

Apparent isotope effects of N₂O during denitrification in two basins with differential mixing

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Nitrous oxide (N₂O) is a potent greenhouse gas with increasing atmospheric mixing ratios. Lakes play an uncertain role regarding their contribution to global N₂O emissions due to a large spatial and temporal heterogeneity. A better understanding of N₂O dynamics in lacustrine systems is needed.

Stable isotopes, $\delta^{15}\text{N}^{\text{bulk}}$ and site-specific $\delta^{15}\text{N}$, of N₂O are powerful tools to investigate N₂O production and consumption processes such as nitrification, nitrifier denitrification or denitrification. Towards a better comprehension of N₂O isotope signature generation and fractionation, we studied N₂O isotope systematics in the meromictic North (NB) and the monomictic South Basin (SB) of Lake Lugano, Switzerland, over one seasonal cycle. In the oxic water column of both basins, N₂O carried a clear signal of nitrification, characterised by a site preference ($\text{SP} = \delta^{15}\text{N}_{\text{center}} - \delta^{15}\text{N}_{\text{outer}}$) ranging from 28.2 to 35.6‰.

Denitrification (i.e. N₂O reduction) dominated N₂O isotope dynamics in the sub-/anoxic water column in both basins, accompanied by normal apparent isotope effects ϵ for SP ($\epsilon_{\text{SP}} = 21.6 \pm 4.7\text{‰}$ for NB and $5.4 \pm 2.6\text{‰}$ for SB) and $\delta^{18}\text{O}$ ($\epsilon_{18\text{O}} = 8.0 \pm 1.5\text{‰}$ for NB and $4.1 \pm 2.4\text{‰}$ for SB). An inverse apparent isotope effect for $\delta^{15}\text{N}^{\text{bulk}}$ of $-7.0 \pm 1.1\text{‰}$ was found throughout the entire year in the hypoxic to euxinic waters of the NB. The SB showed an inverse apparent isotope effect for denitrification only during summer stratification, when the bottom water turned anoxic ($\epsilon_{15\text{N}^{\text{bulk}}} = -9.3 \pm 1.6\text{‰}$). This inverse isotope effect for $\delta^{15}\text{N}^{\text{bulk}}$ contrasts pure culture studies and marine field studies commonly yielding a normal $\epsilon_{15\text{N}^{\text{bulk}}}$ for N₂O consumption. The observed inverse isotope effect during net N₂O consumption in Lake Lugano may likely be due to simultaneously occurring N₂O production during net N₂O consumption or potentially caused by a non-canonical/non-bacterial denitrification process producing differential isotopic patterns. This will be investigated in further experiments.