Determining Reactive Iron Mineral Contributions in Redox Transition Zones with Sequential Extraction

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Reactive iron minerals play an important role in electron transfer between various phases, such as microcosms, contaminants, and nutrients in redox transition zones. To better understand surface chemistry and processes in forming reactive iron minerals in redox transition zones, sequential extraction has been used to distinguish the iron speciation and minerals. In this study, a 60-foot anaerobic core collected was collected from an industrial site where the redox condition was preserved. Based on screening analyses (i.e., x-ray fluorescence (XRF), pH, redox potential, and abundant bacteria), two redox transition zones: the Upper Zone and Zone 1 were identified as potentially sulfide-rich iron minerals. A six-step sequential extraction process was applied to discern ion-exchangeable Fe^{2+}, crystalline Fe(II) minerals (siderite ($FeCO_3$), pyrite (FeS_2), and pyrrhotite (Fe_7S_8)), amorphous iron minerals (ferrihydrite ($Fe_2O_3{\cdot}0.5(H_2O)$), mackinawite (FeS), and greigite (Fe_3S_4)), crystalline Fe(III) oxides (hematite (Fe_2O_3), lepidocrocite (γ-FeOOH), and goethite (α-FeOOH)), and Fe(II)/Fe(III) mineral magnetite (Fe_3O_4). Because the varying grain size in the sediments and the need to work in the glovebox, the reaction time for extractions was examined. Extended extraction times improved recoveries up to a maximum of 21%. Based on extractions, the Upper Zone was (1) abundant in Fe(II) minerals including crystalline iron sulfide and amorphous iron minerals (Fe(II) and Fe(III)); (2) absent of ion-exchangeable Fe^{2+} in most samples; (3) lower recoveries compared to other zones and may be attributed to organically bound iron. The abundance of iron sulfide minerals demonstrated that the Upper Zone is a reduced environment where potentially abiotic dehalogenation is active. In Zone 1, reactive iron minerals included siderite, pyrite and magnetite; this zone was found to be reduced as well. Compared with Zone 1, the Upper Zone revealed a more sulfide-rich mineral coating. In addition, although a chlorobenzene gradient was observed in Zone 1, the Upper Zone was depleted of VOCs suggesting potentially a greater degree in dehalogenation. Differences in reactive iron mineral contributions for abiotic dehalogenation is being investigated in batch studies.