

4.62.14

Sorption of nitroaromatic compounds (NAC) by smectite clay: Geochemical modulation of NAC bioavailability and toxicity

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Nitroaromatic compounds are prominent soil contaminants and potent mutagens. We recently conducted studies on the adsorption mechanisms of NACs by K⁺-saturated smectite clays using macroscopic sorption measurements, thermodynamics, Fourier Transform spectroscopy, X-ray diffraction, quantum calculations and molecular dynamics simulations. Our results indicate that the strong adsorption of NACs on K-clays results from the complexation of –NO₂ groups with the interlayer K⁺ ions and the energy gained by partitioning of these nitroaromatics into the subaqueous environment of the clay interlayers where the sparingly soluble organic compounds are less hydrated than in bulk water. In contrast, adsorption on Ca²⁺-saturated smectite clays was less favorable, presumably because of the greater hydration of Ca²⁺ (vs. K⁺). Cation hydration determines the interlayer distance and hence degree of solute dehydration upon sorption, size of adsorption domains, and ability of –NO₂ groups to complex directly with interlayer cations. The strong influence of cation type on sorption suggests the use of simple ion (e.g., K⁺/Ca²⁺) exchange to manipulate the mobility and the availability of NACs in smectitic soils or geosolids amended with smectite clays. We content that the base-saturation status of clays can be used as geochemical control on the bioavailability/toxicity of energetics during remediation.

4.62.15

Iron (hydr)oxides and electron shuttles govern the fate of 2,4,6-trinitrotoluene by a soil bacterium

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Contamination of surface and subsurface environments with nitroaromatics such as 2,4,6-trinitrotoluene (TNT) is a worldwide problem. Numerous studies have investigated the (bio)transformation of nitroaromatics in aqueous suspensions. In subsurface environments, however, the presence of soil constituents such as iron phases and natural organic matter can have a significant influence on the fate, rate and extent of reaction of pollutant metals and organics. Batch studies with a *Cellulomonas* sp. strain ES6 in the presence of iron phases (hematite, magnetite and ferrihydrite) and the electron shuttle anthraquinone-2,6-disulfonate (AQDS) were conducted to reveal biotic and abiotic mechanisms contributing to the degradation pathway of TNT. AQDS was included as an electron shuttle to facilitate the bioreduction of the iron phases. Mineral phases were characterized by scanning and transmission electron microscopy (SEM and TEM) and by selected area electron and X-ray diffraction (SAED and XRD). The initial characterization of the synthetic ferrihydrite revealed that it matched the diffraction pattern of 6-line ferrihydrite. The 6-line ferrihydrite was still identifiable after 2 weeks of incubation; however, a secondary iron mineral phase had been produced in the inoculated samples. The formed secondary iron mineral phase was identified to be hematite (α -Fe₂O₃). Semi-quantitative XRD analysis indicated that the transformation of ferrihydrite to hematite was more than three times higher in the presence of AQDS. Bioreduction of ferrihydrite had a significant impact on the degradation of TNT. On the one hand, we found that the initial reduction rate of TNT was slightly decreased in the presence of bioreducible iron(III) phases, probably due to competition for electrons by Fe(III) and TNT. On the other hand we found that the reduction rates of the produced TNT metabolites were significantly enhanced in the presence of iron(III) phases. Based on abiotic experiments with ferrihydrite, the increased extent of TNT reduction was a consequence of iron mineral phase associated Fe(II). Batch systems amended with the crystalline hematite instead of the poorly crystalline ferrihydrite showed significantly lower reduction rates of Fe(III). We conclude that the absence of easily reducible Fe(III) in the hematite containing systems impacted the reduction rate and degradation pathway of TNT.