Influence of the bordering shelves on nutrient distribution in the Arctic halocline inferred from water column nitrate isotopes

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Running head: Nitrate isotopes in the Arctic Ocean

Abstract

The East Siberian Sea and contiguous western Arctic Ocean basin are characterized by a subsurface nutrient maximum in the halocline, generally attributed to both Pacific inflow and intensive remineralization in shelf bottom waters that are advected into the central basin. We report nitrogen and oxygen isotopic measurement of nitrate from the East Siberian Sea and western Eurasian Basin, in order to gain insight into how nitrate is processed by the microbial community and redistributed in the Arctic Ocean. A large decoupling between nitrate $\delta^{15}$N and
δ\(^{18}\)O is reported, increasing and decreasing upward from the Atlantic temperature maximum layer toward the surface, respectively. A correlation between water and nitrate δ\(^{18}\)O indicates that most of the nitrate (> 60 %) at the halocline has been regenerated within the Arctic Ocean. The increase in nitrate δ\(^{15}\)N correlates with the fixed N deficit, indicating a causal link between the loss of fixed N and the \(^{15}\)N enrichment. This suggests that a significant share of benthic denitrification is driven by nitrate supplied by remineralization and partial nitrification, allowing residual \(^{15}\)N-enriched ammonium to diffuse out of the sediments. By increasing nutrient concentrations and fixed N deficit in shelf bottom waters, this imprint is attenuated offshore following advection into the halocline by nitrate regeneration and mixing. Estimation of the sedimentary isotope effect related to benthic denitrification yields values in the range of 2.4 – 3.8 ‰, with its magnitude driven by both the degree of coupling between remineralization and nitrification, and fixed N concentrations in shelf bottom waters.

1. Introduction

Primary production in the Arctic Ocean is predominantly controlled by extreme seasonal variation of light, while being modulated further by the growth and decay of sea ice (Wassman and Reigstad, 2011; Slagstad et al., 2015). Primary production is thus restricted to a limited period from late spring to summer and occurs both at the bottom of sea ice and in the euphotic layer (Wassman and Reigstad, 2011; Leu et al., 2015; Janout et al., 2016), with an overall higher primary production over the Arctic shelves and slopes (Pabi et al., 2008). In recent years, Arctic sea ice has been retreating at an unprecedented rate (Cavalieri and Parkinson, 2012). These changes have profound impacts on primary production and upper ocean dynamics, and, therefore, the functioning of the Arctic marine ecosystems (Wassman and Reistag, 2011; Rainville et al., 2011; Yool et al., 2015). Primary production has increased by 30 % from 1998 to
2012 (Arrigo and van Dijken, 2015). Whether this increase in productivity will continue as sea
ice declines further, is difficult to predict (Arrigo and van Dijken, 2015; Vancoppenolle et al.,
2013). In this respect, the availability of fixed nitrogen (i.e., reactive N or non-N\textsubscript{2}; also defined
as biologically available N) also sets a limit on phytoplankton growth in the Arctic Ocean
(Popova et al., 2012; Codispoti et al., 2013). Current understanding in the N dynamics of Arctic
Ocean is limited compared to other ocean regions and reducing these uncertainties would
increase the reliability of projections for future Arctic primary productivity (Chang and Devol,
2009; Vancoppenolle et al., 2013; Arrigo and van Dijken, 2015).

Processes in the Arctic halocline are illustrative of the fixed N pathway into the Arctic Ocean
(Fig. 1b) (Tremblay et al., 2015). The subsurface nutrient maximum in the western Arctic upper
halocline is advected with high-nutrient Pacific water and supplemented with nutrients from the
decomposition of organic matter on the bordering shelves and slopes (Jones and Anderson, 1986;
Anderson et al., 2013; Tremblay et al., 2015). These waters exit the Arctic Ocean with the
predominantly cyclonic Arctic Ocean Boundary Current (AOBC) carrying water from the
Beaufort Gyre toward the Canadian Arctic archipelago and Fram Strait (Rudels, 2012). The
colder lower halocline is thought to be formed either by (i) a combination of deep winter
convection and fresh water input by sea-ice melt when Atlantic water enters the Arctic Ocean
through the eastern Fram Strait and Barents Sea, or (ii) by offshore advection of dense water that
is produced by sea-ice formation over the Arctic shelves during AOBC transport (Aagaard et al.,
1981; Rudels et al., 1994, 1996; Steele and Boyd, 1998; Woodgate et al., 2001; Kikuchi et al.,
2004). Being progressively covered by a less saline upper halocline on its route into the western
Arctic Ocean, the lower halocline water mass initially has characteristics of the relatively
nutrient-poor Atlantic source water, but is subsequently supplemented with nutrients from the
decomposition of organic matter on bordering shelves and slopes during their transport (Anderson et al., 2017). About half of the Atlantic inflow returns immediately out of the Arctic Ocean through Fram Strait whereas the other half is transported with the AOBC across the Arctic Ocean before exiting through the western Fram Strait and Canadian Arctic Archipelago (Fig. 1b) (Rudels, 2012).

While nitrogen and oxygen isotopes ratios of nitrate ($\text{NO}_3^-$; $^{15}\text{N}/^{14}\text{N}, {^{18}\text{O}}/{^{16}\text{O}}$) provide a powerful tool to assess how $\text{NO}_3^-$ is processed by the microbial community and is redistributed through the Arctic Ocean, such measurements have so far only been carried out for the Chukchi Sea shelf and the Canada Basin (Brown et al., 2015). Nitrate assimilation and denitrification (both $\text{NO}_3^-$ consuming processes) preferentially convert $^{14}\text{N}$ and $^{16}\text{O}$, leaving the residual $\text{NO}_3^-$ enriched in $^{15}\text{N}$ and $^{18}\text{O}$. The degree of fractionation is given by the kinetic isotope effect, $\varepsilon$, defined by the ratio of rates at which the two isotopes are converted from one form to another (i.e., for nitrogen, $^{15}\varepsilon$ (‰) = ($^{14}k$/$^{15}k$-1) x 1000; where $^n k$ is the rate coefficient for the $^n\text{N}$-containing reactant). Since denitrifying bacteria and phytoplankton discriminate against $^{15}\text{N}$ and $^{18}\text{O}$ to the same extent ($^{15}\varepsilon \sim ^{18}\varepsilon$) (Granger et al., 2008, 2010; Karsh et al., 2012), the residual $\text{NO}_3^-$ $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values increase in proportion to $\text{NO}_3^-$ consumption (i.e., coupling between N and O isotopes).

Nitrification ($\text{NO}_3^-$ producing process), on the other hand, decouples N from O isotopes (Lehmann et al., 2004; Sigman et al., 2005). During $\text{NO}_3^-$ assimilation and regeneration (i.e., N remineralization + nitrification), the N isotopes are recycled between the fixed N pools, while the O isotopes are removed during $\text{NO}_3^-$ assimilation (since $\text{NO}_3^-$ is reduced to ammonium, $\text{NH}_4^+$, before assimilation) and then re-introduced during nitrification (i.e., oxidation of $\text{NH}_4^+$ to nitrite, $\text{NO}_2^-$, and then to $\text{NO}_3^-$) (Casciotti et al., 2010; Buchwald et al., 2012, 2015). Anaerobic ammonium oxidation into $\text{N}_2$ (i.e., anammox) is another pathway to lose fixed N from marine
sediments (Dalsgaard et al., 2005) but is considered to play a minor role over the Arctic shelves in comparison to denitrification, as these shelves receive high loads of labile organic matter (Dalsgaard et al., 2005; McTigue et al., 2016).

Brown et al. (2015) observed a progressive $^{15}$N-enrichment and $^{18}$O-depletion of NO$_3^-$ over the Chukchi Sea shelf and the adjacent offshore Canada Basin during advection of Pacific waters through the Bering Strait into the Canada Basin. The $^{15}$N-enrichment was inversely correlated with NH$_4^+$ concentrations in shelf bottom waters, suggesting a sediment source of $^{15}$N-enriched NH$_4^+$ in agreement with the process of benthic coupled partial nitrification-denitrification (Lehmann et al., 2007; Granger et al., 2011). The $^{18}$O-depletion relative to the Bering Sea source waters indicated that a significant fraction (~ 50 %) of NO$_3^-$ in the upper halocline was regenerated by nitrification during the transport from the Bering Strait into the Canada Basin.

In the present study we report $\delta^{15}$N and $\delta^{18}$O of NO$_3^-$ along a slope transect in the East Siberian Sea and for the sea ice-covered area of the western Eurasian Basin (Fig. 1), allowing us to test the hypothesis that a decoupling between N and O isotopes as observed in the Bering Strait and Canada Basin may likely be extended to the entire Arctic upper ocean. The primary objectives are to understand how the nutrient maximum in the Arctic halocline is being formed, and what is the influence of the bordering shelves on the reprocessing and redistribution of nutrients throughout the Arctic Ocean. The secondary objective is to improve our mechanistic understanding of the isotope systematics related to benthic fixed N loss.

2. Materials and method

Water samples were collected on full water column profiles during one cruise in the vicinity of Fram Strait (~ 82.5°N and 6.2°W) in the western Eurasian Basin, northeast of Greenland, with 5 hydrocasts (July 2014; R.V. Polarstern, ARKXXVIII/3) and a second across-slope section in the
East Siberian Sea (170 – 175°E) with 6 hydrocasts, including on-shelf and off-shelf stations (August 2014; R.V. Oden, SWERUS-C3) (Fig. 1).

Salinity and temperature were recorded using a Seabird 911C CTD with dual Sea-Bird temperature (SBE 3), conductivity (SBE 04c) and oxygen sensors (SBE 43). Dissolved oxygen \( (O_2) \) was measured onboard soon after sampling via Winkler titration as described in Anderson et al. (2017). Samples were stored frozen (-20°C) in acid-cleaned HDPE 60 ml bottles until their analysis at the home-based laboratory (AMGC, VUB, Brussels, Belgium) for both water \( \delta^{18}O \), and nitrate \( \delta^{15}N \) and \( \delta^{18}O \). Immediately after sampling, the SWERUS-C3 samples were filtered to remove particles using pre-rinsed Acrodisc filters (0.2 µm porosity). Nutrient concentrations (nitrate, \( NO_3^- \), nitrite, \( NO_2^- \), ammonium, \( NH_4^+ \), phosphate, \( PO_4^{3-} \) and silicic acid, \( Si(OH)_4 \)) were measured based on spectrophotometric techniques, using a continuous flow QuAAtro analyzer from Seal Analytical (Hydes et al., 2010), either soon after sampling for SWERUS-C3 or on frozen samples at the home-based laboratory for ARKVIII/3 (Dore et al., 1996).

We used \( N^* \) concentration to estimate the deficit in fixed N (i.e., biologically available N) in comparison to \( PO_4^{3-} \), according to \( N^* = [DIN] -16*[PO_4^{3-}] + 2.9 \) (Deutsch et al., 2001; DIN = dissolved inorganic N = \( NO_3^- + NO_2^- + NH_4^+ \)). Low (negative) \( N^* \) concentrations indicate a sink of fixed N and high (positive) concentrations are indicative of N\(_2\) fixation. Nutrients can be further defined as regenerated vs. preformed nutrients (Ito and Follows, 2005). Below the euphotic layer, regenerated nutrients are derived from the remineralization of organic matter, either exported from the surface with export production (i.e., being equivalent to net community production) or supplied from the rivers. Preformed nutrients originate as euphotic layer nutrients that are left unused following blooms and are then carried into the subsurface by winter vertical mixing or downwelling (Ito and Follows, 2005). One can resolve the contributions of
regenerated and preformed nutrients using the Apparent Oxygen Utilization (AOU), which depends on the observed temperature, salinity, and in-situ oxygen distribution (Broecker et al., 1985), and assuming a fixed stoichiometric ratio between oxygen and nutrients for remineralization (Anderson, 1995). Regenerated $\text{PO}_4^{3-}$ equals AOU divided by the $\text{O}_2/\text{PO}_4^{3-}$ oxidation ratio during aerobic respiration (i.e., $\text{AOU}/150$; $\text{C}_{106}\text{H}_{175}\text{O}_{42}\text{N}_{16}\text{P} + 150\text{O}_2 = 106\text{CO}_2 + 16\text{HNO}_3 + \text{H}_3\text{PO}_4 + 78\text{H}_2\text{O}$). Extensive denitrification over the Arctic shelves and slopes (Chang and Devol, 2009) introduces a complexity in the utilization of both AOU and $\text{O}_2/\text{NO}_3^-$ oxidation ratio, rendering it difficult to infer regenerated $\text{NO}_3^-$.

Nitrate $\delta^{15}$N and $\delta^{18}$O were determined with the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002). Briefly, 20 nmol of $\text{NO}_3^-$ is quantitatively converted to $\text{N}_2\text{O}$ gas by denitrifying bacteria (*Pseudomonas chlororaphis* f. sp. *aureofaciens* ATCC no 13985) that lack an active $\text{N}_2\text{O}$ reductase. The produced $\text{N}_2\text{O}$ is analyzed by gas chromatography/isotope ratio mass spectrometry (Thermo, DeltaV, VUB), using a custom-build ‘purge and trap’ system similar to the one described by Casciotti et al. (2002). Measurements are referenced to air $\text{N}_2$ for $\delta^{15}$N and Vienna Standard Mean Ocean Water (VSMOW) for $\delta^{18}$O using the $\text{NO}_3^-$ reference materials IAEA-NO3, with a $\delta^{15}$N of 4.7‰ and a $\delta^{18}$O of 25.6‰, and USGS-34, with a $\delta^{15}$N of -1.8‰ and a $\delta^{18}$O of -27.9‰ (Böhlke et al., 2003). Prior to the nitrate isotope analyses, $\text{NO}_2^-$ was removed by reaction with sulfamic acid to avoid any interference with $\text{NO}_3^-$ (Granger and Sigman, 2009). Each batch of samples intended for mass spectrometric analysis included $\text{NO}_3^-$ reference materials that was also amended with sulfamic acid to ensure that no contamination originates from this treatment. As a concentration effect is reported for measurements of $\text{NO}_3^-$ $\delta^{18}$O, nitrate reference materials were diluted with low-nutrient Sargasso Sea surface water to generate concentrations that bracket the concentrations of the samples in each batch (Weigand et
We use any trends between the measured $\delta^{18}$O of the two references concentrations bracketing of the sample concentrations to generate a linear correction for this trend (Marconi et al., 2015; Weigand et al., 2016). Replicate analysis (100% of the samples) indicates a median (mean) 1sd reproducibility of 0.15 (0.21) and 0.25 (0.27) ‰ for the NO$_3^-$ $\delta^{15}$N and $\delta^{18}$O, respectively.

Water $\delta^{18}$O was measured using a CO$_2$ equilibration technique (Epstein and Mayeda, 1953). Headspace gastight vials (12 ml) are first flushed with helium gas and 500 µl of water is then added followed by 300 µl of pure CO$_2$. The samples are placed in a shaker for 48h at ambient laboratory temperature allowing CO$_2$ $\delta^{18}$O to fully equilibrate with water $\delta^{18}$O before extraction with a GasBench - Isotope Ratio Mass Spectrometer (Nu Perspective, Nu Instruments). Measurements were referenced to Vienna Standard Mean Ocean Water (VSMOW) for $\delta^{18}$O using in-house standards previously calibrated to the VSMOW scale. The reported standard deviation (1sd) is ~ 0.05 ‰ (Benetti et al., 2017).

3. Results

Temperature vs. salinity diagrams for both the East Siberian Sea and the western Eurasian Basin show presence of cold and saline bottom water, overlaid by warmer Atlantic water centered at ~300 m (i.e., temperature maximum; > 0°C) (Fig. 2a). Overall, most of the density stratification in the Arctic Ocean occurs above ~ 250 m in the halocline, separated into a lower and an upper halocline with an Atlantic and Pacific origin, respectively (McLaughlin et al., 1996; Rudels et al., 1996). In the western Eurasian Basin, only a cold lower halocline was observed near the freezing point of seawater and with a salinity of ~ 34.0 (Fig. 2a), centered around ~ 100 m depth. The lower halocline was warmer and slightly deeper in the East Siberian Sea. The upper
halocline was present in the East Siberian Sea at a depth range of 100-125 m in the salinity range 32.5 to 33.5 and was clearly discernable by the maximum in nutrients, especially $\text{PO}_4^{3-}$ and $\text{Si(OH)}_4$ being indicative of the nutrient-rich Pacific inflow (Fig. 3) (Jones et al., 1998). Water $\delta^{18}$O largely followed salinity (Fig. 2b), as the freshwater supply in the Arctic Ocean is highly $^{18}$O-depleted (Cooper et al., 2008).

In the East Siberian Sea, a large accumulation of nutrients, especially $\text{PO}_4^{3-}$ and $\text{Si(OH)}_4$, was observed at the halocline (Fig. 3). On-shelf stations had roughly similar NO$_3^-$ concentrations at comparable salinity than off-shelf stations but with higher $\text{PO}_4^{3-}$ and $\text{Si(OH)}_4$ concentrations. In the western Eurasian Basin, no maximum in NO$_3^-$ concentration was observed with concentrations steadily increasing from the surface to the deeper layers. On the contrary $\text{PO}_4^{3-}$ and $\text{Si(OH)}_4$ showed a small maximum at the lower halocline (Fig. 3). The accumulation of nutrients in the East Siberian Sea was associated with a clear deficit in fixed N (i.e., biologically available N), as inferred from negative N$^*$ concentrations, and O$_2$ consumption due to remineralization (Figs. 3e, f). This is further confirmed with the proportion of regenerated $\text{PO}_4^{3-}$ being higher at the halocline, and even more so at the lower halocline in the East Siberian Sea (Fig. 3d).

A large decoupling between NO$_3^-$ $\delta^{15}$N and $\delta^{18}$O was observed at the halocline, increasing and decreasing upward, respectively (Figs. 4b, c). For the off-shelf stations of the East Siberian Sea, NO$_3^-$ $\delta^{15}$N increased from 5.0 to 8.6 ‰ from ~300 m depth to just below the mixed layer depth. No measurements were available at shallower depths as NO$_3^-$ concentration was ~0.2 µmol l$^{-1}$, below our detection limit. The two on-shelf stations had contrasting NO$_3^-$ $\delta^{15}$N, with one station following the trend given by the off-shelf stations (up to 9.5 ‰) and one station having relatively lower NO$_3^-$ $\delta^{15}$N values (up to 5.3 ‰) (Fig. 4b). In the western Eurasian Basin, NO$_3^-$ $\delta^{15}$N
increased from 5.0 to 6.9 ‰. We observed a strong negative correlation between N* and NO$_3^-$ $\delta^{15}$N ($R^2 = 0.7$, p value < 0.001) in the East Siberian Sea (Fig. 5a). Only one of the two on-shelf stations falls on this trend with the other station presenting a deficit in fixed N but without $^{15}$N-enrichment of NO$_3^-$. In the western Eurasian Basin, the relationship between N* and NO$_3^-$ $\delta^{15}$N was attenuated, showing a larger scatter, though still significant ($R^2 = 0.3$, p value < 0.001).

In the off-shelf stations of the East Siberian Sea, NO$_3^-$ $\delta^{18}$O decreased from 1.9 to -0.6 ‰ from ~300 m depth to just below the mixed layer depth (Fig. 4b). At a given salinity on-shelf stations had similar NO$_3^-$ $\delta^{18}$O values than off-shelf stations (data not shown). NO$_3^-$ $\delta^{18}$O increased just below the mixed layer for three stations, one on-shelf (up to 4.1 ‰) and two off-shelf stations (up to 2.4 ‰). This likely reflects an increase in the contribution of preformed nutrients toward the surface (Fig. 3d), reflecting $^{18}$O enrichment from past NO$_3^-$ assimilation starting with a NO$_3^-$ initial pool harboring a variable decoupling between N and O isotopes (Fig. 4c). In the western Eurasian Basin, NO$_3^-$ $\delta^{18}$O decreased similarly with depth from ~1.5 to 0.3 ‰ with comparable values in both the lower halocline and surface waters as in the East Siberian Sea. A positive relationship was reported between NO$_3^-$ $\delta^{18}$O and water $\delta^{18}$O in the East Siberian Sea (Fig. 4d; $R^2 = 0.7$, p value < 0.001). This relationship was attenuated and more scattered for the western Eurasian Basin ($R^2 = 0.4$, p value < 0.001).

4. Discussion

The nutrient maximum and fixed N (i.e., biologically available N) deficit in the western Arctic halocline are generally attributed to inflow of nutrient-rich Pacific waters through the shallow Bering Strait (Jones et al., 1998). Episodic intrusion of Pacific waters occurs in the Makarov Basin and the East Siberian Sea, mostly depending on the dominating atmospheric pressure field that determines the extent of the Beaufort Gyre and the position of the Transpolar Drift.
Further remineralization and benthic denitrification in Arctic shelf seas are required to explain the accentuation of these properties within the Arctic Ocean. Although both NO$_3^-$ and PO$_4^{3-}$ concentrations increase in the upper halocline relative to inflowing Pacific waters, the NO$_3^-$ increase is less than expected from Redfield stoichiometry. As a result, the fixed-N deficit is enhanced (Fig. 6) and this is likely due to processes occurring over the productive Arctic shelves and slopes. There, benthic and water column remineralization are confining decay products (i.e., nutrients) in shelf bottom waters that are then advected throughout the basins of the Arctic Ocean to form the halocline (Jones and Anderson, 1986; Anderson et al., 2013, 2017). The substantive production and export of organic material to the shallow benthos stimulates denitrification in sediments, with benthic denitrification rates reported to contribute between 4 to 13% of the total sink of fixed N in the global ocean. This contrasts with the relatively small contribution of the Arctic Ocean (1.4%) to the total ocean volume (Devol et al., 1997; Chang and Devol, 2009; McTigue et al., 2016).

In the East Siberian Sea, the O$_2$ consumption associated with the nutrient maximum cannot result solely from the advection of nutrient-rich Pacific waters through the well-ventilated shallow Bering Strait (Fig. 3e) (Olsen et al., 2016). If this were the case, O$_2$ concentrations would be close to saturation and most nutrients would be preformed nutrients. However, up to 75% of the PO$_4^{3-}$ in the halocline can be considered as regenerated PO$_4^{3-}$ produced by the remineralization of organic matter either exported from the surface waters or supplied from rivers (Fig. 3d) (Ito and Follows, 2005). The maximum contribution of regenerated PO$_4^{3-}$ was also found in the lower halocline carrying the O$_2$ minimum as well as a significant deficit in fixed N (Anderson et al., 2017). The lower halocline waters are essentially of Atlantic origin, being transported and transformed along the cyclonic Arctic Boundary Current (Fig. 1b) (Aagaard et al., 1981; Rudels...
et al., 1994, 1996; Steele and Boyd, 1998; Woodgate et al., 2001; Kikuchi et al., 2004). While originally relatively poor in nutrients, accumulation of nutrients by remineralization during their transport is required, most likely following offshore advection of nutrient-enriched shelf bottom water into the central Arctic Basin (Anderson et al., 2017). Conservative mixing between Atlantic- and Pacific-derived waters, following diapycnal mixing, cannot explain the nutrient accumulation in nutrients, O$_2$ depletion and deficit of fixed N observed at the lower halocline in the East Siberian Sea (red lines in Fig. 3). For the western Eurasian Basin stations, the lower nutrient concentrations in the halocline could indicate that this area is predominantly affected by the Atlantic inflow (Figs. 1c and 3) through the eastern Fram Strait and the Barents Sea and exit the Arctic Ocean mostly through the western Fram Strait (Fig. 1b) (Ruddels, 2012). However, as discussed in the following sections, the NO$_3^-$ $\delta^{15}$N and $\delta^{18}$O values for the western Eurasian Basin indicate that these signatures were partly inherited from the Arctic Ocean and especially from the bordering shelves, implying a widespread influence of the continental shelves on the Arctic nutrient distribution.

The dual nitrogen and oxygen isotopes ratios of NO$_3^-$ give insight on how NO$_3^-$ is processed by the microbial community and redistributed in the Arctic Ocean. The following discussion will start with the utilization of the NO$_3^-$ $\delta^{18}$O to estimate the fraction of NO$_3^-$ regenerated within the Arctic Ocean (section 4.1). Then, NO$_3^-$ $\delta^{15}$N will be discussed, suggesting that benthic coupled partial nitrification-denitrification (CPND) is significant over the Arctic shelves and slopes, and is required to explain the high halocline NO$_3^-$ $\delta^{15}$N values in the East Siberian Sea and to a lower extent in the western Eurasian Basin (section 4.2). Finally, the N isotope systematics associated with CPND are discussed including implications for the utilization of the N isotopes to constrain the marine N budget (section 4.3).
4.1. Regenerated nitrate in the Arctic Ocean

Nitrified NO$_3^-$ $\delta^{18}$O is considered to be close to the $\delta^{18}$O of seawater in which nitrification takes place (Casciotti et al., 2008; Sigman et al., 2009; Buchwald et al., 2012; Rafter et al., 2013). In comparison to the rest of the Ocean, Arctic waters exhibit a large variability in $\delta^{18}$O resulting from the large $^{18}$O-depleted freshwater supply (Fig. 2b) (Cooper et al., 2008). This $^{18}$O-depletion could be transmitted to the newly produced NO$_3^-$, potentially allowing us to quantify the fraction of NO$_3^-$ being regenerated in the Arctic Ocean vs. the fraction being advected with the Pacific and Atlantic inflows.

We observed a positive relationship between the $\delta^{18}$O of NO$_3^-$ and seawater ($R^2 > 0.4$, p value $< 0.001$), indicating that the regional imprint from $^{18}$O-depleted Arctic rivers was indeed transmitted to the Arctic NO$_3^-$ pool through regeneration, both in the East Siberian Sea and the western Eurasian Basin (Fig. 4d). Overall NO$_3^-$ $\delta^{18}$O values decreased toward the surface (i.e., following the trend for water $\delta^{18}$O), but this decrease was stronger for the East Siberian Sea than for the western Eurasian Basin, likely reflecting the larger freshwater contribution (i.e., lower water $\delta^{18}$O and salinity) to the former basin (Fig. 2b) (Cooper et al., 2008; Bluhm et al., 2015). This relationship between seawater $\delta^{18}$O and NO$_3^-$ $\delta^{18}$O appears to be unique to the Arctic and sub-Arctic areas, and so far has only been reported for the Chukchi Sea and the Canada Basin (Brown et al., 2015) and over the northern Bering shelf (Granger et al., 2011, 2013). The present study suggests that it is likely the norm for the whole Arctic Ocean. A deviation from this relationship is observed toward the surface for some stations in both the East Siberian Sea and western Eurasian Basin, with the latter harboring high NO$_3^-$ $\delta^{18}$O ($\sim$1 to 4.3 ‰) for low seawater $\delta^{18}$O ($\sim$1.6 to -2.3 ‰; Fig. 4d). This likely reflects $^{18}$O enrichment from NO$_3^-$ assimilation.
starting with a NO$_3^-$ initial pool harboring a variable decoupling between N and O isotopes (Fig. 4c).

The regeneration of NO$_3^-$ is related to nitrification (NH$_4^+$ to NO$_3^-$), while the O isotopes are removed by NO$_3^-$ assimilation and denitrification (since NO$_3^-$ is reduced to NH$_4^+$ or N$_2$) and then replaced in the nitrification process (NH$_4^+$ to NO$_2^-$ and then to NO$_3^-$) (Sigman et al., 2005). The $\delta^{18}$O of newly produced NO$_3^-$ will depend on the associated isotopic fractionation during nitrification and the sources of O atoms (Sigman et al., 2009; Buchwald et al., 2012). The relatively small range of NO$_3^-$ $\delta^{18}$O reported for deep and intermediate waters in the ocean ($\sim 1.5$ to $2.5\%$), being close to seawater $\delta^{18}$O, has led to the general assumption that NO$_3^-$ $\delta^{18}$O of newly produced NO$_3^-$ is mainly set by O incorporation from water with a little contribution from O$_2$ (Sigman et al., 2009). Field studies have shown that newly produced NO$_3^-$ $\delta^{18}$O is near that of seawater $\delta^{18}$O $\sim 1.1 \%$ (Casciotti et al., 2008; Sigman et al., 2009; Rafter et al., 2013). While culture experiments give a range for newly produced NO$_3^-$ $\delta^{18}$O between $-1.5$ and $1.3 \%$ relative to seawater $\delta^{18}$O (Buchwald et al., 2012), encompassing field estimates, they also demonstrate that this range in $\delta^{18}$O reflects, instead, a combination of large kinetic isotope effects (during O atom incorporation from H$_2$O and O$_2$) and equilibrium isotope effect with H$_2$O (Casciotti, 2007, Casciotti et al., 2010; Buchwald et al., 2012).

Our data clearly highlight the role played by water $\delta^{18}$O in setting the variation of NO$_3^-$ $\delta^{18}$O (Fig. 4d). Halocline waters in the East Siberian Sea and the western Eurasian basin, show a relatively good agreement between observed NO$_3^-$ $\delta^{18}$O and the predicted $\delta^{18}$O for regenerated NO$_3^-$ according to field studies (i.e., seawater $\delta^{18}$O $\sim 1.1 \%$; black line in Fig. 4d). However, a clear deviation from the predicted trend, with higher NO$_3^-$ $\delta^{18}$O than expected, is observed toward the surface (i.e., toward more negative water $\delta^{18}$O; above $\sim 80$ m depth) and could
possibly reflect an increasing proportion of preformed nutrients (Fig 3d). An alternative explanation could be that a mismatch in the timing between NO$_3^-$ regeneration and freshwater accumulation occurs toward the surface, or that regenerated NO$_3^-$, mostly accumulated at the halocline nutrient maximum, diffuse upward and mix with more $^{18}$O-depleted surface waters. Despite this complexity, the relationship between NO$_3^-$ and seawater $\delta^{18}$O clearly indicates that most of the NO$_3^-$ being supplied into the upper Arctic Ocean has been reprocessed at least once within the Arctic Ocean, including the NO$_3^-$ advected with the nutrient-rich Pacific inflow.

Brown et al. (2015) estimated based on ambient NO$_3^-$ $\delta^{18}$O values that roughly 50 % of NO$_3^-$ in the upper halocline was regenerated in the waters of the Bering Strait and the Canada Basin, encompassing the range given by Granger et al. (2013) for the northern Bering Shelf (20 to 80 %). These authors used the following mass and isotopic balance:

$$[	ext{NO}_3^-]_{\text{total}} \times \text{NO}_3^- \delta^{18}\text{O}_{\text{total}} = [	ext{NO}_3^-]_{\text{preformed}} \times \text{NO}_3^- \delta^{18}\text{O}_{\text{preformed}} + [	ext{NO}_3^-]_{\text{regenerated}} \times \text{NO}_3^- \delta^{18}\text{O}_{\text{regenerated}}$$

(1)

Rearranged and simplified as follows:

$$[	ext{NO}_3^-]_{\text{regenerated}}/[	ext{NO}_3^-]_{\text{total}} = (\text{NO}_3^- \delta^{18}\text{O}_{\text{total}} - \text{NO}_3^- \delta^{18}\text{O}_{\text{preformed}})/(\text{NO}_3^- \delta^{18}\text{O}_{\text{regenerated}} - \text{NO}_3^- \delta^{18}\text{O}_{\text{preformed}})$$

(2)

Equation 2 gives the proportion of the ambient NO$_3^-$ pool being regenerated. Setting regenerated NO$_3^-$ $\delta^{18}$O to H$_2$O $\delta^{18}$O + 1.1 ‰, yields NO$_3$ $\delta^{18}$O values of 0.3 ± 0.6 and 0.4 ± 0.5 ‰ for the halocline of the East Siberian Sea and western Eurasian Basin, respectively. Preformed NO$_3^-$ $\delta^{18}$O is set to 1.5 ± 0.5 ‰, encompassing the range for the Atlantic and Pacific inflows (Brown et al., 2015; Deman et al., 2017). Accordingly, the proportion of regenerated NO$_3^-$ to the NO$_3^-$ pool is 80 ± 43 and 65 ± 35 % at the halocline of the East Siberian Sea and western Eurasian Basin, respectively. Despite the large uncertainties, these estimates are similar to the fraction of
regenerated $\text{PO}_4^{3-}$ calculated by assuming a fixed stoichiometric ratio between oxygen and nutrients for remineralization (40 to 75%; Fig. 3d). More data are needed to better constrain preformed $\text{NO}_3^{-} \delta^{18}O$ at the regional scale in the Arctic Ocean, and holds for regenerated $\text{NO}_3^{-} \delta^{18}O$ at the global scale.

4.2. Coupled benthic partial nitrification-denitrification on the bordering shelves

Nitrate $\delta^{15}N$ increased from the Atlantic temperature maximum upward to the halocline and toward the surface, contrasting with the trend observed for $\text{NO}_3^{-} \delta^{18}O$. This increase was larger in the East Siberian Sea than in the western Eurasian Basin (Fig. 4b), reflecting the fact that water in the latter basin is more representative of open water conditions, far from direct shelf to basin interactions and was likely more impacted by regeneration and mixing with less-altered Atlantic inflow (Fig. 1b). The decoupling between $\text{NO}_3^{-} \delta^{15}N$ and $\delta^{18}O$ excludes the possibility that partial $\text{NO}_3^{-}$ assimilation is responsible for this increase in $\text{NO}_3^{-} \delta^{15}N$. Nitrate assimilation preferentially converts $^{14}N$ and $^{16}O$, leaving the residual $\text{NO}_3^{-}$ equally enriched in $^{15}N$ and $^{18}O$ as both $N$ and $O$ isotopes are discriminated to the same extent ($^{15}\varepsilon \sim^{18}\varepsilon$; Fig. 4c) (Granger et al., 2004, 2010; Karsh et al., 2012). This increase in $\text{NO}_3^{-} \delta^{15}N$ toward the surface can neither be explained by regeneration of $\text{NO}_3^{-}$ with nitrification in the water column. Indeed, as is common to Arctic surface waters in summer, $\text{NO}_3^{-}$ is fully consumed in the East Siberian Sea (Codispoti et al., 2013; Humborg et al., 2017). Export production $\delta^{15}N$ (i.e., sinking PN) is therefore equal or close to the $\text{NO}_3^{-}$ source $\delta^{15}N$ (i.e., subsurface $\text{NO}_3^{-} \delta^{15}N$) (Eppley and Peterson, 1979; Altabet and Francois, 1994). In case $\text{NO}_3^{-}$ is only partly assimilated in the surface waters (e.g., in the western Eurasian Basin), export production $\delta^{15}N$ will be lower than ambient $\text{NO}_3^{-} \delta^{15}N$ (Altabet and Francois, 1994). Concerning the regeneration of $\text{NO}_3^{-}$, we can reasonably assume that (i) nitrification is complete on annual to multi-annual scales, and (ii) there is little or no isotopic
fractionation during remineralization of organic matter to NH$_4^+$ (Knapp et al., 2011; Möbius, 2013). Accordingly, buried organic N and nitrified NO$_3^-$ $\delta^{15}$N in the water column are equal or close to the export production $\delta^{15}$N. Violating assumptions (i) and (ii) will tend regenerated NO$_3^-$ $\delta^{15}$N to become lower than sinking PN $\delta^{15}$N (Granger et al., 2011; Fripiat et al., 2014). An input of riverine organic matter will also likely decrease regenerated NO$_3^-$ $\delta^{15}$N upon remineralization, as riverine fixed N $\delta^{15}$N is likely to be low in relative pristine high-latitude rivers (Voss et al., 2006). Instead of remaining constant or decreasing, NO$_3^-$ $\delta^{15}$N rather increased from the Atlantic temperature maximum to the halocline where NO$_3^-$ had accumulated as linked to a consumption of oxygen (Figs 3 and 4). As discussed further below, we suggest that this increase in NO$_3^-$ $\delta^{15}$N is mostly derived from benthic-pelagic interactions (Fig. 7), confining nutrients and a fixed N deficit in shelf bottom waters that are then advected throughout the basins of the Arctic Ocean to be incorporated into the halocline (Jones and Anderson, 1986; Anderson et al., 2013, 2017). For shelf bottom water of the East Siberian Sea this is in agreement with the observed larger nutrient concentrations, N deficit and O$_2$ consumption, which show a tendency to increase toward the sediment interface. Furthermore, we observed that for the off-shelf stations these properties of the halocline become enhanced inshore (Fig. 3).

There was a strong negative correlation between N$^*$ and NO$_3^-$ $\delta^{15}$N in the East Siberian Sea ($R^2 = 0.7$, p value < 0.001), indicating a causal link between the loss of fixed N with benthic denitrification (i.e., N$_2$ production) and the $^{15}$N enrichment in ambient NO$_3^-$ (Fig. 5a). Denitrification cannot take place in the oxygen-containing water column, as observed throughout the Arctic Ocean (Olsen et al., 2016), and is occurring predominantly in the anoxic sedimentary layer of the Arctic shelves and slopes (Chang and Devol, 2009). In case of benthic denitrification, such $^{15}$N-enrichment of NO$_3^-$ can be explained if a significant share of
denitrification consumes NO\textsubscript{3}\textsuperscript{-} that was initially produced from partial benthic nitrification (Fig. 7) (Lehmann et al., 2007). The first step of nitrification (NH\textsubscript{4}\textsuperscript{+} into NO\textsubscript{2}\textsuperscript{-}) strongly discriminates N isotopes, with $^{15}\varepsilon \sim 15$‰ (Casciotti et al., 2003; Santoro and Casciotti, 2011). Residual NH\textsubscript{4}\textsuperscript{+} $\delta^{15}$N increases by producing low NO\textsubscript{2}\textsuperscript{-} $\delta^{15}$N. It is generally assumed that NO\textsubscript{2}\textsuperscript{-} does not accumulate in pore waters and is quantitatively converted by the second step of nitrification (NO\textsubscript{2}\textsuperscript{-} into NO\textsubscript{3}\textsuperscript{-}). As a result of this complete NO\textsubscript{2}\textsuperscript{-} oxidation, the reported inverse kinetic isotope effect ($^{15}\varepsilon \sim -13$‰) is muted (Casciotti, 2009). Newly produced low-$\delta^{15}$N NO\textsubscript{3}\textsuperscript{-} is subsequently reduced to N\textsubscript{2} by denitrification. In case remineralization exceeds nitrification (i.e., partial nitrification) residual $^{15}$N-enriched NH\textsubscript{4}\textsuperscript{+} diffuses out to bottom waters where it is fully nitrified into NO\textsubscript{3}\textsuperscript{-}, increasing the NO\textsubscript{3}\textsuperscript{-} concentration and transmitting the $^{15}$N-enrichment from benthic nitrification into the water column NO\textsubscript{3}\textsuperscript{-} (Fig. 7). This combination of processes is able to explain the observed $^{15}$N enrichment in ambient NO\textsubscript{3}\textsuperscript{-} in the shelf bottom waters and the Arctic halocline layer (Figs. 4b, c and 5a). Sedimentary denitrification sustained by direct NO\textsubscript{3}\textsuperscript{-} diffusion from the overlying water column is unlikely to increase overlying water column NO\textsubscript{3}\textsuperscript{-} $\delta^{15}$N. This denitrification pathway is limited by the diffusion of NO\textsubscript{3}\textsuperscript{-} into the active denitrification layer, with little NO\textsubscript{3}\textsuperscript{-} escaping and therefore not imparting its residual high-$\delta^{15}$N value to the overlying water column NO\textsubscript{3}\textsuperscript{-} (Brandes and Devol, 1997, 2002; Lehmann et al., 2004, 2007).

Benthic coupled partial nitrification-denitrification (CPND) has also been put forward by others to explain a similar $^{15}$N-enrichment and $^{18}$O-depletion of NO\textsubscript{3}\textsuperscript{-} over the Chukchi Sea shelf and the downstream Canada Basin (Brown et al., 2015). The occurrence of this decoupling between N and O isotopes also in the East Siberian Sea, as well as in the lower halocline of predominantly Atlantic origin water, suggests that benthic coupled nitrification-denitrification is
a widespread process over the productive Arctic shelves and slopes. Higher export of organic
matter over the shallow productive Arctic shelves (e.g., the Chukchi and East Siberian Sea) is
likely more favorable to a decoupling between remineralization and nitrification (i.e., lower
nitrification/remineralization ratio), allowing a larger efflux of NH$_4^+$ out of the sediments. This
imprint is likely progressively diluted with increasing distance from the shelves by regeneration
and mixing, implying decreasing NO$_3^-$ $\delta^{15}$N values and an attenuated relationship with N* in the
western Eurasian Basin (Figs. 4b and 5a).

Though the N* and NO$_3^-$ $\delta^{15}$N trend closely fits the line representing conservative mixing
between Atlantic- and modified Pacific-derived waters, this process alone cannot reproduce the
distributions in nutrient, oxygen and N* concentrations found in the East Siberian Sea (red lines
in Figs 3 and 5a). This is further confirmed by the distribution of NO$_3^-$ $\delta^{15}$N vs. the fraction of
fixed N left over by benthic denitrification (see next section). The East Siberian Sea falls on the
fractionation trend given by the preferential removal of $^{14}$N with benthic denitrification, but with
higher than expected NO$_3^-$ $\delta^{15}$N for the conservative mixing (Figs 5b, c). However, in agreement
with the observed attenuation of the NO$_3^-$ $\delta^{15}$N vs. N* concentration relationship away from the
shelf regions, the trend in the western Eurasian Basin, on the contrary, does fit the mixing line
between a fractionated (upper halocline) and an unfractionated pools of NO$_3^-$ (Atlantic derived-
water) (Figs 5b, c).

4.3. Sedimentary isotope effect associated with fixed N loss

The fixed N budget of the Ocean is set by the balance between N inputs (mostly N$_2$ fixation) and
outputs (mostly pelagic and benthic denitrification) (Codispot et al., 2001; Galloway et al.,
2004; Gruber and Galloway, 2008). By knowing the isotope effects related to the fixed N outputs
and the $\delta^{15}$N of the fixed N input, one can estimate the relative imprint of benthic vs. water
column denitrification on the ‘mean’ (i.e., global ocean) oceanic fixed N $\delta^{15}\text{N}$ (Brandes and Devol, 2002; Deutsch et al., 2004; Sigman et al., 2009).

In heterogeneous environments such as sediments, the determination of a ‘mean’ isotope effect related to fixed N loss is not trivial (Lehmann et al., 2007). Indeed, different isotope effects have been defined, depending on where in the system the isotopic fractionation is expressed (pore waters vs. overlying water column) and what fixed N pools are considered (only NO$_3^-$ or total reactive N). The sedimentary isotope effect ($\varepsilon_{\text{sed}}$) takes into account the impact of all fixed N fluxes (including NH$_4^+$) out of the sediments in the expression of the organism-level isotope effects into the overlying water column NO$_3^-$ (Lehmann et al., 2007).

Benthic denitrification has long been assumed to occur with little or no sedimentary isotope effect, as most of the NO$_3^-$ is reduced in the active denitrification layer with little NO$_3^-$ escaping and therefore not imparting its residual high-$\delta^{15}\text{N}$ value to the overlying water column NO$_3^-$ (Brandes and Devol, 1997, 2002; Lehmann et al., 2004, 2007). Recently, higher isotope effects for coupled partial nitrification-denitrification (CPND) have been reported (up to $\sim 8$‰), as the residual NH$_4^+$ diffusing out of the sediments transmits the $^{15}\text{N}$-enrichment from benthic nitrification into overlying water column NO$_3^-$ (Fig. 7) (Lehmann et al., 2007; Granger et al., 2011; Alkhatib et al., 2012). A better assessment of the variability of the sedimentary isotope effect is therefore required to better constrain the ‘mean’ oceanic N isotope budget.

The negative relationship between N* and NO$_3^-$ $\delta^{15}\text{N}$ suggests a causal link between the loss of fixed N (predominantly over the shelves and slopes) (Chang and Devol, 2009) and the $^{15}\text{N}$ enrichment in ambient NO$_3^-$ (Fig. 5a). We propose to use this correlation to estimate the sedimentary isotope effect with the following equations:

$$\text{NO}_3^- \cdot \delta^{15}\text{N} = \text{initial fixed N } \delta^{15}\text{N} - \varepsilon_{\text{sed}} \cdot \ln([\text{DIN}]/([\text{DIN}]-\text{N}^*)) \quad (3)$$
assuming a system in which the reactant N pool is neither replenished nor lost from the system (i.e., Rayleigh fractionation kinetics). The alternative is an open system in steady state for which the input of substrate balances the outputs (residual substrate + product):

\[
\text{NO}_3^- \delta^{15}N = \text{initial fixed N } \delta^{15}N + ^{15}\varepsilon_{\text{sed}} * \left(1 - \frac{[\text{DIN}]}{([\text{DIN}] - N^*)}\right)
\]  

(4)

Several assumptions are inherent to these above equations. The first assumption is that DIN concentration in the water column is representative of the residual fixed N pool. This is a reasonable assumption since the sedimentary DIN pool contributes to a small fraction of the DIN in the combined bottom water and reactive sedimentary layer. The second assumption considers initial fixed N to be the sum of initially available fixed N in the water column (mostly dissolved inorganic N) plus what is derived from organic matter remineralization, in both the bottom water (\(R_{wc}\)) and the reactive sedimentary layer (\(R_{sed}\)) (Fig. 7). Accordingly, the initial fixed N pool is the water column DIN augmented with the N-deficit (\(N^*\)) (Altabet et al., 1999). Hereafter, \(f\) is defined as the ratio between DIN and (DIN-\(N^*\)), and represents the fraction of substrate remaining after the fixed N loss. The third assumption considers \(\text{NO}_3^- \delta^{15}N\) as representative of the residual fixed N \(\delta^{15}N\). It is a reasonable assumption since \(\text{NO}_3^-\) is considered as the end-product of remineralization in the aphotic ocean. To test this last assumption, we also take into account a sedimentary \(\text{NH}_4^+ \delta^{15}N\) of 20 \(\%\) and the relative contribution of \(\text{NH}_4^+\) to the DIN pool to estimate an expected DIN \(\delta^{15}N\). This sedimentary \(\text{NH}_4^+ \delta^{15}N\) value has been reported in the shelf bottom water of the Bering shelf (Granger et al., 2011).

By rearranging equations 3 and 4, the linear relationship between \(\text{NO}_3^- \delta^{15}N\) and either ln(\(f\)) or (1-\(f\)) allows us to estimate a sedimentary isotope effect of \(2.4 \pm 0.4\) and \(3.2 \pm 0.4\) \(\%\) (\(R^2 = 0.7\); p value < 0.001) and an initial fixed N \(\delta^{15}N\) (i.e., at \(N^* = 0\)) of \(6.1 \pm 0.2\) and \(6.2 \pm 0.2\) \(\%\) (p value < 0.001), for closed and open system conditions, respectively (Figs. 5b and 5c). By taking into
account the expected DIN $\delta^{15}$N (assuming a sedimentary NH$_4^+$ $\delta^{15}$N of 20‰), the isotope effect increases to 3.0 ± 0.3 and 3.8 ± 0.3‰ ($R^2 = 0.9$; p value < 0.001) and the fixed N $\delta^{15}$N increases to 6.5 ± 0.1 and 6.6 ± 0.1‰ (p value < 0.001) (not shown). Although more elaborate models (e.g., diffusion-reaction models) might be more appropriate to describe this complex environment, our one-box model is a robust approach to reproduce the observations in the East Siberian Sea ($R^2 > 0.7$, p value < 0.001; Fig. 5). The initial NO$_3^-$ $\delta^{15}$N is close to the observed values at the lower halocline of the offshore East Siberian Sea sites, but little is known about how and from where NO$_3^-$ is advected over the East Siberian shelf. The estimated sedimentary isotope effect fits in the range reported for benthic denitrification (0 - 8‰) (Brandes and Devol, 1997, 2002; Lehmann et al., 2004, 2007; Granger et al., 2011; Alhkatib et al., 2012). The upper limit is usually imparted to the nitrification-driven denitrification and the lower limit to NO$_3^-$ diffusion-driven denitrification (Lehmann et al., 2007; Granger et al., 2011; Alhkatib et al., 2012).

In case of CPND the overall expression of the sedimentary isotope effect into the overlying water column will be mostly a function of the balance between benthic remineralization and nitrification fluxes, which sets the amount of NH$_4^+$ diffusing out of the sediment, its $\delta^{15}$N signature as well as the ambient NO$_3^-$ concentration. Similar to the dilution effect described in Deutsch et al. (2004) for water column denitrification, a fractionated fixed N pool (i.e., efflux out of the sediments) is mixed with an unfractionated fixed N pool (i.e., mostly ambient NO$_3^-$), impacting differently $f$ and NO$_3^-$ $\delta^{15}$N being used to estimate $e_{sed}$ (Eqs. 3 and 4). With a tight coupling between benthic remineralization and nitrification, efflux carries high NH$_4^+$ $\delta^{15}$N out of the sediments but its lower concentration will give less weight in the resulting mixing product NO$_3^-$ $\delta^{15}$N (i.e., efflux + ambient NO$_3^-$ in the overlying water column). In case remineralization
equals CPND, the sedimentary isotope effect is muted, as there is no NH$_4^+$ efflux. In case there is no NO$_3^-$ in the initial water column, the estimated sedimentary isotope effect equals the isotope effect of nitrification ($\sim$15 ‰; Casciotti et al., 2003; Santoro and Casciotti, 2011) and water column NO$_3^-$ $\delta^{15}$N is directly set by the efflux $\delta^{15}$N (i.e., residual product of benthic nitrification). Any intermediate scenario will tend to have a sedimentary isotope effect lying between these two extreme values (i.e., 0 and $\sim$15 ‰). Further mixing with offshore water, not in contact with the reactive sedimentary layer, will also tend to decrease the overall expression of the sedimentary isotope effect (Figs 5b, c).

Accordingly, the relatively low sedimentary isotope effect (2.4 - 3.8 ‰) for the East Siberian Sea may result of benthic CPND characterized by a close coupling between remineralization and nitrification. Note that one station over the shelf (i.e., SWERUS-C3 station 62), presented a clear fixed N deficit but little associated $^{15}$N-enrichment, and was considered an outlier (Fig. 5). This situation may likely result from benthic coupled nitrification-denitrification but with nitrification balancing remineralization, leading to little or no NH$_4^+$ efflux and a sedimentary isotope effect close to 0 ‰ for CPND.

In agreement with previous studies (Lehmann et al., 2007; Granger et al., 2011; Alkhatib et al., 2012) sedimentary isotope effect for benthic fixed N loss is likely to vary considerably for different sedimentary environments. We have shown that, in case of benthic coupled partial nitrification-denitrification, its magnitude also depends on the conditions in the overlying water column (i.e., unfractionated ambient fixed N pools) and especially the degree of coupling between remineralization, and nitrification in the reactive sedimentary layer (i.e., dilution effect). This has profound consequences in the determination of a ‘mean’ sedimentary isotope effect.
needed to assess a relative contribution of benthic vs. water column denitrification to the oceanic fixed N loss, requiring further investigations.

5. Conclusion

Mechanisms generally considered able to explain the halocline nutrient maximum in the Arctic Ocean are; (i) advection of nutrient-rich Pacific water via the shallow Bering Strait, and/or (ii) intensive remineralization over the productive shallow shelves. The latter mechanism implies a temporary confinement of the remineralization products (i.e., nutrients) in shelf bottom waters in interaction with highly reactive sediments, followed by their advection into the central basin to form the halocline (Jones and Anderson, 1986; Anderson et al., 2013, 2017; Tremblay et al., 2015).

Above the Atlantic temperature maximum, a clear relationship was observed between $\delta^{18}$O of water and NO$_3^-$, both for the East Siberian Sea and the western Eurasian Basin. Seawater in the upper Arctic Ocean has extremely low $\delta^{18}$O values due to the large $^{18}$O-depleted freshwater supply. This imprint is transmitted to the ambient NO$_3^-$ $\delta^{18}$O during NO$_3^-$ regeneration. At the halocline, NO$_3^-$ $\delta^{18}$O was close to the value expected for newly produced NO$_3^-$ $\delta^{18}$O (i.e., water $\delta^{18}$O + 1.1‰; Sigman et al., 2009). This suggests that most of the NO$_3^-$ (> 60 %) at the Arctic halocline had been regenerated at least once within the Arctic Ocean, including the nutrients supplied with the Pacific inflow. This proportion increases for the halocline of the East Siberian Sea (~ 80%). These estimates are in agreement with the percentage contribution of regenerated PO$_4^{3-}$ to the whole PO$_4^{3-}$ pool determined based on Apparent Oxygen Utilization and O$_2$:PO$_4^{3-}$ theoretical stoichiometric ratio, and ranging from ~ 40 up to 75 % for the halocline in the western Eurasian Basin and East Siberian Sea, respectively (Ito and Follows, 2005).
The associated increase in $\text{NO}_3^-$ $\delta^{15}\text{N}$ toward the nutrient maximum, which is accompanied by a strong fixed N deficit and a partial O$_2$ consumption, provide some clues on where the regeneration predominantly occurs. The $\text{NO}_3^-$ $\delta^{15}\text{N}$ increase was larger in the East Siberian Sea, particularly for inshore waters compared to the western Eurasian Basin and was significantly related with N* concentrations. In agreement with previous studies focusing on subarctic and arctic shelves, it is suggested here that benthic denitrification consumes to a significant extent the $\text{NO}_3^-$ produced by partial nitrification in the reactive sediment layers (Granger et al., 2011; Brown et al., 2015). Following an imbalance between remineralization and nitrification, high-$\delta^{15}\text{N}$ NH$_4^+$ accumulates in pore waters and diffuses out of the sediments, transmitting the $^{15}\text{N}$-enrichment into the water column. As this process likely occurs over the entire the productive Arctic shelves, it could explain the accentuation in the nutrient enrichment, the high $\text{NO}_3^-$ $\delta^{15}\text{N}$, and low $\text{NO}_3^-$ $\delta^{18}\text{O}$, as well as the fixed N deficit in the Arctic halocline, following advection of shelf bottom waters into the central basin. This imprint is progressively diluted far from the shelves by mixing, implying lower $\text{NO}_3^-$ $\delta^{15}\text{N}$ values and an attenuated relationship with N* with increasing distance from the shelves (e.g., toward the western Eurasian Basin).

These findings clearly highlight the key role of the bordering shelves in setting the nutrient distribution and properties in the Arctic Ocean. The substantive production and export of organic material to the shallow sediments stimulates remineralization and denitrification at the sediment interface, releasing and confining nutrients in shelf bottom water and removing fixed N from the ocean. More investigations are required to develop a mechanistic understanding of this process and how it is likely to evolve in a rapidly changing Arctic Ocean. This benthic-pelagic coupling is still poorly represented in biogeochemical models (Popova et al., 2010; Vancoppenolle et al., 2013).
The relationship between N* and NO$_3^-$ $\delta^{15}$N allows us to estimate an isotope effect related to benthic denitrification expressed in the water column (i.e., sedimentary isotope effect) (Altabet et al., 1999; Lehmann et al., 2007). Over the East Siberian Sea, the sedimentary isotope effect was between 2.4 and 3.8 $\%$, in the middle range of previous estimates. This magnitude can be explained by a close coupling between remineralization and nitrification, implying that the efflux out of the sediments carries a high-$\delta^{15}$N signal but is highly depleted in fixed N. As the latter is being mixed with the unfractionated fixed N pool in the overlying water column (mostly NO$_3^-$), less weight is given for the efflux to set water column NO$_3^-$ $\delta^{15}$N. This process is similar to what has been described as a dilution effect for pelagic denitrification by Deutsch et al. (2004).

Variable sedimentary isotope effects determined by the degree of coupling between remineralization and nitrification, overlying water column fixed N concentration, and variations in the NO$_3^-$ source for benthic denitrification, all have profound consequences when assessing the global fixed N budget based on the ‘mean’ (i.e., global Ocean) isotopic balance and require further investigations (Brandes and Devol, 2002; Deutsch et al., 2004).

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Figures and captions

**Figure 1:** Sea Ice concentration on August 1\textsuperscript{st} 2014 (Malasnik and Stroeve, 1999) (a) and bathymetry and halocline circulation, sources and associated fronts (blue shows Pacific-origin waters, purple shows Atlantic-origin waters, thick black line depicts the front between them) (Rudels et al., 1994, 1996; McLaughlin et al., 1996; Bluhm et al., 2015) (b). The stations reported in this study are represented by the red squares.

**Figure 2:** Potential Temperature – salinity diagram (a) and water $\delta^{18}$O (‰ vs. SMOW) – salinity diagram (b) for the western Eurasian Basin (gray squares) and in the East Siberian Sea for the off-shelf (blue circles) and on-shelf (empty purple triangles) stations. Thin lines connects adjacent samples from the same hydrocast. The light gray shaded area indicates the upper halocline (UH) observed only in the East Siberian Sea. The dark gray shaded area is for the lower halocline (LH) in both the East Siberian Sea and western Eurasian Basin.

**Figure 3:** Concentrations – salinity diagrams for NO$_3^-$ (a), Si(OH)$_4$ (b), PO$_4^{3-}$ (c), regenerated:total PO$_4^{3-}$ ratio (d), dissolved O$_2$ (e), and N* (f) in the western Eurasian Basin (gray squares) and in the East Siberian Sea for the off-shelf (blue circles) and on-shelf (empty purple triangles) stations. Thin lines connects adjacent samples from the same hydrocast. The light gray shaded area indicates the upper halocline (UH) observed only in the East Siberian Sea. The dark gray shaded area is for the lower halocline (LH) in both the East Siberian Sea and western Eurasian Basin. The black arrows indicate the trend for the off-shelf stations with decreasing distance from the East Siberian shelf. The mixing lines between the upper halocline in the East Siberian Sea and the lower halocline in the western Eurasian Basin is represented by the red lines, representative of the Pacific- and Atlantic-derived waters, respectively.
**Figure 4:** Depth profiles of NO$_3^-$ concentration (a) and both NO$_3^-$ $\delta^{15}$N (filled symbols) and $\delta^{18}$O (open symbols) (b) in the western Eurasian Basin (gray squares) and in the East Siberian Sea for the off-shelf (blue circles) and on-shelf (purple triangles) stations. The horizontal gray dashed line represents the 50m isobath, representing approximately the mean outer shelf-depth over the East Siberian Sea, and the blue dashed line represents the Atlantic temperature maximum. The vertical dashed black lines in (b) represent the mean oceanic NO$_3^-$ $\delta^{15}$N and $\delta^{18}$O (Sigman et al., 2009; Marconi et al., 2015). Thin lines connects adjacent samples from the same hydrocast. Nitrate $\delta^{15}$N vs. $\delta^{18}$O (c), and water $\delta^{18}$O vs. NO$_3^-$ $\delta^{18}$O (d) in the western Eurasian Basin (square) and in the East Siberian Sea for the off-shelf (circles) and on-shelf (triangles) stations. The colored symbols in both (c) and (d) represent the halocline with the colors corresponding to salinity (i.e., color bar in panel d). The trends given by both assimilation and benthic coupled partial nitrification-denitrification (CPND) are represented in (c), as well as the predicted newly produced NO$_3^-$ $\delta^{18}$O from nitrification (d) according to field studies.

**Figure 5:** NO$_3^-$ $\delta^{15}$N vs. N* (a), ln(f) (b), and (1-f) (c) in the western Eurasian Basin (gray squares) and in the East Siberian Sea for the off-shelf (blue circles) and on-shelf (purple triangles) stations. F is defined as the fractional loss of fixed N [i.e., $f = \text{DIN}/(\text{DIN} - N^*)$] (Altabet et al., 1999). The linear regression for off-shelf stations in the East Siberian Sea is shown with the dashed blue line. The open symbols represent the data omitted from regression because they appears to have been influenced by past assimilation (Fig. 4c). The mixing lines between the upper halocline in the East Siberian Sea and the lower halocline in the western Eurasian Basin is shown with the red lines, representative of the Pacific- and Atlantic-derived waters, respectively.
Figure 6: Phosphate vs. nitrate concentrations from both GLODAP-v2 database (Olsen et al., 2016) and this study. Black and white circles represent all available data from GLODAP-v2 in the eastern and western Arctic, defined here as the area from the coasts to the North Pole between 0 and 180°E and 0-180°W, respectively. Green and orange circles represent all available data from GLODAP-v2 for the Bering Sea, over the shelf (> 150 m) and in the deep basin, respectively. The arrows show the effect (i.e., slope) of remineralization, denitrification, and a scenario in which denitrification equals remineralization, assuming N to P ratio of 16 and 104 for remineralization and denitrification, respectively (Anderson et al., 1995; Gruber and Sarmiento, 1997).

Figure 7: Conceptual scheme showing the inputs and loss of fixed N in the combined shelf bottom water and reactive sedimentary layer. Initial fixed N is initial DIN and what is supplied from the remineralization of exported particulate N (PN) both in the water column (R_{wc}) and in sediments (R_{sed}). As little isotopic fractionation is expected for remineralization, the newly produced NH$_4^+$ δ$^{15}$N is close to the exported PN δ$^{15}$N, being close to the advected NO$_3^-$ δ$^{15}$N as most of the NO$_3^-$ is consumed in the euphotic layer. Nitrification in the water column is assumed to be quantitative (∼ 100%), and newly produced NO$_3^-$ δ$^{15}$N in the water column is therefore close to the NH$_4^+$ δ$^{15}$N. If benthic remineralization is larger than nitrification, NH$_4^+$ is accumulated in pore waters and can diffuse into the overlying water column (i.e., efflux, E). NH$_4^+$ δ$^{15}$N will increase as being the residual substrate of nitrification, preferentially oxidizing $^{14}$NH$_4^+$ into NO$_3^-$. Low-δ$^{15}$N NO$_3^-$ in the reactive sediment will then be quantitatively converted into N$_2$, transmitting the isotopic fractionation from sedimentary nitrification to denitrification (D).
$\delta^{15}N = \text{adveced NO}_3^- \cdot \delta^{15}N$

**Initial fixed N = initial DIN + R**

**Final fixed N**

- $\text{NH}_4^+$
  - $\varepsilon \sim 0$
  - $N_{\text{sed}} = R_{\text{sed}} - E$
  - $\varepsilon \sim 15$
  - $\sim 100$
  - $\varepsilon \sim 25$

- $\text{NO}_3^-$
  - $\varepsilon \sim 15$
  - $\epsilon = 16O$

**Exported PN**

- $R_{\text{wc}}$
  - $\varepsilon \sim 0$

**Bottom water**

**Reactive sed.**
Nitrate (μmol l⁻¹)

Phosphate (μmol l⁻¹)

Western Arctic (90-180°W)
- Eastern Arctic (90-180°E)
- Pacific
- Bering shelf
- western Eurasian Basin (this study)
- off-shelf East Siberian Sea (this study)
- on-shelf East Siberian Sea (this study)

Remineralization

Denitr. = Rem.

Denitrification
Initial fixed N = initial DIN + R

**Final fixed N**

- \( \text{NH}_4^+ \) with \( \varepsilon \sim 0 \)
- \( \text{N}_{\text{wc}} \) with \( \varepsilon \sim 15 \) and \( 15\text{N} \)
- \( \text{NO}_3^- \) with \( 16\text{O} \)
- \( \text{NH}_4^+ \) with \( 14\text{N} \) and \( \varepsilon \sim 15 \)

Reactive sed.

Bottom water

\( R_{\text{wc}} \) with \( \varepsilon \sim 0 \)

\( R_{\text{sed}} \) with \( \varepsilon \sim 0 \)

\( N_{\text{sed}} = R_{\text{sed}} - E \)

\( \text{N}_2 \) with \( \varepsilon \sim 25 \)

Oxic layer

Anoxic layer

D