Enhancing Microbial Sulfate Reduction of Hydrocarbons in Groundwater Using Permeable Filled Borings

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Abstract

At a service station closed in 1993, groundwater contained benzene that persisted above the cleanup goal of 1 mg/L in zones depleted of background sulfate. The benzene and other petroleum hydrocarbons (PHCs) were present as much as 36 feet (11 m) below the water table and therefore remediation of a thick saturated zone interval was required. Microcosms using site sediments demonstrated that anaerobic benzene biodegradation occurred only if sulfate was added, suggesting sulfate addition as a remediation approach. Twenty-four boreholes (9.1” diameter and 56’ deep) were drilled around four monitoring wells, in which benzene concentrations exceeded 1 mg/L. The boreholes were backfilled with a mixture of gravel and 15,000 pounds of gypsum (which releases sulfate as it dissolves) to create “Permeable Filled Borings” (PFBs). Currently, nine high pressure injections (HPIs) of gypsum slurry were conducted in other site locations (312 pounds of gypsum total). PFBs were expected to release sulfate for up to 20 years, whereas HPIs were expected to produce a short-lived plume of sulfate. Concentrations of benzene and sulfate in groundwater were monitored over a 3-year period in six monitoring wells. In two wells near PFBs, benzene concentrations dropped below the cleanup goal by two to three orders of magnitude; in one well, sulfate concentrations exceeded 500 mg/L for the most recent 18 months. Benzene concentrations in two other PFB monitoring wells declined by a factor of 2 to 4, but remained above 1 mg/L, presumably due to high-dissolved PHC concentrations and possibly greater residual PHC mass in adjacent sediments, and therefore greater sulfate demand. However, hydrogen and sulfur isotopic enrichment in benzene and sulfate, respectively, confirmed biodegradation of benzene and stimulation of sulfate-reducing conditions. Thus, it is hypothesized that the PHC mass in adjacent sediments will decline over time, as will dissolved PHC concentrations, and eventually benzene concentrations will decrease below the cleanup goal. Benzene in two HPI monitoring wells was below the cleanup goal for all but one sampling event before HPIs were conducted and remained below the cleanup goal after HPIs; there was no stimulation of sulfate-reducing conditions. It is concluded that sulfate released from PFBs contributed to declining benzene concentrations.

Introduction

Dissolved benzene can persist at concentrations above 1 mg/L in groundwater at Underground Storage Tank release sites, exceeding regulatory action levels (i.e., California Low Threat Closure Policy 2012). At some of these sites, toluene, ethylbenzene, and xylene (TEX) concentrations are each well below 1 mg/L and do not require remediation.

Research and practice have shown that dissolved petroleum hydrocarbons (PHCs), including gasoline range constituents (BTEX and others) and diesel range constituents (naphthalene, methyl-naphthalene, and others) biodegrade under sulfate-reducing conditions (Meckenstock and Mourtaki 2011) that are common in groundwater impacted by PHCs (Kolhatkar and Schnobrich 2017). Often, the demand for sulfate imposed by dissolved hydrocarbons in the release zone exceeds the amount supplied by the flow of natural sulfate-laden groundwater into the release zone; consequently groundwater flowing through a portion of the release zones is depleted of sulfate. For example, sulfate reduction accounted for 73 to 95% of the total attenuation of PHCs in groundwater at the site described in this paper (Mackay et al. 2018b). Dissolved sulfate concentrations were also found to be depleted within and downdip of the release zone.

In some PHC release zones, anaerobic biodegradation under sulfate-reducing conditions may reduce TEX concentrations but leave benzene at concentrations exceeding regulatory limits (Kolhatkar and Schnobrich 2017). If a portion of the PHC-impacted zone is depleted in terminal electron acceptors (dissolved oxygen, sulfate, and nitrate, or solid phase iron or manganese), a remediation strategy can include the addition of an electron acceptor. Sulfate is a common amendment, which can be effective in enhancing biodegradation of benzene and other PHCs and reduce constituent concentrations below regulatory goals (Anderson and Lovley 2000; Sublette et al. 2006; Kolhatkar et al. 2008; Kolhatkar and...
Schnobrich 2017), Cunningham et al. (2001) conducted field experiments using combined injection of nitrate and sulfate to accelerate in situ bioremediation of BTEX in groundwater compared to the rate of natural attenuation. Benzene degradation appeared to be stimulated by the nitrate and sulfate injection by the end of the 15-month demonstration. Their results demonstrated benzene can be biodegraded anaerobically after other preferentially degraded hydrocarbons have been removed. A variety of sulfate delivery schemes have been applied in practice, including release or injection of solutions, emplacement or injection of slurries, and emplacement of solid amendments (Anderson and Lovley 2000; Cunningham et al. 2001; Kolhatkar and Schnobrich 2017).

High pressure injections (HPIs) of water-based slurries of solid sulfate amendments have been applied with mixed success. For such methods, sulfate distribution and delivery are defined by site geology and the number, spacing, and depths of injection points. Distribution of injected solutions and slurries can be very irregular (e.g., Howe et al. 2013; Bennett et al. 2017), due to preferential pathways for migration of the injectates. Thus, the injected sulfate may not be optimally distributed compared to the zones within which sulfate is needed to accelerate bioremediation, leading to inefficient and patchy treatment. The actual distribution of the injected slurry is generally unknown and can sometimes enter monitoring wells or other subsurface infrastructure, such as piping.

PHC remediation technologies using water-based slurries can also be limited because they contain a relatively low mass of sulfate, which can be rapidly depleted in areas with high PHC concentrations (i.e., high electron-acceptor demand).

Surface application of sulfate solutions was investigated by Wei (2015) and Wei et al. (2018), who conducted controlled field experiments in a relatively uniform sandy medium to remediate a light nonaqueous phase (LNAPL) source located 2.6 to 8.2 feet (0.8 to 2.5 m) below ground and below a shallow water table. Sulfate solution concentrations ranged from 5 to 20 mg/L. Deeper penetration of sulfate into the saturated zone was observed for higher solution concentrations and attributed to density-driven advection. Their study showed the potential for land application of sulfate solutions to enhance biodegradation of benzene and other compounds dissolving from LNAPL or diffusing from PHC-contaminated sediments. In practice, selecting the concentration of the sulfate solution to target a desired depth interval below the water table may be a considerable challenge if there is a thick and heterogeneous vadose zone, or if density-driven advection causes some of the sulfate solution to migrate below the contaminated depth intervals.

Kolhatkar and Schnobrich (2017) tested land application of solid sulfate amendments at a site formerly used for storage, transfer, and blending of various refined petroleum products. Solid sulfate mixed with granular agricultural gypsum (CaSO₄·2H₂O) and/or Epsom salts (MgSO₄) was mixed and blended into surficial soils to target an LNAPL source located 3 to 10 feet (0.9 to 3.1 m) bgs. Benzene concentrations were at least 10 times higher than TEX concentrations in groundwater. The upper 3 feet (0.9 m) of soils had previously been excavated and backfilled with clean soil. Periodic intentional or natural infiltration was used to dissolve some of the solid and carry the sulfate solution to the PHC-impacted portion of the saturated zone. In pilot and larger-scale tests, high concentrations of sulfate (>300 mg/L) could be sustained in groundwater for up to 2 years following an application, and sulfate was delivered approximately 1 to 6 feet (0.3 to 1.8 m) below the water table. The authors concluded that benzene was likely biodegrading and being stimulated by sulfate application, but interpretation was clouded by continued dissolution of LNAPL and the fluctuating water table. In principle, sulfate addition methods should be effective to reduce dissolved PHC concentrations at sites containing residual LNAPL, if the flux of sulfate supply exceeds the flux of sulfate demand imposed by biodegradation of PHCs arising from LNAPL dissolution.

As suggested by Kolhatkar and Schnobrich (2017) or implied by both studies just cited, remediation by land applications of sulfate solutions or solids is most applicable to unpaved sites with relatively permeable soil in the vadose zone and relatively shallow PHC impacts in the saturated zone. Thus, surface application may have limited effectiveness for PHC impacts that extend far below the water table. Kolhatkar and Schnobrich (2017) cautioned that another potential limitation to the land application approach for remediating PHC impacts in groundwater could arise if the vadose zone were thicker than 15 feet (4.6 m) and contained sinks for sulfate other than the target contaminants.

This paper presents a case study using novel “Permeable Filled Borings” (PFBs) to enhance sulfate biodegradation and reduce benzene concentrations in groundwater below regulatory cleanup levels. A PFB is created by using a permeable medium, in this case a mixture of granular gypsum and gravel, to backfill an open borehole within the targeted depth interval of the saturated zone. The gravel functions as a nondissolving porous medium, and the finer-grained gypsum is another porous medium occupying the pore spaces between the gravel particles. As gypsum gradually dissolves into groundwater flowing through the PFB, the structure of the gravel is expected to remain. The design was intended to allow sulfate release at high concentrations for many years, and to any depth interval within the saturated zone. The method relies on the natural groundwater flow to distribute sulfate from the PFBs to the PHC-impacted portions of the subsurface. The study site had been evaluated in detail by Mackay et al. (2018a, 2018b) and was known to have relatively high-background sulfate, a PHC release zone in which sulfate was depleted, and benzene persisting above the cleanup goal. Microcosm studies described in Appendix S1 confirmed the site’s microbial community can reduce benzene if supplied additional sulfate. The PFB method provides a benefit over other sulfate addition techniques for PHC remediation (e.g., HPI or surface applications), which can be limited in both the amount and depth of distribution of sulfate within PHC-impacted saturated zone. This study describes the first field-scale application of PFBs containing gypsum to enhance biodegradation rates at a PHC-contaminated site.

**Background**

**Conceptual Approach of PFBs**

PFBs are an extension of the idea of using arrays of unpumped wells to form discontinuous permeable reactive
barriers (Wilson and Mackay 1995; Wilson et al. 1997). In one application of unpumped wells, each well screen could contain materials that release amendments to groundwater flowing through them to support in situ biodegradation of contaminants within and downgradient of the well screen (e.g., Chapman et al. 1997; Wilson et al. 2002). Prior publications on the theory of borehole dilution tests (Halevy et al. 1967; Drost et al. 1968) and applications of unpumped wells as amendment releasers (Wilson and Mackay 1995; Wilson et al. 1997) have shown that if the permeability of the screen and its contents is much higher than that of the native formation, and the groundwater flow direction is constant, then groundwater will converge into the screen and diverge as it flows out as shown schematically in Figure 1a. In that case, the “convergence factor” (ratio of width captured to diameter of screen) is 2, as is the divergence factor. Figure 1b illustrates approximate amendment distributions expected in groundwater downgradient of PFBs at the study site after an elapsed time of 3 years, based on prior simulations (Wilson et al. 1997); the illustrations depict transport and spreading for this study site, for an elapsed time period of approximately 3 years. Site characteristics and conditions are described later. As shown in Figure 1b, lateral distribution of the amendment, if not consumed by reactions, can be increased by hydrodynamic dispersion. However, as also shown in Figure 1b, relative concentrations above 0.5 (50%) are likely to be restricted laterally to about two to three times the well diameter, assuming there is no consumption of the amendment in or downgradient of the well screen. Relative concentrations of 0.1 (10%) may extend further, perhaps up to four to five times the well diameter, again assuming no consumption. If the hydraulic conductivity of the well screen and its contents is less than approximately 100 times that of the formation, then the convergence and divergence factors will be less than 2. Furthermore, the width of the distribution downgradient of the well screen would be less if the released amendment is utilized by reactions in the well or downgradient. Thus, Figure 1 illustrates the best case of amendment spreading for a constant flow field. On the other hand, groundwater flow directions typically vary cyclically, which will tend to broaden the overall lateral impact of the dissolved amendment. Furthermore, geologic media are never truly homogeneous, so actual flow of water into and out of screens will depart from the idealized distributions, in some cases being broader and in others narrower depending on the distribution of the more permeable native media. However, it is important to note that the dissolved amendment will follow the same permeable paths that the target dissolved contaminants will migrate within, so even if flow divergence is low due to heterogeneities, the amendment will support bioremediation where it is needed downgradient of each well screen. Wilson et al. (1997) discuss how the spacing of vertical amendment-releasers affects lateral distribution of the released amendment, how arrays of such releasers can be used to create more uniform lateral distributions, if needed, and how to compare the flux of amendment released to the flux of dissolved contaminant to be degraded.

The PFB approach described here emplaces amendment-releasing solids directly in boreholes, with no well screen between the emplaced materials and the native formation. If the contents of the boreholes are significantly more permeable than the native formation, then flow convergence into the borehole should be similar to that expected for well screens, as in Figure 1a and the downgradient distribution of the dissolved amendment similar to Figure 1b, with caveats as discussed just above. The design of PFBs used at the study site is described in detail below after discussion of site characteristics.

Figure 1. Plan view conceptualizations of (a) convergence and divergence of groundwater flowlines into and out of an unpumped well screen filled with permeable amendment releasing material or device and (b) dissolved amendment distribution expected downgradient of two well screens containing amendment sources (see text for discussion). Amendment distributions are used to depict hypothesized sulfate distributions downgradient of PFBs in Figure 4.
Site Background and Characteristics

Mackay et al. (2018a, 2018b) discuss in detail the background and characteristics of the site, a former service station that closed in 1993, so only a brief summary is presented here. Groundwater velocity at this silty site is very low and estimated to be approximately 0.57 cm/d. Average rainfall in this urban, West Coast area is approximately 15 inches per year but varies seasonally. Figure 2a presents a map of the unpaved site, a roughly triangular property, showing locations of key monitoring wells and former facilities (removed years ago). The heavy dashed line indicates the area within which groundwater benzene concentrations remained above 1 mg/L at various depths and within which residual LNAPL may have remained (ITRC 2014). Figure 2b illustrates the vertical intervals of the monitoring well screens, projected onto the C-C’ transect, as well as the three vertical intervals (shallow, middle, and deep) defined by the screen depths of all the site wells. Figure 2b also shows monitoring wells discussed in the Results and Discussion section and the location of the soil sample used in the microcosm studies discussed later. Well depths were selected by prior consultants to explore vertical profiles of PHC contamination in the total depth interval monitored within the single hydrogeologic unit. Site operations ceased in 1993 and much of the originally released LNAPL is now submerged and, as discussed by Mackay et al. (2018a, 2018b), most may have been depleted by diffusion into the relatively low permeability media surrounding the thin interconnected more permeable lenses. Prior to installation of PFBs and HPIs, LNAPL had not been detected in any monitoring wells since March 2010. Therefore, we do not depict the location of LNAPL since no continuous LNAPL phase is expected or suggested by any monitoring to date.

Biodegradation of PHCs in the subsurface is expected to cause a decrease of electron acceptors in both groundwater and sediment (Wiedemeier et al. 1999). As discussed by Mackay et al. (2018a) and shown in Appendix S1, historical monitoring at this site confirms that the highest concentration PHC-contaminated zones are depleted of sulfate and contain methane. Methanogenic conditions would be expected to dominate, since sulfate in the groundwater from upgradient is depleted as the groundwater migrates into the source zone.

Methods and Design Considerations

Microcosms

Sediment and groundwater for laboratory microcosm preparation were collected from borehole B-10, which was located near the former underground storage tanks (Figure 2). Details of microcosm construction, analysis, and results are provided in Appendix S1.

Stable Isotope Analysis

For a remediation strategy with sulfate addition, measuring sulfur isotopes ($\delta^{34}$S) in sulfate is useful to understand if sulfate is effective to enhance sulfate-reducing conditions and promote hydrocarbon biodegradation. We also measured carbon and hydrogen isotopes in benzene to demonstrate evidence for compound-specific biodegradation.

Stable isotope analysis can be applied to the electron acceptor of interest (e.g., sulfate) providing process-specific (versus compound-specific) information about biodegradation (Aelion et al. 2010; Clark and Fritz 1997).
Isotope analysis can be used for electron acceptors to differentiate changes due to biodegradation from those due to mixing (Schroth et al. 2001; Bouchard et al. 2018). Microbial sulfate reduction usually results in significant fractionation, that is, an enrichment of δ²⁳⁴S in unconsumed sulfate (Schroth et al. 2001). If there is no δ²³⁴S enrichment, declining sulfate concentrations are likely due to dilution by mixing. Carbon and hydrogen isotope ratios can be measured for the compound of interest (e.g., benzene) to evaluate the performance of remediation at hydrocarbon-impacted sites (Bouchard et al. 2018). Enrichment in ¹³C and ²H suggests biodegradation or another transformation process is occurring. Additional detail on stable isotope analysis is provided in Appendix S1.

Selection of Backfill Materials and Method of Construction of the PFBs

As discussed below in more detail, hollow stem augers (nominal 8” OD, approximately 4” ID) were used to construct the PFBs. The boreholes were backfilled by pouring a mixture of hydrated gypsum and rhyolite gravel (Table 1) into the auger as it was backed out. To avoid bridging in the auger interior, the particle size of the backfill media had to be in the gravel range or smaller.

The rhyolite gravel was used as a proppant, to keep the PFB from subsiding as the gypsum dissolved. Angular rhyolite gravel was selected over other options since it was available in a range of particle sizes and had bulk and solid densities similar to gypsum. The similarity of densities was expected to yield similar settling rates within the open, water-filled boreholes when the mixture was poured into them. A poorly graded gypsum was desirable to allow it to fill the porosity of the gravel proppant as the mixture settled in each borehole. Based on grain size distribution, the hydraulic conductivity of a 1:1 mixture of gypsum and rhyolite by volume was expected to be at least 500 times higher than the hydraulic conductivity of the native fine silty medium comprising most of the contaminated saturated zone at the site. Although it could not be confirmed after emplacement, we expected that the similar densities and porosities of gypsum and rhyolite would lead to relatively uniform composition and permeability of the mixture within the backfilled boreholes.

Installation of PFBs

Twenty-four PFBs were installed in the locations shown in Figure 3, a closeup of the site. The goal was to have at least one of the PFBs upgradient of each monitoring well at all times to allow the earliest possible insight into enhancement of biodegradation under sulfate-reducing conditions. PFBs were installed downgradient and side-gradient of the monitoring wells because the groundwater flow direction had varied considerably in 2 years prior to installations, as discussed in Appendix S1. August 2018 groundwater elevations are shown in Figure 3 for wells in both the middle and deep intervals, confirming the total monitored interval acts as a single hydrogeologic unit and supporting the decision to construct PFBs across the entire contaminated groundwater interval.

Each PFB was constructed by advancing a borehole with a nominal 8-inch (20 cm) outside diameter (OD) auger to the desired total depth. The 8-inch (20 cm) boring diameter was the largest that could be drilled to the maximum desired depth in some locations (56 feet [17.1 m] bgs) with the available hollow stem auger drill rig. The auger was then retracted a short distance, the interval of the borehole beneath the auger backfilled by pouring the 1:1 (v/v) gypsum-rhyolite mixture into the hollow stem, and these steps repeated until the backfill was complete over the desired depth interval: 20 or 25 feet bgs to 56 feet bgs.

Table 1

| Material | Porosity (−) | Bulk Density (g/cm³) | Solid Density (g/cm³) | Images (Same Scale), Illustrating Particle Size Distribution |
|----------|--------------|----------------------|-----------------------|-----------------------------------------------------------|
| Gypsum   | 0.49         | 1.17                 | 2.31                  | ![Image](Note1) Superior Soils, Hanford, CA. Product name: Agri-Gyp 95% pure (dihydrate) |
| Rhyolite | 0.48         | 1.12                 | 2.13                  | ![Image](Note2) Lyngso, Redwood City, CA. Product name: Teffy rock |

1/4” (6.3 mm) screen retention 9.40%, passing = 90.60%, 40 mesh (0.425 mm) retention 37.00%, passing = 63%.

2 Particle size: 3/8 inches (9.5 mm).
Spacing between PFBs was 4 to 5 feet (1.2 to 1.5 m), as close as could practically and safely be conducted by the drilling contractor. The 4- to 5-feet spacing is much tighter than required solely to match flux of PHC contaminants in the plume to flux of sulfate from the PFBs, as discussed in Appendix S1, but likely to allow most of the sulfate released from each PFB to disperse laterally to enhance biodegradation in portions of the plume not directly captured by PFBs (Wilson et al. 1997). In total, these PFBs contained 15,000 pounds (6800 kg) of gypsum containing 8400 pounds (3810 kg) of sulfate. PFBs located near target wells U-4 and U-18 were backfilled with the gypsum/gravel mix from approximately 20 to 56 feet (6 to 17.1 m) bgs, and PFBs near target wells U-1 and U-3 were backfilled from approximately 25 to 56 feet (7.7 to 17.1 m) bgs. In each of the 24 PFBs, the gypsum/gravel mixture was followed by 2 feet of hydrated bentonite chips and Portland neat cement to the surface. The backfill depth of 25 feet (7.7 m) bgs near U-1 and U-3 was selected because depth to water (DTW) measurements on site was approximately 25 to 26 feet (7.6 to 7.9 m) bgs at the time of the installations. The backfill depth of 20 feet (6 m) bgs near wells U-4 and U-18 was selected due to shallower benzene detections historically observed in that area. Thus, if groundwater elevations were to rise, a sulfate source would be present at a shallower depth in that area.

As described in Appendix S1, the maximum sulfate delivery rate from gypsum-filled borings was estimated from expected gypsum solubility under the site geochemical conditions, the groundwater velocity, and the degree of convergence of flow into the PFB. The PFB longevity was estimated to be approximately 20 years based on the mass of sulfate in the borings, the sulfate delivery rate, and other assumptions described in Appendix S1. Groundwater flow directions, which had been very consistent for years prior to 2011 (Mackay et al. 2018a, 2018b), were observed to be much more variable in 2014 to 2015 several years before PFB emplacement (Appendix S1); based on reviews of locations and pumping histories of nearby public supply wells, it is likely the varying local flow directions were due in part to pumping of nearby public supply wells during those years. The most dramatic change in groundwater flow direction occurred in the Winters of 2014 and 2015, both drought years (Appendix S1, Figure S1-1a). As it turned out, during the period of this study the groundwater flow direction returned to the historic stability with a mean direction illustrated in Figures 3 and 4 in this paper (Appendix S1, Figure S1-1b).

PFBs were installed near wells U-1, U-3, U-4, and U-18, because these were the only site wells with benzene concentrations consistently exceeding the California Low-Threat Closure Policy criteria of 1000 μg/L (as of January 2015). Although benzene concentrations in wells U-12 and U-15 had been below cleanup goals for most of the 2.5 years prior to PFB/HPI installations, in March 2015 they exceeded 1000 μg/L. Thus, in case benzene concentrations were to remain above 1000 μg/L, U-12 and U-15 were included, by agreement with the regulators, as target areas for direct-push, HPIs of sulfate slurries to initiate short-term sulfate-reducing conditions (details described below).

**High-Pressure Injections of Gypsum Slurry**

Nine direct-push, HPIs were completed by standard industry techniques using a gypsum slurry. The HPIs were...
completed near wells U-12 and U-15, for reasons described above, and in several other locations throughout the site. The remediation project manager decided to provide more sulfate between the PFB locations, using HPIs, as shown in Figure 3. A gypsum slurry solution was injected under high pressure (up to 1000 psi at the wellhead) in the HPI borings. The water source for the solution was city hydrant water. An estimated total of 312 pounds (141.5 kg) of gypsum and 23,400 gal (88,600 L) of water were injected into the HPI borings, for an overall average sulfate concentration of approximately 900 mg/L, if the gypsum were assumed to dissolve immediately after injection. Since the gypsum dissolution was likely not instantaneous, the dissolved sulfate concentrations in zones directly impacted by the injections were likely to be much lower than 900 mg/L. Following injection, the HPI borings were backfilled from total depth to ground surface using a Portland neat cement grout mixture. For the HPIs completed near U-12 and U-15, three injection depths targeted the middle depth interval monitored by these wells; details for these and other HPIs are provided in Appendix S1.

Expected Sulfate Distribution after 3 Years

Figure 4 illustrates conceptually the sulfate distribution expected downgradient of each PFB and each HPI 3 years after emplacement assuming no sulfate-depleting reactions. Each PFB is expected to sustain the generation of a plume of sulfate for up to 20 years (as calculated in Appendix S1), and the length and width of the plumes shown in the figure expected from the migration and spreading after 3 years given the estimated groundwater velocity at the site (as conceptualized in Figure 1 and discussed in accompanying text). Each HPI was expected to create a limited plume of sulfate initially, given the low mass of gypsum included in each HPI, which would then detach from and migrate downgradient of the injection location.

Results and Discussion

Microcosm Results

The presence and activity of a native microbial community of benzene degraders and sulfate reducers was confirmed in the laboratory microcosms, as discussed in more detail in Appendix S1. Substantial benzene and sulfate removal were observed in live treatments amended with benzene at 43 mg/L and sulfate at 1506 mg/L. The addition of sulfate at a concentration similar to that upgradient from the benzene-contaminated zone resulted in benzene biodegradation in the positive control (86% decrease, i.e., to 6 mg/L average of triplicates) and all treatments amended with sulfate (71 to 100% decrease, i.e., to 12 mg/L or below detection limit) between approximately 300 to 600 days after microcosm setup. Although nitrate is an alternative electron acceptor and phosphate is a potentially limiting nutrient, nitrate and phosphate amendments alone did not result in enhanced benzene removal in comparison to unamended (presumably methanogenic) microcosms or the negative control. Nitrate and phosphate amendments in combination

Figure 4. Hypothesized distributions of dissolved sulfate 3 years after emplacement of PFBs and HPIs, assuming no consumption of sulfate in the aquifer. Symbols are the same as in Figure 3. Darker yellow depicts higher sulfate concentrations near PFBs, and paler yellow depicts lesser concentrations. This conceptualization assumes groundwater flow direction remains constant, PFBs remain permeable, gypsum in PFBs dissolves at a steady rate yielding constant concentration of sulfate in water diverging from PFBs, and thus each PFB creates a plume of dissolved sulfate similar to that idealized in Figure 1b for conditions at the site. The gypsum emplaced by HPIs is assumed to be depleted relatively rapidly of sulfate, yielding a plume of sulfate that detaches from the HPI location. Conceptualizations of sulfate distribution assume no sulfate-consuming reactions. If sulfate is utilized in the aquifer by sulfate-reducing bacteria, the actual sulfate distributions would be more restricted than illustrated. In that case, the drawn plumes could illustrate the extent of groundwater impacted by sulfate-reducing conditions.
with sulfate did not result in greater benzene biodegradation when compared to sulfate-only addition. These results suggested that in situ remediation of dissolved PHCs could be enhanced by release of sulfate into the saturated contaminated zone.

Monitoring of PFB and HPI Performance

Four monitoring wells, shown in Figure 3, are within several feet of PFBs: deep-screened wells U-1, U-3, and U-4, and mid-screened well U-18. Figure 3 also includes mid-screened wells U-12 and U-15, located near two HPBs. All these wells had shown little change in BTEX or TPH (total petroleum hydrocarbons) for years (Mackay et al. 2018a). Prior to this study the most recent evidence of LNAPL near the wells were detections of sheens in March 2010 in U-1 and U-3 and LNAPL was measured in December 2007 in U-1 at a thickness of 0.03 feet.

A few days after PFBs were installed, a sheen was measured in U-1. Three months after PFB installation (December 2015), LNAPL was measured at a thickness of 0.03 feet in U-3. Six months after PFB installation (March 2016), LNAPL was measured at 0.01 feet in both U-1 and U-3, and a sheen was noted in U-18. We hypothesize that sheen and LNAPL occurrences in these three PFB monitoring wells resulted from disturbance of native media during PFB augering that triggered LNAPL release from nearby, probably fine-grained, sediments. Apparently, they were only short-lived releases as there have been no LNAPL or sheen detections at the site since March 2016. Nevertheless, the prior detections of LNAPL and sheens are evidence that PHC was present in sediments near at least those three wells (U-1, U-3, and U-18).

Groundwater Concentrations

Figure 5a to 5d plot TPH-GRO (TPH gasoline residual organics), benzene, TEX, and sulfate concentrations (log scale) vs. time for wells U-12, U-3, U-4, and U-18. Appendix S1 presents such a plot for U-1, which is very similar to U-18, and U-15, which is very similar to U-12 (Figure SI-7a and SI-7b). Figure 5 plots begin in March 2013, providing preremediation trends based on nine monitoring events over 2.5 years. The timing of PFB or HPI installations is shown on each plot. In Appendix S1, Figure SI-8a and SI-8b plots BTEX, sulfate, and DTW for U-1 and U-18, respectively, demonstrating that hydrocarbon concentrations in deep- and mid-screened wells were not influenced by variable groundwater elevations.

Preremediation hydrocarbon concentrations help define potential sulfate demand and appropriate remedial action. PHC concentrations and thus sulfate demand were much lower near U-12 (and U-15 as discussed in Appendix S1) than near other wells in Figure 5; in fact, benzene exceeded 1 mg/L in March 2015 for the first time since January 2000. For this reason, HPBs were conducted near U-12 and U-15. In each of the other wells in Figure 5 (all PFB monitoring wells), benzene concentrations had exceeded 1 mg/L for at least 18 months prior to remediation and TPH-GRO was on the order of 10 mg/L. Therefore, preremediation sulfate demand for dissolved PHCs, including nontarget hydrocarbons as well as benzene, was much higher in the PFB monitoring wells, which is why the PFB approach was selected. Overall, preremediation sulfate demand decreased in this order: U-18, U-1 > U-3, U-4 > U-12, U-15.

Consistent with the expectation that U-12, U-3, and U-4 were relatively low in sulfate demand, they showed post-remediation benzene concentrations that dropped below

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Figure 5. PFB and HPI monitoring wells TPH-GRO, benzene, TEX, and sulfate vs. time (a) U-12, (b) U-3, (c) U-4, and (d) U-18. Vertical dashed lines indicate installation date of noted sulfate release method.
1 mg/L within 6 months. U-3 and U-4 benzene continued to decline, while U-12 benzene, which had been below 1 mg/L before HPI installation, returned to below 1 mg/L but with significant variability. The most significant TPH-GRO reductions occurred in U-3 and U-4. U-18 postremediation benzene and TPH-GRO were variable, with benzene remaining above 1 mg/L through August 2018.

As discussed in Mackay et al. (2018a), background sulfate concentrations in upgradient well U-7 varied between 200 and 1420 mg/L after 2005 (data not shown here), whereas preremediation sulfate in the four wells discussed here was very low (<10 mg/L), as shown in Figure 5a to 5d. As discussed in Appendix S1, we expected the sulfate concentration released from the PFBs to be approximately 1400 mg/L, although the released concentration could vary depending on groundwater velocity, PFB permeability, etc. As discussed earlier, the expected sulfate concentration from the HPIs is at most 900 mg/L, and likely far lower, in portions of the aquifer immediately impacted by injections.

Postremediation, sulfate concentrations changed in all the wells in Figure 5, but with different trends.

- HPI monitoring well: U-12 sulfate was widely variable (>40 mg/L on five events and <10 mg/L on six events); benzene remained below 1 mg/L. The lowest benzene and TPH values co-occurred with the highest sulfate concentrations, suggesting the possibility that benzene reduction was in part due to dilution by the originally irregularly distributed sulfate-laden water from the HPI injections.
- PFB monitoring wells: In U-3, sulfate concentrations peaked at 1840 mg/L in March 2017 and declined significantly thereafter, while benzene concentrations have remained below the cleanup goal in all postremediation sampling events (e.g., 13 μg/L in August 2018). U-4 sulfate concentrations exceeded 500 mg/L after September 2016 and benzene declined to below 1 μg/L (nondetect in most recent sample). U-18 showed the least apparent impact of the PFB installations, with sulfate variable but low (generally below 10 mg/L) and TPH-GRO and benzene more variable than preremediation, but benzene remaining above the cleanup goal.

**Sulfate Isotope Results**

For a remediation strategy with sulfate addition, measuring the $\delta^{34}$S/$\delta^{32}$S ratio in sulfate ($\delta^{34}$S-SO$_4^{2-}$) is useful to understand if sulfate is enhancing sulfate-reducing conditions and promoting biodegradation. Figure 6 illustrates $\delta^{34}$S-SO$_4^{2-}$ results over time for all PFB and HPI monitoring wells and background well U-7. If no $\delta^{34}$S-SO$_4^{2-}$ value is shown for a sampling date in Figure 6, the sulfate concentration was too low to measure the sulfur isotope ratio. For March 2018, due to laboratory issues, there are no $\delta^{34}$S-SO$_4^{2-}$ results for any well.

The PFB and HPI gypsum $\delta^{34}$S-SO$_4^{2-}$ benchmark value (12.4‰) is shown as a horizontal dashed red line in Figure 6. This benchmark value results from gypsum dissolution in water and is isotopically heavier (increased $\delta^{34}$S/$\delta^{32}$S ratio) than sulfur in dissolved sulfate present in background groundwater at the site, which is strongly negative (see U-7 data in Figure 6). $\delta^{34}$S-SO$_4^{2-}$ values that increase with time, and approach the benchmark value, suggest PFB or HPI gypsum is creating sulfate-reducing conditions. If the $\delta^{34}$S-SO$_4^{2-}$ value exceeds the benchmark gypsum value, there is strong evidence for sulfate-reducing conditions enhanced by gypsum dissolution from PFBs or HPIs. Overall, Figure 6 shows that sulfate-reducing conditions were created near the PFBs, but on only one date is there any evidence sulfate-reducing conditions had been stimulated near either HPI.

PFBs near U-3 and U-4: The $\delta^{34}$S-SO$_4^{2-}$ results confirm that the PFBs created sulfate-reducing conditions near U-3 and U-4. U-3 $\delta^{34}$S-SO$_4^{2-}$ exceeds the gypsum benchmark for the last three sampling events when sulfate was detected (June 2017 to December 2017). U-4 $\delta^{34}$S-SO$_4^{2-}$ exceeds the gypsum benchmark for every quarter it was measured, beginning March 2016. As described earlier, benzene concentrations in U-3 and U-4 have declined two to three orders
of magnitude since installation of the PFBs. \( \delta^{34}\text{S-SO}_4 \) results demonstrate sulfate-reducing conditions induced by the PFBs near U-3 and U-4 accelerated hydrocarbon biodegradation near those wells.

PFBs near U-18: \( \delta^{34}\text{S-SO}_4 \) is more strongly enriched (more positive) than in any of the other wells. The higher enrichment indicates greater stimulation of sulfate reduction. This, coupled with the relatively steady benzene concentration, corroborates the hypothesis of other PHCs being degraded under sulfate-reducing conditions, thus limiting sulfate that is available to microorganisms capable of benzene biodegradation. Though U-18 benzene concentrations have not yet been reduced below 1 mg/L, the isotopic evidence demonstrates PFBs are effective in creating sulfate-reducing conditions for PHC biodegradation. Figure 5d (log scale) shows TPH-GRO has declined by a factor of two and TEX has declined by more than a factor of three following PFB installations. After sulfate demand for other hydrocarbons is met, sulfate-enhanced biodegradation of benzene is more likely to proceed near U-1. Because sulfate could not be measured on August 20, 2015, the well was resampled on August 27, 2015, a few days after PFB installations near this well and \( \delta^{34}\text{S-SO}_4 \) was very close to the gypsum benchmark. This is consistent with elevated sulfate concentration on the same date (Appendix S1, Figure SI-7a). Three months after PFB installations (December 2015), Figure 6 shows \( \delta^{34}\text{S-SO}_4 \) exceeded the gypsum benchmark in U-1. Since 2015, there was only one sampling event for U-1 when the sulfate concentration was high enough to allow measurement of \( \delta^{34}\text{S-SO}_4 \). We hypothesize for U-1, as we do for U-18, that after sulfate demand for other hydrocarbons is met, sulfate-enhanced biodegradation of benzene is more likely to proceed near U-1.

HPIs near U-12 and U-15: The \( \delta^{34}\text{S-SO}_4 \) data for monitoring wells near HPIs is less promising. U-12 \( \delta^{34}\text{S-SO}_4 \) data exceeds the baseline value on only 1 of 10 sampling events and has a negative value on six events. For U-15 there were three events when \( \delta^{34}\text{S-SO}_4 \) could be measured, all values were negative and well below the baseline. Therefore, U-12 and U-15 \( \delta^{34}\text{S-SO}_4 \) results suggest that the HPIs had limited success in inducing sulfate-reducing conditions. Neither of those wells, however, had postremediation benzene concentrations that exceeded the cleanup goal (1 mg/L). Given that the preremediation concentrations had already been below the goal for years, except immediately before remediation, we hypothesize that benzene variations in these wells resulted from dilution by the water injected by HPIs, spatial or temporal variability in the PHC plume, and/or movement of the lateral edge of the PHC plume that they monitored (due possibly to small shifts in local groundwater flow directions).

Benzene Isotope Results

\( \delta^{13}\text{C} \) and \( \delta^{2}\text{H} \) for benzene was included in the quarterly sampling plan for each of the PFB and HPI monitoring wells in the first 2 years following PFB and HPI installations. \( \delta^{13}\text{C} \) enrichments were very small; studies conducted at other sites demonstrate long well screens, such as those at the study site, can mask \( \delta^{13}\text{C} \) enrichments occurring within specific depth intervals smaller than the screen length (Buscheck et al. 2017, 2019). Therefore, only \( \delta^{2}\text{H} \) results are presented and discussed here. Hydrogen isotopic enrichment occurred on five of six sampling events for U-3 and on six of seven sampling events for U-4. As remediation progressed, benzene approached the reporting limit in U-3, U-4, U-12, and U-15; thus, it was not possible to measure \( \delta^{2}\text{H} \) for all these wells during later sampling events.

Implications of Sulfate and Benzene Isotope Results

There are multiple monitoring events with enriched \( \delta^{34}\text{S-Sulfate} \) and enriched \( \delta^{2}\text{H-Benzene} \) in U-3 and U-4, coupled with two to three orders of magnitude reduction in benzene. It is therefore reasonable to suggest these benzene reductions are due to sulfate reducing conditions. Figure 7 is a plot for \( \delta^{2}\text{H-Benzene} \) vs. \( \delta^{34}\text{S-Sulfate} \) for the March 2016 monitoring event, the only sampling event when \( \delta^{2}\text{H} \) and \( \delta^{34}\text{S} \) could both be measured for the five wells shown in

![Figure 7. March 2016 \( \delta^{34}\text{S} \) in sulfate vs. \( \delta^{2}\text{H} \) in benzene in PFB and HPI monitoring wells.](image-url)
the figure. Figure 7 illustrates $\delta^2$H enrichment, providing compound-specific evidence of benzene biodegradation, and $\delta^{34}$S enrichment, and thus process-specific evidence of sulfate-reducing conditions. The figure also illustrates enrichment in $\delta^2$H-benzene and $\delta^{34}$S-sulfate in the three PFB monitoring wells (U-3, U-4, and U-18) compared to the two HPI monitoring wells (U-12 and U-15).

### Summary and Implications

For years before and in the 3 years after HPIs were completed, benzene concentrations in nearby mid-screened wells U-12 and U-15 were below or slightly greater than 1000 ug/L for most of the monitoring events. The HPIs conducted near U-12 and U-15 emplaced a relatively small mass of gypsum, and sulfate concentrations in U-12 and U-15 only occasionally exceeded 40 mg/L. There is only limited isotopic or other evidence that HPIs stimulated sulfate-reducing conditions or benzene biodegradation. As mentioned previously, we hypothesize that U-12 and U-15 monitored the lateral edge of the PHC plume. Thus, we conclude that PHC concentration fluctuations in U-12 and U-15 primarily reflect dilution by water injected during the HPI emplacements, spatial variability in the plume, and/or small shifts in groundwater flow directions, not remediation initiated or sustained by HPIs as applied in this study.

In deep-screened wells U-3 and U-4, which monitored PFBs, postremediation benzene declined by two to three orders of magnitude. In August 2018 benzene concentration was below 15 μg/L in well U-3 and below 1 μg/L in well U-4. Postremediation TPH-GRO was also significantly lower than pre-remediation concentrations in these wells. Isotopic evidence ($\delta^{34}$S-SO$_4$) in U-3 and U-4 demonstrates that the PFBs enhanced sulfate-reducing conditions and accelerated hydrocarbon biodegradation.

In mid-screened well U-18, which monitored PFBs, postremediation benzene remained above 1000 μg/L whereas TEX compounds declined by a factor of three. There is strong isotopic evidence ($\delta^{34}$S-SO$_4$) for sulfate-reducing conditions, which is expected to enhance hydrocarbon biodegradation. Therefore, if PFBs maintain sulfate-reducing conditions and total dissolved PHC concentrations decline during the lifetime of sulfate release by the PFBs, benzene biodegradation will eventually be accelerated near U-18.

Gypsum-filled borings have not created any secondary water quality concerns at this site. Calcium concentrations in PFB monitoring wells are very similar to background. Sulfide concentrations have not exceeded 1.7 mg/L. Effective for shallower contamination, yielding a comprehensive overall remediation strategy. Depth-discrete data are useful to determine PFB depth and vertical horizon for treatment. At sites with distinct, multiple water-bearing zones requiring remediation, care must be taken not to create short-circuiting across water-bearing zones. For sites with multiple water-bearing zones, the permeable portion of the borings should be completed for specific hydrogeologic units and borings should be appropriately grouted to prevent short-circuiting.

At this site, sulfate delivery through PFBs supported more demonstrable benzene remediation than did the equally time-consuming installation of HPIs. PFB costs, including labor and materials, were approximately $4000 per 56-feet boring at this site. PFBs are a promising sulfate delivery strategy for deep, submerged hydrocarbon-impacted groundwater. This technology can be applied for saturated zones with fine-grained soils and low groundwater velocities, which are not conducive to groundwater extraction or other remediation approaches. At the study site, the TPH concentrations in the target wells ranged from below 10 to 20 mg/L, suggesting a PFB spacing of 20 to 40 feet based solely on flux considerations. Instead, this study utilized a PFB spacing of approximately 5 feet, the closest practical spacing, and one that potentially would provide far more sulfate than required for the captured plume flux (about 30% of total), leaving the rest of the sulfate to migrate and spread laterally downgradient to enhance biodegradation of the plume not directly captured by the PFBs. Larger diameter borings would contain more sulfate source and allow wider PFB spacing. Cross-gradient, parallel rows of PFBs on offsetting patterns would enhance sulfate delivery by increasing the effective lateral density of the PFBs, as projected onto a transect (Wilson et al. 1997). The hydraulic conductivity of the permeable media should ideally be at least 100 times that of the formation; thus, as for any groundwater remediation design, confident estimates of formation hydraulic conductivity are needed.

Permeable, gypsum-filled trenched could provide a continuous sulfate-releasing medium. We did not select such an approach for this site since the cost would likely have been too high, if indeed it was even possible to reach the required depth of 56 feet (ITRC 2011). While trenchless technologies can reach deep enough, they would have required more staging area than was available at this narrow site and therefore probably more time. For other sites, PFBs or other approaches appropriate for deep groundwater could complement sulfate land application, which may be more effective for shallower contamination, yielding a comprehensive overall remediation strategy.

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Supporting Information

Additional Supporting Information may be found in the online version of this article. Supporting Information is generally not peer reviewed.

Figure SI-1. Groundwater flow directions.

Figure SI-2. (a) Benzene, (b) sulfate and (c) methane distribution projected onto longest X-X' (Figure 2(a)) through the site along the direction of groundwater flow.

Figure SI-3. Benzene and toluene concentrations (μM) in microcosm groundwater versus time (days) for controls.

Figure SI-4. Benzene concentrations (μM) in microcosm groundwater versus time (days) for treatments 1 through 8.

Figure SI-5. Carbon dioxide and methane concentrations (μM) in microcosm headspace versus time (days) for treatments 1 through 8.

Figure SI-6. Monitoring Wells U-3 and U-4 Benzene C/C0 versus Time.

Figure SI-7. Monitoring Well Concentration vs. Time (a) U-1 and (b) U-15.

Figure SI-8. BTEX Concentration and Depth to Water vs. Time (a) U-1 and (b) U-18.

Figure SI-9. Location and numbering of HPI borings.

Table SI-1. Summary table of microcosm control and treatment amendments.

Table SI-2. Microcosm outcomes - amended electron donor removal and headspace accumulation of gaseous degradation products.

Table SI-3. PFB spacing estimated by comparing flux of sulfate demand by a TPH plume to flux of sulfate supply from PFB.

Table SI-4. High Pressure Injections (HPIs) at the site.

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