

Identification of Natural Attenuation Mechanisms of Hexavalent Chromium in Groundwater through Geochemical and Matrix Diffusion Evaluations

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Background/Objectives. Providing a robust conceptual site model for subsurface groundwater contamination including sources and attenuation mechanisms identification is essential to establish the appropriate strategy for effective site management and remediation options. Determinations of attenuation mechanisms and the associated rates, capacities and stability are essential to the evaluations (EPA, 2007). New technologies have recently been developed to understand matrix diffusion of organic compounds in bedrock materials and the associated long term impacts on groundwater (Parker, 2007). Applying similar concepts for hexavalent chromium in limestone and shale bedrock provided an in-depth understanding of the availability of contaminants within a source area to be released into the aquifer and natural attenuation mechanisms (Chapman, 2013).

Approach/Activities. In order to evaluate the mass transfer and attenuation mechanisms of hexavalent chromium into and out of the bedrock matrix at a former ammunition site in Kansas, a series of analyses were performed on discrete core samples collected below the former waste disposal impoundment. Core samples were first evaluated for weathering, active fractures, secondary precipitation, staining, and geochemical transitions. Discrete samples from select cores were then collected in and around existing weathered zones and fractures. Specialty analyses performed on these samples included X-ray fluorescence (XRF), electron microprobe (EMP), X-ray diffraction (mineralogy), and leachate tests to understand the relationship between chromium concentrations in the groundwater and geochemical composition of the solid bedrock matrices. Similar analyses were performed on limestone and shale samples downgradient and below the source area to evaluate attenuation mechanisms. In addition, discrete groundwater samples were analyzed for metagenomics to determine the degree of biological reduction that may be occurring. PHREEQC and CRAFLUSH modeling were used to predict the geochemical and diffusion impacts to the resultant groundwater plume.

Results/Lessons Learned. By performing discrete sample analysis on the suspected source materials and surrounding areas, we were able to determine the likely geochemical and physical processes that are causing elevated hexavalent chromium in groundwater. In particular, EMP analysis identified significant chromate secondary precipitates including copper chromate within the suspected source area which contain significant concentrations of hexavalent chromium. As a result of this precipitation and the low permeability of the bedrock matrix, the ability for aqueous hexavalent chromium to diffuse into the bedrock matrix does not appear significant. The groundwater is thus impacted by a more available precipitated chromate solid phase instead of a diffusion limited source within the bedrock matrix. The analytical techniques, especially EMP, also determined the major attenuation mechanisms and products including solid phase trivalent chromium iron oxyhydroxides and chromium containing iron sulfides and barites. The high-resolution sampling approach and application of multiple analytical tools has allowed the development of a detailed conceptual site model and robust remediation strategy evaluation. Based on these results, an approach to aggressively remediate the primary source

area associated with these precipitates is being implemented to reduce mass flux to groundwater. Based on the low hydraulic gradient at the site, natural attenuation is likely to play a significant role in the final remedy once the mass flux is reduced.