Biogeochemistry of the Arctic halocline and the deep water masses in the Central Arctic: insights from nitrate stable isotopes

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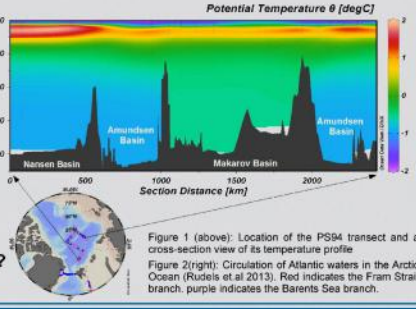
Background

The Arctic Ocean mediates nutrient exchange between Atlantic and Pacific basins. The extent to which water masses travel and mix within the Arctic will influence primary productivity and oxygenation of the water column. However, this basin is warming at a rate twice the global average. The processes that control nutrient cycling and carbon fixation on a Pan-Arctic scale and their sensitivity to sea-ice conditions and climate change remain unclear.

Study Area

Geotraces PS94 cruise sampled Nansen, Amundsen and Makarov basins (fig.1). The water masses analysed are:

Water Mass	Depth Interval	T-S properties
Polar Surface Water	0 - 200m	≤ 33.5 psu, < 0°C
Atlantic Intermediate	200 - 1500m	~34.95 psu, 1.5 - 2.5°C
Arctic Deep Water	1500m - bottom	~34.95 psu, -1 - 0°C



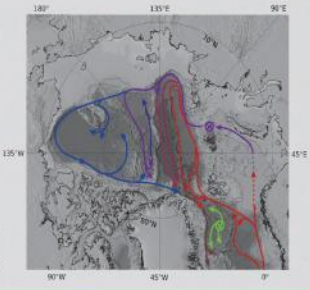


Figure 1 (above): Location of the PS94 transect and a cross-section view of its temperature profile

Figure 2(right): Circulation of Atlantic waters in the Arctic Ocean (Rudels et.al 2013). Red indicates the Fram Strait branch. purple indicates the Barents Sea branch.

Key Questions

- **What controls nutrient uptake and productivity in Central Arctic surface waters?**
- **What are the fractions of preformed and regenerated nutrients throughout the water column?**
- **What is the potential of surface productivity in changing deep Arctic oxygenation?**

Advantages of using NO_3^- isotopes

- Stable isotopes discern between overlapping processes due to their distinct isotopic signatures (fig.3)
- Coupling between $\delta^{15}N(NO_3^-)$ and $\delta^{18}O(NO_3^-)$ differentiates between preformed and regenerated nitrate pools and can thus assess efficiency of organic matter recycling (fig.4).
- Isotopes offer an additional, stoichiometry-independent method to analyse carbon fixation and oxygenation of water masses under changing environmental conditions
- NO_3^- stable isotopes were determined using the Denitrifier Method (Sigman et.al. 2001) and gas chromatography mass spectrometry.

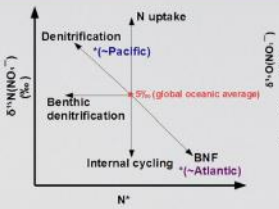


Figure 3: Effect of N-cycling processes on the $\delta^{15}N(NO_3^-)$ signature of the water

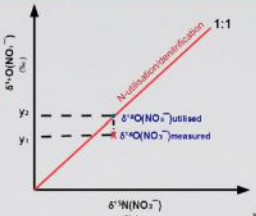


Figure 4: Isotopic method for determining the fraction of regenerated nitrate

$$\delta^{18}O(NO_3^-)_{measured} = \delta^{18}O(NO_3^-)_{nitrified} * (X) + \delta^{18}O(NO_3^-)_{utilised} * (1-X)$$

$$\delta^{18}O(NO_3^-)\ nitrified = \delta^{18}O(H_2O) + \varepsilon(nitrification)$$

$$\varepsilon(nitrification) = 1.1‰$$

$$\delta^{18}O(H_2O) = ~0‰$$

$$\delta^{18}O(NO_3^-)\ nitrified = ~0‰ + 1.1‰ = ~1.1‰$$

$$y_1 = 1.1‰ * (X) + y_2 * (1-X)$$

where X is the fraction of regenerated nitrate and 1-X is the fraction of preformed nitrate

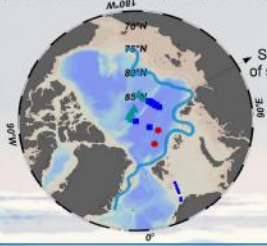
Sea-ice extent and shelf recycling: the main factors shaping nutrient uptake and productivity of the Central Arctic halocline

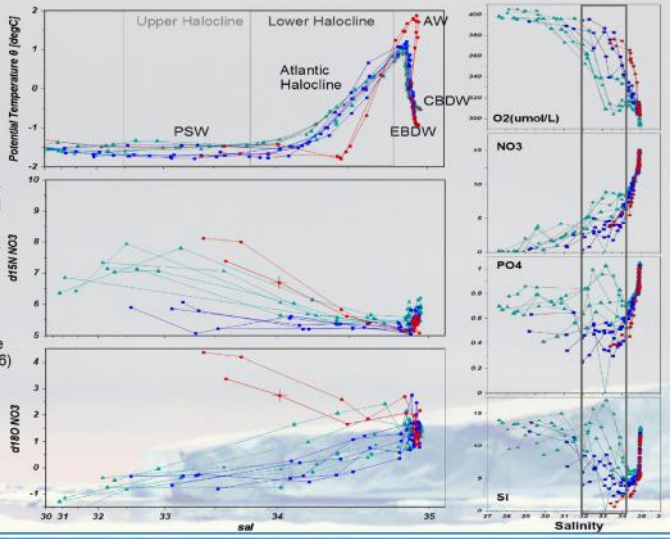
Nansen, Amundsen and Makarov haloclines present distinct biogeochemistry depending on:
-sea-ice extent (all 3 basins are under sea-ice which limits surface uptake and productivity)
-basin location relative to the Arctic shelves and proximity to Atlantic/Pacific inflows

Nansen: halocline dominated by Atlantic inflow; coupling of isotopes indicates nitrate assimilation

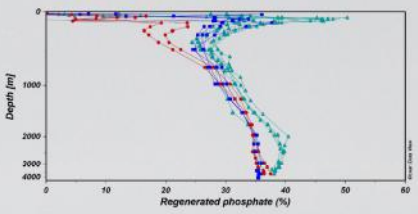
Makarov: Si and PO4 max. and N* min. point to a Pacific sourced halocline; Decoupling of isotopes indicates partial nitrification-denitrification specific to nearby shelves

Amundsen: smaller nutrient peaks indicate weaker Pacific influence; sea-ice prevents extensive nutrient assimilation (weak increase of $\delta^{15}N(NO_3^-)$ towards surface).





Respiration stoichiometry shows ≈40-45% of nutrients are regenerated in Amundsen and Makarov halocline



Isotopes and surface nutrient concentrations reflect under sea-ice conditions for the 3 basins.

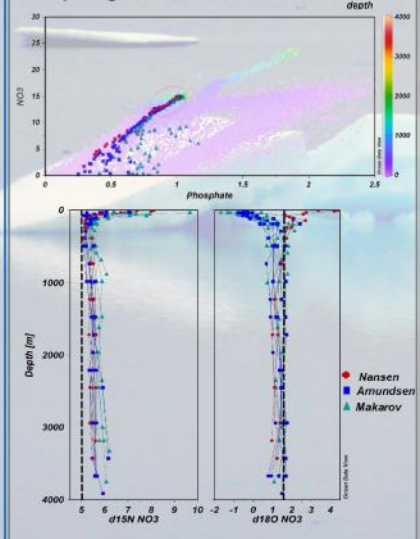
Ice edge inhibits local uptake and productivity => halocline biochemical signatures are imported from shelves/other basins

$\delta^{18}O(NO_3^-)$ reflects the variation of shelf recycling

Shelf productivity and residence time determine the amount of regenerated nutrients in the Central Arctic halocline

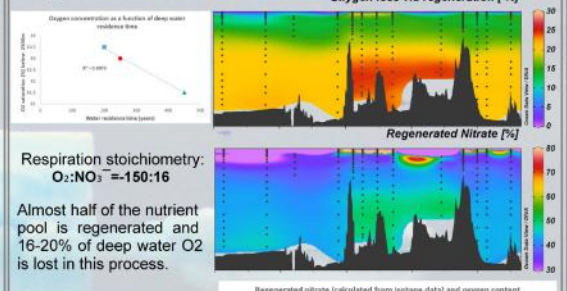
Central Arctic Deep Waters are sensitive to changes in surface productivity

Deep Arctic shares the same nutrient stoichio-metry with Atlantic waters, but not the same isotopic signature



Heavier $\delta^{15}N(NO_3)$ and lighter $\delta^{18}O(NO_3)$ than in the Atlantic source are a result of local nutrient regeneration

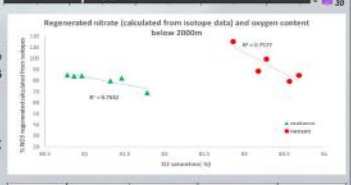
Oxygen sensitivity to nutrient regeneration is shown using two independent methods



Respiration stoichiometry: $O_2:NO_3^-$=-150:16

Almost half of the nutrient pool is regenerated and 16-20% of deep water O2 is lost in this process.

Using N&O isotopes, the % of regenerated nitrate is calculated independently of respiration stoichiometry. This also presents a strong relationship with O2 content



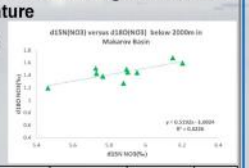
The two methods generate distinct figures for the pool of regenerated nitrate. But, both prove the sensitivity of deep water O2 content to nutrient regeneration

Basin	Ventilation age (years)	O2 saturation (%)	%NO3 regenerated (respiration stoichiometry)	%NO3 regenerated (isotope method)
Nansen	250	83	48	84
Amundsen	200	83.5	45	82
Makarov	450	81.5	50	84

Changes in sea-ice extent = changes in primary productivity = changes in flux of OM to depth = changes in amount of regenerated nutrients = changes in oxygenation of deep waters

Regeneration and benthic denitrification: two antagonistic effects shaping deep Makarov isotopic signature

Both isotopes increase with depth, but $\delta^{15}N$ increases faster than $\delta^{18}O(NO_3^-)$



$\delta^{15}N(NO_3)$ vs N* has $R^2 = 0.768$ and p value <0.0001=> causal link between loss of fixed N and $\Delta^{15}N$ enrichment in NO_3

Sedimentary denitrification rate in Makarov is exceedingly low: 15.4 umol N/m2/d

Station (PS94)	Depth integrated N* (µmol)	Depth interval of integration (m)	Basin ventilation age (years)	µmol N $m^{-2}d^{-1}$
101	1428.136	2000-bottom	450	11.72
96	1274.2	2000-bottom	450	8.42
134	2381.7	2000-bottom	450	26.1

Plotting $\delta^{15}N(NO_3)$ vs. fraction of substrate remaining after fixed N loss, gives an approx. **isotope effect for benthic denitrification of 2.9‰**

Changes in deep Arctic oxygenation will further impact benthic denitrification rates and the isotopic effect they impart onto the water column.

Conclusions

- **Sea-ice coverage and shelf processes modulate subsurface nutrient pools of the Central Arctic halocline.**
- **Oxygenation of deep Arctic basins is sensitive to future changes in surface primary productivity. However the rate of change will differ between the 3 basins**
- **Many questions still to be answered: Which basin it the most sensitive to change? Why does the isotope method show more regenerated nitrate than the stoichiometry method? Why does benthic denitrification have an isotopic effect only in Makarov?**

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References:

- Anderson L. A., 1995. *Deep Sea Research, Part I*, 42(9), pp.1675–1680
- Casciotti, K. and Buchwald, C. 2012. *Frontiers in Microbiology*. 3
- Granger, J. et al., 2011. *Journal of Geophysical Research: Oceans*, 116(11), pp.1–18
- Granger, J et al., 2018. *Journal of Geophysical Research: Oceans*
- Gruber, N. and Sarmiento, J. 1997. *Global Biogeochemical Cycles*. 11(2), pp.235-266
- Rudels, B.,et al., 2013. *Ocean Science*, 9(1), pp.147-169
- Sigman, D.et al., 2001. *Anal. Chem.*, 73, pp.4145–4153