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A high-resolution passive sampling technique for nitrate isotopologues using thin-film gels

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Nitrate transport across interfaces is an area of high interest for hydrology, oceanography, atmospheric and cryospheric sciences. For example, the interfaces between aquifers and rivers or lakes have been identified as biogeochemical hotspots with steep redox gradients. However, a detailed understanding of the spatial heterogeneity and potential temporal variability of these hotspots, and the consequences for nitrogen processing, is hindered by a paucity of adequate measurement techniques.

A novel methodology is presented here, using Diffusive Equilibrium in Thin-film (DET) gels as high-spatial-resolution passive-samplers of $\delta(^{15}\mathrm{N}, \mathrm{NO_3^-})$ and $\delta(^{18}\mathrm{O}, \mathrm{NO_3^-})$ to investigate nitrogen cycling. Fractionation of nitrogen and oxygen isotopes during diffusion of nitrate through the DET gel was determined using varying equilibration times and nitrate concentrations. This demonstrated that nitrogen and oxygen isotopes do not fractionate when sampled with a DET gel. $\delta(^{15}\mathrm{N})$ from the DET gels ranged between (2.3±0.2) and (2.7±0.3) ‰ for a nitrate stock solution value of (2.7±0.4) ‰. $\delta(^{18}\mathrm{O})$ ranged between (18.3±1.0) and (21.5±0.8) ‰ for a nitrate stock solution value of (19.7±0.9) ‰. Nitrate recovery and isotope values were independent of equilibration time and nitrate concentration.

An additional in situ study showed that nitrate concentration and isotopes provide unique, high-resolution data that enable improved understanding of nitrogen cycling in sediments. This technique could be easily extended to other condensed media such as soils or ice matrices.ch as soils or ice matrices.