Geogenic aqueous uranium in an alluvial aquifer

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Groundwater contamination with naturally occurring Uranium (U) has been identified across the US. Groundwater carrying oxidants, such as O_2 and NO_3^-, can lead to the oxidative dissolution of reduced U(IV) yielding mobile aqueous U(VI). Groundwater U and NO_3^- has been demonstrated to co-occur throughout the High Plains. In one particular alluvial aquifer serving as the sole municipal drinking water source for 25,000 people U and NO_3^- concentrations ranged from 1.0 - 345.0 ug L^{-1} and 2.0 - 50.8 mg L^{-1}, respectively. In an effort to geochemically characterize sedimentary U and assess U mobilization potential, groundwater and sediment cores were collected from two boreholes (0 - 55 m). Vadose zone soils maintained oxidized and reduced U (40 - 94% U(IV)). However the majority of the U in sediments below the water table (33.5m), was identified as U(IV) (79 - 95% U(IV)). Groundwater was suboxic (Eh, -100 to +200 mV, O_2 2.1 to 6.8 mg L^{-1}) with U(VI) concentrations determined by KPA ranging from 5.0 - 20.4 ug L^{-1}. Alkalinity in groundwater ranged from 260 to 406 mg L^{-1} (as HCO_3^-). Geochemical simulations using major ion chemistry, mineral equilibrium, and surface complexation PHREEQC models identified calcium-uranyl-carbonate complexes ($Ca_xUO_2(CO_3)_3^x$) as dominant U species in groundwater. Simulations also indicated insignificant U adsorption (< 5%) to mineral surfaces. Thus, desorption is likely not a mechanism mobilizing U rather, the co-occurrence of oxidants, O_2 and NO_3^-, likely drives U mobilization via oxidative dissolution. Organic carbon buried in the sediments (0.01 - 0.3%) and dissolved in groundwater (0.8 - 5.4 mg L^{-1}) could serve as a redox buffer promoting U(VI) reduction and immobilization. However, changes in O_2 or NO_3^- concentrations could alter kinetics promoting oxidation. These results indicate that alkalinity alone is not the primary factor controlling U mobility and suggests oxidative dissolution as a mechanism contributing to geogenic U mobilization of groundwater.