Isotope enabled Reactive Transport Model Describes Cr Reduction via Biogenic Ferrous Iron in Chromium Contaminated Groundwater

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Chromium (Cr) is a commonly used element in many industries, such as paint and steel manufacturing, and tannery. Oxidised chromium (Cr(VI)) is soluble in water and is carcinogenic. Cr(VI) can be reduced to Cr(III), which is less toxic and sparingly soluble, making the reduction of Cr(VI) an effective remediation strategy. Sukinda Valley, in eastern India, supplies over 95% of India's domestic Cr from mining the Sukinda ultramafic complex [1]. Chromite mining operations in the region have resulted in mining overburden that has leached Cr(VI) in the groundwater supply in the valley. Subsequently, Cr(VI) concentrations in groundwater have been found to be up to 115.2 mg/l, well beyond recommended safe limits [2].

We present an isotope enabled reactive transport model (RTM) describing the reduction of Cr(VI) to Cr(III) via a redox couple with biogenic aqueous Fe(II), formed via bacterially mediated, dissimilatory reduction of iron. Bacterial reduction of iron is stimulated through injection of acetic acid. Our model includes Mn(III) associated with goethite in the sedimentary rock which can reoxidise Cr(III). We use the Cr isotope fractionation that accompanies the reduction of Cr(VI) to track remediation progress in terms the modification of the $\delta^{53/52}$ Cr in the groundwater. We use our model to explore the impact that stimulating dissimilatory iron reduction has on the remediation of Cr(VI) as well as on changes to the fluid composition and mineralogy through space and time.

We also report how machine learning enhanced sensitivity analysis [3] was able to direct and support both model development and the accompanying field campaign in Sukinda, by identifying key parameters to be constrained, and uncertainties in the model. Finally, we report a theoretical "optimised" remediation strategy, derived from the reactive transport model that would reduce the most Cr(VI) as quickly as possible, and immobilise it as solid Cr(III).

[1] Das, A. P., & Mishra, S. (2010), *Journal of carcinogenesis*, 9.

[2] Naz, A., Mishra, B. K., & Gupta, S. K. (2016), *Exposure and Health*, 8(2), 253-264

[3] Fotherby et al. (2022), *in review*