Reactivity of chemical reductants as a function of redox zonation

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Abstract To determine the distribution and reactivity of chemical reductants as a function of redox zonation, the reaction kinetics for a series of probe molecules have been measured in sediments for which redox conditions have been well characterized. Redox characterization has included quantifying the major redox-active species in sediment pore waters (NO₃, Mn⁴⁺, Fe²⁺, SO₄²⁻, S²⁻, CH₄, and H₂) and the use of acid extraction to determine the major pools of Fe(II), Fe(III), FeS and FeS₂ associated with the solid phase of the sediments. Reactivity patterns determined for halogenated methanes in iron-reducing and sulphate-reducing sediments and Fe(II)-goethite and FeS model systems suggest that Fe(II) sorbed to iron oxides is the dominant chemical reductant in both the iron-reducing and sulphate-reducing sediments. Reaction kinetics of a nitroaromatic probe chemical studied in sediments as a function of redox zonation provides further evidence for the important role of Fe(II) as a reductant in sediments under iron-reducing, sulphate-reducing and methano­genic conditions.

Key words anaerobic sediment; chemical reductants; halogenated methanes; nitroaromatics; probe molecules; reaction kinetics; redox zonation; reductive transformations

INTRODUCTION

A significant effort is underway at the US Environment Protection Agency’s (EPA) National Exposure Research Laboratory to incorporate reaction kinetics and pathways for reductive transformations into environmental exposure models. This effort comes from the realization that: (a) many agrochemicals, textile dyes, pharmaceuticals, solvents and synthetic building blocks contain functional groups that are susceptible to reduction in anoxic environments; (b) many reductive transformations result in the formation of reaction products that are of more concern than the parent compound; and (c) reducing environments abound in nature (e.g. subsurface waters and soils, aquatic sediments, sewage sludge, waterlogged peats, hypolimnia of stratified lakes, and oxygen-free segments of eutrophic rivers).

Although research efforts to date have identified the types of functional groups that can react in reducing environments, our ability to predict the rates of reduction for a particular chemical in environmental systems remains quite limited. The obvious question remains: What are the sources of electrons in natural reducing environments? The cumulative knowledge in this area suggests that naturally occurring reductants are a complex array of species ranging from chemical or "abiotic" reagents through extracellular biomolecules and redox active enzymes, to microbial populations (Tratnyek & Macalady, 2000). The occurrence of chemical reductants in anaerobic
sediments and aquifers is primarily a result of the reduction of inorganic, electron acceptors coupled to the microbial oxidation of organic matter. Depending on the microbial activity, the bioavailability of organic carbon, and the availability of electron acceptors in subsurface environments, a sequence of redox zones can develop that are characterized by the respective dominant terminal electron accepting process (i.e. nitrate-, manganese-, iron-, sulphate-reducing and methanogenic). Although terminal electron accepting processes (TEAPs) can result in the direct formation of chemical reductants (e.g. $\text{SO}_4^{2-}$ reduction resulting in formation of $\text{S}_2^-$), of greater significance are the subsequent reactions or processes that lead to the formation of chemical reductants that can potentially play a role in the reductive transformation of organic pollutants. Examples include activation of Fe(II) by ligand exchange onto iron oxide surfaces (Klausen et al., 1995; Haderlein & Pecher, 1999), formation of redox active minerals such as FeS and green rust (Butler & Hayes, 2000), and the reduction of quinone functional groups in dissolved organic matter by $\text{S}_2^-$ (Perlinger et al., 1996).

To gain an understanding of how the reactivity of chemical reductants varies as a function of redox zonation as defined by the dominant TEAPs, reaction kinetics have been measured for a series of halogenated aliphatics and nitroaromatics in a number of well-characterized anaerobic sediments. The comparison of reactivity patterns (i.e. the range in reactivity and relative order of reactivity) generated for probe molecules in natural and model systems has been demonstrated as a powerful tool for the characterization of chemical reductants in natural systems (Rugge et al., 1998).

RESULTS AND DISCUSSION

Nitroaromatic reduction as a function of the dominant TEAP

Reduction kinetics were measured for $p$-cyanonitrobenzene (pCNB) in sediment slurries as a function of the dominant TEAP. pCNB has been used as a probe molecule to investigate nitroaromatic reduction in a laboratory sediment column that had been characterized with respect to redox zonation (Simon et al., 2000). Reduction of pCNB occurs through $p$-cyano-N-hydroxylaniline (pCNH) with complete reduction resulting in the formation of $p$-cyanoaniline (pCNA):

\[
\begin{align*}
\text{pCNB} & \rightarrow \text{pCNN} \rightarrow \text{pCNH} \rightarrow \text{pCNA} \\
\end{align*}
\]

Sediment was collected from a river bottom in the Athens, Georgia area. In its natural state, the sediment was aerobic. Upon incubation in sealed serum bottles, the sediment became iron reducing as evidenced by the loss of nitrate and the formation of soluble Mn(II) and Fe(II) over a period of three to four months. The onset of iron
Reduction could be shortened to four to five weeks by the addition of 10 mM acetate. Furthermore, the addition of acetate resulted in methanogenesis, as evidenced by the formation of methane and an increase in soluble H₂ concentrations after a period of 10 to 15 weeks. Sulphate-reducing conditions were achieved by the addition of 10 mM sulphate and 10 mM acetate or lactate to the aerobic sediment. Sulphate reduction typically occurred after a three-week incubation period resulting in formation of soluble S²⁻ and visual change in the colour of the sediment slurry from a dark brown to black, indicating the formation of FeS.

Rate constants for the reduction of pCNB in nitrate-reducing, iron-reducing, iron-reducing/methanogenic, and sulphate-reducing sediment slurries are summarized in Table 1. The aqueous phase concentrations of Fe(II) and S²⁻, as well as the dissolved H₂ concentrations are also provided.

Table 1 Reduction kinetics of p-CNB as a function of the dominant TEAP in freshwater sediment slurries.

<table>
<thead>
<tr>
<th>Dominant TEAP</th>
<th>kₑᵣ</th>
<th>Fe(II)ₐq (µM)</th>
<th>S²⁻ₐq (µM)</th>
<th>H₂ₐq (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate reducing</td>
<td>NR</td>
<td>0</td>
<td>0</td>
<td>0.14</td>
</tr>
<tr>
<td>Iron reducing</td>
<td>1.0</td>
<td>44</td>
<td>0</td>
<td>0.90</td>
</tr>
<tr>
<td>Iron reducing/methanogenic</td>
<td>1.6</td>
<td>53</td>
<td>0</td>
<td>9.33</td>
</tr>
<tr>
<td>Iron reducing/methanogenic</td>
<td>2.4</td>
<td>94</td>
<td>0</td>
<td>14.8</td>
</tr>
<tr>
<td>Sulphate reducing (10 mM acetate)</td>
<td>3.7</td>
<td>28</td>
<td>1.2</td>
<td>6.64</td>
</tr>
<tr>
<td>Sulphate reducing (10 mM lactate)</td>
<td>11.9</td>
<td>418</td>
<td>4.3</td>
<td>7.79</td>
</tr>
</tbody>
</table>

TEAP = terminal electron accepting process. kₑᵣ — normalized to k for iron-reducing sediment. aq = aqueous phase. NR = no reaction.

Under nitrate-reducing conditions, pCNB reduction was not observed indicating that nitrate is a better electron acceptor than pCNB. Under iron-reducing conditions, the facile reduction of pCNB to pCNA was observed with a pseudo first-order rate constant of 6.55 × 10⁻³ h⁻¹ (t₁/₂ = 106 h). An increase in the relative rate for the reduction of pCNB was observed under iron-reducing/methanogenic conditions. The rate of reduction increased with the aqueous phase Fe(II) concentration. We speculate that the fraction of Fe(II) bound through ligand exchange to iron oxide surface hydroxyl groups, which is thought to be the reactive form of Fe(II), increases with increasing aqueous Fe(II) concentration. Control experiments indicate that aqueous phase Fe(II) does not reduce pCNB. A further rate enhancement for the reduction of pCNB in the sulphate-reducing sediments was observed relative to the iron-reducing and iron-reducing/methanogenic sediments. In the sediment treated with 10 mM lactate, the increase in the rate of reduction did correspond to the increase in the Fe(II)ₐq. Control experiments demonstrated that at these low concentrations of aqueous phase concentrations, S²⁻ would not contribute to the reduction of pCNB. Further evidence that Fe(II) plays a role in the reduction of pCNB is that the loss of Fe(II)ₐq is concurrent with the reduction of pCNB to pCNA (Fig. 1). Similar results were obtained in iron-reducing and iron-reducing/methanogenic sediment slurries. In each case, recovery of Fe(II)ₐq concentrations to those prior to addition of pCNB occurred over a two to three week period.
Reactivity patterns for halogenated methanes

Reactivity patterns were measured for a series of halogenated methanes in iron- and sulphate-reducing sediment and in model systems to provide further insight into the effects of redox zonation on the reactivity of chemical reductants. To generate the reactivity patterns, rate constants for the reduction of eight halogenated methanes were measured in an iron-reducing sediment, a sulphate-reducing sediment and two model systems including Fe(II)/goethite and FeS. The sediment experiments were conducted with the silt and clay fraction (<53 μm) of bottom sediment collected from a freshwater pond in the Athens, Georgia area.

As described earlier, iron-reducing conditions were determined by the formation of aqueous phase Fe(II) after an incubation period of two months in sealed serum bottles. Sulphate reduction was initiated by the addition of 10 mM SO$_4^{2-}$ and lactate. After a two-week incubation period, H$_2$S was detected in the headspace and the sediment had turned black, indicative of FeS formation. Acid extraction of the sediment phase and trapping of the acid volatile sulphide with zinc acetate demonstrated that FeS accounted for 3 to 7% of the biogenic Fe(II) associated with the sulphate-reducing sediment (Kennedy et al., 1999). The Fe(II)-goethite model system consisted of 0.5 mg ml$^{-1}$ slurry of goethite buffered to pH 6.8 with MES (2-[N-morpholino] ethanesulphonic acid) buffer and 1 mM Fe(II) under an argon atmosphere. The Fe(II)-goethite slurry was equilibrated for 24 h prior to the addition of the halogenated methanes. Anoxic slurries of FeS (0.044 g ml$^{-1}$) were prepared in argon sparged, deionized water. Comparison of the reactivity patterns indicates that the range and relative order of reactivity for the halogenated methanes in the iron- and sulphate-reducing sediments were quite similar suggesting that the probe chemicals were responding to the same reductant in both sediment systems (Fig. 2). Comparison of the reactivity patterns of those measured in the sediment systems to the model systems indicates strong similarities to the reactivity pattern for the Fe(II)-goethite model system and strong dissimilarities to the reactivity pattern for the FeS model system. These data suggest that surface bound Fe(II) complexed to iron oxide surfaces is a dominant reductant in the iron- and sulphate-reducing sediments.
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![Fig. 2 Reactivity patterns for the reductive transformation of halogenated methanes in natural sediment and model systems.](image)

CONCLUSIONS

Measuring the reactivity of probe chemicals in well-characterized natural sediments is providing useful information concerning the characterization of chemical reductants in anoxic sediments as a function of redox zonation. Comparison of reactivity patterns for a series of halogenated methanes measured in natural sediments and model systems suggests that surface-bound Fe(II) is the dominant reductant under both iron-reducing and sulphate-reducing conditions. Reaction kinetics of a nitroaromatic probe chemical studied in sediments as a function of redox zonation provides further evidence for the important role of Fe(II) as a reductant in sediments under iron-reducing, sulphate-reducing and methanogenic conditions. Studies are in progress with a larger set of iron reducing, sulphate reducing and methanogenic sediments and aquifer materials to determine the generality of these observations.

REFERENCES


