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

F. Fripiat[1,2], M. Declercq[3], C.J. Sapart[3], L.G. Anderson[4], V. Bruechert[5], F. Deman[1], D. Fonseca-Batista[6], C. Humborg[7], A. Roukaerts[1], I.P. Semiletov[8], and F. Dehairs[1]

[1]Analytical, Environmental, and Geochemistry, Earth Sciences Research Group, Vrije Universiteit Brussel, Brussels, Belgium

[2]Max Planck Institute for Chemistry, Mainz, Germany

[3]Laboratoire de glaciologie, department of Earth and Environmental Sciences, Université Libre de Bruxelles, Brussels, Belgium

[4]Department of Marine Sciences, University of Gothenburg, Gothenburg, Sweden

[5]Department of Geological Sciences, Stockholm University, Stockholm, Sweden

[6]Oceanography Department, Dalhousie University, Halifax, Nova Scotia, Canada

[7]Baltic Nest Institute BNI, Stockholm University, Stockholm, Sweden

[8]International Arctic Research Center/University of Alaska Fairbanks, Fairbanks, AK, USA

f.fripiat@mpic.de

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

27 $\delta^{18}O$ is reported, increasing and decreasing upward from the Atlantic temperature maximum

28 layer toward the surface, respectively. A correlation between water and nitrate $\delta^{18}O$ indicates that

29 most of the nitrate (> 60 %) at the halocline has been regenerated within the Arctic Ocean. The

30 increase in nitrate $\delta^{15}N$ correlates with the fixed N deficit, indicating a causal link between the

31 loss of fixed N and the ^{15}N enrichment. This suggests that a significant share of benthic

32 denitrification is driven by nitrate supplied by remineralization and partial nitrification, allowing

33 residual ^{15}N-enriched ammonium to diffuse out of the sediments. By increasing nutrient

34 concentrations and fixed N deficit in shelf bottom waters, this imprint is attenuated offshore

35 following advection into the halocline by nitrate regeneration and mixing. Estimation of the

36 sedimentary isotope effect related to benthic denitrification yields values in the range of 2.4 – 3.8

37 ‰, with its magnitude driven by both the degree of coupling between remineralization and

38 nitrification, and fixed N concentrations in shelf bottom waters.

39 1. Introduction

40 Primary production in the Arctic Ocean is predominantly controlled by extreme seasonal

41 variation of light, while being modulated further by the growth and decay of sea ice (Wassman

42 and Reigstad, 2011; Slagstad et al., 2015). Primary production is thus restricted to a limited

43 period from late spring to summer and occurs both at the bottom of sea ice and in the euphotic

44 layer (Wassman and Reigstad, 2011; Leu et al., 2015; Janout et al., 2016), with an overall higher

45 primary production over the Arctic shelves and slopes (Pabi et al., 2008). In recent years, Arctic

46 sea ice has been retreating at an unprecedented rate (Cavalieri and Parkinson, 2012). These

47 changes have profound impacts on primary production and upper ocean dynamics, and,

48 therefore, the functioning of the Arctic marine ecosystems (Wassman and Reistag, 2011;

49 Rainville et al., 2011; Yool et al., 2015). Primary production has increased by 30 % from 1998 to

50   2012 (Arrigo and van Dijken, 2015). Whether this increase in productivity will continue as sea

51   ice declines further, is difficult to predict (Arrigo and van Dijken, 2015; Vancoppenolle et al.,

52   2013). In this respect, the availability of fixed nitrogen (i.e., reactive N or non-N_2; also defined

53   as biologically available N) also sets a limit on phytoplankton growth in the Arctic Ocean

54   (Popova et al., 2012; Codispoti et al., 2013). Current understanding in the N dynamics of Arctic

55   Ocean is limited compared to other ocean regions and reducing these uncertainties would

56   increase the reliability of projections for future Arctic primary productivity (Chang and Devol,

57   2009; Vancoppenolle et al., 2013; Arrigo and van Dijken, 2015).

58   Processes in the Arctic halocline are illustrative of the fixed N pathway into the Arctic Ocean

59   (Fig. 1b) (Tremblay et al., 2015). The subsurface nutrient maximum in the western Arctic upper

60   halocline is advected with high-nutrient Pacific water and supplemented with nutrients from the

61   decomposition of organic matter on the bordering shelves and slopes (Jones and Anderson, 1986;

62   Anderson et al., 2013; Tremblay et al., 2015). These waters exit the Arctic Ocean with the

63   predominantly cyclonic Arctic Ocean Boundary Current (AOBC) carrying water from the

64   Beaufort Gyre toward the Canadian Arctic archipelago and Fram Strait (Rudels, 2012). The

65   colder lower halocline is thought to be formed either by (i) a combination of deep winter

66   convection and fresh water input by sea-ice melt when Atlantic water enters the Arctic Ocean

67   through the eastern Fram Strait and Barents Sea, or (ii) by offshore advection of dense water that

68   is produced by sea-ice formation over the Arctic shelves during AOBC transport (Aagaard et al.,

69   1981; Rudels et al., 1994, 1996; Steele and Boyd, 1998; Woodgate et al., 2001; Kikuchi et al.,

70   2004). Being progressively covered by a less saline upper halocline on its route into the western

71   Arctic Ocean, the lower halocline water mass initially has characteristics of the relatively

72   nutrient-poor Atlantic source water, but is subsequently supplemented with nutrients from the

73   decomposition of organic matter on bordering shelves and slopes during their transport

74   (Anderson et al., 2017). About half of the Atlantic inflow returns immediately out of the Arctic

75   Ocean through Fram Strait whereas the other half is transported with the AOBC across the Arctic

76   Ocean before exiting through the western Fram Strait and Canadian Arctic Archipelago (Fig. 1b)

77   (Rudels, 2012).

78   While nitrogen and oxygen isotopes ratios of nitrate (NO_3^-; $^{15}N/^{14}N$, $^{18}O/^{16}O$) provide a powerful

79   tool to assess how NO_3^- is processed by the microbial community and is redistributed through the

80   Arctic Ocean, such measurements have so far only been carried out for the Chukchi Sea shelf

81   and the Canada Basin (Brown et al., 2015). Nitrate assimilation and denitrification (both NO_3^-

82   consuming processes) preferentially convert ^{14}N and ^{16}O, leaving the residual NO_3^- enriched in

83   ^{15}N and ^{18}O. The degree of fractionation is given by the kinetic isotope effect, ε, defined by the

84   ratio of rates at which the two isotopes are converted from one form to another (i.e., for nitrogen,

85    $^{15}\varepsilon$ (‰) = (($^{14}k/^{15}k$)-1) x 1000); where $^n k$ is the rate coefficient for the $^n N$-containing reactant).

86   Since denitrifying bacteria and phytoplankton discriminate against ^{15}N and ^{18}O to the same

87   extent ($^{15}\varepsilon \sim {}^{18}\varepsilon$) (Granger et al., 2008, 2010; Karsh et al., 2012), the residual NO_3^- $\delta^{15}N$ and $\delta^{18}O$

88   values increase in proportion to NO_3^- consumption (i.e., coupling between N and O isotopes).

89   Nitrification (NO_3^- producing process), on the other hand, decouples N from O isotopes

90   (Lehmann et al., 2004; Sigman et al., 2005). During NO_3^- assimilation and regeneration (i.e., N

91   remineralization + nitrification), the N isotopes are recycled between the fixed N pools, while the

92   O isotopes are removed during NO_3^- assimilation (since NO_3^- is reduced to ammonium, NH_4^+,

93   before assimilation) and then re-introduced during nitrification (i.e., oxidation of NH_4^+ to nitrite,

94   NO_2^-, and then to NO_3^-) (Casciotti et al., 2010; Buchwald et al., 2012, 2015). Anaerobic

95   ammonium oxidation into N_2 (i.e., anammox) is another pathway to lose fixed N from marine

96   sediments (Dalsgaard et al., 2005) but is considered to play a minor role over the Arctic shelves

97   in comparison to denitrification, as these shelves receive high loads of labile organic matter

98   (Dalsgaard et al., 2005; McTigue et al., 2016).

99   Brown et al. (2015) observed a progressive ^{15}N-enrichment and ^{18}O-depletion of NO_3^- over the

100   Chukchi Sea shelf and the adjacent offshore Canada Basin during advection of Pacific waters

101   through the Bering Strait into the Canada Basin. The ^{15}N-enrichment was inversely correlated

102   with NH_4^+ concentrations in shelf bottom waters, suggesting a sediment source of ^{15}N-enriched

103   NH_4^+ in agreement with the process of benthic coupled partial nitrification-denitrification

104   (Lehmann et al., 2007; Granger et al., 2011). The ^{18}O-depletion relative to the Bering Sea source

105   waters indicated that a significant fraction (~ 50 %) of NO_3^- in the upper halocline was

106   regenerated by nitrification during the transport from the Bering Strait into the Canada Basin.

107   In the present study we report δ^{15}N and δ^{18}O of NO_3^- along a slope transect in the East Siberian

108   Sea and for the sea ice-covered area of the western Eurasian Basin (Fig. 1), allowing us to test

109   the hypothesis that a decoupling between N and O isotopes as observed in the Bering Strait and

110   Canada Basin may likely be extended to the entire Arctic upper ocean. The primary objectives

111   are to understand how the nutrient maximum in the Arctic halocline is being formed, and what is

112   the influence of the bordering shelves on the reprocessing and redistribution of nutrients

113   throughout the Arctic Ocean. The secondary objective is to improve our mechanistic

114   understanding of the isotope systematics related to benthic fixed N loss.

2. Materials and method

115

116   Water samples were collected on full water column profiles during one cruise in the vicinity of

117   Fram Strait (~ 82.5°N and 6,2°W) in the western Eurasian Basin, northeast of Greenland, with 5

118   hydrocasts (July 2014; R.V. Polarstern, ARKXXVIII/3) and a second across-slope section in the

119   East Siberian Sea (170 – 175°E) with 6 hydrocasts, including on-shelf and off-shelf stations

120   (August 2014; R.V. Oden, SWERUS-C3) (Fig. 1).

121   Salinity and temperature were recorded using a Seabird 911C CTD with dual Sea-Bird

122   temperature (SBE 3), conductivity (SBE 04c) and oxygen sensors (SBE 43). Dissolved oxygen

123   (O_2) was measured onboard soon after sampling via Winkler titration as described in Anderson et

124   al. (2017). Samples were stored frozen (-20°C) in acid-cleaned HDPE 60 ml bottles until their

125   analysis at the home-based laboratory (AMGC, VUB, Brussels, Belgium) for both water $\delta^{18}O$,

126   and nitrate $\delta^{15}N$ and $\delta^{18}O$. Immediately after sampling, the SWERUS-C3 samples were filtered

127   to remove particles using pre-rinsed Acrodisc filters (0.2 µm porosity). Nutrient concentrations

128   (nitrate, NO_3^-, nitrite, NO_2^-, ammonium, NH_4^+, phosphate, PO_4^{3-} and silicic acid, $Si(OH)_4$) were

129   measured based on spectrophotometric techniques, using a continuous flow QuAAtro analyzer

130   from Seal Analytical (Hydes et al., 2010), either soon after sampling for SWERUS-C3 or on

131   frozen samples at the home-based laboratory for ARKVIII/3 (Dore et al., 1996).

132   We used N* concentration to estimate the deficit in fixed N (i.e., biologically available N) in

133   comparison to PO_4^{3-}, according to N* = [DIN] −16*[PO_4^{3-}] + 2.9 (Deutsch et al., 2001; DIN =

134   dissolved inorganic N = $NO_3^- + NO_2^- + NH_4^+$). Low (negative) N* concentrations indicate a sink

135   of fixed N and high (positive) concentrations are indicative of N_2 fixation. Nutrients can be

136   further defined as regenerated vs. preformed nutrients (Ito and Follows, 2005). Below the

137   euphotic layer, regenerated nutrients are derived from the remineralization of organic matter,

138   either exported from the surface with export production (i.e., being equivalent to net community

139   production) or supplied from the rivers. Preformed nutrients originate as euphotic layer nutrients

140   that are left unused following blooms and are then carried into the subsurface by winter vertical

141   mixing or downwelling (Ito and Follows, 2005). One can resolve the contributions of

142　regenerated and preformed nutrients using the Apparent Oxygen Utilization (AOU), which

143　depends on the observed temperature, salinity, and in-situ oxygen distribution (Broecker et al.,

144　1985), and assuming a fixed stoichiometric ratio between oxygen and nutrients for

145　remineralization (Anderson, 1995). Regenerated PO_4^{3-} equals AOU divided by the O_2/PO_4^{3-}

146　oxidation ratio during aerobic respiration (i.e., AOU/150; $C_{106}H_{175}O_{42}N_{16}P + 150O_2 = 106CO_2 +$

147　$16HNO_3 + H_3PO_4 + 78H_2O$). Extensive denitrification over the Arctic shelves and slopes (Chang

148　and Devol, 2009) introduces a complexity in the utilization of both AOU and O_2/NO_3^- oxidation

149　ratio, rendering it difficult to infer regenerated NO_3^-.

150　Nitrate $\delta^{15}N$ and $\delta^{18}O$ were determined with the denitrifier method (Sigman et al., 2001;

151　Casciotti et al., 2002). Briefly, 20 nmol of NO_3^- is quantitatively converted to N_2O gas by

152　denitrifying bacteria (*Pseudomonas chlororaphis* f. sp. *aureofaciens* ATCC no 13985) that lack

153　an active N_2O reductase. The produced N_2O is analyzed by gas chromatography/isotope ratio

154　mass spectrometry (Thermo, DeltaV, VUB), using a custom-build 'purge and trap' system

155　similar to the one described by Casciotti et al. (2002). Measurements are referenced to air N_2 for

156　$\delta^{15}N$ and Vienna Standard Mean Ocean Water (VSMOW) for $\delta^{18}O$ using the NO_3^- reference

157　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 -

158　1.8‰ and a $\delta^{18}O$ of -27.9‰ (Böhlke et al., 2003). Prior to the nitrate isotope analyses, NO_2^- was

159　removed by reaction with sulfamic acid to avoid any interference with NO_3^- (Granger and

160　Sigman, 2009). Each batch of samples intended for mass spectrometric analysis included NO_3^-

161　reference materials that was also amended with sulfamic acid to ensure that no contamination

162　originates from this treatment. As a concentration effect is reported for measurements of NO_3^-

163　$\delta^{18}O$, nitrate reference materials were diluted with low-nutrient Sargasso Sea surface water to

164　generate concentrations that bracket the concentrations of the samples in each batch (Weigand et

165   al., 2016). We use any trends between the measured $\delta^{18}O$ of the two references concentrations

166   bracketing of the sample concentrations to generate a linear correction for this trend (Marconi et

167   al., 2015; Weigand et al., 2016). Replicate analysis (100% of the samples) indicates a median

168   (mean) 1sd reproducibility of 0.15 (0.21) and 0.25 (0.27) ‰ for the NO_3^- $\delta^{15}N$ and $\delta^{18}O$,

169   respectively.

170   Water $\delta^{18}O$ was measured using a CO_2 equilibration technique (Epstein and Mayeda, 1953).

171   Headspace gastight vials (12 ml) are first flushed with helium gas and 500 µl of water is then

172   added followed by 300 µl of pure CO_2. The samples are placed in a shaker for 48h at ambient

173   laboratory temperature allowing CO_2 $\delta^{18}O$ to fully equilibrate with water $\delta^{18}O$ before extraction

174   with a GasBench - Isotope Ratio Mass Spectrometer (Nu Perspective, Nu Instruments).

175   Measurements were referenced to Vienna Standard Mean Ocean Water (VSMOW) for $\delta^{18}O$

176   using in-house standards previously calibrated to the VSMOW scale. The reported standard

177   deviation (1sd) is ~ 0.05 ‰ (Benetti et al., 2017).

3. Results

179   Temperature vs. salinity diagrams for both the East Siberian Sea and the western Eurasian Basin

180   show presence of cold and saline bottom water, overlaid by warmer Atlantic water centered at ~

181   300 m (i.e., temperature maximum; > 0°C) (Fig. 2a). Overall, most of the density stratification in

182   the Arctic Ocean occurs above ~ 250 m in the halocline, separated into a lower and an upper

183   halocline with an Atlantic and Pacific origin, respectively (McLaughlin et al., 1996; Rudels et

184   al., 1996). In the western Eurasian Basin, only a cold lower halocline was observed near the

185   freezing point of seawater and with a salinity of ~ 34.0 (Fig. 2a), centered around ~ 100 m depth.

186   The lower halocline was warmer and slightly deeper in the East Siberian Sea. The upper

187   halocline was present in the East Siberian Sea at a depth range of 100-125 m in the salinity range

188   32.5 to 33.5 and was clearly discernable by the maximum in nutrients, especially PO_4^{3-} and

189   $Si(OH)_4$ being indicative of the nutrient-rich Pacific inflow (Fig. 3) (Jones et al., 1998). Water

190   $\delta^{18}O$ largely followed salinity (Fig. 2b), as the freshwater supply in the Arctic Ocean is highly

191   ^{18}O-depleted (Cooper et al., 2008).

192   In the East Siberian Sea, a large accumulation of nutrients, especially PO_4^{3-} and $Si(OH)_4$, was

193   observed at the halocline (Fig. 3). On-shelf stations had roughly similar NO_3^- concentrations at

194   comparable salinity than off-shelf stations but with higher PO_4^{3-} and $Si(OH)_4$ concentrations. In

195   the western Eurasian Basin, no maximum in NO_3^- concentration was observed with

196   concentrations steadily increasing from the surface to the deeper layers. On the contrary PO_4^{3-}

197   and $Si(OH)_4$ showed a small maximum at the lower halocline (Fig. 3). The accumulation of

198   nutrients in the East Siberian Sea was associated with a clear deficit in fixed N (i.e., biologically

199   available N), as inferred from negative N* concentrations, and O_2 consumption due to

200   remineralization (Figs. 3e, f). This is further confirmed with the proportion of regenerated PO_4^{3-}

201   being higher at the halocline, and even more so at the lower halocline in the East Siberian Sea

202   (Fig. 3d).

203   A large decoupling between NO_3^- $\delta^{15}N$ and $\delta^{18}O$ was observed at the halocline, increasing and

204   decreasing upward, respectively (Figs. 4b, c). For the off-shelf stations of the East Siberian Sea,

205   NO_3^- $\delta^{15}N$ increased from 5.0 to 8.6 ‰ from ~ 300 m depth to just below the mixed layer depth.

206   No measurements were available at shallower depths as NO_3^- concentration was ~0.2 μmol l^{-1},

207   below our detection limit. The two on-shelf stations had contrasting NO_3^- $\delta^{15}N$, with one station

208   following the trend given by the off-shelf stations (up to 9.5 ‰) and one station having relatively

209   lower NO_3^- $\delta^{15}N$ values (up to 5.3 ‰) (Fig. 4b). In the western Eurasian Basin, NO_3^- $\delta^{15}N$

210   increased from 5.0 to 6.9 ‰. We observed a strong negative correlation between N* and NO_3^-

211    $\delta^{15}N$ ($R^2 = 0.7$, p value < 0.001) in the East Siberian Sea (Fig. 5a). Only one of the two on-shelf

212   stations falls on this trend with the other station presenting a deficit in fixed N but without ^{15}N-

213   enrichment of NO_3^-. In the western Eurasian Basin, the relationship between N* and NO_3^- $\delta^{15}N$

214   was attenuated, showing a larger scatter, though still significant ($R^2 = 0.3$, p value < 0.001).

215   In the off-shelf stations of the East Siberian Sea, NO_3^- $\delta^{18}O$ decreased from 1.9 to -0.6 ‰ from ~

216   300 m depth to just below the mixed layer depth (Fig. 4b). At a given salinity on-shelf stations

217   had similar NO_3^- $\delta^{18}O$ values than off-shelf stations (data not shown). NO_3^- $\delta^{18}O$ increased just

218   below the mixed layer for three stations, one on-shelf (up to 4.1 ‰) and two off-shelf stations

219   (up to 2.4 ‰). This likely reflects an increase in the contribution of preformed nutrients toward

220   the surface (Fig. 3d), reflecting ^{18}O enrichment from past NO_3^- assimilation starting with a NO_3^-

221   initial pool harboring a variable decoupling between N and O isotopes (Fig. 4c). In the western

222   Eurasian Basin, NO_3^- $\delta^{18}O$ decreased similarly with depth from ~ 1.5 to 0.3 ‰ with comparable

223   values in both the lower halocline and surface waters as in the East Siberian Sea. A positive

224   relationship was reported between NO_3^- $\delta^{18}O$ and water $\delta^{18}O$ in the East Siberian Sea (Fig. 4d;

225    $R^2 = 0.7$, p value < 0.001). This relationship was attenuated and more scattered for the western

226   Eurasian Basin ($R^2 = 0.4$, p value < 0.001).

4. Discussion

228   The nutrient maximum and fixed N (i.e., biologically available N) deficit in the western Arctic

229   halocline are generally attributed to inflow of nutrient-rich Pacific waters through the shallow

230   Bering Strait (Jones et al., 1998). Episodic intrusion of Pacific waters occurs in the Makarov

231   Basin and the East Siberian Sea, mostly depending on the dominating atmospheric pressure field

232   that determines the extent of the Beaufort Gyre and the position of the Transpolar Drift

233   (Woodgate et al., 2001; Proshutinsky et al., 2015). Further remineralization and benthic

234   denitrification in Arctic shelf seas are required to explain the accentuation of these properties

235   within the Arctic Ocean. Although both NO_3^- and PO_4^{3-} concentrations increase in the upper

236   halocline relative to inflowing Pacific waters, the NO_3^- increase is less than expected from

237   Redfield stoichiometry. As a result the fixed-N deficit is enhanced (Fig. 6) and this is likely due

238   to processes occurring over the productive Arctic shelves and slopes. There, benthic and water

239   column remineralization are confining decay products (i.e., nutrients) in shelf bottom waters that

240   are then advected throughout the basins of the Arctic Ocean to form the halocline (Jones and

241   Anderson, 1986; Anderson et al., 2013, 2017). The substantive production and export of organic

242   material to the shallow benthos stimulates denitrification in sediments, with benthic

243   denitrification rates reported to contribute between 4 to 13 % of the total sink of fixed N in the

244   global ocean. This contrasts with the relatively small contribution of the Arctic Ocean (1.4 %) to

245   the total ocean volume (Devol et al., 1997; Chang and Devol, 2009; McTigue et al., 2016).

246   In the East Siberian Sea, the O_2 consumption associated with the nutrient maximum cannot result

247   solely from the advection of nutrient-rich Pacific waters through the well-ventilated shallow

248   Bering Strait (Fig. 3e) (Olsen et al., 2016). If this were the case, O_2 concentrations would be

249   close to saturation and most nutrients would be preformed nutrients. However, up to 75% of the

250   PO_4^{3-} in the halocline can be considered as regenerated PO_4^{3-} produced by the remineralization of

251   organic matter either exported from the surface waters or supplied from rivers (Fig. 3d) (Ito and

252   Follows, 2005). The maximum contribution of regenerated PO_4^{3-} was also found in the lower

253   halocline carrying the O_2 minimum as well as a significant deficit in fixed N (Anderson et al.,

254   2017). The lower halocline waters are essentially of Atlantic origin, being transported and

255   transformed along the cyclonic Arctic Boundary Current (Fig. 1b) (Aagaard et al., 1981; Rudels

256   et al., 1994, 1996; Steele and Boyd, 1998; Woodgate et al., 2001; Kikuchi et al., 2004). While

257   originally relatively poor in nutrients, accumulation of nutrients by remineralization during their

258   transport is required, most likely following offshore advection of nutrient-enriched shelf bottom

259   water into the central Arctic Basin (Anderson et al., 2017). Conservative mixing between

260   Atlantic- and Pacific-derived waters, following diapycnal mixing, cannot explain the nutrient

261   accumulation in nutrients, O_2 depletion and deficit of fixed N observed at the lower halocline in

262   the East Siberian Sea (red lines in Fig. 3). For the western Eurasian Basin stations, the lower

263   nutrient concentrations in the halocline could indicate that this area is predominantly affected by

264   the Atlantic inflow (Figs. 1c and 3) through the eastern Fram Strait and the Barents Sea and exit

265   the Arctic Ocean mostly through the western Fram Strait (Fig. 1b) (Ruddels, 2012). However, as

266   discussed in the following sections, the NO_3^- $\delta^{15}N$ and $\delta^{18}O$ values for the western Eurasian

267   Basin indicate that these signatures were partly inherited from the Arctic Ocean and especially

268   from the bordering shelves, implying a widespread influence of the continental shelves on the

269   Arctic nutrient distribution.

270   The dual nitrogen and oxygen isotopes ratios of NO_3^- give insight on how NO_3^- is processed by

271   the microbial community and redistributed in the Arctic Ocean. The following discussion will

272   start with the utilization of the NO_3^- $\delta^{18}O$ to estimate the fraction of NO_3^- regenerated within the

273   Arctic Ocean (section 4.1). Then, NO_3^- $\delta^{15}N$ will be discussed, suggesting that benthic coupled

274   partial nitrification-denitrification (CPND) is significant over the Arctic shelves and slopes, and

275   is required to explain the high halocline NO_3^- $\delta^{15}N$ values in the East Siberian Sea and to a lower

276   extent in the western Eurasian Basin (section 4.2). Finally, the N isotope systematics associated

277   with CPND are discussed including implications for the utilization of the N isotopes to constrain

278   the marine N budget (section 4.3).

279   4.1.Regenerated nitrate in the Arctic Ocean

280   Nitrified NO_3^- $\delta^{18}O$ is considered to be close to the $\delta^{18}O$ of seawater in which nitrification takes

281   place (Casciotti et al., 2008; Sigman et al., 2009; Buchwald et al., 2012; Rafter et al., 2013). In

282   comparison to the rest of the Ocean, Arctic waters exhibit a large variability in $\delta^{18}O$ resulting

283   from the large ^{18}O-depleted freshwater supply (Fig. 2b) (Cooper et al., 2008). This ^{18}O-depletion

284   could be transmitted to the newly produced NO_3^-, potentially allowing us to quantify the fraction

285   of NO_3^- being regenerated in the Arctic Ocean vs. the fraction being advected with the Pacific

286   and Atlantic inflows.

287   We observed a positive relationship between the $\delta^{18}O$ of NO_3^- and seawater ($R^2 > 0.4$, p value <

288   0.001), indicating that the regional imprint from ^{18}O-depleted Arctic rivers was indeed

289   transmitted to the Arctic NO_3^- pool through regeneration, both in the East Siberian Sea and the

290   western Eurasian Basin (Fig. 4d). Overall NO_3^- $\delta^{18}O$ values decreased toward the surface (i.e.,

291   following the trend for water $\delta^{18}O$), but this decrease was stronger for the East Siberian Sea than

292   for the western Eurasian Basin, likely reflecting the larger freshwater contribution (i.e., lower

293   water $\delta^{18}O$ and salinity) to the former basin (Fig. 2b) (Cooper et al., 2008; Bluhm et al., 2015).

294   This relationship between seawater $\delta^{18}O$ and NO_3^- $\delta^{18}O$ appears to be unique to the Arctic and

295   sub-Arctic areas, and so far has only been reported for the Chukchi Sea and the Canada Basin

296   (Brown et al., 2015) and over the northern Bering shelf (Granger et al., 2011, 2013). The present

297   study suggests that it is likely the norm for the whole Arctic Ocean. A deviation from this

298   relationship is observed toward the surface for some stations in both the East Siberian Sea and

299   western Eurasian Basin, with the latter harboring high NO_3^- $\delta^{18}O$ (~1 to 4.3 ‰) for low seawater

300    $\delta^{18}O$ (~-1.6 to -2.3 ‰; Fig. 4d). This likely reflects ^{18}O enrichment from NO_3^- assimilation

301   starting with a NO_3^- initial pool harboring a variable decoupling between N and O isotopes (Fig.

302   4c).

303   The regeneration of NO_3^- is related to nitrification (NH_4^+ to NO_3^-), while the O isotopes are

304   removed by NO_3^- assimilation and denitrification (since NO_3^- is reduced to NH_4^+ or N_2) and then

305   replaced in the nitrification process (NH_4^+ to NO_2^- and then to NO_3^-) (Sigman et al., 2005). The

306    $\delta^{18}O$ of newly produced NO_3^- will depend of the associated isotopic fractionation during

307   nitrification and the sources of O atoms (Sigman et al., 2009; Buchwald et al., 2012). The

308   relatively small range of NO_3^- $\delta^{18}O$ reported for deep and intermediate waters in the ocean (~ 1.5

309   to 2.5‰), being close to seawater $\delta^{18}O$, has led to the general assumption that NO_3^- $\delta^{18}O$ of

310   newly produced NO_3^- is mainly set by O incorporation from water with a little contribution from

311   O_2 (Sigman et al., 2009). Field studies have shown that newly produced NO_3^- $\delta^{18}O$ is near that of

312   seawater $\delta^{18}O$ + ~ 1.1 ‰ (Casciotti et al., 2008; Sigman et al., 2009; Rafter et al., 2013). While

313   culture experiments give a range for newly produced NO_3^- $\delta^{18}O$ between -1.5 and 1.3 ‰ relative

314   to seawater $\delta^{18}O$ (Buchwald et al., 2012), encompassing field estimates, they also demonstrate

315   that this range in $\delta^{18}O$ reflects, instead, a combination of large kinetic isotope effects (during O

316   atom incorporation from H_2O and O_2) and equilibrium isotope effect with H_2O (Casciotti, 2007,

317   Casciotti et al., 2010; Buchwald et al., 2012).

318   Our data clearly highlight the role played by water $\delta^{18}O$ in setting the variation of NO_3^- $\delta^{18}O$

319   (Fig. 4d). Halocline waters in the East Siberian Sea and the western Eurasian basin, show a

320   relatively good agreement between observed NO_3^- $\delta^{18}O$ and the predicted $\delta^{18}O$ for regenerated

321   NO_3^- according to field studies (i.e., seawater $\delta^{18}O$ + ~ 1.1 ‰; black line in Fig. 4d). However, a

322   clear deviation from the predicted trend, with higher NO_3^- $\delta^{18}O$ than expected, is observed

323   toward the surface (i.e., toward more negative water $\delta^{18}O$; above ~ 80 m depth) and could

324 possibly reflect an increasing proportion of preformed nutrients (Fig 3d). An alternative

325 explanation could be that a mismatch in the timing between NO_3^- regeneration and freshwater

326 accumulation occurs toward the surface, or that regenerated NO_3^-, mostly accumulated at the

327 halocline nutrient maximum, diffuse upward and mix with more ^{18}O-depleted surface waters.

328 Despite this complexity, the relationship between NO_3^- and seawater $\delta^{18}O$ clearly indicates that

329 most of the NO_3^- being supplied into the upper Arctic Ocean has been reprocessed at least once

330 within the Arctic Ocean, including the NO_3^- advected with the nutrient-rich Pacific inflow.

331 Brown et al. (2015) estimated based on ambient NO_3^- $\delta^{18}O$ values that roughly 50 % of NO_3^- in

332 the upper halocline was regenerated in the waters of the Bering Strait and the Canada Basin,

333 encompassing the range given by Granger et al. (2013) for the northern Bering Shelf (20 to 80

334 %). These authors used the following mass and isotopic balance:

335 $\qquad [NO_3^-]_{total} * NO_3^- \delta^{18}O_{total} = [NO_3^-]_{preformed} * NO_3^- \delta^{18}O_{preformed} + [NO_3^-]_{regenerated} * NO_3^-$

336 $\qquad\qquad\qquad\qquad\qquad \delta^{18}O_{regenerated}$ (1)

337 Rearranged and simplified as follows:

338 $\qquad [NO_3^-]_{regenerated}/[NO_3^-]_{total} = (NO_3^- \delta^{18}O_{total} - NO_3^- \delta^{18}O_{preformed})/(NO_3^- \delta^{18}O_{regenerated} - NO_3^-$

339 $\qquad\qquad\qquad\qquad\qquad \delta^{18}O_{preformed})$ (2)

340 Equation 2 gives the proportion of the ambient NO_3^- pool being regenerated. Setting regenerated

341 $NO_3^- \delta^{18}O$ to $H_2O \delta^{18}O + 1.1$ ‰, yields $NO_3 \delta^{18}O$ values of 0.3 ± 0.6 and 0.4 ± 0.5 ‰ for the

342 halocline of the East Siberian Sea and western Eurasian Basin, respectively. Preformed NO_3^-

343 $\delta^{18}O$ is set to 1.5 ± 0.5 ‰, encompassing the range for the Atlantic and Pacific inflows (Brown et

344 al., 2015; Deman et al., 2017). Accordingly, the proportion of regenerated NO_3^- to the NO_3^- pool

345 is 80 ± 43 and 65 ± 35 % at the halocline of the East Siberian Sea and western Eurasian Basin,

346 respectively. Despite the large uncertainties, these estimates are similar to the fraction of

347 regenerated PO_4^{3-} calculated by assuming a fixed stoichiometric ratio between oxygen and

348 nutrients for remineralization (40 to 75%; Fig. 3d). More data are needed to better constrain

349 preformed NO_3^- $\delta^{18}O$ at the regional scale in the Arctic Ocean, and holds for regenerated NO_3^-

350 $\delta^{18}O$ at the global scale.

351   4.2.Coupled benthic partial nitrification-denitrification on the bordering shelves

352 Nitrate $\delta^{15}N$ increased from the Atlantic temperature maximum upward to the halocline and

353 toward the surface, contrasting with the trend observed for NO_3^- $\delta^{18}O$. This increase was larger in

354 the East Siberian Sea than in the western Eurasian Basin (Fig. 4b), reflecting the fact that water

355 in the latter basin is more representative of open water conditions, far from direct shelf to basin

356 interactions and was likely more impacted by regeneration and mixing with less-altered Atlantic

357 inflow (Fig. 1b). The decoupling between NO_3^- $\delta^{15}N$ and $\delta^{18}O$ excludes the possibility that

358 partial NO_3^- assimilation is responsible for this increase in NO_3^- $\delta^{15}N$. Nitrate assimilation

359 preferentially converts ^{14}N and ^{16}O, leaving the residual NO_3^- equally enriched in ^{15}N and ^{18}O as

360 both N and O isotopes are discriminated to the same extent ($^{15}\varepsilon \sim {}^{18}\varepsilon$; Fig. 4c) (Granger et al.,

361 2004, 2010; Karsh et al., 2012). This increase in NO_3^- $\delta^{15}N$ toward the surface can neither be

362 explained by regeneration of NO_3^- with nitrification in the water column. Indeed, as is common

363 to Arctic surface waters in summer, NO_3^- is fully consumed in the East Siberian Sea (Codispoti

364 et al., 2013; Humborg et al., 2017). Export production $\delta^{15}N$ (i.e., sinking PN) is therefore equal

365 or close to the NO_3^- source $\delta^{15}N$ (i.e., subsurface NO_3^- $\delta^{15}N$) (Eppley and Peterson, 1979; Altabet

366 and Francois, 1994). In case NO_3^- is only partly assimilated in the surface waters (e.g., in the

367 western Eurasian Basin), export production $\delta^{15}N$ will be lower than ambient NO_3^- (Altabet and

368 Francois, 1994). Concerning the regeneration of NO_3^-, we can reasonably assume that (i)

369 nitrification is complete on annual to multi-annual scales, and (ii) there is little or no isotopic

16

370   fractionation during remineralization of organic matter to NH_4^+ (Knapp et al., 2011; Möbius,

371   2013). Accordingly, buried organic N and nitrified NO_3^- $\delta^{15}N$ in the water column are equal or

372   close to the export production $\delta^{15}N$. Violating assumptions (i) and (ii) will tend regenerated NO_3^-

373    $\delta^{15}N$ to become lower than sinking PN $\delta^{15}N$ (Granger et al., 2011; Fripiat et al., 2014). An input

374   of riverine organic matter will also likely decrease regenerated NO_3^- $\delta^{15}N$ upon remineralization,

375   as riverine fixed N $\delta^{15}N$ is likely to be low in relative pristine high-latitude rivers (Voss et al.,

376   2006). Instead of remaining constant or decreasing, NO_3^- $\delta^{15}N$ rather increased from the Atlantic

377   temperature maximum to the halocline where NO_3^- had accumulated as linked to a consumption

378   of oxygen (Figs 3 and 4). As discussed further below, we suggest that this increase in NO_3^- $\delta^{15}N$

379   is mostly derived from benthic-pelagic interactions (Fig. 7), confining nutrients and a fixed N

380   deficit in shelf bottom waters that are then advected throughout the basins of the Arctic Ocean to

381   be incorporated into the halocline (Jones and Anderson, 1986; Anderson et al., 2013, 2017). For

382   shelf bottom water of the East Siberian Sea this is in agreement with the observed larger nutrient

383   concentrations, N deficit and O_2 consumption, which show a tendency to increase toward the

384   sediment interface. Furthermore, we observed that for the off-shelf stations these properties of

385   the halocline become enhanced inshore (Fig. 3).

386   There was a strong negative correlation between N* and NO_3^- $\delta^{15}N$ in the East Siberian Sea (R^2

387   = 0.7, p value < 0.001), indicating a causal link between the loss of fixed N with benthic

388   denitrification (i.e., N_2 production) and the ^{15}N enrichment in ambient NO_3^- (Fig. 5a).

389   Denitrification cannot take place in the oxygen-containing water column, as observed throughout

390   the Arctic Ocean (Olsen et al., 2016), and is occuring predominantly in the anoxic sedimentary

391   layer of the Arctic shelves and slopes (Chang and Devol, 2009). In case of benthic

392   denitrification, such ^{15}N-enrichment of NO_3^- can be explained if a significant share of

393   denitrification consumes NO_3^- that was initially produced from partial benthic nitrification (Fig.

394   7) (Lehmann et al., 2007). The first step of nitrification (NH_4^+ into NO_2^-) strongly discriminates

395   N isotopes, with $^{15}\varepsilon \sim 15$ ‰ (Casciotti et al., 2003; Santoro and Casciotti, 2011). Residual NH_4^+

396    $\delta^{15}N$ increases by producing low NO_2^- $\delta^{15}N$. It is generally assumed that NO_2^- does not

397   accumulate in pore waters and is quantitatively converted by the second step of nitrification

398   (NO_2^- into NO_3^-). As a result of this complete NO_2^- oxidation, the reported inverse kinetic

399   isotope effect ($^{15}\varepsilon \sim -13$ ‰) is muted (Casciotti, 2009). Newly produced low-$\delta^{15}N$ NO_3^- is

400   subsequently reduced to N_2 by denitrification. In case remineralization exceeds nitrification (i.e.,

401   partial nitrification) residual ^{15}N-enriched NH_4^+ diffuses out to bottom waters where it is fully

402   nitrified into NO_3^-, increasing the NO_3^- concentration and transmitting the ^{15}N-enrichment from

403   benthic nitrification into the water column NO_3^- (Fig. 7). This combination of processes is able to

404   explain the observed ^{15}N enrichment in ambient NO_3^- in the shelf bottom waters and the Arctic

405   halocline layer (Figs. 4b, c and 5a). Sedimentary denitrification sustained by direct NO_3^-

406   diffusion from the overlying water column is unlikely to increase overlying water column NO_3^-

407    $\delta^{15}N$. This denitrification pathway is limited by the diffusion of NO_3^- into the active

408   denitrification layer, with little NO_3^- escaping and therefore not imparting its residual high-$\delta^{15}N$

409   value to the overlying water column NO_3^- (Brandes and Devol, 1997, 2002; Lehmann et al.,

410   2004, 2007).

411   Benthic coupled partial nitrification-denitrification (CPND) has also been put forward by others

412   to explain a similar ^{15}N-enrichment and ^{18}O-depletion of NO_3^- over the Chukchi Sea shelf and

413   the downstream Canada Basin (Brown et al., 2015). The occurrence of this decoupling between

414   N and O isotopes also in the East Siberian Sea, as well as in the lower halocline of

415   predominantly Atlantic origin water, suggests that benthic coupled nitrification-denitrification is

416   a widespread process over the productive Arctic shelves and slopes. Higher export of organic

417   matter over the shallow productive Arctic shelves (e.g., the Chukchi and East Siberian Sea) is

418   likely more favorable to a decoupling between remineralization and nitrification (i.e., lower

419   nitrification/remineralization ratio), allowing a larger efflux of NH_4^+ out of the sediments. This

420   imprint is likely progressively diluted with increasing distance from the shelves by regeneration

421   and mixing, implying decreasing NO_3^- $\delta^{15}N$ values and an attenuated relationship with N* in the

422   western Eurasian Basin (Figs. 4b and 5a).

423   Though the N* and NO_3^- $\delta^{15}N$ trend closely fits the line representing conservative mixing

424   between Atlantic- and modified Pacific-derived waters, this process alone cannot reproduce the

425   distributions in nutrient, oxygen and N* concentrations found in the East Siberian Sea (red lines

426   in Figs 3 and 5a). This is further confirmed by the distribution of NO_3^- $\delta^{15}N$ vs. the fraction of

427   fixed N left over by benthic denitrification (see next section). The East Siberian Sea falls on the

428   fractionation trend given by the preferential removal of ^{14}N with benthic denitrification, but with

429   higher than expected NO_3^- $\delta^{15}N$ for the conservative mixing (Figs 5b, c). However, in agreement

430   with the observed attenuation of the NO_3^- $\delta^{15}N$ vs. N* concentration relationship away from the

431   shelf regions, the trend in the western Eurasian Basin, on the contrary, does fit the mixing line

432   between a fractionated (upper halocline) and an unfractionated pools of NO_3^- (Atlantic derived-

433   water) (Figs 5b, c).

434   4.3.Sedimentary isotope effect associated with fixed N loss

435   The fixed N budget of the Ocean is set by the balance between N inputs (mostly N_2 fixation) and

436   outputs (mostly pelagic and benthic denitrification) (Codispoti et al., 2001; Galloway et al.,

437   2004; Gruber and Galloway, 2008). By knowing the isotope effects related to the fixed N outputs

438   and the $\delta^{15}N$ of the fixed N input, one can estimate the relative imprint of benthic vs. water

439   column denitrification on the 'mean' (i.e., global ocean) oceanic fixed N δ^{15}N (Brandes and

440   Devol, 2002; Deutsch et al., 2004; Sigman et al., 2009).

441   In heterogeneous environments such as sediments, the determination of a 'mean' isotope effect

442   related to fixed N loss is not trivial (Lehmann et al., 2007). Indeed, different isotope effects have

443   been defined, depending on where in the system the isotopic fractionation is expressed (pore

444   waters vs. overlying water column) and what fixed N pools are considered (only NO_3^- or total

445   reactive N). The sedimentary isotope effect (ε_{sed}) takes into account the impact of all fixed N

446   fluxes (including NH_4^+) out of the sediments in the expression of the organism-level isotope

447   effects into the overlying water column NO_3^- (Lehmann et al., 2007).

448   Benthic denitrification has long been assumed to occur with little or no sedimentary isotope

449   effect, as most of the NO_3^- is reduced in the active denitrification layer with little NO_3^- escaping

450   and therefore not imparting its residual high-δ^{15}N value to the overlying water column NO_3^-

451   (Brandes and Devol, 1997, 2002; Lehmann et al., 2004, 2007). Recently, higher isotope effects

452   for coupled partial nitrification-denitrification (CPND) have been reported (up to ~ 8 ‰), as the

453   residual NH_4^+ diffusing out of the sediments transmits the ^{15}N-enrichment from benthic

454   nitrification into overlying water column NO_3^- (Fig. 7) (Lehmann et al., 2007; Granger et al.,

455   2011; Alkhatib et al., 2012). A better assessment of the variability of the sedimentary isotope

456   effect is therefore required to better constrain the 'mean' oceanic N isotope budget.

457   The negative relationship between N* and NO_3^- δ^{15}N suggests a causal link between the loss of

458   fixed N (predominantly over the shelves and slopes) (Chang and Devol, 2009) and the ^{15}N

459   enrichment in ambient NO_3^- (Fig. 5a). We propose to use this correlation to estimate the

460   sedimentary isotope effect with the following equations:

461            $$NO_3^- \; \delta^{15}N = \text{initial fixed N } \delta^{15}N - {}^{15}\varepsilon_{sed} * \ln([DIN]/([DIN]-N*)) \quad (3)$$

462   assuming a system in which the reactant N pool is neither replenished nor lost from the system

463   (i.e., Rayleigh fractionation kinetics). The alternative is an open system in steady state for which

464   the input of substrate balances the outputs (residual substrate + product):

465   NO_3^- $\delta^{15}N$ = initial fixed N $\delta^{15}N$ + $^{15}\varepsilon_{sed}$ * (1-[DIN]/([DIN]-N*))   (4)

466   Several assumptions are inherent to these above equations. The first assumption is that DIN

467   concentration in the water column is representative of the residual fixed N pool. This is a

468   reasonable assumption since the sedimentary DIN pool contributes to a small fraction of the DIN

469   in the combined bottom water and reactive sedimentary layer. The second assumption considers

470   initial fixed N to be the sum of initially available fixed N in the water column (mostly dissolved

471   inorganic N) plus what is derived from organic matter remineralization, in both the bottom water

472   (R_{wc}) and the reactive sedimentary layer (R_{sed}) (Fig. 7). Accordingly, the initial fixed N pool is

473   the water column DIN augmented with the N-deficit (N*) (Altabet et al., 1999). Hereafter, f is

474   defined as the ratio between DIN and (DIN-N*), and represents the fraction of substrate

475   remaining after the fixed N loss. The third assumption considers NO_3^- $\delta^{15}N$ as representative of

476   the residual fixed N $\delta^{15}N$. It is a reasonable assumption since NO_3^- is considered as the end-

477   product of remineralization in the aphotic ocean. To test this last assumption, we also take into

478   account a sedimentary NH_4^+ $\delta^{15}N$ of 20 ‰ and the relative contribution of NH_4^+ to the DIN pool

479   to estimate an expected DIN $\delta^{15}N$. This sedimentary NH_4^+ $\delta^{15}N$ value has been reported in the

480   shelf bottom water of the Bering shelf (Granger et al., 2011).

481   By rearranging equations 3 and 4, the linear relationship between NO_3^- $\delta^{15}N$ and either ln(f) or

482   (1- f) allows us to estimate a sedimentary isotope effect of 2.4 ± 0.4 and 3.2 ± 0.4 ‰ (R^2 = 0.7; p

483   value < 0.001) and an initial fixed N $\delta^{15}N$ (i.e., at N* = 0) of 6.1 ± 0.2 and 6.2 ± 0.2 ‰ (p value

484   < 0.001), for closed and open system conditions, respectively (Figs. 5b and 5c). By taking into

485 account the expected DIN δ^{15}N (assuming a sedimentary NH_4^+ δ^{15}N of 20 ‰), the isotope effect

486 increases to 3.0 ± 0.3 and 3.8 ± 0.3 ‰ ($R^2 = 0.9$; p value < 0.001) and the fixed N δ^{15}N increases

487 to 6.5 ± 0.1 and 6.6 ± 0.1 ‰ (p value < 0.001) (not shown). Although more elaborate models

488 (e.g., diffusion-reaction models) might be more appropriate to describe this complex

489 environment, our one-box model is a robust approach to reproduce the observations in the East

490 Siberian Sea ($R^2 > 0.7$, p value < 0.001; Fig. 5). The initial NO_3^- δ^{15}N is close to the observed

491 values at the lower halocline of the offshore East Siberian Sea sites, but little is known about

492 how and from where NO_3^- is advected over the East Siberian shelf. The estimated sedimentary

493 isotope effect fits in the range reported for benthic denitrification (0 - 8 ‰) (Brandes and Devol,

494 1997, 2002; Lehmann et al., 2004, 2007; Granger et al., 2011; Alhkatib et al., 2012). The upper

495 limit is usually imparted to the nitrification-driven denitrification and the lower limit to NO_3^-

496 diffusion-driven denitrification (Lehmann et al., 2007; Granger et al., 2011; Alhkatib et al.,

497 2012).

498 In case of CPND the overall expression of the sedimentary isotope effect into the overlying

499 water column will be mostly a function of the balance between benthic remineralization and

500 nitrification fluxes, which sets the amount of NH_4^+ diffusing out of the sediment, its δ^{15}N

501 signature as well as the ambient NO_3^- concentration. Similar to the dilution effect described in

502 Deutsch et al. (2004) for water column denitrification, a fractionated fixed N pool (i.e., efflux out

503 of the sediments) is mixed with an unfractionated fixed N pool (i.e., mostly ambient NO_3^-),

504 impacting differently f and NO_3^- δ^{15}N being used to estimate ε_{sed} (Eqs. 3 and 4). With a tight

505 coupling between benthic remineralization and nitrification, efflux carries high NH_4^+ δ^{15}N out of

506 the sediments but its lower concentration will give less weight in the resulting mixing product

507 NO_3^- δ^{15}N (i.e., efflux + ambient NO_3^- in the overlying water column). In case remineralization

508   equals CPND, the sedimentary isotope effect is muted, as there is no NH_4^+ efflux. In case there is

509   no NO_3^- in the initial water column, the estimated sedimentary isotope effect equals the isotope

510   effect of nitrification (~15 ‰; Casciotti et al., 2003; Santoro and Casciotti, 2011) and water

511   column NO_3^- $\delta^{15}N$ is directly set by the efflux $\delta^{15}N$ (i.e., residual product of benthic

512   nitrification). Any intermediate scenario will tend to have a sedimentary isotope effect lying

513   between these two extreme values (i.e., 0 and ~15 ‰). Further mixing with offshore water, not in

514   contact with the reactive sedimentary layer, will also tend to decrease the overall expression of

515   the sedimentary isotope effect (Figs 5b, c).

516   Accordingly, the relatively low sedimentary isotope effect (2.4 - 3.8 ‰) for the East Siberian Sea

517   may result of benthic CPND characterized by a close coupling between remineralization and

518   nitrification. Note that one station over the shelf (i.e., SWERUS-C3 station 62), presented a clear

519   fixed N deficit but little associated ^{15}N-enrichment, and was considered an outlier (Fig. 5). This

520   situation may likely result from benthic coupled nitrification-denitrification but with nitrification

521   balancing remineralization, leading to little or no NH_4^+ efflux and a sedimentary isotope effect

522   close to 0 ‰ for CPND.

523   In agreement with previous studies (Lehmann et al., 2007; Granger et al., 2011; Alkhatib et al.,

524   2012) sedimentary isotope effect for benthic fixed N loss is likely to vary considerably for

525   different sedimentary environments. We have shown that, in case of benthic coupled partial

526   nitrification-denitrification, its magnitude also depends on the conditions in the overlying water

527   column (i.e., unfractionated ambient fixed N pools) and especially the degree of coupling

528   between remineralization, and nitrification in the reactive sedimentary layer (i.e., dilution effect).

529   This has profound consequences in the determination of a 'mean' sedimentary isotope effect

530   needed to assess a relative contribution of benthic vs. water column denitrification to the oceanic

531   fixed N loss, requiring further investigations.

5. Conclusion

533   Mechanisms generally considered able to explain the halocline nutrient maximum in the Arctic

534   Ocean are; (i) advection of nutrient-rich Pacific water via the shallow Bering Strait, and/or (ii)

535   intensive remineralization over the productive shallow shelves. The latter mechanism implies a

536   temporary confinement of the remineralization products (i.e., nutrients) in shelf bottom waters in

537   interaction with highly reactive sediments, followed by their advection into the central basin to

538   form the halocline (Jones and Anderson, 1986; Anderson et al., 2013, 2017; Tremblay et al.,

539   2015).

540   Above the Atlantic temperature maximum, a clear relationship was observed between $\delta^{18}O$ of

541   water and NO_3^-, both for the East Siberian Sea and the western Eurasian Basin. Seawater in the

542   upper Arctic Ocean has extremely low-$\delta^{18}O$ values due to the large ^{18}O-depleted freshwater

543   supply. This imprint is transmitted to the ambient NO_3^- $\delta^{18}O$ during NO_3^- regeneration. At the

544   halocline, NO_3^- $\delta^{18}O$ was close to the value expected for newly produced NO_3^- $\delta^{18}O$ (i.e., water

545    $\delta^{18}O$ + 1.1 ‰; Sigman et al., 2009). This suggests that most of the NO_3^- (> 60 %) at the Arctic

546   halocline had been regenerated at least once within the Arctic Ocean, including the nutrients

547   supplied with the Pacific inflow. This proportion increases for the halocline of the East Siberian

548   Sea (~ 80%). These estimates are in agreement with the percentage contribution of regenerated

549   PO_4^{3-} to the whole PO_4^{3-} pool determined based on Apparent Oxygen Utilization and O_2:PO_4^{3-}

550   theoretical stoichiometric ratio, and ranging from ~ 40 up to 75 % for the halocline in the

551   western Eurasian Basin and East Siberian Sea, respectively (Ito and Follows, 2005).

552   The associated increase in NO_3^- $\delta^{15}N$ toward the nutrient maximum, which is accompanied by a

553   strong fixed N deficit and a partial O_2 consumption, provide some clues on where the

554   regeneration predominantly occurs. The NO_3^- $\delta^{15}N$ increase was larger in the East Siberian Sea,

555   particularly for inshore waters compared to the western Eurasian Basin and was significantly

556   related with N* concentrations. In agreement with previous studies focusing on subarctic and

557   arctic shelves, it is suggested here that benthic denitrification consumes to a significant extent the

558   NO_3^- produced by partial nitrification in the reactive sediment layers (Granger et al., 2011;

559   Brown et al., 2015). Following an imbalance between remineralization and nitrification, high-

560    $\delta^{15}N$ NH_4^+ accumulates in pore waters and diffuses out of the sediments, transmitting the ^{15}N-

561   enrichment into the water column. As this process likely occurs over the entire the productive

562   Arctic shelves, it could explain the accentuation in the nutrient enrichment, the high NO_3^-- $\delta^{15}N$,

563   and low NO_3^--$\delta^{18}O$, as well as the fixed N deficit in the Arctic halocline, following advection of

564   shelf bottom waters into the central basin. This imprint is progressively diluted far from the

565   shelves by mixing, implying lower NO_3^- $\delta^{15}N$ values and an attenuated relationship with N* with

566   increasing distance from the shelves (e.g., toward the western Eurasian Basin).

567   These findings clearly highlight the key role of the bordering shelves in setting the nutrient

568   distribution and properties in the Arctic Ocean. The substantive production and export of organic

569   material to the shallow sediments stimulates remineralization and denitrification at the sediment

570   interface, releasing and confining nutrients in shelf bottom water and removing fixed N from the

571   ocean. More investigations are required to develop a mechanistic understanding of this process

572   and how it is likely to evolve in a rapidly changing Arctic Ocean. This benthic-pelagic coupling

573   is still poorly represented in biogeochemical models (Popova et al., 2010; Vancoppenolle et al.,

574   2013).

575   The relationship between N* and NO_3^- $\delta^{15}N$ allows us to estimate an isotope effect related to

576   benthic denitrification expressed in the water column (i.e., sedimentary isotope effect) (Altabet et

577   al., 1999; Lehmann et al., 2007). Over the East Siberian Sea, the sedimentary isotope effect was

578   between 2.4 and 3.8 ‰, in the middle range of previous estimates. This magnitude can be

579   explained by a close coupling between remineralization and nitrification, implying that the efflux

580   out of the sediments carries a high-$\delta^{15}N$ signal but is highly depleted in fixed N. As the latter is

581   being mixed with the unfractionated fixed N pool in the overlying water column (mostly NO_3^-),

582   less weight is given for the efflux to set water column NO_3^- $\delta^{15}N$. This process is similar to what

583   has been described as a dilution effect for pelagic denitrification by Deutsch et al. (2004).

584   Variable sedimentary isotope effects determined by the degree of coupling between

585   remineralization and nitrification, overlying water column fixed N concentration, and variations

586   in the NO_3^- source for benthic denitrification, all have profound consequences when assessing

587   the global fixed N budget based on the 'mean' (i.e., global Ocean) isotopic balance and require

588   further investigations (Brandes and Devol, 2002; Deutsch et al., 2004).

Acknowledgments

600   References

601   Aagaard, K., L.K. Coachman, and C. Carmack. 1981. On the halocline of the Arctic Ocean. Deep Sea Res. 28: 529-

602   545.

603   Alkhatib, M., M.F. Lehmannn, and P.A. del Giorgio. 2012. The nitrogen isotope effect of benthic remineralization-

604   nitrification-denitrification coupling in an estuarine environment. Biogeosciences 9: 1633-1646, doi:10.5194/bg-9-

605   1633-2012.

606   Altabet, M.A., R. Francois. 1994. Sedimentary nitrogen isotope ratio as a recorder for surface ocean nitrate

607   utilization. Global Biogeochem. Cycles 8:130-116.

608   Altabet, M.A., C. Pilskaln, R. Thunell, C. Pride, D. Sigman, F. Chavez, and R. Francois. 1999. The nitrogen isotope

609   biogeochemistry of sinking particles from the margin of the Eastern North Pacific. Deep Sea Res. I 46: 655-679.

610   Anderson, L.A. 1995. On the hydrogen and oxygen content of marine phytoplankton. Deep Sea Res. I 42: 1675-

611   1680.

612   Anderson, L.G., P.S. Andersson, G. Bjork, E.P. Jones, S. Jutterstrom, and I. Wahlstrom. 2013. Source and formation

613   of the upper halocline of the Arctic Ocean. J. Geophys. Res. 118: 410-421, doi:10.1029/2012JC008291.

614   Anderson, L.G., G. Björk, O. Holby, S. Jutterström, M. O'Regan, C. Pearce, I. Semiletov, C. Stranne, T. Stöven, T.

615   Tanhua, A. Ulfsbo, M. Jakobsson. 2017. Shelf –Basin interaction along the Laptev – East Siberian Seas. Ocean

616   Science, 13, 349-363, doi:10.5194/os-13-349-2017.

617   Arrigo, K.R., and G.L. van Dijken. 2015. Continued increases in Arctic Ocean primary production. Prog. Oceanogr.

618   136: 60-70.

619   Benetti, M., A.E. Sveinbjörnsdottir, R. Olafsdottir, M.J. Leng, C. Arrowsmith, K. Debondt, F. Fripiat, and G. Aloisi.

620   2017. Inter-comparison of salt effect correction for $\delta^{18}O$ and δ^2H measurements in seawater by CRDS and IRMS

621   using the gas-H2O equilibration method. Mar. Chem. 194: 114-123.

622   Bluhm, B.A., K.N. Kosobokova, and E.C. Carmack. 2015. A tale of two basins: An integrated physical and

623   biological perspective of the deep Arctic Ocean. Prog. Oceanogr. 139: 89-121.

624   Böhlke, J.K., S.J. Mroczkowski, and T.B. Coplen. 2003. Oxygen isotopes in nitrate: new reference materials for

625   $^{18}O{:}^{17}O{:}^{16}O$ measurements and observations on nitrate-water equilibration. Rapid Commun. Mass Spectrom. 17:

626   1835-1846.

627   Brandes, J.A., and A.H. Devol. 1997. Isotopic fractionation of oxygen and nitrogen in coastal marine sediments.

628   Geochim. Cosmochim. Acta 61(9): 1793-1801.

629   Brandes, J.A., and A.H. Devol. 2002. A global marine-fixed nitrogen isotopic budget: Implications for Holocene

630   nitrogen cycling. Global Biogeochem. Cycles 16(4): 1120, doi:10.1029/2001GB001856.

631   Broecker, W.S., T. Takahashi, and T. Takahashi. 1985. Sources and flow pattern of deep ocean waters as deduced

632   from potential temperature, salinity, and initial phosphate concentration. J. Geophys. Res. 90: 6925-6939.

633   Brown, Z.W., K.L. Casciotti, R.S. Pickart, J.H. Swift, and K.R. Arrigo. 2015. Aspects of the marine nitrogen cycle

634   of the Chukchi Sea shelf and Canada basin. Deep Sea Res. II 118: 73-87.

635   Buchwald, C., A.E. Santoro, M.R. McIlvin, and K.L. Casciotti. 2012. Oxygen isotopic composition of nitrate and

636   nitrite produced by nitrifying cocultures and natural marine assemblages. Limnol. Oceanogr. 57(5) : 1391-1375.

637   Buchwald, C., A.E. Santoro, R.H.R. Stanley, and K.L. Casciotti. 2015. Nitrogen cycling in the secondary nitrite

638   maximum of the eastern tropical North Pacific off Costa Rica. Global Biogeochem. Cycles 29: 2061-2081,

639   doi:10.1002/2015GB005187.

640   Casciotti, K.L., D.M. Sigman, M. Galanter Hastings, J.K. Böhlke, and A. Hilkert. 2002. Measurement of the oxygen

641   isotopic composition of nitrate in seawater and freshwater using the denitrifier method. Anal. Chem. 74 : 4905-

642   4912.

643   Casciotti, K.L., D.M. Sigman, and B.B. Ward. 2003. Linking diversity and stable isotope fractionation in ammonia-

644   oxidizing bacteria. Geomicrobiol. J. 20 : 335-353.

645   Casciotti, K.L., J.K. Böhlke, M.R. McIlvin, S.J. Mroczkowski, and J.E. Hannon. 2007. Oxygen isotopes in nitrite :

646   Analysis, calibration, and equilibration. Anal. Chem. 79 : 2427-2436.

647   Casciotti, K.L., T.W. Trull, D.M. Glover, and D. Davies. 2008. Constraints on nitrogen cycling at the subtropical

648   North Pacific Station ALOHA from isotopic measurements of nitrate and particulate nitrogen. Deep-Sea Res. II 55:

649   1661-1672.

650   Casciotti, K.L. 2009. Inverse kinetic isotope fractionation during bacterial nitrite oxidation. Geochim. Cosmochim.

651   Acta 73: 2061-2076.

652　Casciotti, K.L., M. McIlvin, and C. Buchwald. 2010. Oxygen isotopic exchange and fractionation during bacterial

653　　ammonia oxidation. Limnol. Oceanogr. 55(7): 753-762.

654　Cavalieri, D.J., and C.L. Parkinson. 2012. Arctic sea ice variability and trends, 1979-2010. The cryosphere 6: 881-

655　　889, doi:10.5194/tc-6-881-2012.

656　Chang, B.X., and A.H. Devol. 2009. Seasonal and spatial patterns of sedimentary denitrification rates in the Chukchi

657　　sea. Deep Sea Res. II 56: 1339-1350.

658　Codispoti, L.A., J.A. Brandes, J.P. Christensen, A.H. Devol, S.W.A. Naqvi, H.W. Paerl, and T. Yoshinari. 2001.The

659　　oceanic fixed nitrogen and nitrous oxide budgets: Moving targets as we enter the Anthropocene? Sci. Mar. 65: 85-

660　　105.

661　Codispoti, L.A., V. Kelly, A. Thessen, P. Matrai. S. Suttles, V. Hill, M. Steele, and B. Light. 2013. Synthesis of

662　　primary production in the Arctic Ocean: III. Nitrate and phosphate based estimates of net community production.

663　　Prog. Oceanogr. 110 : 126-150.

664　Cooper, L.W., J.W. McClelland, R.M. Holmes, P.A. Raymond, J.J. Gibson, C.K. Guay, and B.J. Peterson. 2008.

665　　Flow-weighted values of runoff tracers ($\delta18O$, DOC, Ba, alkalinity) from the six largest Arctic rivers. Geophys.

666　　Res. Let. 35: L18606, doi :10.1029/2008GL035007.

667　Dalsgaard, T., B. Thamdrup, and D.E. Canfield. 2005. Anaerobic ammonium oxidation (anammox) in the marine

668　　environment. Research in Microbiology 156: 457-464.

669　Deman, F., D. Fonseca-Batista, F. Fripiat, E. Le Roy, D. Thilakarathne, N. Lemaitre, A. Roukaerts, and F. Dehairs.

670　　2017. N_2-fixation footprint on nitrate isotopic composition in temperate northeast Atlantic Ocean. Abstract at the

671　　Goldschmidt international conference on geochemistry 2017, Paris.

672　Deutsch, C., N. Gruber, R.M. Key, and J.L. Sarmiento. 2001. Denitrification and N_2 fixation in the Pacific Ocean.

673　　Global Biogeochem. Cycles 15(2): 483-506.

674　Deutsch, C., D.M. Sigman, R.C. Thunell, A.N. Meckler, and G.H. Haug. 2004. Isotopic constraints on

675　　glacial/interglacial changes in the oceanic nitrogen budget. Global Biogeochem. Cycles 18: GB4012,

676　　doi:10.1029/2003GB002189.

677　Devol, A.H., L.A. Codispoti, J.P. Christensen. 1997. Summer and winter denitrification rates in western Arctic shelf

678　　sediments. Cont. Shelf Res. 9 : 1029-1050.

679   Dore, J.E., T. Houlihan, D.V. Hebel, G. Tien, L. Tupas, and D.M. Karl. 1996. Freezing as a method of sample

680   preservation for the analysis of dissolved inorganic nutrient in seawater. Mar. Chem. 53: 173-185.

681   Eppley, R.W., and B.J. Peterson. 1979. Particulate organic matter flux and planktonic new production in the deep

682   ocean. Nature 282: 677-680.

683   Epstein, S., and T.K. Mayeda. 1953. Variations of the 18/16O ratio in natural waters. Geochim. Cosmochim. Acta

684   4(5): 213-224.

685   Fripiat, F., D.M. Sigman, S.E. Fawcett, P.A. Rafter, M.A. Weigand, and J.-L. Tison. 2014. New insights into sea ice

686   nitrogen biogeochemical dynamics from the nitrogen isotopes. Global Biogeochem. Cycles 25:

687   doi:10.1002/2013GB004729.

688   Granger, J., D.M. Sigman, J.A. Needoba, and P.J. Harrison. 2004. Coupled nitrogen and oxygen isotope

689   fractionation of nitrate during assimilation by cultures of marine phytoplankton. Limnol. Oceanogr. 49(5) : 1763-

690   1773.

691   Granger, J., D.M. Sigman, M.F. Lehmannn, and P.D. Tortell. 2008. Nitrogen and oxygen isotope fractionation

692   during dissimilatory nitrate reduction by denitrifying bacteria. Limnol. Oceanogr. 53(6) : 2533-2545.

693   Granger, J., and D.M. Sigman. 2009. Removal of nitrite with sulfamic acid for nitrate N and O isotope analysis with

694   the denitrifier method. Rapid Commun. Mass Spectrom. 23: 3753-3762, doi:10.1002/rcm.4307.

695   Granger, J., D.M. Sigman, M.M. Rohde, M.T. Maldonado, and P.D. Tortell. 2010. N and O isotope effects during

696   nitrate assimilation by unicellular prokaryotic and eukaryotic plankton cultures. Geochim. Cosmochim. Acta 74:

697   1030-1040.

698   Granger, J., M.G. Prokopenko, D.M. Sigman, C.W. Mordy, Z.M. Morse, L.V. Morales, R.N. Sambrotto, and B.

699   Plessen. 2011. Coupled nitrification-denitrification in sediment of the eastern Bering Sea shelf lea to [15]N

700   enrichment of fixed N in shelf waters. J. Geophys. Res. 116: C11006, doi:10.1029/2010JC006751.

701   Granger, J., M.G. Prokopenko, C.W. Mordy, and D.M. Sigman. 2013. The proportion of remineralized nitrate on the

702   ice-covered eastern Bering Sea shelf evidenced from the oxygen isotope ratio of nitrate. Global Biogeochem.

703   Cycles 27: 962-971, doi:10.1002/gbc.20075.

704   Gruber, N., and J.L. Sarmiento. 1997. Global patterns of marine nitrogen fixation and denitrification. Global

705   Biogeochem. Cycles 11(2): 235-266.

706 Gruber, N., and J.N. Galloway. 2008. An Earth-system perspective of the global nitrogen cycle. Nature 451: 293-
707   296, doi:10.1038/nature06592.

708 Humborg, C., M.C. Geibel, L.G. Anderson, G. Björk, C.M. Sundbom, B.F. Thornton, B. Deutsch, E. Gustafsson,
709   and others. 2017. Sea-air exchange patterns along the central and outer East Siberian Arctic Shelf as inferred from
710   continuous CO2, stable isotope and bulk chemistry measurements. Global Biogeochem. Cy. 31,
711   doi:10.1002/2017GB005656.

712 Hydes, D.J., M. Aoyama, A. Aminot, K. Bakker, S. Becker, et al. 2010. Determination of dissolved nutrients (N, P,
713   Si) in seawater with high precision and inter-comparability using gas-segmented continuous flow analysers. The
714   GO-SHIP Repeat Hydrograhy Manual: A collection of Expert Reports and Guidelines.

715 Ito, T., and M.J. Follows. 2005. Preformed phosphate, soft tissue pump and atmospheric CO_2. J. Mar. Res. 63: 813-
716   839.

717 Janout, M.A., J. Holemann, A.M. Waite, T. Krumpen, W.-J. von Appen, and F. Martynov. 2016. Sea-ice retreat
718   controls timing of summer plankton blooms in the Eastern Arctic Ocean. Geophys. Res. Lett. 43: 12493-12501,
719   doi:10.1002/2016GL071232.

720 Jones, E.P., and L.G. Anderson. 1986. On the origin of the chemical properties of the Arctic Ocean Halocline. J.
721   Geophys. Res. 91(C9): 10759-10767.

722 Jones, E.P., L.G. Anderson, and J.H. Swift. 1998. Distribution of Atlantic and Pacific waters in the upper Arctic
723   Ocean: Implications for circulation. Geophys. Res. Let. 25(6) : 765-768.

724 Karsh, K.L., J. Granger, K. Kritee, and D.M. Sigman. 2012. Eukaryotic assimilatory nitrate reductase fractionate N
725   and O isotopes with a ratio near unity. Environ. Sci. Technol. 46 : 5727-5735, dx.doi.org/10.1021/es204593q.

726 Kikuchi, T., K. Hatakeyama, and J.H. Morison. 2004. Distribution of convective Lower Halocline Water in the
727   eastern Arctic Ocean. J. Geophys. Res. 109, C12030, doi:10.1029/2003JC002223

728 Knapp, A.N., D.M. Sigman, F. Lipschultz, A.B. Kustka, and D.G. Capone. 2011. Interbasin isotopic correspondence
729   between upper-ocean bulk DON and subsurface nitrate and its implications for marine nitrogen cycling. Global
730   Biogeochem. Cycles 25: GB4004, doi:10.1029/2010GB003879.

731 Lehmannn, M.F., D.M. Sigman, and W.M. Berelson. 2004. Coupling the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ of nitrate as a
732   constraint on benthic nitrogen cycling. Mar. Chem. 88: 1-20.

733   Lehmannn, M.F., D.M. Sigman, D.C. McCorkle, J. Granger, S. Hoffman, G. Cane, and B.G. Brunelle. 2007. The

734   distribution of nitrate ^{15}N/^{14}N in marine sediments and the impact of benthic nitrogen loss on the isotopic

735   composition of oceanic nitrate. Geochim. Cosmochim. Acta 71: 5384-5404.

736   Leu, E., C.J. Mundy, P. Assmy, K. Campbell, T.M. Gabrielsen, M. Gosselin, T. Juul-Pedersen, and R. Gradinger.

737   2015. Arctic spring awakening – Steering principles behind the phenology of vernal ice algal blooms. Prog.

738   Oceanogr. 139 : 151-170.

739   Maslanik, J., and J. Stroeve. 1999. Updated daily. Near-Real-Time DMSP SSMIS Daily Polar Gridded Sea Ice

740   Concentrations. Boulder, Colorado USA: NASA DAAC at the National Snow and Ice Data Center.

741   Marconi, D., M.A. Weigand, P.A. Rafter, M.R. McIlvin, M. Forbes, K.L. Casciotti, and D.M. Sigman. 2015. Nitrate

742   isotope distribution on the US GEOTRACE North Atlantic cross-basin section: Signal of polar nitrate source and

743   low latitude nitrogen cycle. Mar. Chem. 177:143-156.

744   McLaughlin, F.A., E.C. Carmack, R.W. Macdonald, and J.K.B. Bishop. 1996. Physical and geochemical properties

745   across the Atlantic/Pacific water mass front in the southern Canadian Basin. J. Geophys. Res. 101: 1183-1197.

746   McTigue, N.D., W.S. Gardner, K.H. Dunton, and A.K. Hardison. 2016. Biotic and abiotic controls on co-occuring

747   nitrogen   cycling   processes   in   shallow   Arctic   shelf   sediments.   Nature   communications   7:13145,

748   doi:10.1038/ncomms13145.

749   Möbius, J. 2013. Isotope fractionation during nitrogen remineralization (ammonification) : Implications for nitrogen

750   isotope biogeochemistry. Geochim. Cosmochim. Acta 105 : 422-432.

751   Olsen, A., R.M. Key, S. van Heuven, S.K. Lauvset, A. Velo, X. Lin, C. Schirnick, A. Kozyr, and others. 2016. The

752   Global Ocean Data Analysis Project version 2 (GLODAPv2) – An internally consistent data product for the world

753   ocean. Earth Syst. Sci. Data 8: 297-323, doi:10.5194/essd-8-297-2016.

754   Pabi, S., G.L. van Dijken, and K.R. Arrigo. 2008. Primary production in the Arctic Ocean, 1998-2006. J. Geophys.

755   Res. 113, doi:10.1029/2007JC004578.

756   Popova, E.E., A. Yool, A.C. Coward, F. Dupont, C. Deal, S. Elliott, E. Hunke, M. Jin, and others. 2012. What

757   controls primary production in the Arctic Ocean? Results from an intercomparison of five general circulation

758   models with biogeochemistry. J. Geophys. Res. 117, C00D12, doi:10.1029/2011JC007112.

759   Proshutinsky, A., D. Dukhovskoy, M.L. Timmermans, R. Krishfield, and J.L. Bamber. 2015. Arctic circulation

760   regimes. Phil. Trans. R. Soc. A. 373: 20140160, doi:10.1098/rsta.2014.0160.

761   Rafter, P.A., P.J. DiFiore, and D.M. Sigman. 2013. Coupled nitrate nitrogen and oxygen isotopes and organic matter

762   remineralization in the Southern and Pacific Oceans. J. Geophys. Res. 118: 1-14, doi:10.1002/jgrc.20316.

763   Rainville, L., C.M. Lee, and R.A. Woodgate. 2011. Impact of wind-driven mixing in the Arctic Ocean.

764   Oceanography 24(3): 136-145.

765   Rudels, B., E.P. Jones, L.G. Anderson, and G. Kattner. 1994. On the intermediate depth waters of the Arctic Ocean.

766   In O.M. Johannessen, R.D. Muechn, and J.E. Overland [eds.], The polar oceans and their roles in shaping the

767   global environment. American Geophysical Union, Washington D.C., doi:10.1029/GM085p0033.

768   Rudels, B., L.G. Anderson, and E.P. Jones. 1996. Formation and evolution of the surface mixed layer and halocline

769   of the Arctic Ocean. J. Geophys. Res. 101: 8807-8821.

770   Rudels, B. 2012. Arctic Ocean circulation and variability – advection and external forcing encounter constraints and

771   local processes. Ocean Sci. 8: 261-286, doi:10.5194/os-8-261-2012.

772   Santoro, A.E., and K.L. Casciotti. 2012. Enrichment and characterization of ammonia-oxidizing archaea from the

773   open ocean: phylogeny, physiology and stable isotope fractionation. ISME 5: 1769-1808.

774   Sigman, D.M., K.L. Casciotti, M. Andreani, C. Barford, M. Galanter, and J.K. Böhlke. 2001. A bacterial method for

775   the nitrogen isotopic analysis of nitrate in seawater and freshwater. Anal. Chem. 73: 4145-4153.

776   Sigman, D.M., J. Granger, P.J. DiFiore, M.M. Lehmannn, R. Ho, G. Cane, and A. van Green. 2005. Coupled

777   nitrogen and oxygen isotope measurements of nitrate along the eastern North Pacific margin. Global Biogeochem.

778   Cycles. 19: GB4022, doi:10.1029/2005GB002458.

779   Sigman, D.M., P.J. DiFiore, M.P. Hain, C. Deutsch, Y. Wang, D.M. Karl, A.N. Knapp, M.F. Lehmannn, and others.

780   2009. The dual isotope of deep nitrate as a constraint on the cycle and budget of oceanic fixed nitrogen. Deep Sea

781   Res. I 56: 1479-1439.

782   Slagstad, D., P.F.J. Wassman, and I. Ellingsen. 2015. Physical constraints and productivity in the future Arctic

783   Ocean. Front. Mar. Sci. 2(85): doi:10.3389/fmars.2015.00085.

784   Steele, M., and T. Boyd. 1998. Retreat of the cold halocline layer in the Arctic Ocean. J. Geophys. Res. 103(C5):

785   10419-10435, doi:10.1029/98JC00580

786   Tremblay, J.E., L.G. Anderson, P. Matrai, P. Coupel, S. Bélanger, C. Michel, and M. Reigstad. 2015. Global and

787   regional drivers of nutrient supply, primary production and CO2 drawdown in the changing Arctic Ocean. Prog.

788   Oceanogr. 139: 171-196.

789   Vancoppenolle, M., L. Bopp, G. Madec, J. Dunne, T. Ilyina, P.R. Halloran, and N. Steiner. 2013. Future Arctic

790   Ocean primary productivity from CMIP5 simulations: Uncertain outcome, but consistent mechanisms. Global

791   Biogeochem. Cycles 27: 605-619, doi:10.1002/gbc.20055.

792   Voss, M., B. Deutsch, R. Elmgren, C. Humborg, P. Kuupo, M. Pastuszak, C. Rolff, and U. Shulte. 2006. Source

793   identification of nitrate by means of isotopic tracers in the Baltic Sea catchments. Biogeosciences 3: 663-676.

794   Wassmann, P., and M. Reigstad. 2011. Future Arctic Ocean seasonal ice zones and implications for pelagic-benthic

795   coupling. Oceanography 24(3): 220-231, http://dx.doi.org/10.5670/oceanog.2011.74.

796   Weigand, M.A., J. Foriel, B. Barnett, S. Oleynik, and D.M. Sigman. 2016. Updates to instrumentation and protocols

797   for isotopic analysis of nitrate by the denitrifier method. Rapid Commun. Mass Spectrom. 30: 1365-1383.

798   Woodgate, R.A., K. Aagaard, R.D. Muench, J. Gunn, G. Björk, B. Rudels, A.T. Roach, and U. Schauer. 2001. The

799   Arctic ocean boundary current along the Eurasian slope and the adjacent Lomonosov Ridge: Water mass

800   properties, transports and transformations from moored instruments. Deep Sea Res. I 48: 1757-1792.

801   Yool, A., E.E. Popova, and A.C. Coward. 2015. Future change in ocean productivity: Is the Arctic the new Atlantic?

802   J. Geophys. Res. 120: 2169-9261, doi:10.1002/2015JC011167

803 ## Figures and captions

804 **Figure 1:** Sea Ice concentration on August 1st 2014 (Malasnik and Stroeve, 1999) (a) and

805 bathymetry and halocline circulation, sources and associated fronts (blue shows Pacific-origin

806 waters, purple shows Atlantic-origin waters, thick black line depicts the front between them)

807 (Rudels et al., 1994, 1996; McLaughlin et al., 1996; Bluhm et al., 2015) (b). The stations

808 reported in this study are represented by the red squares.

809 **Figure 2:** Potential Temperature – salinity diagram (a) and water $\delta^{18}O$ (‰ vs. SMOW) – salinity

810 diagram (b) for the western Eurasian Basin (gray squares) and in the East Siberian Sea for the

811 off-shelf (blue circles) and on-shelf (empty purple triangles) stations. Thin lines connects

812 adjacent samples from the same hydrocast. The light gray shaded area indicates the upper

813 halocline (UH) observed only in the East Siberian Sea. The dark gray shaded area is for the

814 lower halocline (LH) in both the East Siberian Sea and western Eurasian Basin.

815 **Figure 3:** Concentrations – salinity diagrams for NO_3^- (a), $Si(OH)_4$ (b), PO_4^{3-} (c),

816 regenerated:total PO_4^{3-} ratio (d), dissolved O_2 (e), and N* (f) in the western Eurasian Basin (gray

817 squares) and in the East Siberian Sea for the off-shelf (blue circles) and on-shelf (empty purple

818 triangles) stations. Thin lines connects adjacent samples from the same hydrocast. The light gray

819 shaded area indicates the upper halocline (UH) observed only in the East Siberian Sea. The dark

820 gray shaded area is for the lower halocline (LH) in both the East Siberian Sea and western

821 Eurasian Basin. The black arrows indicate the trend for the off-shelf stations with decreasing

822 distance from the East Siberian shelf. The mixing lines between the upper halocline in the East

823 Siberian Sea and the lower halocline in the western Eurasian Basin is represented by the red

824 lines, representative of the Pacific- and Atlantic-derived waters, respectively.

825   **Figure 4:** Depth profiles of NO_3^- concentration (a) and both NO_3^- $\delta^{15}N$ (filled symbols) and $\delta^{18}O$

826   (open symbols) (b) in the western Eurasian Basin (gray squares) and in the East Siberian Sea for

827   the off-shelf (blue circles) and on-shelf (purple triangles) stations. The horizontal gray dashed

828   line represents the 50m isobath, representing approximately the mean outer shelf-depth over the

829   East Siberian Sea, and the blue dashed line represents the Atlantic temperature maximum. The

830   vertical dashed black lines in (b) represent the mean oceanic NO_3^- $\delta^{15}N$ and $\delta^{18}O$ (Sigman et al.,

831   2009; Marconi et al., 2015). Thin lines connects adjacent samples from the same hydrocast.

832   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

833   (square) and in the East Siberian Sea for the off-shelf (circles) and on-shelf (triangles) stations.

834   The colored symbols in both (c) and (d) represent the halocline with the colors corresponding to

835   salinity (i.e., color bar in panel d). The trends given by both assimilation and benthic coupled

836   partial nitrification-denitrification (CPND) are represented in (c), as well as the predicted newly

837   produced NO_3^- $\delta^{18}O$ from nitrification (d) according to field studies.

838   **Figure 5:** NO_3^- $\delta^{15}N$ vs. N* (a), ln(f) (b), and (1-f) (c) in the western Eurasian Basin (gray

839   squares) and in the East Siberian Sea for the off-shelf (blue circles) and on-shelf (purple

840   triangles) stations. F is defined as the fractional loss of fixed N [i.e., f = DIN/(DIN - N*)]

841   (Altabet et al., 1999). The linear regression for off-shelf stations in the East Siberian Sea is

842   shown with the dashed blue line. The open symbols represent the data omitted from regression

843   because they appears to have been influenced by past assimilation (Fig. 4c). The mixing lines

844   between the upper halocline in the East Siberian Sea and the lower halocline in the western

845   Eurasian Basin is shown with the red lines, representative of the Pacific- and Atlantic-derived

846   waters, respectively.

847   **Figure 6:** Phosphate vs. nitrate concentrations from both GLODAP-v2 database (Olsen et al.,

848   2016) and this study. Black and white circles represents all available data from GLODAP-v2 in

849   the eastern and western Arctic, defined here as the area from the coasts to the North Pole

850   between 0 and 180°E and 0-180°W, respectively. Green and orange circles represent all available

851   data from GLODAP-v2 for the Bering Sea, over the shelf (> 150 m) and in the deep basin,

852   respectively. The arrows show the effect (i.e., slope) of remineralization, denitrification, and a

853   scenario in which denitrification equals remineralization, assuming N to P ratio of 16 and 104 for

854   remineralization and denitrification, respectively (Anderson et al., 1995; Gruber and Sarmiento,

855   1997).

856   **Figure 7:** Conceptual scheme showing the inputs and loss of fixed N in the combined shelf

857   bottom water and reactive sedimentary layer. Initial fixed N is initial DIN and what is supplied

858   from the remineralization of exported particulate N (PN) both in the water column (R_{wc}) and in

859   sediments (R_{sed}). As little isotopic fractionation is expected for remineralization, the newly

860   produced NH_4^+ $\delta^{15}N$ is close to the exported PN $\delta^{15}N$, being close to the advected NO_3^- $\delta^{15}N$ as

861   most of the NO_3^- is consumed in the euphotic layer. Nitrification in the water column is assumed

862   to be quantitative (~ 100%), and newly produced NO_3^- $\delta^{15}N$ in the water column is therefore

863   close to the NH_4^+ $\delta^{15}N$. If benthic remineralization is larger than nitrification, NH_4^+ is

864   accumulated in pore waters and can diffuse into the overlying water column (i.e., efflux, E).

865   NH_4^+ $\delta^{15}N$ will increase as being the residual substrate of nitrification, preferentially oxidizing

866    $^{14}NH_4^+$ into NO_3^-. Low-$\delta^{15}N$ NO_3^- in the reactive sediment will then be quantitatively converted

867   into N_2, transmitting the isotopic fractionation from sedimentary nitrification to denitrification

868   (D).

Legend:
- ○ 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

UH

Initial fixed N = initial DIN + R