EGU22-11261, updated on 16 Aug 2022
https://doi.org/10.5194/egusphere-egu22-11261
EGU General Assembly 2022

Investigation of the potential use of the supersaturation ratio of N_2 (ΔN_2) for the estimation of the seasonal and spatial variability of denitrification and anammox in the water column of the Baltic Proper

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Denitrification and anammox are the main nitrogen (N) removal pathways in seawaters. Both processes are important in regions, such as the Baltic Sea, which receive high nutrient loads, that enhance primary production and eutrophication. The Baltic Sea is also characterized by a strong vertical salinity gradient and the presence of a permanent halocline hampering mixing in the water column and ventilation of the deep water layers. Rare events of deep water renewal, together with high oxygen consumption, lead to suboxic and anoxic conditions in the Baltic Sea, which are favorable for denitrification and anammox – processes for which the end product is a non-reactive N_2. In seawater, the concentration of dissolved gases is controlled by biological and physical processes. The latter can be traced by measuring inert gases such as argon (Ar). Hence, the N_2/Ar ratio can be used to separate physical and biological effects influencing N_2 fields. This approach may suit especially to the stratified water bodies, where deep waters are separated from the surface water layer influenced by the gas exchange with the atmosphere.

The study aimed at investigating the potential use of the supersaturation ratio – ΔN_2 as a tracer of denitrification and anammox processes in the water column of the Baltic Proper. The ΔN_2 ratio was derived as an anomaly from the N_2/Ar ratio in seawater being at equilibrium with the atmosphere. The used technique was Membrane Inlet Mass Spectrometry, which allows performing high-precision measurements of dissolved N_2 and Ar in water (masses 28 and 40 were detected, respectively). Seawater samples were collected between 2017 and 2021 from nineteen stations, including Gdańsk, Gotland, and Bornholm Deeps.

The ΔN_2 indicated N_2 accumulation in the oxygen minimum zones below the halocline with the highest values found in the bottom layers. This can be explained by both denitrification and possibly anammox in the water column and with N_2 release from sediments. ΔN_2 values ranged from 1.0 to 32.6 μmol L^{-1}. In autumn 2021 a significant difference in ΔN_2 ($p = 0.0008$) between the studied sites was observed. For example on station located in Gotland Deep ΔN_2 values were in the range from 17.6 to 32.6 μmol L^{-1}, while on station located in the Central Baltic Proper the maximum was 6.1 μmol L^{-1}. The seasonal ΔN_2 changes (autumn, spring, and winter) were

investigated for two stations located in the Gdańsk Deep and indicated statistically significant variability ($p=0.0077$) with the highest ΔN_2 observed in winter. Additionally, ΔN_2 was negatively correlated with nitrate ($R^2=0.5469$) and oxygen ($R^2=0.6382$), positively with phosphate ($R^2=0.4382$) and ammonium ($R^2=0.2898$), while no clear dependency was observed for nitrite ($R^2=0.0388$).

The presented study was the first attempt performed on such a large scale in the Baltic Proper. It demonstrates a high potential in the use of supersaturation ratio for identification of the active sites for denitrification and anammox processes.

The results were obtained within the framework of the statutory activities of the Institute of Oceanology Polish Academy of Sciences and the research project: 2019/34/E/ST10/00217 funded by the Polish National Science Centre.