Tales from the Crypt(ic): The Phantoms of the Nitrogen Cycle

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The nitrogen cycle is one of the most complex biogeochemical cycles due to nitrogen's nine redox states ranging from -3 to +5. The most stable nitrogen oxidation states in nature are -3, 0, +1, +3, and +5. Cryptic intermediates, such as hydroxylamine (NH_2OH; -1) and nitric oxide (NO; +2), occur fleetingly. Transient detection of pico- to nano-molar abundances of NH_2OH and NO in soils, coastal seawater, and oxyclines suggests the existence of a hidden nitrogen cycle originating from "leaky" microbial pathways. The fate of these leaked intermediates remains unclear. Laboratory experiments suggest that NH_2OH and NO are rapidly converted to more stable gaseous forms (e.g. N_2O and N_2) in the presence of particulate oxidized manganese and soluble ferrous iron, respectively. New approaches, such as isotopic site preference between the two nitrogen atoms in N_2O and meta-omics sequencing, may aid in the difficult task of discriminating between biotic, abiotic and coupled biotic-abiotic processes in the nitrogen cycle (Zhu-Barker et al., 2015). While abiotic and biotic NH_2OH oxidation have identical nitrogen isotope site preference, we found that abiotic NO reduction to N_2O via Fe^{2+} oxidation yields a site preference value in between that of ammonia oxidation and bacterial denitrification. We also observed kinetic oxygen isotope fractionation during abiotic NO reduction to N_2O, a potentially recognizable signature for distinguishing N_2O production via enzymatic vs. "chemo-" denitrification of NO. Turning to omics datasets, we observed that maximal transcription of genes involved in NH_2OH and NO production was co-incident with the peak in N_2O overlying the Eastern Tropical North Pacific oxygen minimum zone. Integrating these results, we theorize that abiotic reactions between reactive intermediates, catalysed by chemical constituents such as metals or organic matter, may cryptically link canonical pathways in the nitrogen cycle.

Zhu-Barker X, AR Cavazos, NE Ostrom, WR Horwath, JB Glass. 2015. The importance of abiotic reactions for nitrous oxide production Biogeochemistry 126:251-267