Electron Shuttle Effects on Iron(III) Reduction, Methane Production, and Microbial Community Dynamics

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Dissimilatory metal-reducing bacteria (DMRB) gain energy by coupling the oxidation of reduced organic compounds or H2 to the reduction of iron and other metal oxides. These oxides are poorly soluble at the temperature and pH ranges typical of most subsurface environments, and consequently many DMRB use soluble electron-shuttling compounds to aid the extracellular transfer of electrons to these electron acceptors. Pure culture studies suggest these shuttles enhance the overall rate of iron reduction, yet little is known about how the presence of these compounds affects complex native communities of microorganisms under iron-reducing conditions. Using wetland sediment microcosms amended with goethite (α-FeOOH) and either acetate or H2, we examined the effect(s) that individual quinone-based electron shuttles with differing redox potentials have on the rate of iron reduction, the time-to-onset of methanogenesis, and the trajectory of microbial community development. We found the effects of electron shuttles on Fe(III) reduction and methanogenesis were compound specific. 5-hydroxy-1,4-naphthoquinone (lawsone, or NQL) and 1,2-dihydroxy-9,10-anthraquinone (AQZ) had a minimal effect on Fe(III) reduction and methanogenesis relative to the no shuttle (NS) control, while the presence of 9,10-anthraquinone-2,6-disulfonate (AQDS) and 9,10-anthraquinone-2-sulfonate (AQS) lead to more rapid Fe(III) reduction and an earlier onset of methanogenesis. Systems amended with 9,10-anthraquinone-2-carboxylic acid (AQC) showed an initially slower rate of Fe(III) reduction and complete inhibition of methanogenesis despite the availability of excess electron donor. Previous work under axenic conditions (Shewanella putrefaciens CN32) had indicated a robust relationship between the reduction potential of an electron shuttle and the rate of Fe(II) production, such that AQC>AQS>AQDS>AQZ>NQL>NS. However, in these wetland sediment microcosms, AQDS>NQS≈AQZ≈NQL>AQC, suggesting that the reduction potential is not an effective predictor of the effectiveness of a putative electron shuttle in systems with a diverse microbial community. Members of the Geobacteraceae and Desulfuromonadaceae dominated in the absence of added electron shuttles and in the presence of AQZ. The Geobacteraceae alone dominated NQL- and AQS-amended systems, but were of lower relative abundance in the presence of AQC, in which case Pelobacteraceae (acetate-amended) or Shewanellaceae (H2-amended) were dominant depending on the electron donor present. It is not yet clear if AQC acts by directly promoting these taxa, although enrichment of Geobacteraceae in one of the three acetate-amended enrichments suggest that they are not specifically inhibited by AQC. The complete inhibition of methanogenesis by AQC highlights the possibility for electron shuttles to influence microbial processes in addition to those involving respiration with insoluble terminal electron acceptors.