Nitrogen cycling in Yellowstone National Park thermal waters

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Sedimentary rock derived from organic-rich depositional environments can be an ecologically-significant source for nitrogen. In Yellowstone National Park, geologic sources for nitrogen include Mesozoic marine sedimentary rocks (50 to 240 mg N kg^{-1}), Eocene lacustrine deposits, and glacial deposits. Geologic nitrogen is transferred to thermal waters primarily in the form of ammonium ($NH_4^+{}_{(aq)}$ + $NH_3^0{}_{(aq)}$). Geothermal processes, including enhanced dissolution at high temperatures, sorption to clays, boiling, volatilization of $NH_3^0{}_{(aq)}$, recondensation of $NH_4^+{}_{(aq)}$ into vapor-dominated vadose zones, and mixing of meteoric and hydrothermal waters, result in a broad range ammonium concentrations (<0.3 µM to 46 mM N-NH_4^+). The highest ammonium concentrations are in fluids that are derived from 1) meteoric waters with hot gas discharge and 2) from hydrothermal waters with subsurface boiling and hot gas discharge. Release of H^+ through H_2S oxidation with gas discharge results in increasing N-NH_4^+ with decreasing pH. The isotopic composition of dissolved ammonium is highly variable ($\delta^{15}N$ = -6‰ to +30‰) in comparison to the presumptive Mesozoic source material (+1‰ to +7‰ $\delta^{15}N$) and hydrothermal $\delta^{15}N$ values are positively correlated with pH, reflecting extensive isotopic fractionation of nitrogen through multiple processes.

Elevated ammonium concentrations can persist for 10s of meters or more in thermal water drainages, with the formation of trace nitrogen species NO_2^- and N_2O through nitrification and denitrification. In Nymph Creek, ammonium concentrations decreased from 92 to 74 µM N-NH_4^+ over 148 m from the acidic (pH 2.9) source vent, with the isotopic composition of ammonium increasing from +6.9‰ to +7.3‰ in the first 25m of the drainage, consistent with the microbial transformation of ammonium. Drainage from a circumneutral (pH 6.5) thermal feature in the Washburn Hot Springs group with 15.8 mM ammonium exhibited greater isotopic fractionation (22.1‰ to +25.1‰), reflecting the incomplete oxidation of a much larger pool of reduced nitrogen. Isotopic evaluation of nitrogen cycling and biologic uptake in thermal drainages should account for variations in source characteristics, as well as subsequent isotopic alterations.