

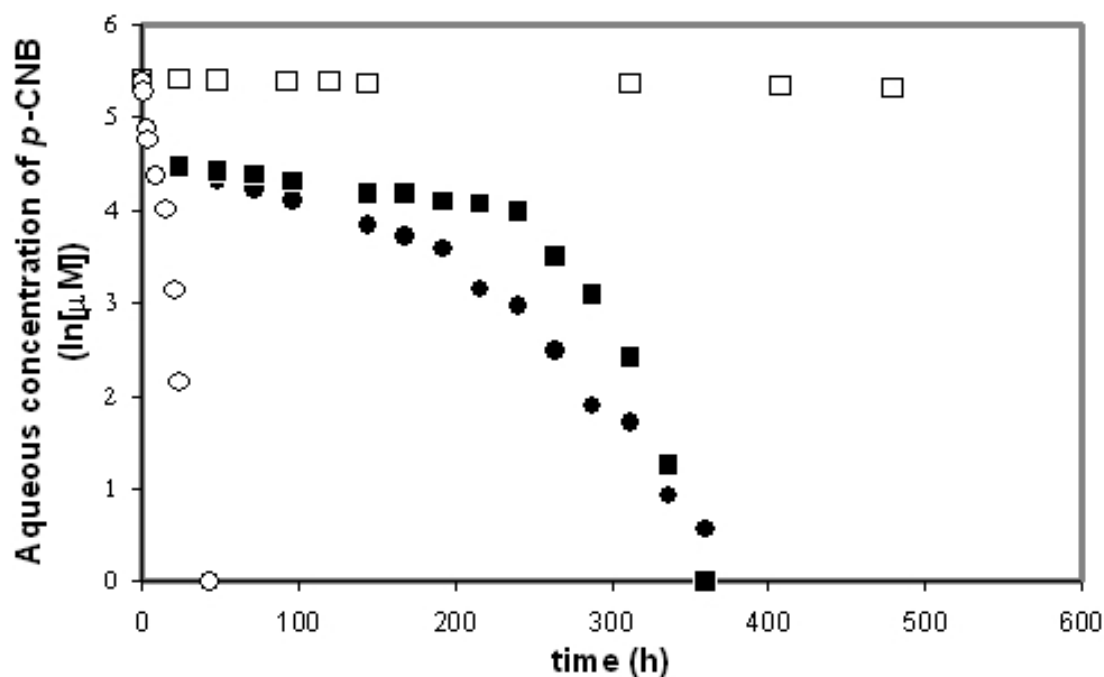
Characterization of the Abiotic Reductants for Nitroaromatic Compounds as a Function of Redox Zonation in Anoxic Sediments

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Reductive transformation is the dominant reaction pathway for the degradation of nitroaromatic compounds in anaerobic environments (Larson and Weber, 1994). Proposed reductants cover a spectrum ranging from reduced minerals and organic matter to microbial enzyme systems. Transformation studies carried out in an anaerobic aquifer have implicated specific reductants such as surface-bound Fe(II) and dissolved sulphide species as the primary reducing agents for a series of nitroaromatics (Rugge *et al.*, 1998). The involvement of these various agents in electron transfer can be expected to vary with the redox zonation of a given sediment system. The development of redox zones is associated with sequential utilisation of the available electron acceptors by the microbial consortium present in groundwater-infiltrated sediments. At the sediment-water interface dissolved oxygen is the most thermodynamically accessible terminal electron acceptor followed by nitrate, manganese(IV) and iron(III) bearing minerals, sulphate and finally carbon dioxide. The successive reduction of these sediment components results in a series of zones usually associated with depth and identified by variations in concentration of the relevant redox indicators (NO_3^- , Mn(II), Fe(II), SO_4^{2-} and CH_4 , respectively). With the objective of characterising the role of chemical reductants as a function of redox zonation, studies were carried out using a representative nitroaromatic compound, *p*-cyanonitrobenzene (*p*-CNB) and a river sediment obtained from the Oconee River (OR) in Athens, GA, USA. The mineralogy of this sediment is dominated by quartz, feldspar, kaolinite and iron phases. Electron microprobe examination of representative samples indicated a fine layer of iron oxide on quartz grains. Earlier column studies with OR sediment demonstrated that the reduction kinetics of *p*-CNB varied as a function of redox zonation as assessed by solution phase concentrations of the redox-active species (Simon *et al.*, 2000). Preliminary experiments in anoxic batch systems designed to monitor the concentration of redox active species were carried out with OR sediment and filtered OR water, with and without 10 mM acetate. These batch studies demonstrated the establishment of a typical series of redox zones over the course of several months.

Significant levels of solution-phase Fe(II) were detected at 28 days (672 h) in un-amended and 11 days (264 h) in acetate-amended batch systems. Batch studies were also carried out in which additions of *p*-CNB to un-amended and acetate-amended systems were made initially and changes in the concentrations of *p*-CNB and its transformation product, *para*-cyanoaniline (*p*-CNA) were monitored as redox zonation progressed. While reduction of the probe compound did occur prior to the establishment of detectable levels of solution-phase ferrous ion in both the amended and un-amended batch systems, a significant increase in the rate of reduction after ~11 days in the batch system containing acetate coincided with a prominent increase in Fe(II)(aq) concentration (Figure 1). These results are consistent with previous studies implicating surface-bound Fe(II) ion as a reductant for xenobiotic species in laboratory columns and model systems (Haderlein, 1999; Klausen, 1995). Subsequent batch experiments have involved poisoning the sediment at a particular redox zone, adding the probe compound and determining the relevant reduction rate constants. Addition of sodium acetate hastened the onset of iron-reducing conditions while addition of potassium nitrate inhibited the system from advancing beyond nitrate reduction. Introduction of the probe compound to batch samples under these various redox conditions indicated pseudo first-order reduction kinetics, but differing rate constants relative to one another (Figure 1). The calculated rate constant for the reduction of *p*-CNB to *p*-CNA under iron-reducing conditions was found to be significantly larger (0.12 h^{-1}) relative to the nitrate-reducing sediment (0.0002 h^{-1}). Continuing this course of investigation will yield rate constants for the OR sediment under both sulphate-reducing and methanogenic conditions. Sequential extractions of sediment slurries at the various stages of zonation will provide information on the various pools of iron present and allow conclusions concerning the role of adsorbed versus solution-phase ferrous ion in the pathway for electron transfer. Electron microscopy of sediment samples at various stages of redox zonation will reveal topographic features that can be associated with the relevant reductive processes (Fredrickson, 1998).



- OR Sediment (unamended)
- OR Sediment with acetate
- OR Sediment under nitrate-reducing conditions
- OR Sediment under iron-reducing conditions (p-CNB added after establishment of Fe-reducing conditions)

Figure 1: Reduction of p-CNB in OR sediment.

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