Effect of Oxygenation on Speciation, Behavior, and Fate of Chromium in Estuarine Sediments

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The main objective of this research is to determine the conditions that favor toxic hexavalent chromium (Cr^{VI}) formation in estuarine sediments upon oxidation of the relatively non-toxic trivalent chromium (Cr^{III}). Grab surficial sediments were collected from various locations in the Baltimore Harbor and characterized for total metals, total organic carbon (TOC), and acid volatile sulfides (AVS). Cr speciation performed using EPA methods 3051A and 3060A in conjunction with our HPLC-ICP-MS analytical technique revealed that Cr in these sediments is predominantly precipitated Cr^{III} – $Cr(OH)_3(s)$ and/or $Cr_xFe_{1-x}(OH)_3(s)$ with concentrations varying from 68 – 1050 µg/g dry wt. Continuously-mixed batch reaction experiments were performed to examine the influence of sediment oxygenation and mimic possible biogeochemical changes resulting from sediment resuspension during flood events, dredging activities, and bioturbation. In these batch reaction experiments, anoxic sediment suspensions were spiked with aqueous Cr^{III} and simultaneously aerated to monitor for Cr^{VI} formation. Cr^{VI} formed in 11 of the 16 sediment samples under aerobic conditions but not under anaerobic conditions. The rate of Cr^{VI} formation correlated negatively with the AVS concentration in the sediments and positively with the porewater-manganese / AVS ratio indicating that the long-term persistence of Cr^{VI} is a function of the sediment reductive capacity despite the ability of these sediments to oxidize Cr^{III}. In another set of batch reaction experiments, Cr^{VI} reoccurrence was observed following the oxygenation of Cr^{VI}-spiked anoxic sediment suspensions after the spiked Cr^{VI} was completely reduced to Cr^{III} under anaerobic conditions. The findings from this research suggest the need to monitor long-term stability of Cr^{III} under changing biogeochemical conditions in Cr contaminated sediments and soils.

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