Effectiveness of Monitored Natural Attenuation at Predicting In Situ Biodegradation in a TCE Contaminated Metasedimentary Bedrock.

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Until recently, there was almost no information available on the microbial communities that inhabit fractured rock. Recent research at pristine and contaminated bedrock sites in a variety of geologic formations has demonstrated that there is an extensive community of microbes on fracture surfaces and in the groundwater that are known to be capable of degrading both chlorinated and petroleum-based organics. This is reassuring as biodegradation is one of the cornerstone processes in natural attenuation. Monitored natural attenuation (MNA) is one of the strategies used at contaminated bedrock sites where the risk to receptors is minimal and other more aggressive remedial strategies are judged to be impractical. Use of MNA assumes that chemical data on biologically important parameters (e.g., organic contaminants, DOC, electron acceptors (EAs)), collected by analyzing groundwater from bedrock boreholes, is indicative of the type and extent of biodegradation occurring *in situ*. The Bedrock Bioremediation Center (BBC) operates a research facility at Site 32 of the former Pease Air Force Base in Portsmouth, NH. The site was contaminated with TCE from a leaking waste storage tank. Most of the contamination in the competent metasandstone and metashale that underlies the site is cis 1, 2 DCE (33-620 ug/L) with smaller quantities of TCE (3-330 ug/L) and VC (3-31 ug/L). DOC in the groundwater at the site ranges from 0.1-4.0 mg/L. The predominant potential EA for biodegradation of the *in situ* natural organic matter (NOM) is sulfate (21-170 mg/L). Some Fe^{+2} and Fe^{+3} are present in the groundwater (0.1-2.13 mg/L and ND-1.6 mg/L, respectively), but no nitrate is detected. The pH and alkalinity of the groundwater are quite high (8.00-10.10 and 130-199 mg/L, respectively), controlled largely by the precipitation and dissolution of carbonate minerals (i.e., calcite, dolomite, ankerite). From a biodegradation potential standpoint, the competent bedrock at Site 32 is a low energy environment. The groundwater data suggest that biodegradation of the chlorinated solvents is stalled at cis-DCE, perhaps because of the low electron donor (ED) concentrations and the high native sulfate concentrations. Data from Site 32 indicates that there is a community of microbes present both in the groundwater and on the fracture surfaces that are capable of degrading the chlorinated solvents to ethene and CO_2, including *Dehalococcoides*. However, the surface associated and groundwater microbial populations are different. The presence of potential TCE degrading microbes suggests that some biodegradation of the chlorinated solvents may be occurring in the competent rock, however, it is not likely as extensive as what occurs in the overlying more porous media (i.e., the overburden and weathered rock). Several observations have been made about the efficacy of the MNA data in predicting what is occurring in the competent bedrock at Site 32. The groundwater collected with open borehole low flow or straddle packer sampling may not be representative of the majority of the fracture porewater and hence, may not indicate the amount of natural attenuation occurring *in situ*. In addition, the activity in the open water-bearing fractures that are more hydraulically conductive may not be representative of what is occurring in the smaller microfractures that also contain chlorinated solvents. The bedrock system is highly ED limited and it is not clear if the microbes can only use the NOM that is in the groundwater or if they can use what is sorbed to the fracture surfaces. If the latter is true, then measuring the DOC in the groundwater may underestimate the biodegradation potential of the system. It appears that the type of EA used at Site 32 may vary, even over short distances (e.g., <0.3m depth intervals), between Fe^{+3}, SO_4^{-2} and CO_3^{-2} reduction. It is not clear if the minerals on the fracture surfaces can serve as sources of EAs. Unfortunately, the MNA methane data can be difficult to interpret because of this compound's ability to travel significant distances from its source. H_2 data can also be confusing in MNA analysis and may not indicate the type of *in situ* biological processes occurring. Perhaps most importantly, the hydraulics of an MNA site must be well understood, For example, at Site 32 in BBC well 5, biodegradation may change from sulfate reduction at 32.6 m depth to carbonate reduction at 40.5 m and back to sulfate reduction at 54.5 m. This seeming disparity is explained by the fact that the fracture zones at 32.6 and 54.5 m are hydraulically connected, as determined in slug and pumping tests at the site. Finally, the typical MNA regime of one or two rounds of sampling annually may not be indicative of what is occurring in the bedrock system, where seasonal changes can be observed in groundwater chemistry and microbiology. Perhaps modified *in situ* microcosms can supplement annual or semi-annual MNA sampling, but again will not unequivocally indicate what is happening in the fracture network.

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