

Moving beyond mineral solubility: Physical and hydrologic constraints on Cr(VI) formation

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Chromium(VI) produced from the oxidation of indigenous Cr(III) minerals is increasingly being recognized as a threat to groundwater quality. Predicting vulnerable environments, however, remains a challenge as groundwater Cr(VI) concentrations can vary greatly even within a given aquifer due to physical and hydrologic heterogeneity. A critical determinant of Cr(VI) generation within soils and sediments is the necessary interaction of two low solubility phases that lead to its production: Cr(III) silicates or (hydr)oxides and Mn(III/IV) oxides. However, it remains unknown to what extent the physical structure of soils may control Cr(VI) production by dictating the separation distance between reactive phases, determining the diffusion distance from Cr(VI) generation sites to advecting groundwater, or regulating infiltration rates and porewater velocity. In this study, we use a dual-pore domain model to investigate the relative control of these parameters, together with Cr-mineral solubility. Indeed, the reaction distance between Cr(III)-bearing minerals and Mn oxides predominantly controls Cr(VI) export to advecting groundwater. Changes in diffusion distance between sites of Cr(VI) generation and advective flow channels has little impact on steady-state Cr(VI) concentrations, but long diffusion distances may suppress Cr(VI) transport under fluctuating hydrologic and biogeochemical conditions by increasing the time required for groundwater Cr(VI) concentrations to reach steady-state. Finally, we show that high porewater flow velocities effectively dilute Cr(VI) diffusing from soil/sediment aggregates, thus minimizing Cr(VI) export relative to lower porewater velocities. In combination, our results recommend consideration of factors beyond Cr(III)-mineral solubility when predicting Cr(VI) production within soils and sediments. Physical and hydrologic controls on Cr(VI) production appear to be capable of overwhelming the impact of Cr(III)-mineral solubility in soils and sediments.