Quantifying rock-nitrogen export from a shale hillslope to floodplain in the East River watershed, Colorado

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Subsurface rock-nitrogen (N) is unaccounted for in most models of N cycling, despite evidence of its return to Earth's surface. Most previous evidence comes from weathering and erosion on exposed surfaces. Weathering below the soil and its contributions to N cycling has been overlooked because direct measurements are rare and challenging. We conducted a study in the East River watershed, part of a much broader area underlain by Mancos Shale. Four deep boreholes were drilled into parent bedrock along a hillslope for sediment characterization and instrumentation for depth- and time-resolved hydrologic and pore water geochemical measurements over two years. We identified two rock-N release processes. One is the result of rock-organic matter (OM) weathering dissolution, and the other is cation exchange of rock-NH_4^+ being displaced by Ca^{2+} (also released by weathering). These processes occur primarily within the zone undergoing seasonal water table fluctuations, which we defined as the weathering zone. We also found that NO_3^- concentrations in the weathering zone pore waters are disproportionally high, resulting from nitrification of shale weathering-released N. Advected by seasonally varying water fluxes, the calculated rock-N exports to the floodplain exceed the predicted fluxes from atmospheric deposition. These findings are also supported by δ^{14}C-DOC ages, $\delta^{15}N/\delta^{18}O$-$NO_3^-$ isotope compositions, and DOM compound classes and abundance (FTICR MS).