

# Cr(VI) ADSORPTION ON ORGANIC RICH SOIL FROM KLEINSTUCK MARSH, KALAMAZOO, MI

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## Abstract

Chromium is a highly toxic chemical species that has leaked into natural systems via many industrial processes. There is much about Cr(VI) bioavailability and mobility that remains poorly understood, but past studies have demonstrated that Cr(VI) is typically mobile in the environment. Cr(VI) mobility can be diminished via adsorption onto sediments, especially sediments containing reduced organic matter, iron (FeII) or manganese (MnII) because these can reduce Cr(VI) to Cr(III) which is more readily sorbed. The objective of this study is to measure the adsorption of Cr(VI) onto organic-rich sediment as a function of pH, time and after step-wise removal of operationally defined sediment fractions.

Sediment cores (10 replicates) were collected to a depth of 50 cm with a Russian peat corer from Kleinstuck Marsh, a minerotrophic fen in Kalamazoo, MI. The upper 10 cm and the lower 10 cm of each core was separated and combined with the same depth interval from the other cores, homogenized in ziplock bags, and promptly freeze-dried. A 4-step sequential extractions procedure [1] was used to selectively remove exchangeable, carbonate, reducible, and oxidizable fractions. Supernatants from each extraction step were analyzed for a suite of metals via ICP-OES. The bulk sediment, together with sediment remaining after each progressive sequential extraction were used to measure Cr(VI) adsorption as a function of pH and time. Adsorption was tested using kinetic edge experiments in which 1 g/L sediment, 10<sup>-5</sup> M Cr(VI), and 0.01 M NaNO<sub>3</sub> were combined in 15 mL plastic centrifuge tubes. Each tube was titrated to a particular pH (spanning 3-10) and placed on a shaker. After 24 hr, 48 hr, 1 week, and 2 weeks, pH was retested in each tube and subsamples (~15 mL) were removed, centrifuged, syringe-filtered (0.2 µm) and the supernatant tested for Cr(VI) and total Cr, using the colorimetric diphenylcarbazide procedure and ICP-OES, respectively. For all sediments except those with the oxidizable fraction removed, Cr(VI) sorption edges are very similar, with nearly 100% sorbed below pH 4, decreasing to less than 5% sorbed above pH 7. In contrast, adsorption is greatly diminished with removal of the oxidizable fraction: after 2 weeks, a maximum of 50% Cr(VI) is sorbed at pH 3, with <20% sorbed between pH 4 and 7. This suggests that much of the Cr(VI) binds to organic matter or other reduced fractions of the soil (e.g. Fe(II)-bearing clays). For all experiments, sorption increased significantly for the first week, with much smaller increases between 1 and 2 weeks. For pH 3-6.5, agreement between colorimetric and ICP data suggests that Cr in solution was primarily Cr(VI). Above pH 6.5, however, there is an increasing divergence between ICP and colorimetric data, demonstrating that up to 40% of the Cr at alkaline pH is reduced to Cr(III) and released into solution. These data will be used to develop surface complexation models, based on both the component additivity and composite sediment approaches.

[1] Tessier, Campbell and Bisson (1979) *Analytical Chemistry* **51**, 844-851.