

Isotopic Insights into Nitrogen Cycling in the Rifle Subsurface

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Nitrogen is a key nutrient supporting microbial activity in the subsurface sediments. The biological availability of nitrogen is dependent on several important processes including nitrogen fixation (conversion of atmospheric N₂ to ammonia), nitrification (conversion of ammonia to nitrate) and denitrification (anaerobic reduction of nitrate to N₂). Other processes include assimilation by microbes, oxidation of various intermediates and anammox (anaerobic oxidation of ammonia and nitrite to N₂). Isotopic measurements of the different reactants, intermediary compounds and products are very useful for distinguishing the occurrences of these different processes in nature. As part of the LBNL SFA at the Rifle site in western Colorado, we have been monitoring the concentrations and isotopic compositions of N₂O, an important intermediary in several of the processes listed above, in soil gas samples collected from the unsaturated zone. In addition, measurements of the concentrations and isotopic compositions of nitrate in pore water from the same wells have also been done. These samples were collected from suction lysimeters installed in the Rifle vadose zone with sampling ports at 0.5 m intervals down to the groundwater table. During the late spring/early summer, snowmelt causes the level of water in the adjacent Colorado River and groundwater to increase by as much as 2 m, inundating the lower sampling ports. During and just after this high-water episode, the concentrations of N₂O in soil gas from the deeper intervals increase to as high as 39 ppmv (versus normal background concentrations of ~5-10 ppmv). Coinciding with these sharp increases in N₂O is a decrease in pore water nitrate concentrations from >5mM to <1mM in the deeper sampling ports. $\delta^{15}\text{N}$ values of the nitrate increased from a background composition of approximately 2‰ to as high as 13‰ during the groundwater level rise before slowly recovering to background compositions. Conversely, the $\delta^{15}\text{N}$ of the N₂O decreased from background compositions averaging about -5‰ to as low as -16‰ before slowly increasing to background. Despite the changes in the difference between the nitrogen isotopic compositions of the N₂O and nitrate ($\Delta^{15}\text{N}_{\text{Nitrate-N}_2\text{O}} = 10\text{‰}$ in the winter and ~30‰ following the rise in the water table), the isotopic compositions are consistent with denitrification being the primary source of the N₂O. The changes in the concentrations and nitrogen isotopic compositions of the nitrate and N₂O suggest that slow build up of pore water nitrate occurs during fall through early spring with low levels of denitrification to N₂O and subsequent denitrification of the N₂O to N₂. During the water level rise and shortly thereafter, flooding of the lower vadose zone rapidly depletes the pore water nitrate, producing a pulse of low $\delta^{15}\text{N}$ N₂O.