

## RESEARCH LETTER

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## Key Points:

- There are marked differences in the DON:DOP ratio between the Eurasian and Amerasian Arctic Ocean
- The Arctic Ocean exports DON and DOP to the North Atlantic
- Lack of observations hinder the ability to resolve temporal changes in nutrient transports and budgets

## Supporting Information:

- Supporting Information S1
- Figure S1
- Figure S2
- Data Set S1

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## Relevance of dissolved organic nutrients for the Arctic Ocean nutrient budget

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**Abstract** We ask whether dissolved organic nitrogen (DON) and phosphorus (DOP) could account for previously identified Arctic Ocean (AO) inorganic nutrient budget imbalances. We assess transports to/from the AO by calculating indicative budgets. Marked DON:DOP ratio differences between the Amerasian and Eurasian AO reflect different physical and biogeochemical pathways. DON and DOP are exported to the North Atlantic via Davis Strait potentially being enhanced in transit from Bering Strait. Fram Strait transports are balanced. Barents Sea Opening transports may provide an additional nutrient source to the Barents Sea or may be locked within the wider AO Atlantic Water circulation. Gaps in our knowledge are identified and discussed.

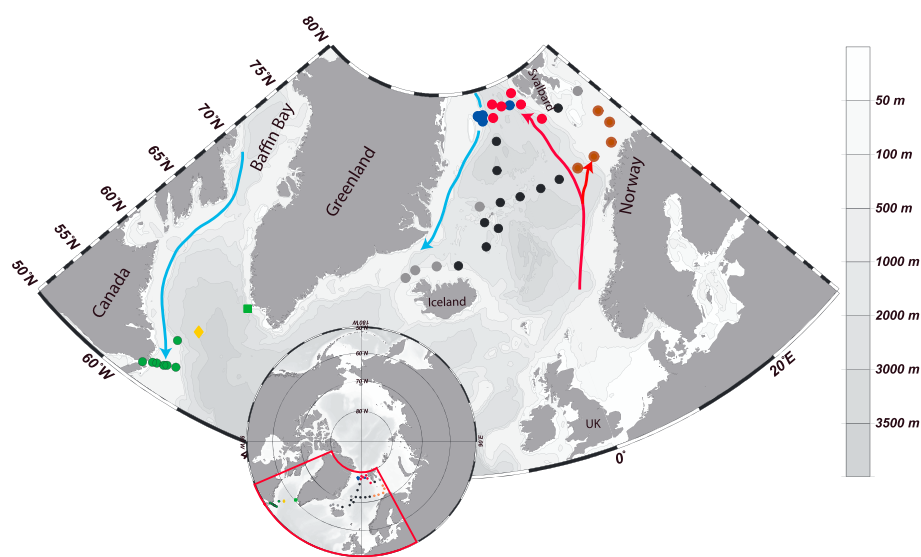
## 1. Introduction

Dissolved nutrients contain elements essential for ocean life, including nitrogen and phosphorus. In the Arctic Ocean (AO), rivers and adjacent oceans supply nutrients that support primary production over the Arctic shelf seas but are limiting toward the central AO as they are depleted [Tremblay and Gagnon, 2009]. Changes in the AO have resulted in impacts to primary production and carbon cycling as open water areas expand [e.g., Arrigo et al., 2008; Pabi et al., 2008; Brown and Arrigo, 2012], highlighting the need to constrain and better understand nutrient sources to the upper, productive layers [e.g., Arrigo et al., 2011; Le Fouest et al., 2013; Tremblay et al., 2015]; modification of freshwater inputs [Peterson et al., 2006, 2002; Shiklomanov and Lammers, 2009] and riverine nutrient loads as materials previously locked in the permafrost are released by enhanced melting [Frey and McClelland, 2009; Frey et al., 2007; Raymond et al., 2007]. Ultimately, a proportion of nutrients delivered to the AO are exported to the North Atlantic (NAtl) [Torres-Valdés et al., 2013, TV13 hereafter].

TV13 showed that the AO exports  $1.0 \pm 0.3 \text{ kmol s}^{-1}$  of phosphate to the NAtl but that known supplies of total dissolved phosphorus (TDP), mainly from rivers [Holmes et al., 2011], accounted for only ~7% of that export. The nitrate budget was balanced ( $1.0 \pm 1.6 \text{ kmol s}^{-1}$ ; TV13) despite the substantial AO denitrification rate (average  $29.4 \text{ kmol-N s}^{-1}$ , range  $14\text{--}66 \text{ kmol-N s}^{-1}$ ) [Chang and Devol, 2009]. Known nitrogen sources comprising riverine dissolved inorganic [Holmes et al., 2011] and remineralized organic [Tank et al., 2011], and fixation [Blais et al., 2012], total only 2–12% of the denitrification rates (TV13), implying additional and unknown sources of both N and P. Hence, we hypothesized that oceanic transports of dissolved organic nutrients—nitrogen (DON) and phosphorus (DOP)—could supply the imbalances, perhaps following ultraviolet (UV) photo-oxidation and bacterial remineralization.

Riverine dissolved organic matter (DOM) supplied to the AO was believed to be mostly refractory [e.g., Cauwet and Sidorov, 1996; Dittmar and Kattner, 2003]. However, 10–30% can be degraded over time scales from weeks to years [Alling et al., 2010; Mann et al., 2012; Wickland et al., 2012; Letscher et al., 2011, 2013b] despite high content of recalcitrant substances in terrigenous DOM [Lara et al., 1998; Para et al., 2013]. Oceanic DOM originates from productive regions, and semilabile forms can be transported downstream, supporting biological production elsewhere [e.g., Torres-Valdés et al., 2009; Reynolds et al., 2014]. Pacific and Atlantic waters may supply DON and DOP to the AO, because they are downstream from the highly productive Bering and Nordic Seas.

We present a first-order quantitative assessment for AO DON and DOP imports and exports by calculating “indicative budgets,” and draw inferences regarding sources/sinks of DON and DOP.



**Figure 1.** Labrador Current and Nordic Seas station locations. Symbols: Atlantic Water inflow (red arrows) via the West Spitsbergen Current (red) and Barents Sea Opening (brown); Polar Outflow (blue arrows) via the East Greenland Current (blue) and Labrador Current (dark-green). Additional stations: central (yellow diamond) and east (green square) Labrador Sea. Also shown: Atlantic Water-dominated stations (black) and stations with Polar (upper 50 m) and Atlantic Waters (grey-filled) characteristics. Color coding is used in further figures. Inset: the wider Arctic Ocean.

## 2. Data and Methods

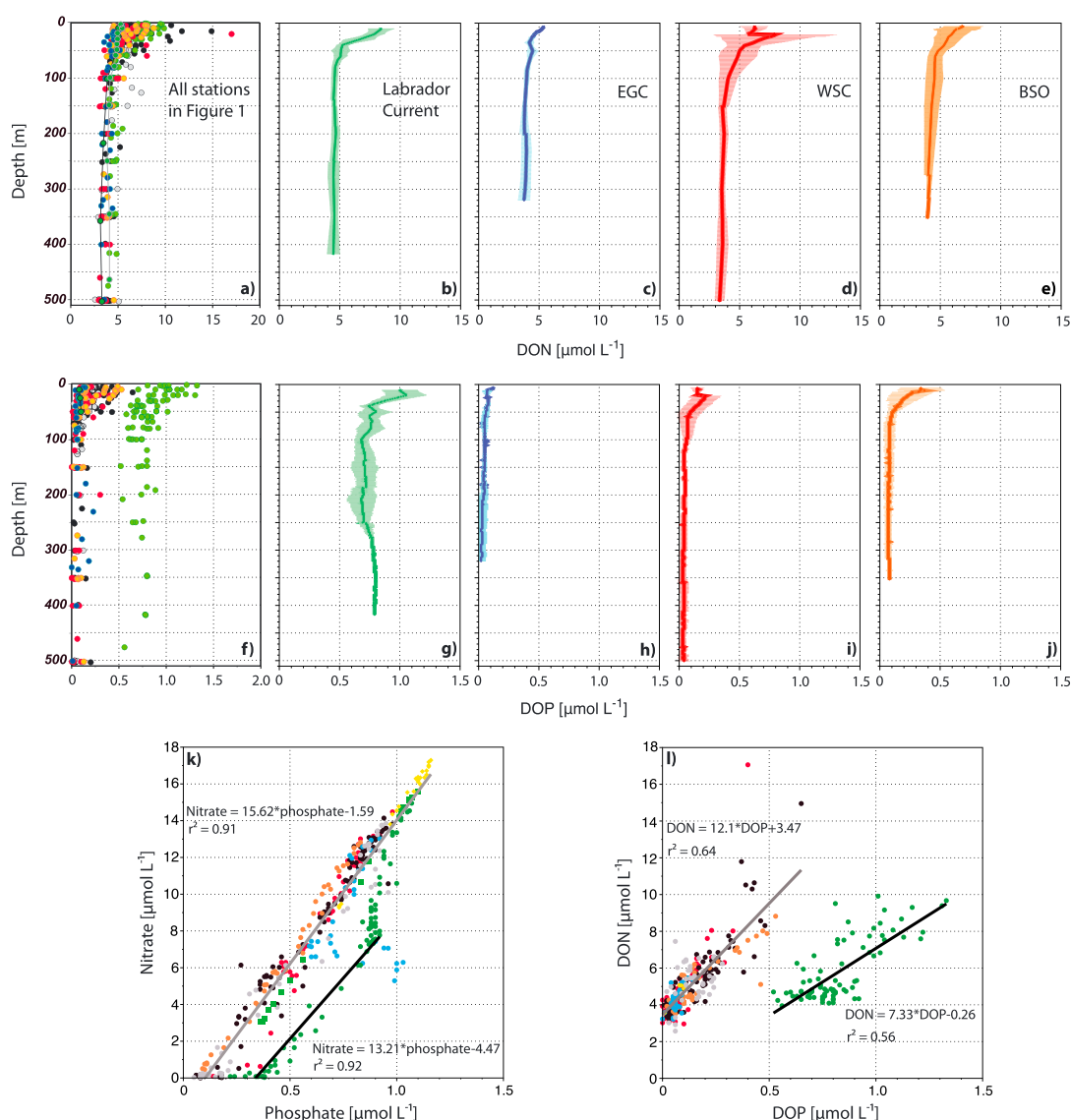
TV13 combined the Arctic boundary velocity field of *Tsubouchi et al.* [2012, T2012 hereafter] with dissolved inorganic nutrient concentrations to generate pan-Arctic inorganic nutrient budgets. Here we adopt a different approach. DON and DOP data collocated with the AO boundary sections are not available. However, enough regional measurements exist to enable the characterization of circum-Arctic water masses with mean DON and DOP concentrations. By combining these concentrations with the velocities of T2012 at appropriate vertical and horizontal scales, we calculate indicative budgets, which are sufficiently accurate to allow us to assess whether AO nutrient budget imbalances could be closed by organic nutrients.

Samples for the analysis of DON, DOP, and inorganic nutrients were collected from the upper 500 m of the water column in the Nordic Seas in June 2012 aboard the RRS *James Clark Ross* (JR271) from 32 stations and in the Labrador Current (LC) in May 2013 aboard the CCGS *Hudson* (HUD13-008) from seven stations, with two additional stations in central and east Labrador Sea (Figure 1). Text S1 in the supporting information provides analytical details.

The measurements of *Simpson et al.* [2008] in the southeastern Beaufort Sea provided DON and DOP as an estimate for Bering Strait. We used their Pacific Water-associated mean DOP concentration ( $0.76 \pm 0.27 \mu\text{mol L}^{-1}$ ) and a mean DON concentration ( $3.15 \pm 1.51 \mu\text{mol L}^{-1}$ ) within their mean DOP depth range. River data were taken from *Holmes et al.* [2011], who reported TDP river supply. *Chang and Devol* [2009] estimated a pan-Arctic average denitrification rate of  $29.4 \text{ kmol N s}^{-1}$  (range  $14\text{--}66 \text{ kmol N s}^{-1}$ ), with the highest rates in the Barents Sea ( $12.9 \text{ kmol N s}^{-1}$ ).

Inorganic nutrient vertical distributions are typical: low surface concentrations increase monotonically with depth (Figure S1). Nitrate and phosphate are lowest in the upper 100 m (undetectable to  $\sim 12 \mu\text{mol-nitrate L}^{-1}$ ,  $0.05\text{--}1.0 \mu\text{mol-phosphate L}^{-1}$ ), increasing to  $12\text{--}16 \mu\text{mol-nitrate L}^{-1}$  and  $0.8\text{--}1.1 \mu\text{mol-phosphate L}^{-1}$  at 500 m. In contrast, dissolved organic nutrients (Figures 2a and 2f) are highest in the upper 100 m, averaging  $5.6 \pm 1.7 \mu\text{mol-DON L}^{-1}$  (range  $3.2\text{--}17.0 \mu\text{mol L}^{-1}$ ) and  $0.17 \pm 0.11 \mu\text{mol-DOP L}^{-1}$  (range undetectable to  $0.65 \mu\text{mol L}^{-1}$ ) in the Nordic Seas. Below 100 m, they average  $3.9 \pm 0.7 \mu\text{mol-DON L}^{-1}$  and  $0.06 \pm 0.04 \mu\text{mol-DOP L}^{-1}$  (range  $2.6\text{--}7.4 \mu\text{mol-DON L}^{-1}$  and undetectable to  $0.2 \mu\text{mol-DOP L}^{-1}$ ).

LC DOP concentrations are high, ranging from  $0.56 \mu\text{mol L}^{-1}$  at 475 m to  $1.33 \mu\text{mol L}^{-1}$  at  $\sim 3.5 \text{ m}$  (Figure 2). DOP averaged  $0.85 \pm 0.18 \mu\text{mol L}^{-1}$  in the upper 100 m and  $0.72 \pm 0.09 \mu\text{mol L}^{-1}$  below. DON and DOP vertical distributions in central and east Labrador Sea (Figures 1 and 2) are instead consistent with those in the



**Figure 2.** (a) DON and (f) DOP vertical distributions (central and east Labrador Sea, grey and black lines, respectively). Horizontally averaged (b–e) DON and (g–j) DOP profiles for selected water masses; LC ( $n = 7$ ), EGC ( $n = 5$  DON,  $n = 4$  DOP), WSC ( $n = 6$ ) and BSO ( $n = 5$ ). Envelope: 1 standard deviation about the mean. Nitrate versus phosphate (k) and DON versus DOP (l).

Nordic Seas. LC DON concentrations ( $6.2 \pm 1.7 \mu\text{mol L}^{-1}$  above 100 m and  $4.4 \pm 0.3 \mu\text{mol L}^{-1}$  at greater depths) are only slightly higher than those in the Nordic Seas.

DON contributes 15–42% of the total dissolved nitrogen (TDN) pool below 100 m and 22–100% above. In the Nordic Seas, DOP contributes  $\leq 17\%$  to the TDP pool below 100 m, and it ranges from negligible to  $\sim 85\%$  above. Across the LC, DOP contributes 34–47% below 100 m and 38–82% above. With the exception of DON and DOP in the East Greenland Current (EGC), dissolved organic pools dominate total dissolved nutrient pools in the surface layer. LC DOP also contributes significantly at depth. These data are shown in Figures S1b and S1d.

JR271 and HUD13-008 hydrographic data were used to characterize inflowing/outflowing water masses nutrient content. We selected nutrient concentrations within their temperature and salinity ( $T$ ,  $S$ ) limits using water mass definitions from Aksenov *et al.* [2010]. Atlantic Water (AW;  $T \geq 2^\circ\text{C}$ ,  $S \geq 34.7$ ) enters the AO through the Barents Sea Opening (BSO) and via the West Spitsbergen Current (WSC) in Fram Strait. Polar outflows comprise near-freezing surface and halocline waters, with  $T < 0^\circ\text{C}$ ,  $30.2 \leq S \leq 33.3$  and  $T < 0^\circ\text{C}$ ,  $33.3 \leq S \leq 34.4$  for

upper (UHW) and lower (LHW) halocline waters, respectively. They exit the AO within the EGC in Fram Strait, and through west Davis Strait, where they join the LC. DON and DOP in  $T$ - $S$  space are shown in Figure S2.

Mean profile nutrient concentrations ( $C_n$ ,  $\text{mmol m}^{-3}$ ) were generated for the LC (i.e., west Davis Strait outflow), EGC, WSC, and BSO (Figure 2; further details in the supporting information Text S2). DON and DOP transports ( $\text{kmol s}^{-1}$ ) were calculated as the product of  $C_n$ , including *Simpson et al.* [2008] data, and volume transports ( $V$ ,  $\text{m}^3 \text{s}^{-1}$ ) for west Davis Strait, Bering Strait, and upper 100 m EGC, WSC, and BSO from T2012. Transport uncertainties (sd) were estimated as  $\sigma^2 = [V \text{sd}(C_n)]^2 + [C_n \text{sd}(V)]^2 + 2VC_n \rho \text{sd}(V) \text{sd}(C_n)$ , with  $V$  and  $C_n$  as above, associated uncertainties  $\text{sd}(V)$  and  $\text{sd}(C_n)$ , and uncertainty correlation  $|\rho| \leq 1$ . Uncertainties are assessed in supporting information Text S3.

Upper 100 m DON and DOP transports were calculated for the EGC, WSC, and BSO. Organic nutrients are concentrated in near-surface waters (Figure 2). Upper layers are likely to contain semilabile forms, whereas at depth (if detectable) organic nutrients are probably refractory [Hansell, 2013]. DON and DOP transports will be most important near the surface where velocities are highest. Deep DOP concentrations there are near or below the detection limit, so we assume that deep transports are low and/or negligible. DON is similar, since concentrations at depth are rather constant (average  $3.9 \pm 0.7 \mu\text{mol L}^{-1}$ ), and volume transports across Fram Strait are nearly balanced (T2012). Hence, sub-100 m DON transports are likely balanced.

LC DON and DOP transports were calculated for the full available depth, prompted by the comparatively high DON and DOP concentrations down to the deepest measurement (475 m). Accordingly, we combined mean nutrient profiles with volume transport down to 620 m, west Davis Strait (T2012).

### 3. Results

Above 100 m nitrate is broadly similar across inflowing and outflowing water masses:  $6.7 \pm 1.4$ ,  $7.2 \pm 0.8$ ,  $7.92 \pm 2.2$ , and  $7.2 \pm 1.4 \mu\text{mol L}^{-1}$  for the LC, EGC, WSC, and BSO, respectively. Phosphate is higher in outflowing waters ( $0.78 \pm 0.07$  and  $0.77 \pm 0.08 \mu\text{mol L}^{-1}$  for the LC and EGC, respectively) than in inflowing waters ( $0.62 \pm 0.12$  and  $0.51 \pm 0.08 \mu\text{mol L}^{-1}$  for the WSC and BSO, respectively). DON is highest in the LC ( $5.58 \pm 0.58 \mu\text{mol L}^{-1}$ ), similar in the WSC and BSO ( $5.30 \pm 1.57$  and  $5.10 \pm 0.90 \mu\text{mol L}^{-1}$ , respectively) and lowest in the EGC ( $4.35 \pm 0.25 \mu\text{mol L}^{-1}$ ). DOP is highest in the LC ( $0.81 \pm 0.10 \mu\text{mol L}^{-1}$ ), similar in the WSC ( $0.11 \pm 0.07 \mu\text{mol L}^{-1}$ ) and BSO ( $0.14 \pm 0.08 \mu\text{mol L}^{-1}$ ), and lowest in the EGC ( $0.06 \pm 0.02 \mu\text{mol L}^{-1}$ ).

LC DON and DOP transports are  $-17.7 \pm 2.33 \text{ kmol-DON s}^{-1}$  and  $-2.82 \pm 0.36 \text{ kmol-DOP s}^{-1}$  and are ultimately delivered to the Natl. Fram Strait transports in the EGC ( $-3.79 \pm 0.77 \text{ kmol-DON s}^{-1}$ ,  $-0.05 \pm 0.02 \text{ kmol-DOP s}^{-1}$ ) and the WSC ( $3.39 \pm 1.46 \text{ kmol-DON s}^{-1}$ ,  $0.07 \pm 0.05 \text{ kmol-DOP s}^{-1}$ ) approximately balance. Transports via the BSO are  $8.36 \pm 1.83 \text{ kmol-DON s}^{-1}$  and  $0.23 \pm 0.13 \text{ kmol-DOP s}^{-1}$ , representing an important supply of organic nutrients to the Eurasian AO. The inferred Bering Strait DON import ( $3.15 \pm 1.54 \text{ kmol s}^{-1}$ ) is approximately half that via the BSO, but the DOP import ( $0.76 \pm 0.28 \text{ kmol s}^{-1}$ ) is 3 times larger. Riverine transports are comparatively small ( $1.92 \text{ kmol-DON s}^{-1}$  and  $0.07 \text{ kmol-DOP s}^{-1}$ ). Combined BSO, Bering Strait, and river imports ( $\sim 13.43 \text{ kmol-DON s}^{-1}$  and  $1.06 \text{ kmol-DOP s}^{-1}$ ) are smaller than LC exports. Net transports suggest a modest DON export ( $-4.66 \pm 3.08 \text{ kmol-DON s}^{-1}$ ) and an important DOP export ( $-1.74 \pm 0.50 \text{ kmol-DOP s}^{-1}$ ) to the Natl. Summarizing, major DON and DOP imports occur via the BSO and Bering Strait, respectively, and major DON and DOP exports occur via the LC. Results are summarized in Table 1.

### 4. Discussion

#### 4.1. Comparison With Measurements Elsewhere

Our DON measurements are consistent with the broad range of observations elsewhere in the upper ocean ( $5.1 \pm 1.7 \mu\text{mol L}^{-1}$ ), which show that DON contributes  $76 \pm 22\%$  of the TDN [Sipler and Bronk, 2015]. DON in the Nordic Seas ( $5.6 \pm 1.7 \mu\text{mol L}^{-1}$ ) and LC ( $6.2 \pm 1.7 \mu\text{mol L}^{-1}$ ) is slightly higher than in the subpolar Natl ( $4.5 \pm 0.6 \mu\text{mol L}^{-1}$ ) [Letscher et al., 2013a; Sipler and Bronk, 2015]. In the upper layers of the AO ( $\leq 100 \text{ m}$ ) DON occurs at  $3.9$ – $8 \mu\text{mol L}^{-1}$  [Sipler and Bronk, 2015], with some of the highest values observed in the Chukchi Sea ( $6$ – $8 \mu\text{mol L}^{-1}$ ) [Letscher et al., 2013b] and close to river mouths;  $7.4 \pm 1.3 \mu\text{mol L}^{-1}$  along the Siberian Shelf [Dittmar et al., 2001] and  $15 \mu\text{mol L}^{-1}$  in the Mackenzie [Tremblay et al., 2014]. Within the AO, high concentrations are likely the result of DON enhancement from biological production [Letscher et al., 2013b]. Lower concentrations have been observed in the Canada Basin ( $3$ – $4 \mu\text{mol L}^{-1}$ ) and Amundsen and Nansen Basins

**Table 1.** Indicative Transports and Budgets of Dissolved Organic Nutrients for the Arctic Ocean<sup>a</sup>

	LC Mean $\pm$ sd	EGC Mean $\pm$ sd	WSC Mean $\pm$ sd	BSO Mean $\pm$ sd	BS Mean $\pm$ sd	Rivers	Net Mean $\pm$ sd
Vol <sub>T</sub>	$-3.71 \pm 0.37$	$-0.87 \pm 0.17$	$0.64 \pm 0.2$	$1.64 \pm 0.21$	$1 \pm 0.1^b$	0.07 <sup>d</sup>	
DON	$4.77 \pm 0.41$	$4.35 \pm 0.25$	$5.30 \pm 1.57$	$5.10 \pm 0.90$	$3.15 \pm 1.51^c$		
DON <sub>Tn</sub>	$-17.70 \pm 2.33$	$-3.79 \pm 0.77$	$3.39 \pm 1.46$	$8.36 \pm 1.83$	$3.15 \pm 1.54$	1.92 <sup>d</sup>	$-4.66 \pm 3.08$
DOP	$0.76 \pm 0.06$	$0.06 \pm 0.02$	$0.11 \pm 0.07$	$0.14 \pm 0.08$	$0.76 \pm 0.27^c$		
DOP <sub>Tn</sub>	$-2.82 \pm 0.36$	$-0.05 \pm 0.02$	$0.07 \pm 0.05$	$0.23 \pm 0.13$	$0.76 \pm 0.28$	0.07 <sup>d</sup>	$-1.74 \pm 0.50$

<sup>a</sup>Volume transport (Vol<sub>T</sub>) is given in sverdrup (Sv; 1 Sv =  $10^6$  m<sup>3</sup> s<sup>-1</sup>), mean profile concentrations (e.g., DON) in  $\mu\text{mol L}^{-1}$  and nutrient transport (e.g., DON<sub>Tn</sub>) in kmol s<sup>-1</sup>. Outflowing waters: Labrador Current (LC); East Greenland Current (EGC). Inflowing waters: West Spitsbergen Current (WSC); Atlantic Waters flowing through the Barents Sea Opening (BSO); Bering Strait (BS); River discharge (Rivers).

<sup>b</sup>Data from Tsubouchi *et al.* [2012].

<sup>c</sup>Data from Simpson *et al.* [2008].

<sup>d</sup>Data from Holmes *et al.* [2011]; total dissolved phosphorus (includes the inorganic and organic fractions).

( $5 \mu\text{mol L}^{-1}$ , <30 m) [Letscher *et al.*, 2013b]. Our DON observations in the Nordic Seas and LC agree, therefore, with prior observations within the AO.

Our DOP measurements are also consistent with observations elsewhere in the open ocean and continental shelves; ranging from low/undetectable to  $0.45 \mu\text{mol L}^{-1}$ , and contributing 40–100% of the TDP in the upper 100 m [Karl and Björkman, 2015]. Our average Nordic Seas DOP concentration ( $0.17 \pm 0.11 \mu\text{mol L}^{-1}$ ) is higher than, but consistent with, the Natl average ( $\sim 0.12 \pm 0.02 \mu\text{mol L}^{-1}$ ) [Karl and Björkman, 2015]. DOP within the AO (and environs) range from low/undetectable to  $\sim 2.6 \mu\text{mol L}^{-1}$  [Simpson *et al.*, 2008; Lin *et al.*, 2012; Tremblay *et al.*, 2014]. Some of the highest concentrations have been observed in the Bering Sea (up to  $0.45 \mu\text{mol L}^{-1}$ ) and Chukchi Sea (up to  $0.41 \mu\text{mol L}^{-1}$ ) [Lin *et al.*, 2012], Kugmallit Bay (Canadian Beaufort Shelf; up to  $1.33 \mu\text{mol L}^{-1}$ ) [Tremblay *et al.*, 2014], and associated with Pacific-derived waters at 150–200 m ( $0.76 \pm 0.27 \mu\text{mol L}^{-1}$ , southeastern Beaufort Sea) [Simpson *et al.*, 2008]. Hence, our observations across the LC ( $0.85 \pm 0.18 \mu\text{mol L}^{-1}$ , upper 100 m) are among the highest recorded in the Arctic-Subarctic environment.

#### 4.2. Relevance of DON and DOP for the AO Nutrient Budget

We set out to investigate whether net oceanic transports of dissolved organic nutrients could account for (i) AO N loss via denitrification ( $29.4 \text{ kmol s}^{-1}$ ), and (ii) the export of phosphate ( $-1.0 \pm 0.3 \text{ kmol s}^{-1}$ ). Our simple assessment suggests the AO to be a minor/modest exporter of DON ( $-4.66 \pm 3.08 \text{ kmol s}^{-1}$ ) and a large exporter of DOP ( $-1.74 \pm 0.50 \text{ kmol s}^{-1}$ ). The results therefore, do not support our hypothesis. To support it, results should yield net imports equivalent to the denitrification rate and to the phosphate export. However, given the AO circulation, patterns emerge with regard to sources and sinks of DON and DOP, and how these might have further impacts downstream.

Figures 2k and 2l plot concentrations of nitrate versus phosphate and DON versus DOP. The inorganic N:P relationship from profiles in the Nordic Seas sector and from profiles in central and east Labrador Sea (nitrate =  $15.6 \times \text{phosphate} - 1.59$ ) is consistent with Atlantic waters, while that from profiles across the LC (nitrate =  $13.2 \times \text{phosphate} - 4.47$ ) is consistent Pacific-derived polar waters. We see the expected offset between waters of Atlantic and Pacific origin (e.g., nitrate =  $17.4 \times \text{phosphate} - 3.07$  and nitrate =  $12.36 \times \text{phosphate} - 10.5$ , respectively) [Jones *et al.*, 1998]. With our new organic nutrient data, we find clear relationships between DON and DOP concentrations associated with Atlantic waters and inferred Pacific-derived waters, analogous to the inorganic nutrient relationships. For the Atlantic waters,  $\text{DON} = 12.1 \times \text{DOP} + 3.47$  and for Pacific waters,  $\text{DON} = 7.33 \times \text{DOP} - 0.26$  (Figure 2l), with the intercept in the former possibly representing the refractory pool at depth. There is a clear offset between the two relationships equivalent to  $0.5 \mu\text{mol-DOP L}^{-1}$  at  $4 \mu\text{mol-DON L}^{-1}$ , increasing to  $0.8 \mu\text{mol-DOP L}^{-1}$  at  $8 \mu\text{mol-DON L}^{-1}$ .

There are biogeochemical implications of this DON:DOP difference. The consistency of the slopes in DON:DOP relationships may be indicative of a common biological origin, but influenced by different removal processes (e.g., denitrification), additional autochthonous and allochthonous sources, and/or water mass modification.

LC DON and DOP transports (i.e., polar outflow) seem enhanced (5.5- and 3.7-fold, respectively) relative to the inferred Pacific-water-derived transports (Table 1). While the latter may be a point for discussion given



the complex nature of water mass transformation via winter convection and halocline water formation, and organic matter decomposition upstream [e.g., Anderson *et al.*, 2013; Lowry *et al.*, 2015; Tremblay *et al.*, 2015], hence, not truly representing annual average transports across Bering Strait, our assumption provides a reference point enabling us to make first-order inferences.

LC DON and DOP transports hold relevant nonetheless and are somewhat consistent with the export of inorganic nutrients via Davis Strait, which were found to be 2 to  $\geq 3$  times larger than the import across Bering Strait (TV13). The above possibly reflects the net effect of physical and biogeochemical processes upstream and/or the composition of DOM: (1) a fraction of the organic nutrients imported via Bering Strait may get locked in the halocline under a strong stratified surface layer; (2) the DON:DOP ratio of this DOM pool may render it unappealing to bacteria and phytoplankton alike (i.e., it cannot relieve nitrogen limitation); and/or (3) biological production of semilabile and refractory dissolved organic matter over the Chukchi Sea and adjacent shelf seas dominates over sinks along the pathway to Davis Strait. If the latter holds true and the increase of open water primary production due to summer sea ice retreat [Arrigo *et al.*, 2008; Brown and Arrigo, 2012] yields larger biologically derived DOM, it is likely this will also affect the quality and quantity of nutrients exported to the NATl.

Deep transports of DON across Fram Strait may be balanced, since concentrations in inflowing and outflowing waters are similar:  $3.6 \pm 0.4 \mu\text{mol L}^{-1}$  for the WSC between 101 and 501 m, and  $3.7 \pm 0.4 \mu\text{mol L}^{-1}$  for the EGC between 101 and 320 m. These concentrations are consistent with DON observations in the Laptev Sea of  $3.6 \pm 0.4 \mu\text{mol L}^{-1}$  (200–500 m) and  $3.4 \pm 0.3 \mu\text{mol L}^{-1}$  ( $>500$  m) [Dittmar *et al.*, 2001; Sipler and Bronk, 2015], which may be typical in deep Eurasian AO waters. We are not aware of concomitant DOP measurements. Across Fram Strait these are near or below the detection limit at depth. We have already shown that Fram Strait surface water transports are approximately in balance.

DON and DOP imports through the BSO ( $8.36 \pm 1.83 \text{ kmol-DON s}^{-1}$  and  $0.23 \pm 0.13 \text{ kmol-DOP s}^{-1}$ ) might (1) become relevant for Eurasian AO biogeochemistry if these organic pools are recycled during transit through the Barents Sea; (2) alternatively, if unused, these might be incorporated into the wider AO scale Atlantic Water driven circulation [e.g., Dmitrenko *et al.*, 2015; Rudels *et al.*, 2004]. If the former held true, the DON transport could potentially offset  $\sim 65 \pm 11\%$  of the N lost to Barents Sea denitrification ( $12.9 \text{ kmol-N s}^{-1}$ ) [Chang and Devol, 2009], and the DOP transport could account for 23% of the phosphate export. If the latter, then organic nutrient pools might be locked under/within AW and/or AW-derived halocline waters in the Eurasian Basin. However, with current data availability, the above scenarios remain to be tested.

#### 4.3. Conclusions

We have assessed the hypothesis that DON and DOP are important for the AO nutrient budget. Indicative budgets allowed us to investigate whether DON could account for the nitrogen lost via denitrification in the AO, and whether DOP could account for the phosphate exported to the NATl, as previously suggested by TV13.

Results do not support our hypothesis, but do provide insights concerning sources and sinks of dissolved organic pools within the AO and how these may influence nutrient transports downstream. We find a clear difference in the DON:DOP relationship between the Amerasian and Eurasian sectors of the AO analogous to the N:P ratio of inorganic nutrients. DON and DOP exported to the NATl via Davis Strait seem to be enhanced relative to the inferred Pacific-derived transports. This may reflect the net effect of a combination of processes upstream such as water mass transformation, halocline formation, DOM production, and organic matter decay. Furthermore, this may be indicative of how current/future changes in the AO may influence the quality and quantity of nutrients (inorganic and organic) exported to the NATl. Transports across Fram Strait seem balanced. BSO transports may potentially contribute toward offsetting denitrification and the export of phosphate. Alternatively, these nutrient pools could be incorporated into the wider AW-derived circulation and be kept away from sunlit layers.

#### 4.4. Implications

TV13 calculated AO inorganic nutrient budgets with sufficient data leading to acceptable accuracy so that it was possible to reach two conclusions. First, that the balanced nitrate budget together with known interior sinks (through denitrification) implied an unknown N source; and second, that the AO contained an unknown source of P to support the net phosphate export. The hypothesis tested herein—that these unknown sources might derive from dissolved organic nutrients—has not been supported. What, therefore, are the logically possible ways forward, whereby these problems may be solved?

1. *Seasonality.* TV13 inorganic nutrient data were collected from late spring through to autumn. Might these budgets be different through winter (late autumn to early spring)?

- a. There is seasonal variability in terms of quantity and quality of riverine nutrient supply; e.g., DON is highest in spring and lowest in winter, while nitrate is higher in winter than in spring, when it gets diluted and consumed [Holmes *et al.*, 2011]. Although the contribution of river nutrient supply is small relative to oceanic nutrient transports, could it influence the AO nutrient budget in winter?
- b. Denitrification rates are linked to primary production and associated particulate organic matter flux to bottom sediments over Arctic shelves [Chang and Devol, 2009]. If the absence of photosynthetic activity in winter is reflected in winter denitrification rates, the N sink could be lower in winter, reducing the apparent annual mean denitrification rate.
- c. Likewise, microbiologically mediated DOM production over productive areas (i.e., Bering, Barents, and Nordic Seas) most likely ceases in winter, so how does this affect nutrient transports (e.g., amount and proportion of organic versus inorganic) into the AO?

Certainly the winter inflow of high-nutrient waters across Bering Strait conditions the winter water over the Chukchi Sea, which later on influences phytoplankton blooms there [Lowry *et al.*, 2015].

2. *Organic nutrients and representativeness.*

- a. Given the lack of DON and DOP data across Bering Strait, we “inferred” their transport across this gateway using data collected in the southeastern Beaufort Sea from Simpson *et al.* [2008]. They observed a DOP enrichment at middepth (150–200 m) associated with Bering Sea water. We in turn selected the associated DON data to obtain a mean for our calculations. However, given the complex interactions of physical and biological processes upstream as discussed above, it is likely that our inference is not accurate enough. We need data across Bering Strait with enough resolution to resolve the signals of the inflowing water masses: e.g., the nutrient-rich Anadyr current on the Russian side, which is difficult to sample.
- b. Perhaps our “indicative” budgets are not representative. As shown in TV13, nutrient fields show substantial horizontal and vertical structure. Our approach here employs data with low spatial resolution, which may not adequately resolve the net effect of mesoscale features, such as the complex recirculation patterns of AW across Fram Strait [Hattermann *et al.*, 2016] or narrow coastal currents that could carry large amounts of terrigenous material: the coasts of Baffin Island, west and east Greenland, Svalbard, mainland Norway, east Siberia, and Alaska.
- c. Denitrification is highly uncertain. We have used the estimated pan-Arctic average of  $29.4 \text{ kmol-N s}^{-1}$  as reference, but with a range of 14 to  $66 \text{ kmol-N s}^{-1}$  [Chang and Devol, 2009], it requires to be constrained.

3. *Alternative nutrient sources.*

- a. Information regarding atmospheric deposition of nutrients to the AO is scarce, but some global modeling assessments suggest these may be negligible; e.g.,  $7.0 \times 10^{-3} \text{ kmol s}^{-1}$  total P [Mahowald *et al.*, 2008],  $\leq 1.13 \times 10^{-13} \text{ kmol m}^{-2} \text{ s}^{-1}$  reactive N [Dentener *et al.*, 2006].
- b. It has recently been suggested that the melting of the Greenland Ice Sheet (GrIS) may drive large nutrient supplies to the fjord systems around Greenland [e.g., Hawkings *et al.*, 2015]. Certainly, the fraction of any supply delivering nutrients to Baffin Bay would contribute to the AO nutrient budget as assessed by us. Hawkings *et al.* [2016] estimated the GrIS melt runoff to supply  $\sim 0.011 \text{ kmol s}^{-1}$  ( $\sim 11 \text{ Gg yr}^{-1}$ ) of bioavailable P, i.e., 1% of the phosphate exported from the AO (TV13) or 0.7% of the DOP export estimated here. They also estimated total phosphorus inputs at  $\sim 0.42 \text{ kmol s}^{-1}$  ( $408 \text{ Gg yr}^{-1}$ ), though what proportion of this may become bioavailable and on what times scales, is yet to be determined.

Perhaps not surprisingly, our simple assessment prompts more questions than provides answers. However, addressing these questions is important if we are to understand how current and future changes in the Arctic environment affect the complex interaction of physical and biogeochemical processes that ultimately lead to nutrient pools (both inorganic and organic) becoming available (or not) to primary producers and bacteria, which has implications for ecosystem functioning and for nutrient transports to the NAtl. It is evident that we lack the data to resolve temporal changes in nutrient transports and budgets, in particular, oceanic biologically derived organic nutrient pools. Our simple analysis provides information to serve as starting point to evaluate the role of dissolved organic nutrients in AO biogeochemistry at the pan-Arctic scale and also beyond AO gateways.

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