

Redox reactions of Fe(II)-organic complexes and Fe-bearing clay minerals

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Iron-bearing clay minerals and organic ligands are both widely found in natural environments. Under anoxic conditions, iron-reducing bacteria are known to produce aqueous Fe(II) and organic ligands, which may form redox active complexes that can directly reduce a range of environmentally relevant contaminants. Additionally, aqueous Fe(II) can reduce Fe in the structure of clay minerals and the resulting structural Fe(II) is capable of facilitating the reduction of contaminants. However, in anaerobic aquifers and soils, it is likely that combined systems of redox active mineral phases and metal-organic complexes exist, yet little is currently known concerning their reactivity.

Here, we used nitroaromatic compounds (NACs) as reactive probe molecules to assess the reactivity of our combined systems. We compared the reduction kinetics of the NAC in the presence of the Fe(II)-organic ligand complex alone to batch reactors also containing nontronite NAu-1, either in its native (oxidized) form or pre-reduced to produce a range of structural Fe(II)/Fe(tot) ratios. Our results show that Fe(II)-organic complexes were capable of reducing structural Fe in NAu-1 and the resulting structural Fe(II) was capable of reducing the NACs. We observed a linear relationship between the reduction potential (E_H) of the organic Fe(II)-complexes and the NAC reduction rate constant ($\log k$) in the mineral-free experiments. In the combined mineral-Fe(II)-complex system, we observed slower NAC reduction kinetics compared to Fe(II)-complexes only, suggesting that the aqueous Fe(II)-complexes were the dominant reactive species rather than clay mineral Fe(II). However, the previously observed linear relationship between E_H and $\log k$ did not hold in the presence of the native mineral, although E_H -values were corrected for the measured partial oxidation of the Fe(II)-complexes due to electron transfer to clay mineral Fe. Interestingly, the Fe(II)/Fe(tot) ratio of the clay mineral added to the Fe(II)-organic complex had a determinative effect on the overall observed reactivity. We are currently investigating the underlying mechanism to provide a new framework for assessing the redox reactivity of combined systems of Fe-bearing minerals and Fe-organic complexes.