ABSTRACT: Few effective remedial technologies exist to remove or immobilize uranium in situ in a highly contaminated acidic aquifer at the Integrated Field Research Challenge (IFRC) site in Oak Ridge, Tennessee. This research was conducted to evaluate geochemical pH controls on chemical speciation and immobilization of contaminant metal ions and radionuclides and microbial activity in both laboratory and field studies. We performed laboratory batch/column and field titrations and geochemical modeling to better understand and quantify the reactions governing the speciation and fate of contaminant metals and radionuclides in the subsurface. We show that the addition of strong base can provide a rapid yet effective means of sequestering U(VI), Tc(VII), and other toxic metals such as Cr(VI) and Co(II) in the soil and groundwater. Greater than 94% of soluble U(VI) can be immobilized at pH above 4.5 by the co-precipitation and/or adsorption with Al-oxyhydroxides, and the presence of sediment minerals facilitates the immobilization of these contaminants. An extended geochemical model with fewer adjustable parameters described well the concentration and speciation of metal ions and precipitates in these titration studies. In > 1-year field plot studies, the pH of recirculated groundwater was slowly increased from an ambient value of approximately 3.5 to about 5.5 in the injection well, and we observed corresponding decrease in U(VI) and Al (> 90% reduction), confirming our laboratory observations. Downgradient wells and the extraction well have shown similar behavior with approximately 80% decrease in U(VI) and Al, despite the fact that the extraction well did not exhibit a discernible change in pH. The response of the groundwater microbial communities was investigated on a monthly basis. The abundance and activity of microorganisms (oxygen consumption, denitrification) generally decreased with time in wells in which the pH substantially increased from base addition. Wells that showed a slower response to bromide tracer tests (FW115, FW130) exhibited a more variable response or no response to base addition in agreement with the smaller pH changes observed in these wells. Microbial communities are well adapted to moderately acidic pH in the OR-IFRC subsurface after decades of exposure to acidity. An elevation of pH could thus act as a stressor that inhibits microbial activity over the short term, or base addition may have unintended consequences for microbial communities. Nevertheless, our results indicate that the field plot acted as a barrier (or a sorbent) for Al, U(VI) and other toxic metals, thus validating our original hypothesis that the master variable for U(VI) and metals attenuation and microbial activity is pH. Aluminum hydrolysis and the presence of carbonates are the dominant pH buffering reaction impeding U and toxic metal precipitation and adsorption at Oak Ridge IFRC.