

# Carbon-limitation in a carbon-rich system: seasonal limitation of benthic denitrification in the coastal northern Baltic Sea

Hellemann D<sup>1,2\*</sup>, Aalto SL<sup>3</sup>, Asmala E<sup>1,2,4</sup>, Kiljunen M<sup>5</sup>, Koch B<sup>6</sup>

<sup>1</sup>Ecosystems and Environment Research Unit, University of Helsinki, Helsinki, Finland; <sup>2</sup>Tvärminne Zoological Station, University of Helsinki, Hanko, Finland; <sup>3</sup>National Institute of Aquatic Resources, Technical University of Denmark, Hirtshals, Denmark; <sup>4</sup>Geological Survey of Finland, Espoo, Finland; <sup>5</sup>Department of Biology and Environmental Science, University of Jyväskylä, Jyväskylä, Finland; <sup>6</sup>Department of Ecological Chemistry, Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany; \*dana.hellemann@helsinki.fi, @DanaHellemann.

## Background

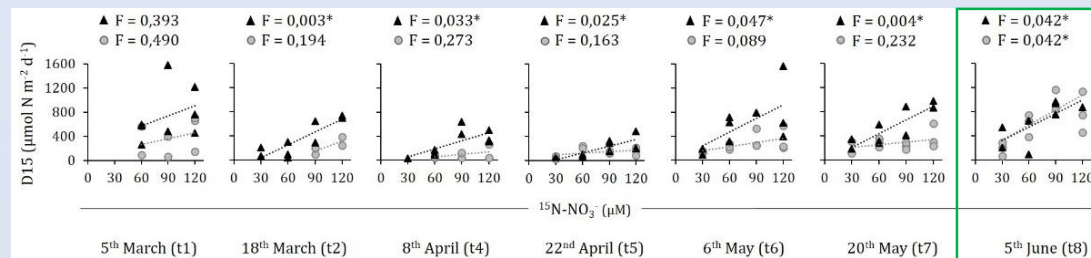
Early spring organic carbon (OC) limitation of benthic denitrification at the northwestern Gulf of Finland has been suggested by Hellemann et al. 2020, Bartl & Hellemann et al. 2019, Jäntti et al. 2011, and Hietanen & Kuparinen 2008, based on **non-significant correlation of D15-denitrification with  $^{15}\text{N-NO}_3^-$  tracer when applying the Isotope Pairing Technique** (Nielsen 1992), indicating that (i) the denitrification layer was not  $\text{NO}_3^-$  limited, thus (ii) denitrifying bacteria were not properly active. We hypothesize, that the available OC in this OC-rich system degrades over winter in such a way that it limits heterotrophic microbial metabolism until fresh OC becomes available again, e.g. via the annual spring bloom.

## Approach

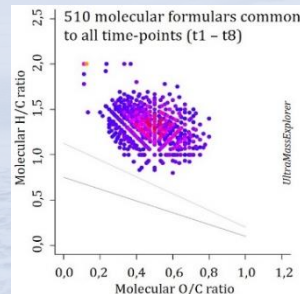
Samples were taken bi-weekly from photic and aphotic sites in the Tvärminne Archipelago pre- to post-spring bloom (March–June 2020) to follow the effect of fresh OC availability on denitrification, measured both 'in situ' and after addition of 1 mM glucose as very labile OC source. Benthic OC-quality was analyzed via natural isotopes, Fourier-transform mass spectrometry (FTMS), and optical measures.

## Results & Discussion

Aphotic site (phytoplankton is main source of benthic OC):



D15-denitrification in unamended 'in situ' sediment did not correlate significantly with  $^{15}\text{N-NO}_3^-$  tracer until beginning of June, whereas D15-denitrification in glucose-amended sediment correlated significantly with tracer from 18<sup>th</sup> March onwards ( $F \leq 0,05^*$ ), **proving OC-limitation of denitrifying bacteria throughout early spring**. The end of limitation in June followed the peak concentration of sediment Chl a on 20<sup>th</sup> May, suggesting that the bacteria were lacking sufficient availability of high quality OC, which, however, was not visible in CN-ratio ( $7,6 \pm 0,1$ ) or  $\delta^{13}\text{C-POC}$  ( $-23,2 \pm 0,2 \text{ ‰}$ ).



Currently, the FTMS-derived molecular composition of pore-water dissolved organic matter is used to characterize the benthic OC-quality at each time-point, using the molecular formulae common to all time-points as base for comparison. *Preliminary* results indicate differences in the nominal oxidation state of OC (LaRowe & Van Cappellen 2011), which leads to differences in the energy gain during OC oxidation, affecting heterotrophic microbial metabolism.

Photic sites (phytoplankton and microphytobenthos are sources of benthic OC):

Denitrifying bacteria were not limited by labile OC.

## Conclusion

Denitrification in coastal sediments that receive OC mainly from phytoplankton was OC-limited in early spring before the input of fresh spring bloom matter, likely due to molecular-level degradation of OC-quality over the winter.

Denitrification in coastal sediments that receive OC from both phytoplankton and microphytobenthos was not OC-limited in early spring, likely due to a more constant fresh OC supply from microphytobenthos.

Microbial bioavailability of OC cannot necessarily be derived from traditional measures of OC-quality, such as natural isotopes or CN-ratios.

The shown seasonally limited denitrification activity in a substantial part of coastal sediments needs to be taken into account when calculating annual budgets of nitrogen-turnover in the northern Baltic Sea.

*All results shown are still unpublished.*

## Acknowledgement



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