Uranium(VI) binding by dissolved organic matter: Influence of water chemistry and dissolved organic matter properties

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Dissolved organic matter (DOM) influences uranium speciation in aquatic environments. Little is known about the effects of water chemistry and DOM quality on the uranyl-DOM complexation strength. Additionally, experimental evidence on the functional groups that drive U(VI) binding under various environmental conditions is limited. In this study we used hydrophobic organic acid (HPoA) fractions of natural DOM and an unfractionated DOM sample to investigate the influence of DOM quality, pH, calcium concentration, and the U:DOM ratio on conditional U(VI)-DOM binding constants (K^c_{DOMU}) by means of a modified equilibrium dialysis ligand exchange approach. Conditional binding constants for eight HPoA samples isolated from different natural waters were found to be relatively constant, although the HPoA samples differed with respect to elemental composition and aromaticity. However, conditional K^c_{DOMU} constants strongly increased with higher pH values. At pH 6, calcium is shown to effectively compete with uranium for weak binding sites, which results in lower K^c_{DOMU} values if calcium concentrations increase. Differences in U:DOM ratio of four orders of magnitude translate to K^c_{DOMU} values ranging from $10^{4.5}$ to $10^{6.6}$ (L g^{-1}) at pH 6 and 0.05 M ionic strength. The results of this study provide experimental evidence that U(VI)-DOM binding is predominantly achieved by acidic oxygen containing moieties. At weak binding sites, U(VI) is bound by Coulombic attraction or complexed to monocarboxylic groups. Strong binding sites, however, consist of chelate forming groups that bind U(VI) in a multidentade complex. Binding strength with porewater from a uraniferous peatbog showed similar U(VI) binding strength as the HPoA fractions. The derived binding constants are independent of DOM fraction and can hence be transferred to natural systems with sufficient reliability.