Determining the Speciation of Reactive Iron Mineral Coatings in Redox Transition Zones with Sequential Extraction

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In subsurface redox transition zones, reactive iron mineral coatings play an important role in electron transfer between bacteria and contaminants. To better understand surface chemistry and potential reaction mechanisms in redox transition zones, sequential extraction is an important tool in addressing iron speciation. In this study, sediment samples were collected from an 18.3 m anoxic core where the redox condition was preserved. Based on screening analyses using x-ray fluorescence (XRF) for sediment composition, sediment pH, sediment redox potential, VOC concentration, and abundant bacteria, two redox transition zones: the Upper Zone and Zone 1 were identified with elevated iron sulfide mineral coatings. A six-step sequential extraction process was applied to discern reduced and oxidized forms of Fe minerals in these two zones. Based on the extractions, the Upper Zone revealed amorphous Fe sulfide minerals mackinawite and greigite that increased in concentration as a function of depth while the crystalline iron sulfide pyrite decreased with depth. The abundance of amorphous iron sulfide minerals observed in the Upper Zone without evidence of VOCs suggests that in this reduced enviroment (a)biotic attenuation may be an important process. In the Zone 1, iron sulfide minerals including amorphous and crystalline forms were present at greater concentrations than Fe(II/III) and Fe(III) minerals indicating a reduced environment. Compared to the Upper Zone, Zone 1 has a greater total concentration of iron sulfide minerals. Based on reactive iron mineral coating contributions, a preliminary bench study was conducted with 1,4-dichlorobenzene, one of the dominant contaminants at the site. The time to achieve 90% dehalogenation was 202 d in the Upper zone and 52 d in Zone 1.