

## Characterising Redox Processes in a Chemically Stressed Contaminated Aquifer using Dissolved H<sub>2</sub>

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Understanding the distribution of microbially catalysed terminal electron accepting processes (TEAPs) is fundamental to characterising the microbiology and geochemistry of groundwater systems. This knowledge is important in predicting the fate of organic contaminants in aquifers, where degradation processes are the dominant mechanism responsible for natural attenuation. Because the potential for degradation of many organic contaminants is determined by the ambient redox conditions, it is necessary to deduce these using reliable indicators of in situ processes. Commonly, distributions of electron acceptors, metabolic end products and, increasingly, transient intermediate products such as molecular hydrogen (H<sub>2</sub>), are used to characterise the redox environments in contaminated aquifers. Empirical evidence from some studies suggests that H<sub>2</sub> produced during fermentation of organic matter is maintained at different steady-state concentrations by respiratory micro-organisms, which allows the identification of the dominant TEAP. The use of H<sub>2</sub> measurements as a bio-indicator of TEAPs is evaluated in a sandstone aquifer contaminated with a complex mixture of phenols (phenol, cresols, xylenols). Two detailed vertical profiles through the plume show that biodegradation is occurring under aerobic and NO<sub>3</sub> reducing conditions at the fringe, but simultaneously by Mn, Fe and SO<sub>4</sub>-reduction and methanogenesis in the plume core at TOC concentrations up to at least 6500 mg/l

(7500 mg/l total phenolics). Speciation modelling indicates mixed, disequilibrium, redox conditions in the plume, which prevents the identification of the dominant TEAP from chemical data. Measured dissolved H<sub>2</sub> concentrations reach 110 nmol/l in the plume and are significantly higher than steady-state values found in other anaerobic aquifers. In addition, the dominant TEAP cannot be inferred from the measured H<sub>2</sub> concentrations. Fermentation and respiratory processes in the plume are strongly correlated with pollutant concentration and indicate degradation is occurring under chemically stressed conditions in the plume. The high H<sub>2</sub> concentrations reflect continuous production from fermentation but subsequent slow metabolism of H<sub>2</sub> by respiratory processes, which are inhibited by toxicity from the contaminant matrix. Measured H<sub>2</sub> concentrations in this system are therefore determined more by the kinetics of respiratory degradation processes, as controlled by contaminant toxicity, than steady-state microbial ecology. Contaminant degradation in this plume is rate-limited by the kinetics of microbial respiratory processes, rather than production of H<sub>2</sub> from fermentation. The results indicate that H<sub>2</sub> measurements in anaerobic groundwater may not be a precise indicator of TEAPs in some contaminated aquifers, but nevertheless can assist in understanding environmental controls on in situ degradation, when considered with other hydrochemical data.