S).
[d][Ad/Al] = Acid aldehydes product ratios reflecting ratio between acid and aldehydes of vanillyl (Vd/Vl) and syringyl (Sd/Sl) groups.

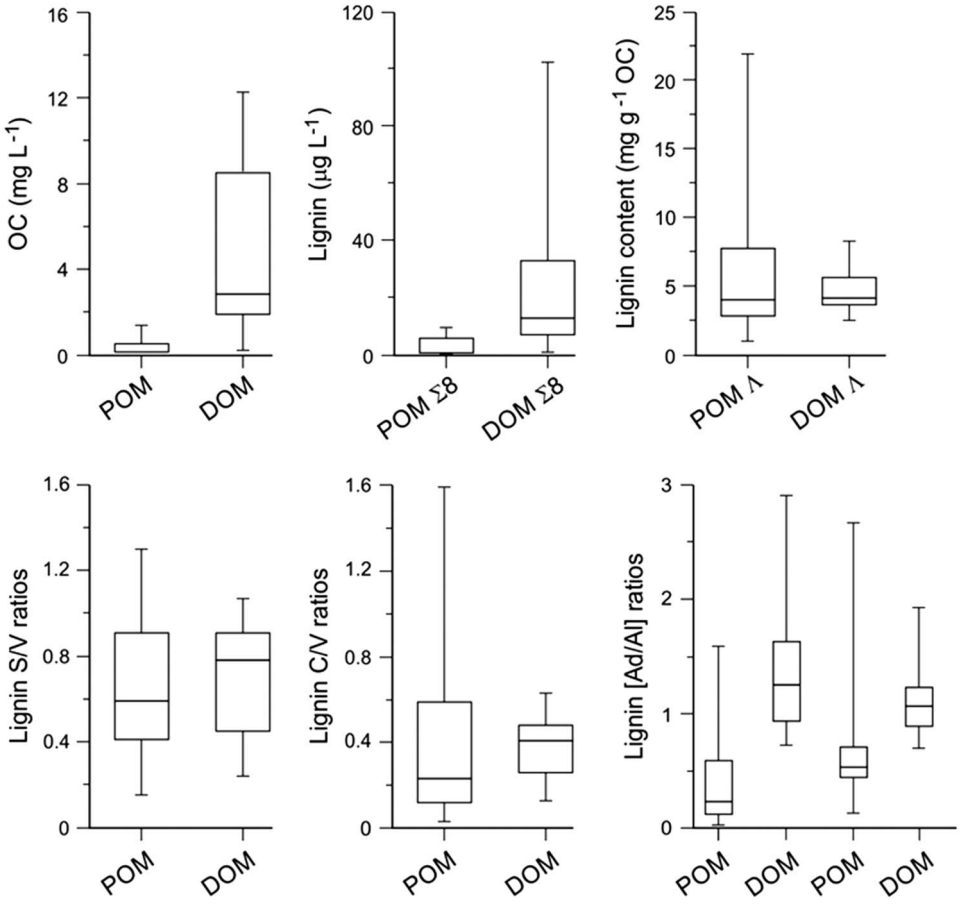

Figure 5. A box and whisker plot displaying descriptive statistics for the parameters measured in this study including median values (horizontal line), first quartile (white box), and third quartile (end bars). Note that the various units are provided with the parameters given below the horizontal axis.

of variances) show below tree line samples are characterized by significantly higher values ($p < 0.05$) for several parameters, including TSS, POC, TDS, DOC, and dissolved lignin concentrations. In terms of lignin compositional parameters, statistically significant differences between above and below tree line samples are observed for dissolved S/V ratios, which are lower below tree line, and dissolved $[Ad\backslash Al]_S$ and $[Ad/Al]_V$ ratios, which are higher in below tree line samples. The nonlignin reaction products also display statistically significant differences between above and below tree line samples. For example, POM samples from below tree line exhibit significantly lower B/V ratios than their above tree line counterparts. With regard to DOM compositions, below tree line samples are characterized by significantly lower 3,5-Bd/V, B/V, and P/V ratios and significantly higher Pn/(Pl + Pd) ratios than their above tree line counterparts, suggesting marked contrasts in the composition of DOM exist between northern and southern rivers.

Finally, isotopic compositions provide additional information for the eight selected DOC samples. In Table 2, the average $\delta^{13}C$ (-27.0 ± 0.6‰), which is typical of terrigenous OC fixed by C3 plants, is similar to values found widely in other Arctic Rivers [e.g., *Goñi et al.*, 2005; *Stein and Macdonald*, 2004; *van Dongen et al.*, 2008]. Given the wide latitudinal and vegetative range of the basins drained by these rivers (Figure 2), the range of observed values is restricted, but it does appear that the more northerly rivers draining northern Arctic ecozones (Josephine, Inuksuak, and Povungnituk) exhibit the highest $\delta^{13}C$ values (-26.5 to -25.1‰). $\Delta^{14}C$ values exhibit a wider range among the rivers, spanning OC recently fixed from atmospheric CO_2 ($\Delta^{14}C$ values near zero) and depleted values (-300‰ for Churchill and Nastapoka Rivers) indicative of contributions from older material that has depleted ^{14}C through radiodecay.

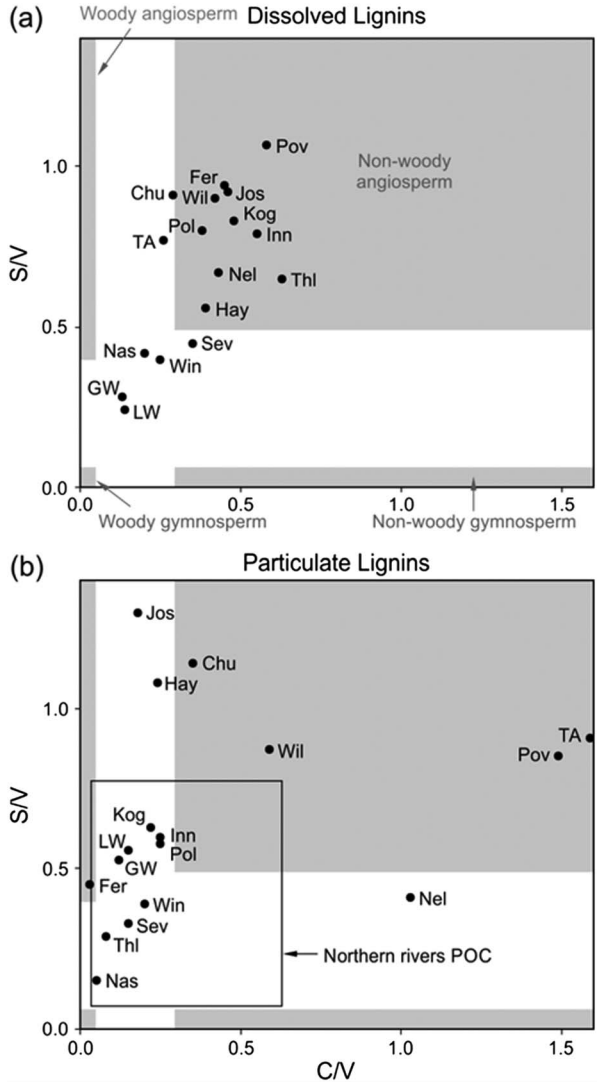

Figure 6. Lignin product reaction ratios for Syringyl/Vanillyl (S/V) and Cinnamyl/Vanillyl (C/V) in (a) DOC and (b) POC from the 17 HBRs. Also shown are classification boundaries for woody versus nonwoody and angiosperm versus gymnosperm sources of lignin phenols. Specific rivers are indicated by the first three letters except for the Tha-Anne (TA), Great Whale (GW), and Little Whale (LW) rivers.

5. Discussion

Here we examine the distributions of POC, DOC, lignin, and $\Delta^{14}C$ compositions in HBRs by comparing and contrasting the various rivers entering the margins of the Bay. From Figures 1 and 2, it is clear that the river basins vary widely in permafrost distribution and dominant vegetation as represented by ecozones. Furthermore, permafrost and vegetation strongly reflect mean annual temperature, which declines with latitude. Accordingly, a strong relationship between latitude and OC sources to rivers is to be expected, but this can be confounded by other factors including, for example, the latitudinal span of a given river basin, differences between west, east, and south rivers in their vegetation patterns (e.g., location of ecozone boundaries (Figure 2b in the supporting information)), hydrology, thermal regimes, and, therefore, organic matter processing in the soils and water. For this reason, we compare rivers by displaying them clockwise starting at the northwest corner of the Bay (Figure 3) rather than displaying them latitudinally.

5.1. Spatial Trends in Concentrations of Particulate and Dissolved Matter

Perhaps the most obvious feature of the HBR data is the cluster of high concentrations of key variables (e.g., TSS, TDS, POC, DOC, particulate, and dissolved lignin) exhibited by the southern rivers (Figures 3a–3d). As illustrated by the permafrost distributions (Figure 1 and Figure 3, top), these southern rivers generally have substantive regions of their drainage basins where permafrost is discontinuous, sporadic, or, in the southernmost parts, completely absent. The broad latitudinal distribution of permafrost cover shown in Figure 1 has developed over the past ~10,000 years as the large glacial ice mass retreated northward and then disappeared. During that time, climate and hydrology have continuously readjusted to the altered ice regime, which has been followed by a slow transition to the present ecozone distribution (Figure 2). With lags in time, OC inventories have, accordingly, accumulated in plants and in active layers of soils appropriate to the postglacial climatic conditions. Very recently, warming appears to be promoting more vigorous permafrost thaw, which will be followed by further response in ecozones.

We infer from the observed concentration patterns in rivers along the HB margin that thawing of permafrost, as has occurred since the last ice age, manifests itself by increasing OC and lignin concentrations in affected rivers, which is in alignment with a recent consensus on how the flux of organics in Arctic rivers will respond

to permafrost thaw [*Abbott et al.*, 2016] and observations elsewhere [*Frey and Smith*, 2005]. The differences in POC, DOC, particulate, and dissolved lignin concentrations between regions having a complete permafrost cover and those having substantial areas without permafrost in Figure 3b suggest that such increases for HBRs may well exceed the "up to 75% increase" consensus in that report. A caveat here is that the Churchill and Nelson Rivers have been impacted by hydrodevelopment (damming and diversion), which may contribute to the elevated DOC and dissolved lignin concentrations [see, e.g., *Butman et al.*, 2012, 2015]. In particular, the age of the DOC in the Churchill River (~2800 years; Table 2), which is older than the DOC in most of the other HBRs (Nastapoka excepted) and in other Arctic rivers where there are measurements [e.g., *Eglinton and Repeta*, 2006; *Guo and Macdonald*, 2006; *Guo et al.*, 2007], could indicate the release of old carbon from various regions of the watershed. Given that both DOC and dissolved lignin concentrations are elevated in the Churchill River, this old DOC contains significant contributions from vascular plants and its great age likely signals the release of old DOC from a deepening active layer due to permafrost thaw expanding northward in the Churchill River basin [e.g., see *Feng et al.*, 2015; *Guo et al.*, 2007]. But even neglecting the Nelson and Churchill Rivers we are led to the same inference that the loss of permafrost would lead to increased TOC concentration in affected rivers. Other factors associated with permafrost conditions may contribute to the high OC and lignin concentrations of the south rivers including type of vegetation (e.g., woody plant material, and lichen) and shallow topography which affects drainage and depth of soil [*Hudon et al.*, 1996; *Kuzyk et al.*, 2008].

Dominance of DOC over POC concentration is typical of Arctic rivers that drain regions where peat and permafrost are present [*Benner et al.*, 2005; *Meybeck*, 1982; *Raymond et al.*, 2007]. Therefore, dominance of DOC (Figure 3b) and dissolved lignin (Figure 3c) observed for south HBRs is to be expected given the extensive peatlands and bogs of the Hudson Plains Ecozone [*Dyke and Sladen*, 2010; *Smith and Burgess*, 2004], which constitute the largest wetland in North America. One consequential result of the transport of DOM by these rivers is the pervasive spread of colored dissolved organic matter into surface layers along the Bay's southern coast [*Granskog et al.*, 2009], which affects ocean light climate within Hudson Bay's coastal regions [*Granskog et al.*, 2007]. High lignin yields measured in dated sediment cores collected from the southern regions of Hudson Bay show that terrigenous POC has been an important component of the OC buried in these coastal sediments for at least the last hundred years [*Kuzyk et al.*, 2008], but there is insufficient evidence from the sparse set of cores to say conclusively whether or not the riverine supply of POC from these southern rivers has been recently increasing.

Although the DOC, POC, and total lignin concentrations in the southern rivers (Figure 3b–3d) imply that permafrost-free areas contribute disproportionally to these organic loads, there are no appropriate river-water benchmarks from which to draw inferences of recent change in riverine OC concentrations associated with increased thawing [*Dyke and Sladen*, 2010; *Smith et al.*, 2010]. It is also unclear how much OC is contributed by each of the distinct permafrost zones crossed by any given river along its route to the river mouth where the measurements were made (top bars in Figure 3). All of the southern rivers presently pass through a zone of continuous permafrost near the coast (Figure 1). However, comparison of southern river compositions with those from northern rivers where permafrost cover is complete (e.g., Josephine, Wilson, Ferguson, Kogaluq, Povungnituk, and Polemund) clearly shows the influence of the southern regions that hold extensive peat deposits, wetlands, and boreal forests [*Dyke and Sladen*, 2010; *Raymond et al.*, 2007; *Smith and Burgess*, 2004]. *Dyke and Sladen* [2010] suggest that thawing at a plateau edge results in thermokarst subsidence and erosion that eventually lead to a transition from peat plateau to fen. During this process, we may expect large peat inventories in southern river basins to release elevated amounts of DOC, dissolved lignins, and nonlignin compounds into the hydrological cycle [e.g., see *Carey*, 2003; *Onstad et al.*, 2000; *Philben et al.*, 2015].

5.2. Lignin Composition and Inferences of POM and DOM Sources

Traditionally, C/V and S/V ratios have been used in tandem to infer sources of lignin [*Goñi et al.*, 1998; *Hedges and Mann*, 1979; *Hu et al.*, 1999; *Kuzyk et al.*, 2008] with high S/V-C/V ratios indicating organic inputs from nonwoody, angiosperm plants (top right of Figures 6a and 6b), which are abundant in arctic tundra, and low S/V-C/V ratios indicating organic inputs from woody gymnosperm species (bottom left of Figures 6a and 6b). These latter include conifers in the boreal forest south of the tree line. Thus, the general patterns

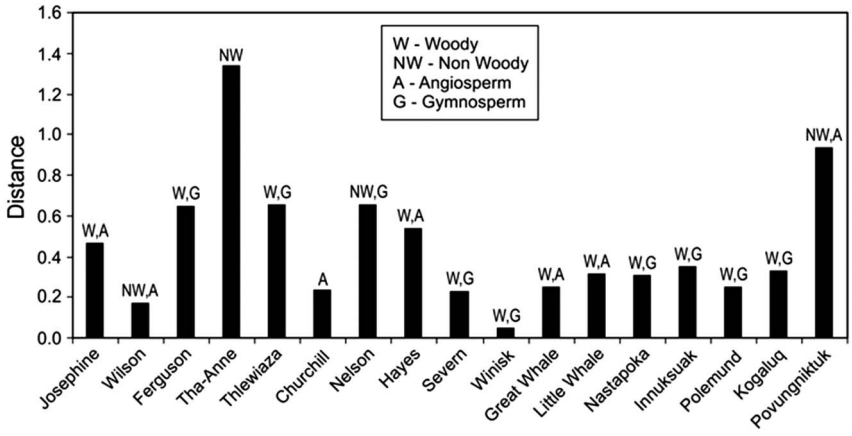

Figure 7. A diagram showing linear distance between the dissolved and particulate compositions (S/V versus C/V in Figure 6). The letters at the top of the bar indicate the direction of the difference on going from the dissolved to particulate organic carbon in any given river as W = woody, NW = non woody, and A = angiosperm, G = gymnosperm. For example, particulates in the Josephine River are woodier and favor angiosperms relative to the dissolved component.

in Figures 3e and 3f broadly reflect dominant vegetation in the respective drainage basins, as was inferred from lignin patterns in Hudson Bay sediments [*Kuzyk et al.*, 2008]. The dissolved lignin ratios (Figure 6a) are particularly clear: all of the rivers north of the tree line plot in the nonwoody-angiosperm box, reflecting the southern Arctic Tundra. Most of the rivers draining regions south of the tree line (Severn, Winisk, Great and Little Whale, and Nastapoka) plot to the lower left suggesting mixed sources.

As can be seen from the distribution of the data in Figure 6b, the particulate lignin ratios do not form such a tidy picture. Although many of the rivers south of the tree line plot to the lower left, suggesting mixed sources so do several of the rivers north of the tree line (Ferguson, Kogaluq, Innuksuak, and Polemund). Three rivers have a significantly higher nonwoody composition in the POC (Tha-Anne, Nelson, and Povungnituk). Of these, the Nelson River has been disturbed by hydro development. Perhaps a more interesting question is how different are the particulate and dissolved lignin compositions within any given river? To answer this question, we calculated the linear distance between dissolved and particulate plot points in Figure 6 and have displayed these as bars in Figure 7. Above each bar we give the direction of difference on going from the dissolved to the particulate phase as would be indicated by a vector on the S/V-C/V plot. For most of the rivers (12 out of 17), the POC is "woodier" than the DOC, and for eight of these rivers, the POC has a larger gymnosperm contribution. These observations suggest that lignin contributions from gymnosperm woody sources are prevalent in particulate samples in HBRs, which perhaps makes intuitive sense, and suggest that monitoring for change should include both dissolved and particulate components.

Two caveats suggest caution when interpreting the lignin compositional data. First, given that we have only single observations for each river collected during postfreshet discharge, it is likely that the OM in transport at that time is not representative of the average annual export. This would be especially true for the particulate load given the large contrasts in concentration and composition as a function of discharge for most rivers [e.g., *Goñi et al.*, 2013b]. Second, processes such as degradation and sorption-desorption reactions of lignin moieties can alter the vegetation-specific signatures of lignin phenols [e.g., *Goñi et al.*, 1993; *Hernes et al.*, 2007]. We thus conclude that for the most part, the lignin compositional signatures of POM and DOM in HBRs reflect the prevalent vegetation patterns but that further evaluation through additional sampling and analyses is needed to constrain other possible sources of variability.

Overall, with the exception of the Povungnituk, Tha-Anne, and Nelson Rivers, the POC in most of the HBRs is similar in composition to other tundra-dominated rivers in Arctic locations in Russia and Canada [*Amon et al.*, 2012; *Goñi et al.*, 2000; *Lobbes et al.*, 2000] (see Northern Rivers box in Figure 6b). All these Arctic rivers have some, or all, of their drainage basins farther north than Hudson Bay. It is noteworthy that the Ob River, whose basin is most similar to that of Hudson Bay, having a relatively mild climate, variable vegetation cover and one of the largest peat bog systems in the world [*Amon et al.*, 2012], also has a relatively high S/V ratio for its POC. Like most HBRs, DOC dominates the TOC in Russian Arctic rivers, contributing up to 82% of the TOC [*Lobbes*

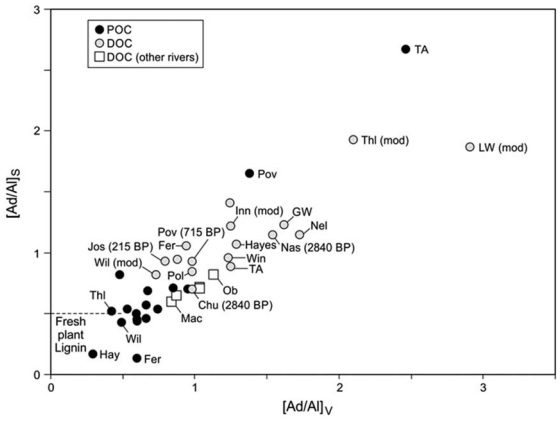

Figure 8. A diagram showing vanillyl ([Ad/Al]v) versus syringyl ([Ad/Al]s) aldehyde to acid ratios for dissolved (gray circles) and particulate (black circles) organic carbon for the 17 Hudson Bay rivers. Also shown are the Ad/Al ratios in DOC for the Ob, Yenesey, Kolyma, and Mackenzie Rivers. Lignin from fresh plant material would have ratios in the small region at the bottom left of the diagram.

et al., 2000], further highlighting the importance of DOC transfers from terrestrial to marine systems in the Arctic. A caveat to this estimate is that all the samples were collected under low-flow conditions (middle to late July) when dissolved loads tend to dominate over particulate loads, which are frequently much larger during periods of high flow.

5.3. Lignin Alteration and Extent of OM Processing

Early experimental studies of lignin degradation by white-rot fungi showed that oxidative decay of the three-carbon sidechain in the lignin polymer by these organisms leads to the production of excess acidic CuO oxidation products at the expense of their aldehyde counterparts [*Goñi et al.*, 1993; *Hedges et al.*, 1988]. Experiments with other tissues and degradative microbes further demonstrated this effect and showed that most vascular plant detritus that has undergone significant lignin degradation displays elevated [Ad/Al] ratios relative to fresh counterparts [e.g., *Nelson et al.*, 1994; *Opsahl and Benner*, 1995; *Weliky and Hedges*, 1989]. The observations of elevated ([Ad/Al] ($>$0.5) ratios in natural samples (e.g., soils and sediments) relative to fresh vascular plant tissues ($<$0.3) have thus been interpreted primarily as an indication of a history of oxidative lignin decay [*Goñi and Hedges*, 1992; *Goñi et al.*, 2005; *Opsahl and Benner*, 1998]. A quantitative interpretation of these ratios, especially for dissolved lignins, is complicated by studies that show marked changes in lignin [Ad/Al] ratios can occur during sorption/desorption processes and are independent of microbial oxidation [e.g., *Hernes et al.*, 2007; *Spencer et al.*, 2012]. It is in this context that we examine lignin [Ad/Al] ratios in the Hudson Bay river samples as semiquantitative indicators of microbial and abiotic alterations. Previous studies have used these lignin-derived compounds to infer origins and processes of POC entering the Arctic's shelves from large rivers [e.g., *Broder et al.*, 2016; *Lobbes et al.*, 2000; *Winterfeld et al.*, 2015], and one small river, the Colville [*Schreiner et al.*, 2013; *Zhang et al.*, 2015]. However, there remain almost no data for the composition of these compounds in the OM carried by smaller, truly Arctic rivers.

For the HBRs, high correlations between the syringyl and vanillyl [Ad/Al] ratios in particulate lignins (r^2 = 0.90) and dissolved lignins (r^2 = 0.74) suggest that these two ratios contain similar information, which displays as scatter along an elongated diagonal (Figure 8) indicating relatively undegraded or processed material toward the bottom left and relatively oxidized lignins toward the upper right. Most of the [Ad/Al] ratios are $>$0.5, indicating that organic matter has undergone significant oxidation and alteration within watersheds, with these processes being most pronounced for the dissolved lignin components relative to their particulate counterparts (Figure 8). The dissolved lignin Ad/Al ratio may have been altered due to degradation or fractionation during sorption-desorption processes [e.g., *Hernes et al.*, 2007].

In general, there is a tendency for the [Ad/Al] ratios to decrease from south to north in the HBRs (Figures 3g and 3h), which likely reflects both permafrost and vegetation conditions (Figures 1 and 2). There are a few exceptional rivers. For example, the Ad/Al ratios in the POC are very high for the Tha-Anne (mixed forest/taiga) (Figure 8) and Povungnituk (southern Arctic) Rivers, indicating exceptionally altered or degraded particulates entering these rivers (Table 3 and Figures 3g and 3h). Previous workers have found that deep mineral soils are associated with fivefold to tenfold higher Ad/Al ratios compared to surface organic soils [*Houel et al.*, 2006]. C/V ratios similarly are increased by the combined effects of leaching and sorption between organic (surface) soil horizons and the mineral subsoil horizons. Thus, the high Ad/Al ratios in the POC for the Tha-Anne and Povungnituk Rivers, together with the high C/V ratios, support the inference that subsoils affected by sorbed DOM are important sources of POC for these rivers. In contrast, the Hayes River

Table 4. Comparison of DOC and Lignin Ratios of the Southwest HBRs (Nelson and Churchill Rivers) and Other Arctic Rivers

Arctic River DOM Worldwide Comparison								
Arctic Rivers	Nelson	Churchill	Mackenzie[a]	Yukon[a]	Lena[a]	Ob[a]	Yenesei[a]	Kolyma[a]
Discharge ($km^3\ yr^{-1}$)	94.1	20.6	298	208	581	427	636	111
DOC ($Tg\ yr^{-1}$)*	0.84	0.25	1.20	1.75	6.47	3.04	5.08	0.71
S/V	0.67	0.91	0.33	0.47	0.28	0.48	0.31	0.41
C/V	0.43	0.29	0.10	0.14	0.08	0.14	0.07	0.10
Ad/Al_v	1.73	0.98	0.84	0.87	1.16	1.13	1.03	1.03
Ad/Al_s	1.15	0.70	0.60	0.65	0.79	0.82	0.72	0.71

[a]Sampled means from 2003–2007 [*Amon et al.*, 2012].

and possibly the Nelson, Ferguson, Wilson, and Thlewiaza Rivers all exhibit relatively undegraded and unaltered POC according to their [Ad/Al] ratios (Figures 8, 3g, and 3h).

Most of the HBRs display dissolved [Ad/Al] ratios that are higher than those observed in other large Arctic Rivers where measurements have been made (Mackenzie, Lena, Yenesey, Ob, Kolyma, and Yukon (Figure 8 and Table 4)). In particular, the Little Whale and Thlewiaza rivers stand out with very elevated Ad/Al ratios suggestive of a very high degree of oxidative and sorptive/desorptive alteration. HBRs resemble the Ob River, which exhibits moderately high dissolved [Ad/Al] ratios and low S/V and C/V ratios (Figure 6a and Table 4), characteristics that, perhaps, derive from the mild climate within the Ob River basin and variable vegetation cover. The Ob River basin includes the largest peat bog system in the world [*Amon et al.*, 2012]; the southwest HBR basins like those of the Churchill, Nelson, Winisk, and Severn Rivers also feature large peat bogs.

5.4. Nonlignin Compositions and OM Character

While not the main focus of this study, the p-hydroxybenzenes and benzoic acids, which are CuO reaction products for nonwoody organic matter, could provide useful indicators of peatland sources in the various river basins [*Philben et al.*, 2014, 2015]. Furthermore, these compounds may prove useful in future studies for providing specific information on the sources and distributions of runoff within Hudson Bay waters [e.g., see *Amon et al.*, 2012; *Kaiser et al.*, 2017]. The Hudson Plains, which lie along the southern boundary of Hudson Bay, contain one of the world's great wetlands, rich in peat. In particular, sphagnum mosses (bryophytes), which dominate these peats, are major contributors to DOC and produce sphagnum acid, which is converted to p-hydroxy phenols under CuO oxidation [*Philben et al.*, 2015; *Williams et al.*, 1998]. Despite these circumstances, we do not see higher amounts of the p-hydroxybenzene or benzoic acid reaction products in DOC for the Hayes, Severn, or Winisk Rivers (Figure 2 and Table S1 in the supporting information), all of which have extensive areas of peatland in their drainage basins. In fact, the DOC in these rivers has lower than average B/V, P/V and 3,5 Bd/V ratios (Figures 9a–9c), indicating higher lignin relative to nonlignin reaction products. On the other hand, the DOC from these rivers does have higher Pn/(Pl + Pd) ratios (Figure 9d). This parameter has been shown to be a useful specific indicator of Sphagnum contributions [*Philben et al.*, 2015] because it is independent of contributions from higher vascular plant sources with elevated V yields. Thus, this latter observation provides evidence for the potential export of peat-derived DOM into Hudson Bay from rivers with high Sphagnum peatlands. More quantitative evaluation of this OM source will require much more thorough characterization of the source signals throughout the study area [cf. *Moingt et al.*, 2016] and a seasonal sampling of the hydrograph.

5.5. Age and Cycling of DOM in HBR Watersheds

Most of the HBRs exhibit high (modern) $\Delta^{14}C$ in their DOC, similar to the Yukon and Mackenzie Rivers [*Guo et al.*, 2007]. The Churchill and Nastapoka (forest tundra ecozone) and the Povungnituk and Josephine (southern Arctic ecozone) Rivers are intriguing because they exhibit DOC with depleted $\Delta^{14}C$ indicating relatively old carbon. These four rivers display intermediate carbon-normalized dissolved lignin contents (Λ_8 of 3–8 mg/g OC), varied plant origins according to the S/V and C/V ratios and intermediate [Ad/Al] ratios (0.8 to 1.0) consistent with moderate alteration of the lignin components within the watershed (Figure 8). Such findings are consistent with a period of preservation in permafrost prior to release as DOM due possibly to

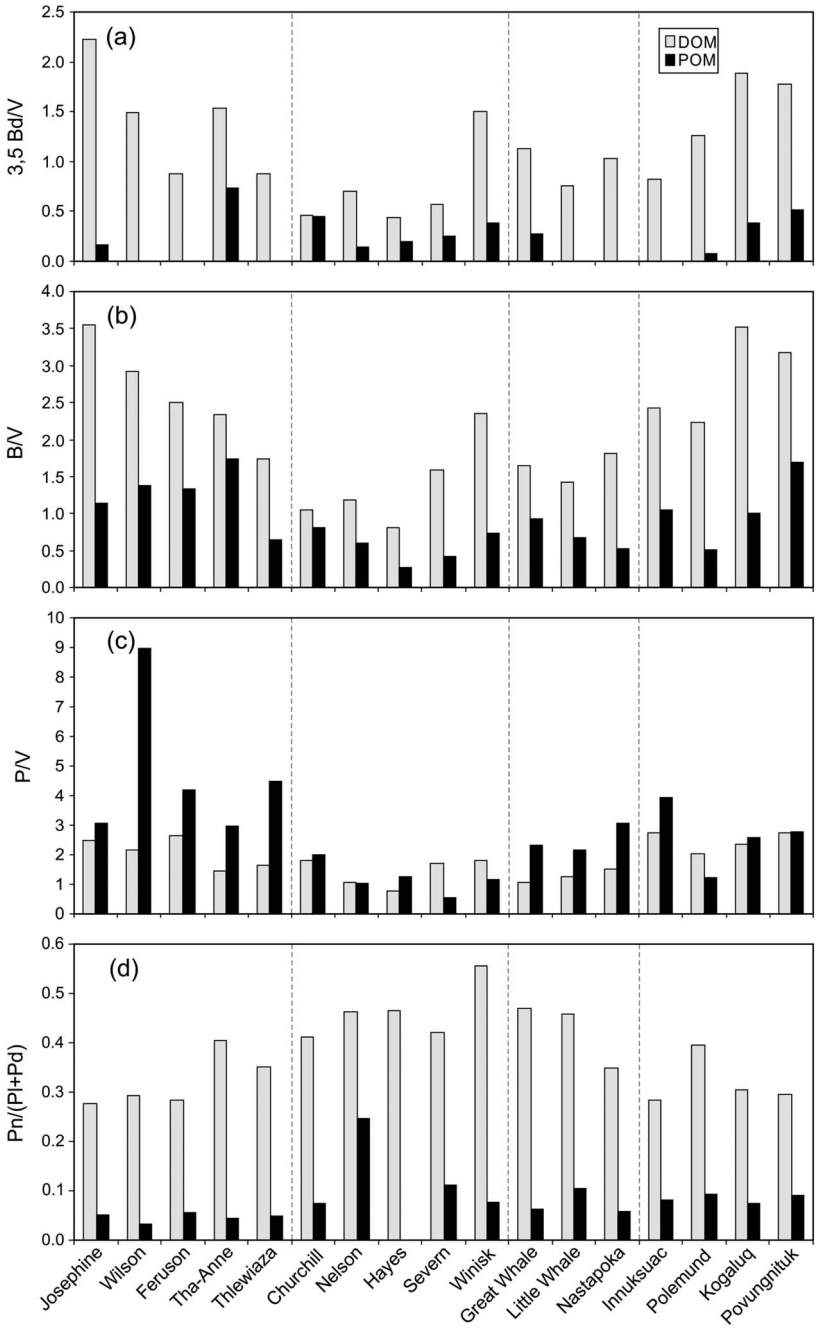

Figure 9. A diagram showing (a) 3,5 Bd/V, (b) B/V, (c) P/V, and (d) Pn/(Pl + Pd) ratios in dissolved and particulate samples for the rivers arranged in counterclockwise order around the Hudson Bay margin (as in Figure 3).

permafrost alteration. A similar conclusion was drawn for organic carbon in some of the Russian Arctic rivers [*Gustafsson et al.*, 2011; *Vonk et al.*, 2010].

The Churchill River has undergone massive hydrodevelopment within its basin, likely triggering the rapid release of dissolved material into the river (Figures 3a and 3b). This is likely mixed material including old DOC or old POC converted to DOC during transport. For the other rivers there are two plausible mechanisms that could favor old DOC at a given HB river mouth: (1) Old DOC released from permafrost is more slowly oxidized in cold, ice-covered river water and therefore survives transport to the river mouth [*Vonk et al.*, 2013] and (2) there is an enhanced release of old soil carbon into the riverine DOC pool. Regarding this first mechanism, it is likely that old DOC components do not survive transport to the river mouth in southern

rivers due to warmer, and longer, ice-free conditions. There are scant data to test this hypothesis, but it is clear that air temperatures of HBR watersheds decline with increase in latitude. For example, there is an approximate decrease in average air temperature of 8°C from the southern reaches of the Winisk (~51.7°N) to the northern reaches of the Josephine (~63°N) [see, e.g., *Déry et al.*, 2005, Table 2]. Perhaps more important would be the length of the open-water season where water temperatures as high as ~18°C could be attained. If the date of maximum discharge is any indication, then the northernmost rivers have an open-water season delayed by as much as 2 months relative to the southernmost rivers [see, e.g., *Déry et al.*, 2005, Figure 9], and an earlier freezeup date depending on when local air temperatures drop below 0°C. Finally, the larger drainage basins to the south, which include many lakes, likely contribute to longer residence times of water within the river system. All of these circumstances would favor the loss of old DOC in southern rivers. However, a plot of $\Delta^{14}C$ versus 1/DOC (not shown) shows no trend that could be interpreted as a selective loss of either ancient or modern components of DOC [e.g., see *Galy et al.*, 2007]. While it is clear that the apparent $\Delta^{14}C$ age of DOC can be affected by thermal regimes, our data do not point toward a selective loss of ancient DOC.

The second mechanism would require enhanced release of old DOC from land to rivers. A general characteristic observed globally for disturbed rivers is increased DOC and increased DOC age [*Butman et al.*, 2012; *Butman et al.*, 2015; *Marwick et al.*, 2015]. For the Nastapoka, disturbance by the onset of thawing would not be surprising given that the basin presently spans the domains of continuous and discontinuous permafrost and is likely undergoing change in vegetative cover as boundaries shift northward due to warming. The Povungnituk and Josephine River basins, however, are the most northern of the study; their basins are small and lie completely within continuous permafrost, and yet both show a significant component of aged DOC. Because these northern rivers have low DOC concentrations and smaller flows relative to the southern rivers (Figure 3b), they would show greater response to the addition of small amount of old DOC. Snow, glacial melt, and groundwater have been shown to transport old DOC [e.g., *Aiken et al.*, 2014], and these sources, therefore, could be the source of aged DOC in the most northern rivers. On the other hand, lignin:DOC ratios, which are not significantly different than in southern rivers, do not reflect low values normally associated with groundwater and snow. It may be relevant that sea ice cover in Hudson Bay [*Hochheim and Barber*, 2014] and in the Canadian Arctic Archipelago [*Howell et al.*, 2015] have declined over the past 10–15 years, with several recent exceptionally low ice cover years. A possibility, therefore, is that these northernmost rivers are vulnerable to recent thawing mediated by warmer summer-fall periods due to lack of ice cover in their adjacent seas. We have very few data points, and only for 1 year. Clearly, confirmation and further investigation of the $\Delta^{14}C$ content of bulk OC components (DOC and POC) and selected compounds are needed to resolve the question of why older DOC is found in the northern rivers, and especially why the Nastapoka River DOC is so anomalous.

6. Conclusions

In Hudson Bay rivers, DOC dominates the TOC, and the southern rivers, especially the Nelson and Churchill, which have been impacted by hydro development, dominate the supply of terrigenous OM to the Bay. In general, DOC, POC, and lignin concentration in HBRs decrease with increasing latitude, but trends in these properties and lignin compositions are controlled more directly by the vegetation and permafrost within individual drainage basins, with the tree line providing an obvious divide in lignin source characteristics. Climate change (warming) will likely be exhibited in the riverine OM as alteration in lignin composition reflecting shifts in vegetation types, which could be slow (northward migration of the tree line) or rapid (invasion by bushes and other plants), and by enhanced release of old soil carbon with deepening of the active layer as permafrost thaws. Based on lignin composition, the riverine OC generally indicates mixed organic sources including woody, gymnosperm plants, and nonwoody angiosperms. The relative contributions from these two sources shift from woody plants below the tree line to nonwoody plants further north. All of the samples show evidence of organic matter alteration. Based on $\Delta^{14}C$ values for selected DOC samples, four rivers have modern DOC whereas the Churchill River, which has been disturbed by hydro development, and three of the northernmost rivers have older DOC. We infer that these northern rivers may be releasing old carbon from soils, possibly as a response to warming associated with diminished sea ice cover in adjacent seas.

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