

Enhancement of Microbial Sulfate Reduction for the Remediation of Hydrocarbon Contaminated Aquifers - A Laboratory and Field Scale Demonstration

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Title: Enhancement of Microbial Sulfate Reduction for the Remediation of Hydrocarbon Contaminated Aquifers - A Laboratory and Field Scale Demonstration

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Research Category: Groundwater remediation

Description:

1.0 Project Goals and Objectives

The primary goal of this project is to design, implement, and monitor a simple but effective enhanced anaerobic bioremediation technology for treating hydrocarbon contamination in aquifers. The specific goals of this project are to:

- 1) Evaluate existing data for long-term trends in benzene, toluene, ethylbenzene and xylenes (BTEX) concentrations.
- 2) Use laboratory experiments coupled with geochemical, hydrological, and contaminant characterizations to design the sulfate injection process and to evaluate the feasibility of this approach.
- 3) Establish baseline contaminant, geochemical, and microbiological conditions prior to nutrient injection.
- 4) Monitor the performance of the enhanced anaerobic biodegradation process.
- 5) Identify the applicability and limitations of enhanced sulfate reduction.

2.0 Results and Discussion

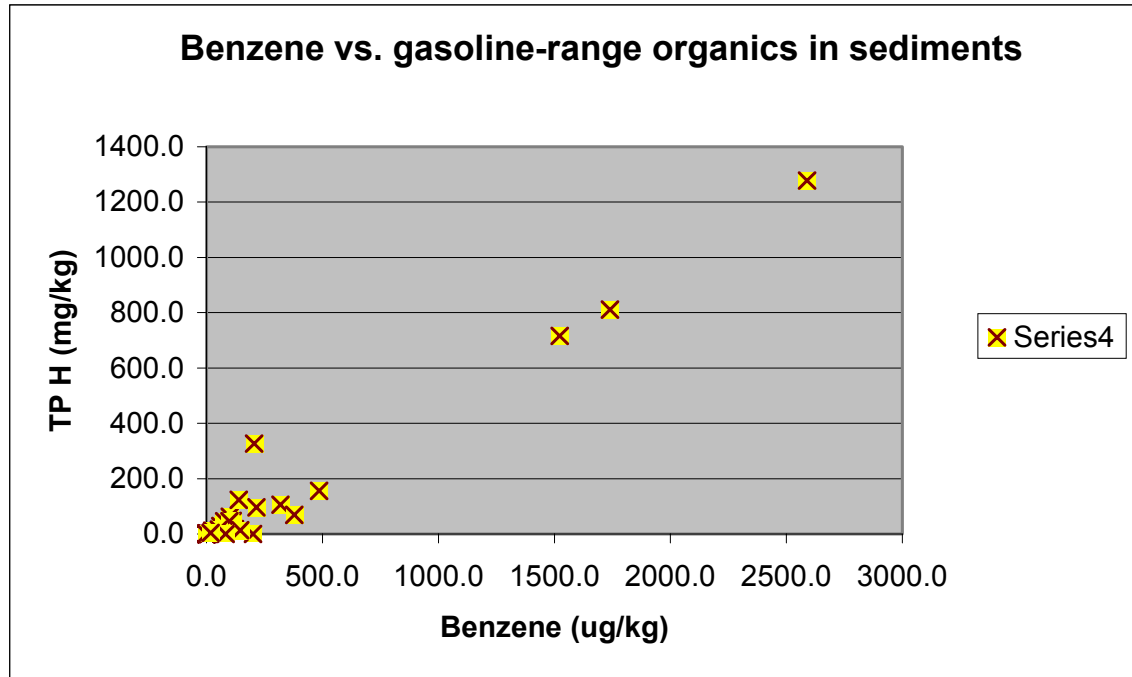
2.1 Hydrocarbon composition and distribution of groundwater and sediments

Gasoline range organics (GRO) ranged from below detection limits to 1,277 mg/kg. GRO and BTEX were below detection in sediments collected at location 400 and 800 ft. east of the N-S line of injection wells. Sediments collected to the north of highway 60 contained high concentrations of GRO. Hydrocarbons were not detected in samples collected from the unsaturated zone. Sediment collected from the deeper portions of the aquifer generally contained higher concentrations of hydrocarbons.

The xylenes (o, m, and p-xylene combined) represented the largest BTEX component in sediment samples followed by ethyl benzene, toluene, and benzene. The concentration of

GRO correlated positively with the concentration of benzene in sediment samples (Figure 1). GRO concentrations were generally 500 times higher than benzene concentration in the sediments indicating that benzene represents only a small portion of the hydrocarbon in the aquifer sediments.

Figure 1.



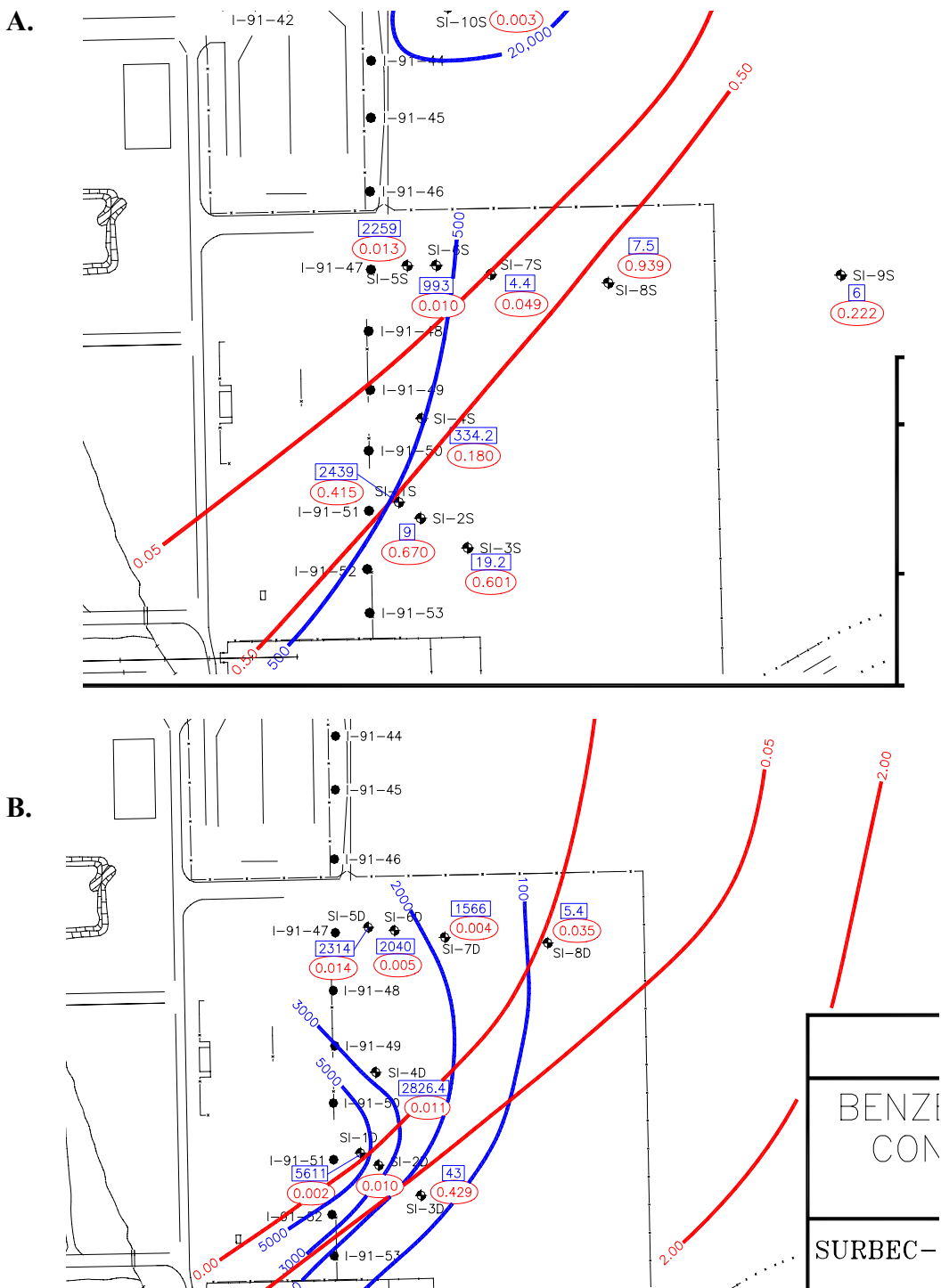
In contrast to the sediment samples, benzene accounted for up to 60% of the dissolved hydrocarbons due to its increased solubility. Dissolved benzene concentrations ranged from below detection limits (2-5 ug/L) to 50 mg/L in well SI-10 D (deep). Dissolved benzene south of the highway usually occurred at levels greater than 2 orders of magnitude higher than dissolved toluene, the second most abundant dissolved BTEX component in the samples. In contrast, several samples collected to the north of the highway contained more toluene than benzene.

Dissolved BTEX occurred at higher concentrations near the base of the alluvium throughout the aquifer except at locations SI-5 and SI-14. There was little difference in the dissolved benzene concentration with depth at location SI-5 located approximately 50 ft. east of the injection wells. However, benzene concentrations decreased much more rapidly along the flow path in the shallow interval than at the base of the alluvium (Figure 2). The dissolved benzene plume near the base of the alluvium extends approximately 100 to 200 ft. further downgradient than the shallow benzene plume (Figure 2). The increased levels of contamination in sediments at the base of the alluvium coupled with increased flow likely account for the increased length of the benzene plume at the base of the aquifer.

Dissolved sulfate was below detection in areas of the aquifer that contained substantial

quantities of hydrocarbon except one location where dissolved nitrate was detected. The downgradient edge of the benzene plume to the east of the south plant correlated with the presence of dissolved sulfate. This was noted for both shallow and deep intervals. The strong correlation between the hydrocarbon plume and the absence of sulfate indicates that sulfate is consumed by anaerobic hydrocarbon biodegradation. It might be anticipated that increased levels of benzene biodegradation occur at the fringe of the plume where sulfate occurs. Indeed, benzene biodegradation was observed in many of the samples along the fringe of the plume without sulfate addition suggesting that the naturally occurring sulfate in this region supports benzene biodegradation.

Figure 2. Comparison of dissolved benzene and sulfate near the water table (A) and at the base of the alluvium (B).



2.2 Dissolved Biogeochemical Indications of the Active Microbial Processes. With a few exceptions, groundwater throughout the sampled interval is depleted of oxygen, nitrate and sulfate, and contains high concentrations of reduced iron and methane. Dissolved sulfide was below detection limits in all of the samples. Low concentrations of dissolved oxygen (0.2 mg/L) were detected primarily in the shallow groundwater south east of the South Plant. This profile suggests that methanogenesis and iron reduction are important processes within the aquifer. The finding that dissolved methane is widely distributed suggests that methanogenesis is also widely distributed in the aquifer. The geochemical evaluation suggests that the conditions are conducive for sulfate addition towards enhancing anaerobic hydrocarbon biodegradation.

2.3 Sulfate reduction and Iron sulfide Distributions

Sulfate reducing activity was identified in sediment samples supplemented with sulfate in an effort to identify where sulfate reduction will likely occur after sulfate amendment. Several samples obtained on the southern side of highway 60 exhibited increased sulfate reducing activity relative to more highly contaminated samples obtained to the north. The average sulfate-reducing activity measured in samples to the south of the highway was 42.5 μM sulfate/d versus 1.29 μM sulfate/d to the north. Sulfate reduction was not detected in four samples to the north of the highway.

Iron sulfide minerals were detected in all of the sediment samples ranging from just under 0.1 $\mu\text{mol S/g}$ to 3 $\mu\text{mol S/g}$ sediment. Sediments collected south of highway 60 that exhibited increased levels of sulfate reducing activity generally had higher levels of iron sulfide minerals. This indicates that increased sulfate reduction activity that occurs in these sediments has resulted in the precipitation of iron sulfide minerals in the sediments. Sulfate reduction activity and iron sulfide content did not correlate in samples collected north of the highway suggesting that the sulfate reduction activity measured in the sediment slurries that were supplemented with sulfate may not represent in-situ sulfate reduction activity. The in-situ concentration of sulfate was near the detection limits in all of the samples north of the highway.

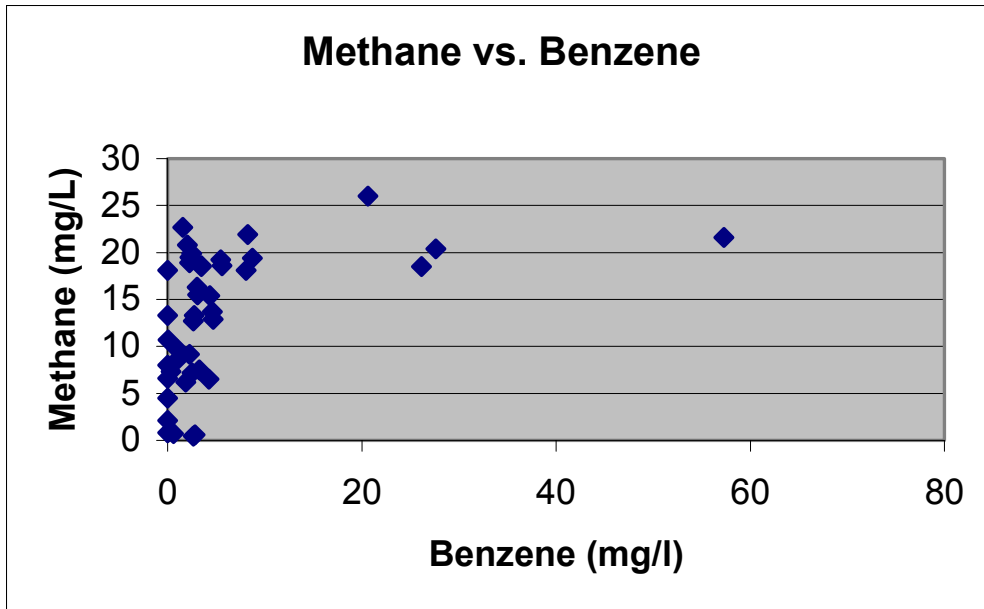
Overall, the sulfate reduction experiments indicate that the majority of sediments support sulfate reduction activity. The highest rates were detected near the edge of the dissolved plume.

2.4 Dissolved Methane Distributions

Dissolved methane was detected at concentrations ranging from 0.4 to 26 mg/L (Figure 3). Increased levels of methane were detected in regions containing increased levels of hydrocarbons including dissolved benzene. Groundwater containing dissolved benzene at concentrations greater than 20 mg/L contained greater than 20 mg/L methane suggesting that high concentrations of benzene, the most toxic BTEX component, does not preclude methanogenesis. This correlation however does not provide direct evidence for the absence of benzene toxicity to methanogenesis because the measured methane may have been produced upgradient from the sampled intervals.

The high concentrations of methane detected in the aquifer, especially in deeper portions of the aquifer is consistent with an environment depleted of electron acceptors.

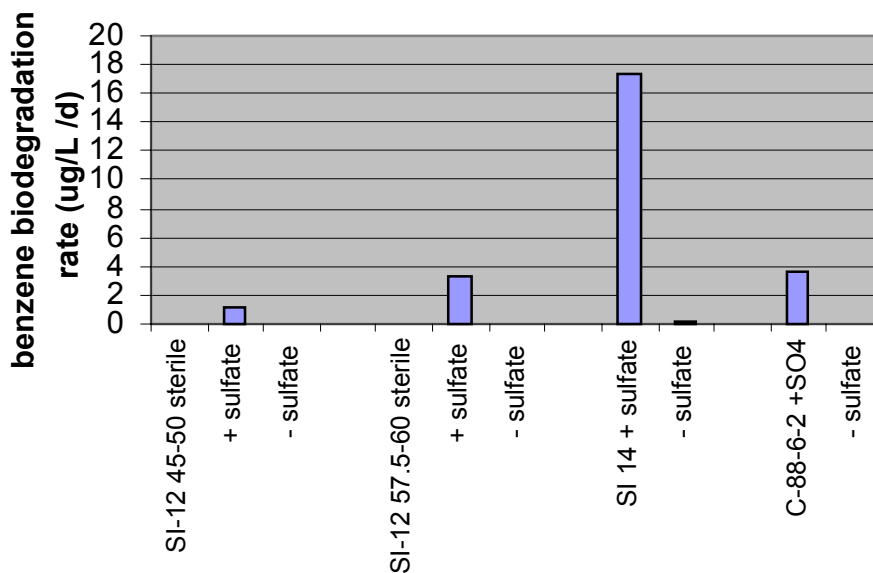
Figure 3.



2.5 Anaerobic Benzene Biodegradation With and Without Sulfate

Sediment samples slurried with groundwater collected from roughly the same interval as the sediments, were amended with sulfate to identify whether sulfate addition stimulated benzene biodegradation activity above that detected in incubations that were not supplemented with sulfate. As seen in figure 4 below, the addition of sulfate stimulated benzene biodegradation in many of the samples. The measured rates of benzene biodegradation ranged from less than one ug benzene/L/d to 37 ug benzene/L/d. Sulfate addition did not stimulate benzene biodegradation in sediments collected south of highway 60 where sulfate was detected in many of the samples. High concentrations of benzene (20 mg/L) detected in the SI-12 45-50 sediment slurry did not preclude anaerobic benzene decomposition upon sulfate addition suggesting that benzene toxicity was not problematic in this sample. Overall, the benzene biodegradation experiments indicate that the addition of sulfate will stimulate benzene biodegradation in many locations that are depleted of sulfate.

Figure 4 Comparison of benzene biodegradation rates with and without sulfate addition. Values are the average of duplicate incubations.



3.0 Tentative Conclusions

- (1) Sediment and groundwater at the base of the alluvium at most locations are more highly contaminated than in shallower regions (including near the water table). However, the smear zone is not continuous with depth. Because higher levels of methane were detected near the base of the alluvium this hydrocarbon appears to support increased levels of methanogenesis.
- (2) The BTEX plume at the base of the alluvium east of the south plant is longer than the shallow BTEX plume.
- (3) Sulfate is depleted in contaminated portions of the aquifer but is present at the fringe of the plume and in uncontaminated areas.
- (4) Sulfate stimulated the anaerobic biodegradation of benzene in many of the samples but not in sediments obtained from near the fringe of the benzene plume east of the South Plant where sulfate occurred naturally in the aquifer.

4.0 Ongoing Work

Sulfide precipitation capacity

Experiments have been initiated to identify the quantity of sulfide that sediment samples are capable of precipitating. The total quantity of sulfide that can be precipitated with solid phase iron in the sediments combined with dissolved iron will be determined to identify the sulfide precipitation capacity of the aquifer. Flow through sediment core

experiments will be used to identify whether iron sulfide precipitation impacts hydraulic conductivity.

Biodegradation experiments and quantification of anaerobic benzene degrading microorganisms

Laboratory incubations have been prepared with groundwater collected from four wells at the study site. These samples are being analyzed a variety of microbial activities and numbers to identify baseline (before sulfate injection) conditions and to evaluate some of the factors that may impact benzene biodegradation. The wells will be sampled at a later time to identify whether the injection of sulfate stimulated the activity and or growth of anaerobic benzene biodegrading bacteria. The specific analyses that are being performed on these water samples include sulfate reduction rates, the number of sulfate reducing bacteria, benzene biodegradation rates, and the number of anaerobic benzene degrading bacteria with and without sulfate. The benzene biodegradation activity assays are also being conducted in samples in which hydrocarbons other than benzene have been removed from the groundwater to identify whether the presence of complex hydrocarbon mixtures impacts anaerobic benzene biodegradation.

Baseline Monitoring

Groundwater samples are being collected from approximately 35 wells on a routine basis for a variety of geochemical and hydrocarbon analyses. These analyses will be used to establish the baseline conditions to which post-sulfate injection data will be compared.

Sulfate Injection System

The sulfate injection system has been constructed and will be mobilized to the site within the next month.

