Cost and Performance Report
for
Enhanced In Situ Anaerobic Bioremediation of Fuel-Contaminated Ground Water

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1. Executive Summary

We have demonstrated the application of an enhanced in situ anaerobic bioremediation technology to clean up ground water contaminated with fuel hydrocarbons, particularly benzene, toluene, ethylbenzene, and xylenes (BTEX). The technology is based on introduction of electron acceptors such as sulfate and nitrate, coupled with removal of toxic or inhibitory compounds such as sulfide, in order to stimulate anaerobic ground water bacteria. The bacteria use the fuel hydrocarbons as a source of carbon and energy, mineralizing BTEX and other hydrocarbons to harmless carbon dioxide in the process. The details of this demonstration have been provided in the project Final Report, and are summarized in this document.

A key issue in the implementation of this technology is the ability to effectively introduce the electron acceptors into the contaminated aquifer region while simultaneously removing toxic or inhibitory compounds. To accomplish this, we installed three injection wells and one extraction well into the contaminated region of the demonstration aquifer. Extracted water was treated to remove toxic and inhibitory compounds, as well as target compounds that were not degraded in situ, then augmented with electron acceptors at the appropriate concentrations, then re-injected via the injection wells. This design allowed the development of three treatment zones (one zone between the extraction well and each of the three injection wells). This methodology is particularly effective at contaminated sites where the target contaminants are sorbed to the aquifer solids and/or are present as small globules of non-aqueous-phase liquids (NAPLs), because the treatment zones are created in the same portion of the aquifer as where the contamination is located. However, we note that the technology will be effective at NAPL-contaminated sites only if the trapped NAPL can be remediated, i.e., if the amount of residual NAPL is small, and if the presence of any perched aquifers does not affect the results.

We demonstrated this technology at the Naval Weapons Station (NWS), Seal Beach, in southern California. A portion of the shallow ground water at NWS Seal Beach was contaminated with fuel hydrocarbons that had leaked from an underground storage tank. Previous investigations had shown that the shallow ground water in the nearby Seal Beach National Wildlife Refuge was being contaminated as a result of the leak. The hydraulic gradient at this site is very low, such that natural ground water flow is very slow to remove inhibitory by-products or to introduce electron acceptors to the site. As a result, it was unclear if intrinsic bioremediation would be able to prevent contamination of the wildlife refuge. Thus, this site was an ideal location at which to demonstrate the enhanced bioremediation technology.

We found that this treatment technology was effective at removing all BTEX compounds from the ground water. Specifically:

- Toluene appeared to be preferentially degraded, and was rapidly degraded even without augmentation of the electron acceptors. A few feet below the water table, toluene concentration was typically below 10 µg/L.

- Biodegradation of ethylbenzene appeared to be stimulated by the introduction of nitrate. In the zone where nitrate was introduced, ethylbenzene concentration was reduced from 250 µg/L to less than 10 µg/L.
- Biodegradation of ortho-xylene appeared to be stimulated by the introduction of sulfate. In one of the zones where sulfate was introduced, the o-xylene concentration was quickly reduced from over 400 µg/L to less than 10 µg/L.
- Biodegradation of meta- and para-xylene appeared to be stimulated by the introduction of nitrate. In the zone where nitrate was introduced, the combined m+p-xylene concentration was reduced from 500 µg/L to less than 20 µg/L.
- Benzene was effectively removed from the ground water, but it appears that most of the removal was due to flushing by the extraction well, with a small contribution from biodegradation. In the zone that was augmented with nitrate and sulfate, benzene concentration was reduced from 3 mg/L to about 50 µg/L, but removal was slow. In the zone that received neither nitrate nor sulfate (i.e., methanogenic conditions), benzene concentration was reduced from 4 mg/L to about 0.4 mg/L, and also was slow. Benzene concentrations often rebounded when pumps were temporarily shut off.

Based on the results from the demonstration, we have estimated the cost of using this technology to clean up a representative site where approximately 3,000 m^3 of ground water and aquifer solids have been contaminated with about 250 gallons (820 kg) of fuel hydrocarbons. The endpoint for the remediation is assumed to be that concentrations of all BTEX compounds are reduced to below their drinking water maximum contaminant levels (MCLs). We assume that the fuel hydrocarbons are present below the water table in three forms: as globules of non-aqueous-phase liquid (NAPL), dissolved in the ground water, and sorbed to aquifer solids. Under the assumed conditions, the estimated present value of the remediation cost is $1.09 million for a five-year clean-up. The estimated capital cost is $470,000 and the estimated present value of the operating and maintenance (O&M) cost is $615,000. The largest capital cost is site characterization, and the largest O&M cost is sampling and analysis. For remediation of the same site via pump-and-treat, the estimated present value of the remediation cost is $1.54 million for a fifteen-year clean-up, with $397,000 for capital costs and a present value of the O&M costs equal to $1,143,000.

This technology is relatively easy to install and to operate. As compared to conventional pump-and-treat remediation, the enhanced in situ bioremediation technology is expected to offer shorter clean-up times and lower overall costs. Also, it is likely to be effective in some situations where intrinsic bioremediation is not, e.g., sites where the natural ground water flow is very slow, such as NWS Seal Beach.

2. Technology Description

2.1. Technology Background

In situ bioremediation is now being investigated, evaluated, and, in some cases, applied as a remediation technology at contaminated ground water sites. The principle of in situ bioremediation is that certain bacteria, found naturally in ground water aquifers, can metabolize particular contaminants, reducing the contaminant concentrations to a safe level. When naturally-occurring metabolic processes are used to remediate a contaminated site without any additional alteration of site conditions, the process is referred to as intrinsic in situ bioremediation. When conditions at the site are engineered or altered in order to stimulate or accelerate the biological destruction of contaminants, the process is referred to as enhanced in situ bioremediation.

In the case of fuel hydrocarbons, it is now well known that many microorganisms indigenous to soil can oxidize (mineralize) the contaminants to harmless carbon dioxide and water. This process can occur rapidly under aerobic conditions, i.e., in the presence of oxygen. Under anaerobic conditions (in the absence of oxygen), the process can still occur, but is not as well understood. Nitrate, sulfate, ferric iron, or carbon dioxide can replace oxygen as the terminal electron acceptor (oxidant). Intrinsic bioremediation is inexpensive, but it can be slow, it is often unpredictable, and it may be inadequate for many sites, particularly under anaerobic conditions. Thus, engineered intervention (enhancement) might be necessary in order for the oxidation to proceed at acceptable rates. Enhanced bioremediation might consist of augmenting the contaminated zone with electron acceptor(s), removing compounds that inhibit the oxidation reaction, or both.

The potential benefits from this technology are large. The principal advantage of bioremediation over conventional pump-and-treat remediation is that most of the contamination is destroyed in situ, and little or no secondary waste is produced. In situ bioremediation might be susceptible to some of the same impediments that limit the efficiency of the pump-and-treat method; for example, slow contaminant leaching of adsorbed contaminants from aquifers, solids can present a continuing source of contamination. However, maintaining the presence of electron acceptors in the contaminated aquifer via periodic injections should be far less expensive than continuous ground water extraction. Therefore, for sites where it can be shown that enhanced in situ bioremediation is technically feasible, it should be less expensive to implement than a pump-and-treat system.

2.2 Theory of Operation and Limitations

Microorganisms are able to use BTEX contaminants as substrates for energy and growth, and electron acceptors such as oxygen, nitrate, and sulfate to convert the contaminants into harmless products (principally carbon dioxide and water), cell mass, and inorganic salts. In almost all cases, oxygen is consumed preferentially over alternate electron acceptors like sulfate or nitrate; after oxygen is consumed, anaerobic microorganisms use a series of alternate electron acceptors. Nitrate and sulfate offer the advantage that they can be injected into an aquifer at much higher concentrations than oxygen. When water and air are in equilibrium at 20 °C, oxygen has a solubility of about 9 mg/L in water, which, stoichiometrically, can oxidize about 2.9 mg/L toluene. By contrast, a practical limit for nitrate or sulfate introduction is around 80 mg/L.

Eighty mg/L of either nitrate or sulfate can oxidize about 16–17 mg/L toluene. The practical limit for nitrate introduction is based on the fact that nitrate is a regulated compound and that excessive nitrate introduction can result in the formation of nitrogen gas. Also, the practical limit for sulfate introduction is based on the fact that sulfate reduction can result in the accumulation of sulfide, which is inhibitory to many biodegradation processes.

Aromatic hydrocarbons including benzene and toluene have also been observed to degrade under fermentative-methanogenic conditions [Wilson, et. al., 1986; Grbic-Galic and Vogel, 1987]. However, BTEX fermentation is poorly understood. Under fermentative conditions, no external electron acceptor is required, because microorganisms use the substrate (i.e., one or more of the BTEX compounds) as both an electron donor and an electron acceptor. The products of fermentation can include carbon dioxide, organic acids (e.g., acetic acid, propionic acid), alcohols (e.g., ethanol), and/or hydrogen gas [National Research Council, 1993]. Fermentation products are biodegraded by other species of bacteria, ultimately resulting in the production of carbon dioxide, methane, and water. Methanogenesis is inhibited by the presence of other electron acceptors or oxidants (e.g., oxygen, nitrate, or sulfate) and so only occurs in very reduced environments.

Because it is difficult to maintain aerobic conditions in a contaminated aquifer, the principle behind this technology is to inject alternate electron acceptors to stimulate anaerobic in situ biodegradation of the target compounds. Limitations to this technology include the following:

1. Anaerobic bioremediation is still not thoroughly understood, especially under field conditions, making clean-up times difficult to predict.
2. Because there is little operational experience with anaerobic bioremediation, the process is not always considered acceptable by regulators.
3. Benzene, the most toxic of the BTEX compounds, has not been conclusively shown to degrade under all anaerobic conditions that exist in the field.

2.3 Technology Specifications

Figure 1 shows a schematic of the injection/extraction well system. Samples are taken at monitoring wells located between the injection and the extraction wells in order to measure the concentrations of the electron acceptors and of the target contaminants. The extraction well is used to remove water that contains the target contaminants (in this case, BTEX) and/or compounds that inhibit the bioremediation process (e.g., sulfide). The extracted water is treated to remove the appropriate compounds, then augmented with electron acceptors in order to stimulate in situ biodegradation of the target contaminants, then re-injected into the contaminated region of the aquifer.

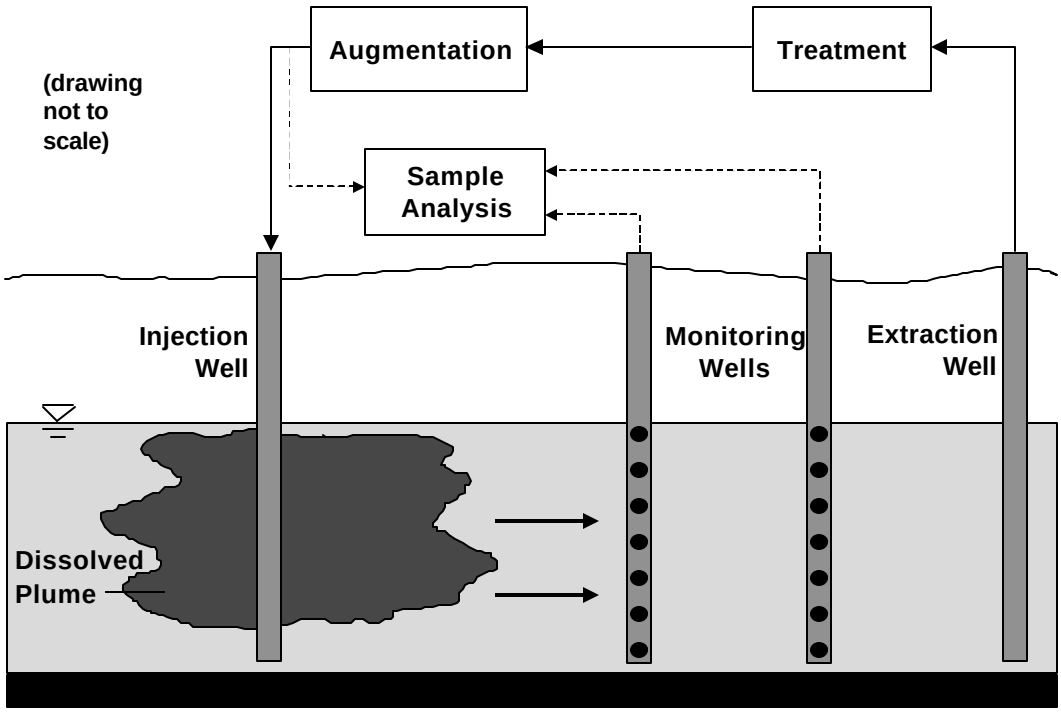

Figure 1: Schematic of the injection/extraction well system.

The system can be operated in three modes:

1. Injection/extraction with no augmentation of electron acceptors, i.e., flushing of the treatment zones with unaugmented treated water;
2. Injection/extraction with augmentation of electron acceptors in the injection wells;
3. No flow, i.e., both injection and extraction wells are off.

A treatment cycle generally consists of operating in these three modes sequentially. The flushing stage allows removal of inhibitory or toxic by-products, the augmentation stage allows introduction of the electron acceptors into the treatment zones, and the no-flow stage provides the microorganisms time to use the electron acceptors and to degrade the target contaminants.

In applying this technology, the items that must be specified include:

- Number and location of injection and extraction wells
- Injection and extraction rates
- Method for above-ground water treatment (to remove inhibitory products and/or target contaminants that are not degraded in situ)
- Selection of electron acceptors to be injected
- Concentration of electron acceptors at injection well
- Duration of flushing, augmentation, and no-flow stages of treatment cycle.

2.4. Key Design Criteria

The expected time frame for complete remediation can be estimated based on the amount of contamination initially present, the injection/extraction rate, the concentrations of electron acceptors in the injection wells, and the approximate stoichiometry of the biodegradation reactions. The actual time required could be longer if any of the following conditions apply:

1. The rate of biodegradation is limited by contaminant mass transfer from globules of NAPL or by contaminant desorption from solid aquifer materials.
2. The rate of biodegradation is limited by contaminant mass transfer out of low-conductivity regions that are inaccessible to the injected electron acceptors.
3. One or more of the target compounds are resistant to biodegradation under the biogeochemical conditions established.

The actual time required might also be shorter than estimated, particularly if fermentation-methanogenesis is found to be a significant removal mechanism in regions where injected electron acceptor concentrations remain low.

The enhanced in situ anaerobic bioremediation technology produces a very low volume of secondary waste, because the majority of contaminant attenuation is performed in situ. However, the above-ground treatment system might produce some waste that requires proper disposal. For instance, if activated carbon is used in the treatment system, the spent carbon must be disposed of and replaced at regular intervals.

After construction, the technology is expected to require very little labor. The injection wells, extraction wells, above-ground treatment system, and chemical injection system require routine maintenance. Electron acceptors must be regularly purchased and supplied to the chemical injection system. A regular monitoring program, including sample collection and analysis must be implemented.

2.5. Mobilization, Construction, and Operation Requirements

This technology is not expected to demand any unusual mobilization, construction, or operation requirements. Once the technology specifications and design criteria (discussed above) have been addressed, and the necessary permits have been obtained, qualified contractors can be hired to install the wells (including monitoring wells), the above-ground treatment system, and the chemical delivery system. One to two months would be expected for mobilization, including the time for readying the equipment and transporting it to the site. An additional 2 to 4 weeks should be expected for construction. The equipment required for this technology is relatively standard and should not require special construction.

Operation of the technology would require regular purchase of the electron acceptors (nitrate, sulfate, and some form of oxygen, such as peroxide) and regular maintenance of the above-ground treatment system. If the above-ground treatment system uses activated carbon, then this includes regular replacement of the spent carbon. Operation of the technology also requires regular sampling to test for the concentrations of the electron acceptors and the target contaminants. A laboratory would be hired to perform the sample analysis.

3. Demonstration Design

3.1. Demonstration Site: Background

The site for the demonstration was a contaminated portion of an aquifer at the Naval Weapons Station (NWS), Seal Beach, in southern California (Figures 2 and 3). A gasoline station located on the premises of the weapons station is contaminated with fuel hydrocarbons that leaked from a steel underground storage tank, as described in the report "Delineation of a hydrocarbon (weathered gasoline) plume in shallow deposits at the U.S. Naval Weapons Station, Seal Beach, California" [Schroeder, 1991]. The gasoline leak was discovered in 1984. The NWS Seal Beach is located on the transition of geologic formations called Landing Hill and the Sunset Gap. The physiographic and hydrogeologic settings are described in detail by [Schroeder, 1991]. The weapons station also contains the Seal Beach National Wildlife Refuge, a wetland located in the Sunset Gap formation. Investigation by the U.S. Geological Survey [Schroeder, 1991] found that the contamination from the leaking tank had migrated to the ground water underlying the Refuge. The Navy's concern about the possible adverse effects of the contamination on the Wildlife Refuge made the Seal Beach facility a potential site at which to demonstrate this remediation technology.

Figure 2: Location of the Naval Weapons Station (NWS), Seal Beach, and the Seal Beach National Wildlife Refuge.

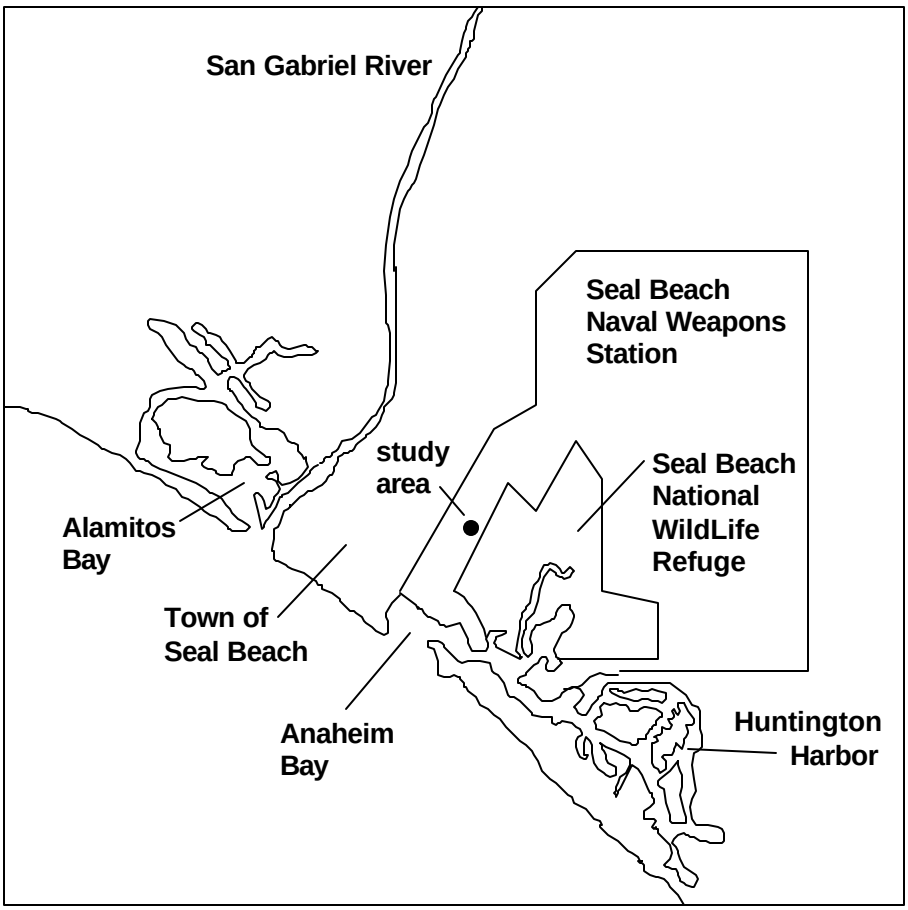

Figure 3: Location of the NWS Seal Beach, the Seal Beach National Wildlife Refuge, and the Demonstration Area.

The following conditions made the NWS Seal Beach site especially well suited for this demonstration:

1. The ground water in the contaminated zone had been anaerobic for at least a decade. Both laboratory and field studies had demonstrated the presence of anaerobic bacteria that are capable of degrading fuel hydrocarbons.
2. The aquifer is shallow and the cost of placing wells is relatively low.
3. At some sites where the ground water is contaminated with fuel hydrocarbons, the prevailing ground water flow may supply sufficient doses of electron acceptors and remove inhibitory products at rates that render engineered simulation unnecessary. At the Seal Beach site, however, the regional ground water velocity is very small. Previous studies at the site [Reinhard, et. al, 1997] indicate that the supply of electron acceptors and/or the removal of inhibitors are limiting, suggesting the need for enhancement of intrinsic bioremediation processes.
4. The aquifer solids are sufficiently permeable to allow pumping of at least a few gallons per minute, i.e., transmissivity is higher than 2 ft^2/day. The interbedding of clay lenses within silty sand (possibly sandy silt) are typical for alluvial deposits along the California Coast.

5. The regulatory agency, the California Regional Water Quality Control Board (CRWQCB), has been supporting research at this site for many years, including controlled release experiments.
6. Laboratory and field data from previous studies [Haag, et. al, 1991; Edwards, et. al, 1992; Edwards and Grbic-Galic, 1992; Ball and Reinhard, 1996; Reinhard, et. al, 1997] had suggested the probability of success of such a demonstration at the Seal Beach site.

A summary of some site characteristics is listed in Table 1.

Table 1. Standard Terminology for the Demonstration Site

Site Background:
Historical Activity that Generated Contamination:
Leaking underground storage tank
Management Practices that Contributed to Contamination:
Underground storage tank (fuel)
Site Characteristics:
Media Treated:
Ground water
Soil (in situ)
Light non-aqueous-phase liquids (LNAPL)
Contaminants Treated:
Organic Compounds, Volatile, Non-halogenated: BTEX
Organic Compounds, Petroleum Hydrocarbons

3.2. Demonstration Site: Characteristics

The hydrogeology of the NWS Seal Beach has been described in detail by [Schroeder, 1991]. About 5800 gallons of fuel leaked from an underground storage tank and contaminated the soil and ground water in the region, as shown in Figure 4. The leak was discovered in 1984 when the steel storage tank was being replaced by a pair of fiberglass tanks. Between 1984 and 1996, observation wells monitored by the Orange County Water District indicated that the contaminant plume in the ground water was slowly retracting, and by the beginning of this demonstration, the plume was concentrated around the source area. The ground water velocity in the region is low, approximately 0.7 cm/day. The ground water flow rate and direction might fluctuate somewhat with the season and with the tides.

The area contaminated by the fuel leak was on the order of 20 acres, but this demonstration was conducted in a relatively small portion of the impacted area (see Figure 4).

Table 2. Shows the Site Characteristics that affect the Treatment Cost and Performance.

Parameter	Value	Measurement Procedure
Soil Types (Soil Classification and Clay Content)	Varies spatially; here we give the extraction well as an example. 0–2 feet below ground surface (BGS): silty, fine to coarse sand	visual inspection by well logger, reviewed by registered geologist
	2–4 ft BGS: silty clay 4–5 ft BGS: silty, medium to coarse sand 5–8 ft BGS: coarse sand, some gravel	
	8–10 ft BGS: silt 10–12 ft BGS: silty fine sand 12–14 ft BGS: fine to medium sand	
	14–14.5 ft BGS: silty clay 14.5–15 ft BGS: medium sand	
Hydraulic Conductivity	0.0005–0.002 cm/sec	pump tests on 6 wells
pH	6.9–8.2 (usually 7.1–7.8) pH units	pH probe
Total Organic Carbon	0.015%–0.028%, bulk value 0.024%	
Non-aqueous phase liquids (NAPL)	Yes, light (less dense than water)	Found in monitoring wells

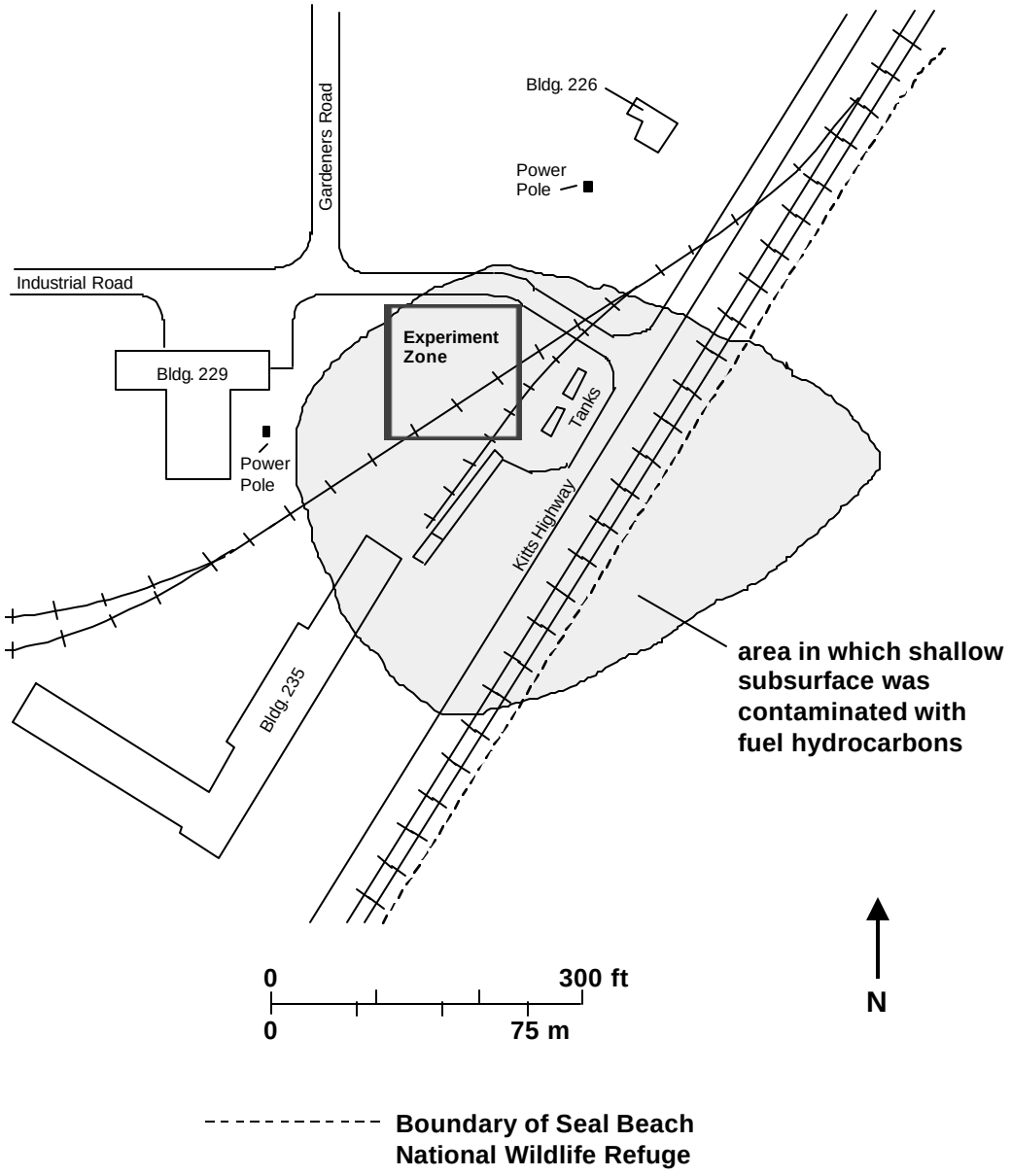

Figure 4: Contaminated region of the shallow ground water aquifer at NWS Seal Beach [Schroeder, 1991].

3.3. Physical Setup and Operation

The treatment system consisted of one extraction well and three injection wells, with relative locations as indicated in Figure 5. Each injection well was fully screened across the saturated zone of the aquifer and was located 10 m away from the extraction well. The extraction well was also fully screened across the saturated zone. The rate of injection in each well was about 1.5 L/min; the rate of extraction was about 4.5 L/min. Different electron acceptors were added at each injection well, creating three different treatment zones with different geochemical sequences. These three zones are labeled Zones 2, 3, and 4, according to the number of the injection well pertaining to each zone (see Figure 5). Zone 3 received no augmentation of electron acceptors, and was therefore expected to develop methanogenic conditions; Zone 2 was augmented with sulfate, and was expected to develop first sulfate-reducing and then methanogenic conditions; Zone 4 was augmented with nitrate and sulfate, and was expected to develop first denitrifying, then sulfate-reducing, then methanogenic conditions. The three zones were established in this manner specifically because one of the objectives of this project was to evaluate the efficacy of anaerobic biodegradation under different geochemical conditions. A full-scale implementation of this technology might employ a different number of injection/extraction wells, and might inject different levels of electron acceptors in order to optimize the bioremediation.

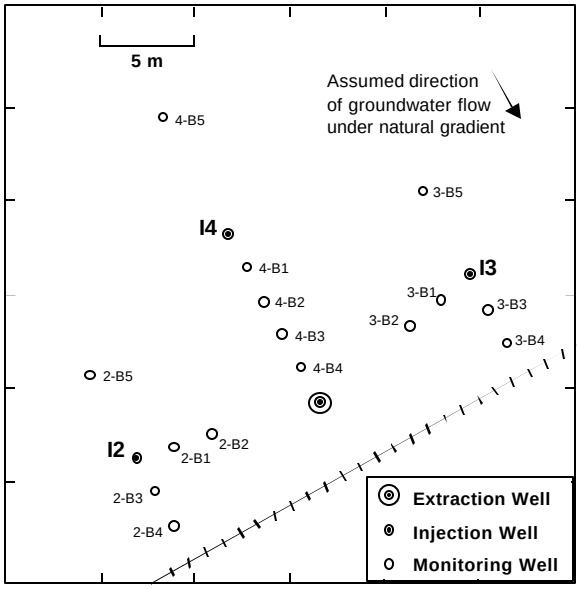

Figure 5: Plan view of the contaminated site and the location of injection, extraction, and monitoring wells.

A treatment evaluation consisted of three stages. First, the three treatment zones were flushed with water that had been treated to remove hydrocarbons, gases, and anions, but had not been augmented with electron acceptors. This served to remove inhibitory products, to remove background concentrations of the electron acceptors, and to reduce the initial BTEX concentration in each zone. The flushing stage was implemented mainly to establish base-line conditions in the treatment zones for evaluation purposes; at a full-scale implementation of this technology, the flushing stage might be omitted depending on whether or not inhibitory by-products are present. The second stage of a treatment evaluation consisted of injecting the zones with treated water that

had also been augmented with the appropriate electron acceptor(s). The augmentation stage lasted for about 4–5 weeks, which was sufficient time to develop treatment zones of about 180 m^3 in size. The third stage was a no-flow stage, in which both injection and extraction wells were shut off. During this time, the treatment zones were monitored to determine how the BTEX concentrations in each zone responded to the established geochemical conditions.

This technology demonstration lasted about 17 months and consisted of three treatment evaluations. The first augmentation period ran from 9/14/97–10/16/97; the second augmentation ran from 5/24/98-6/23/98; the third augmentation period ran from 9/2/98–10/14/98. The third augmentation was not preceded with a flushing stage. Each augmentation consisted of different concentrations of electron acceptors being injected, as summarized in Table 3. The concentrations of the injected electron acceptors were increased from one augmentation to the next in order to slowly build up the proper microbial population. A conservative tracer was injected during the flushing period of the first treatment evaluation in order to establish that the monitoring wells were hydraulically connected to the injection wells.

Table 3: Injected Electron Acceptor Concentrations during Treatment Evaluations

Evaluation #	Zone 2	Zone 3	Zone 4
1	15–20 mg/L sulfate	no electron acceptors added	15 mg/L nitrate, 15 mg/L sulfate
2	70–90 mg/L sulfate	no electron acceptors added	45–55 mg/L nitrate, 70–80 mg/L sulfate
3	40–50 mg/L nitrate, then 75–95 mg/L sulfate	no electron acceptors added	85–125 mg/L nitrate, 70–100 mg/L sulfate

Figure 1 shows a schematic for the ground water recirculation system used in this demonstration. We used treatment and augmentation systems that were unusual in the following respects:

1. The treatment system was designed to remove not only target contaminants and inhibitory products, but also excess electron acceptors (oxygen, nitrate, and sulfate). This was done in order to provide careful control over the composition of the re-injected water so that we could investigate the effects of particular geochemical conditions on the bioremediation process. Under typical operating conditions at a full-scale remediation site, excess electron acceptors would not be removed prior to augmentation and re-injection.
2. The augmentation system did not always provide the optimum mixture of electron acceptors for bioremediation. For instance, no oxygen was added during this demonstration. This was done because one of the goals of the project was to compare bioremediation under three different types of anaerobic conditions (denitrifying, sulfate-reducing, and methanogenic). Under typical operating conditions at a full-scale remediation site, some form of oxygen (e.g., peroxide) would be introduced along with nitrate and sulfate.

3.4. Monitoring Procedures

Sampling was performed automatically via an Automated Sampling and Analysis Platform (ASAP) from Analytic and Remedial Technology (Milpitas, CA). The automated on-line

sampling manifold consisted of 111 sample ports, of which 105 ports were connected directly to the multi-level sample bundles of the monitoring wells. Connections were 0.1875-inch stainless steel sample lines. The remaining six ports were connected to the treatment system and to the three injection wells. After flushing the sample lines, the ASAP extracts a sample and prepares separate aliquots for analysis of volatile organic compounds, anions, pH, and dissolved oxygen. The ASAP provided samples directly to the instrumentation without operator intervention and was operated continuously from August 1997 until November 1998. Results from the ASAP analyses were automatically logged in a computer database. Sample waste water was recycled back to the inlet of the water treatment system.

Each of the three treatment zones had five monitoring wells, as shown in Figure 5. Each monitoring well consisted of seven 0.1875-inch stainless steel tubes with the inlets spaced vertically 14 inches apart, thus providing seven discrete sample locations covering the length of the injection well screens at each monitoring well location. In each monitoring well, the top tube was placed very close to the water table; the bottom tube was located about 7 feet below the water table, with the middle five tubes spaced evenly in between. The inlet of each sample tube was enclosed in glass wool filter protected by nylon "horse hair" fabric, a double weave knit. The monitoring wells were installed by placing the sample bundles in 2-inch boreholes and backfilling with sand; this minimizes the required flush volumes required to obtain representative samples.

For each zone, one multilevel sample well was located approximately 7 m upgradient of the injection well, and two multilevel sample wells were located 2 and 4 m in the direction of the extraction well. In Zones 2 and 3, additional monitoring wells were placed 2 and 4 m downgradient from the injection well. In Zone 4, where the injection well was directly upgradient of the extraction well, monitoring wells were placed 2, 4, 6, and 8 m from the injection well.

3.5. Analytical Procedures

Connections between the monitoring wells and the ASAP were stainless steel tubing. After flushing the sample lines, the ASAP extracted a sample and prepared separate aliquots for analysis of:

1. concentrations of volatile organic compounds (including BTEX) via a modified purge-and-trap method with gas chromatography (GC), photo-ionization detection (PID), and flame ionization detection (FID);
2. concentrations of anions (including bromide, sulfate, and nitrate) via ion chromatography; and
3. pH, dissolved oxygen, and concentration of sulfide via specific probes.

Although the modified purge-and-trap system is not of the design used in standard methods, it has been demonstrated successful by the U.S. Environmental Protection Agency [U.S. EPA, 1993]. The gas chromatograph was not able to resolve meta- and para-xylene, so the concentrations of these two compounds were measured as a sum. Photo-ionization detection was used for the measurement of BTEX concentrations; flame ionization detection was used for the measurement of the concentrations of aliphatic hydrocarbons. Results from the ASAP analyses were automatically logged in a computer database. All samples were stamped with date and time, and had unique names for sample locations.

Table 4: Compounds Analyzed by Automatic Sampling and Analysis Platform

Compound	Gas Chromatography	Ion Chromatography	Specific Probe
Methane	X		
3-methyl-pentane	X		
Hexane	X		
Benzene	X		
Toluene	X		
Ethylbenzene	X		
Xylenes	X		
Trimethyl-benzenes	X		
Chloride		X	
Bromide		X	
Nitrate		X	
Sulfate		X	
Dissolved Oxygen			X
pH			X
Sulfide			X

3.6. Performance Objectives

The principal objective of this project was to demonstrate the technical viability of enhanced intrinsic anaerobic bioremediation of fuel-contaminated ground water. In particular, our goal was to stimulate biodegradation of BTEX compounds in ground water by the addition of the electron acceptors nitrate and sulfate. The primary performance metric for the demonstration is the historical change in BTEX concentrations in the ground water at the site. The secondary performance metric for the demonstration is the historical change in the concentrations of the injected nitrate and sulfate. In addition to the observed change in BTEX concentrations, the destruction of fuel hydrocarbon compounds can be assessed from stoichiometric considerations by quantifying the biological utilization of the sulfate and nitrate injected.

Over recent years, in situ bioremediation has become accepted by regulatory agencies for the remediation of fuel-contaminated sites [U.S. EPA, 1997]. In general, there are two performance criteria that must be met for regulatory acceptance of this technology:

1. The ability of the technology to reduce the BTEX concentrations in ground water to below their drinking water maximum contaminant levels (MCLs): 0.005 mg/L for benzene, 1 mg/L for toluene, 0.7 mg/L for ethylbenzene, and 10 mg/L for (total) xylenes.
2. Sufficient utilization of injected nitrate such that the nitrate concentration does not exceed regulatory standards.

There are no specific performance criteria that will determine whether or not the Department of Defense (DoD) will accept this technology. The acceptance of the technology by DoD is mainly an economic question and will depend on site-specific conditions.

4. Performance Assessment

As discussed in Section 3.6., above, the evaluation of the technology's performance is based primarily on the historical change in contaminant (BTEX) concentrations, and secondarily on the historical change in electron acceptor concentrations. These concentrations were measured through monitoring wells. Each monitoring well had seven sampling points, spaced vertically about 14 inches apart. Each sampling point had a unique name that is given in three parts: the first part indicates in which treatment zone the monitoring well is located; the second part indicates the number of the well bundle within the zone (see Figure 5); and the third part indicates the vertical location of the sampling point, where 1 indicates the uppermost sampler and 7 indicates the lowest sampler. For example, a designation "2-B1-4" means Zone 2, well bundle 1, the fourth sampler from the top. The injection wells are designated I2, I3, and I4, as indicated in Figure 5.

In the subsections below, we present the demonstration results graphically. On some of the figures, different periods in time are labeled with the letters F, A, or N. These letters correspond to the three stages of a treatment evaluation: "F" indicates the first (flushing) stage, in which the treatment zone was flushed with treated but unaugmented water; "A" indicates the second (augmentation) stage, in which the treatment zone was augmented with electron acceptors; and "N" indicates the third (no-flow) stage, in which the injection and extraction wells were shut off such that there was no flow through the treatment zones.

4.1. Summary of Field Observations

The Final Report for this demonstration project provides an in-depth analysis of the technology performance. In this report we briefly summarize the most important findings. Figure 6 shows the BTEX concentration histories in Zone 2, which was augmented with only sulfate during the first two augmentations, and augmented with sulfate and nitrate during the third augmentation. The toluene concentration was very low even at the beginning of the demonstration, indicating that toluene is preferentially degraded among the BTEX compounds under natural conditions. Benzene, ethylbenzene, and xylene concentrations in Zone 2 all decreased over the course of the demonstration. However, only o-xylene appears to have been degraded as a result of sulfate augmentation: note the rapid decrease in concentration during first augmentation period. Benzene, ethylbenzene, and m+p-xylene were removed slowly, apparently due more to flushing than to biodegradation. The ethylbenzene concentration did drop sharply during the third augmentation, when nitrate was added along with sulfate, indicating that nitrate addition can stimulate biodegradation of ethylbenzene.

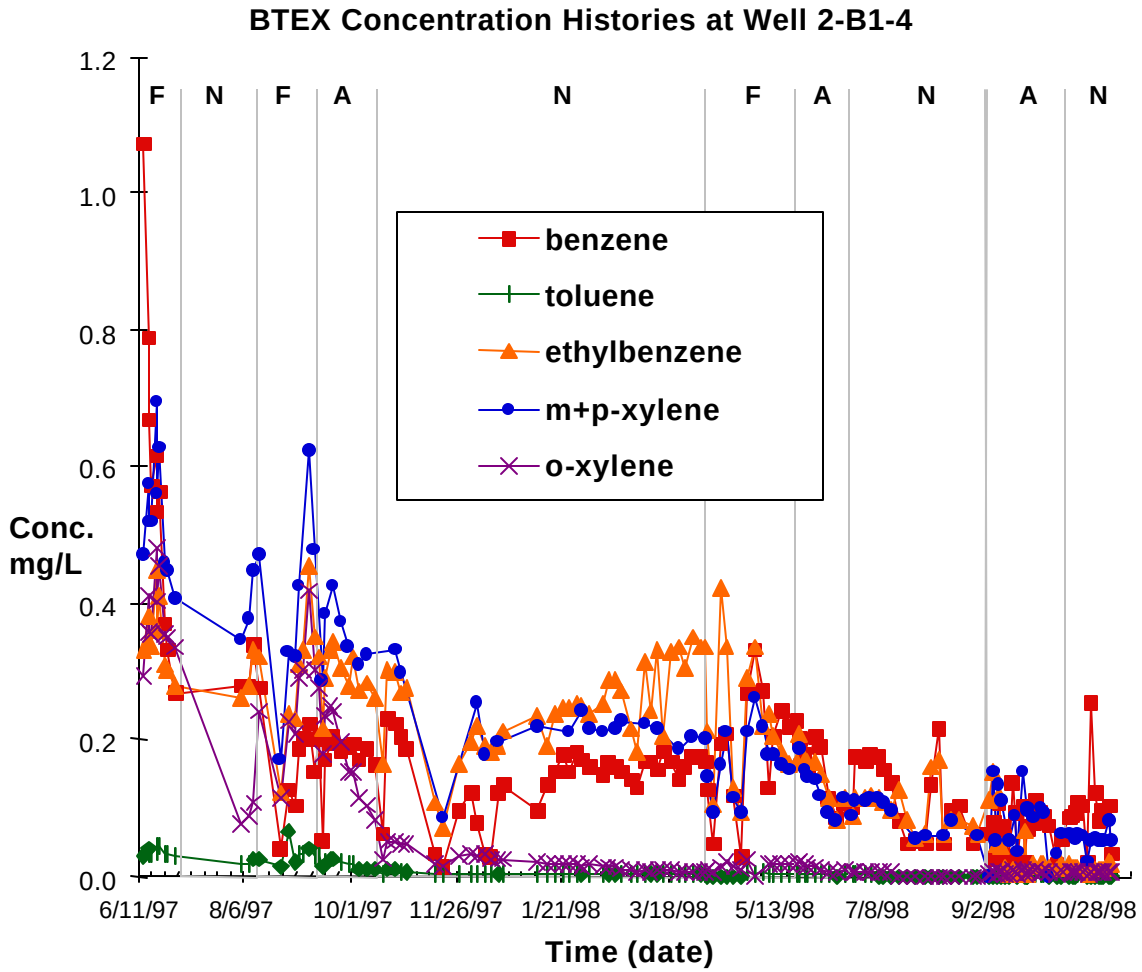

Figure 6: BTEX concentration histories in Zone 2.

Figure 7 shows the BTEX concentration histories in Zone 3, which received no electron acceptors, and therefore developed fermentative-methanogenic conditions. Methane concentrations (not shown) reached concentrations as high as 6 mg/L at monitoring point 3-B1-4. In this region, the concentrations of toluene, ethylbenzene, and xylenes were all low even at the beginning of the demonstration, making it difficult to assess whether or not fermentation-methanogenesis is an effective removal mechanism for these compounds. The benzene data show that benzene concentrations decreased during flushing periods, but rebounded during no-flow periods; the rebound could be a result of benzene dissolution from a non-aqueous phase, benzene desorption from aquifer solids, and/or slow encroachment of benzene-laden ground water from another part of the site. The strong production of methane indicates that a relatively large quantity of petroleum hydrocarbons was being degraded via methanogenesis, but it is impossible to determine which petroleum compounds in particular were degraded. The data suggest that fermentation-methanogenesis is not an effective removal mechanism for benzene, especially if a continuing source of benzene is present in a sorbed or NAPL phase.

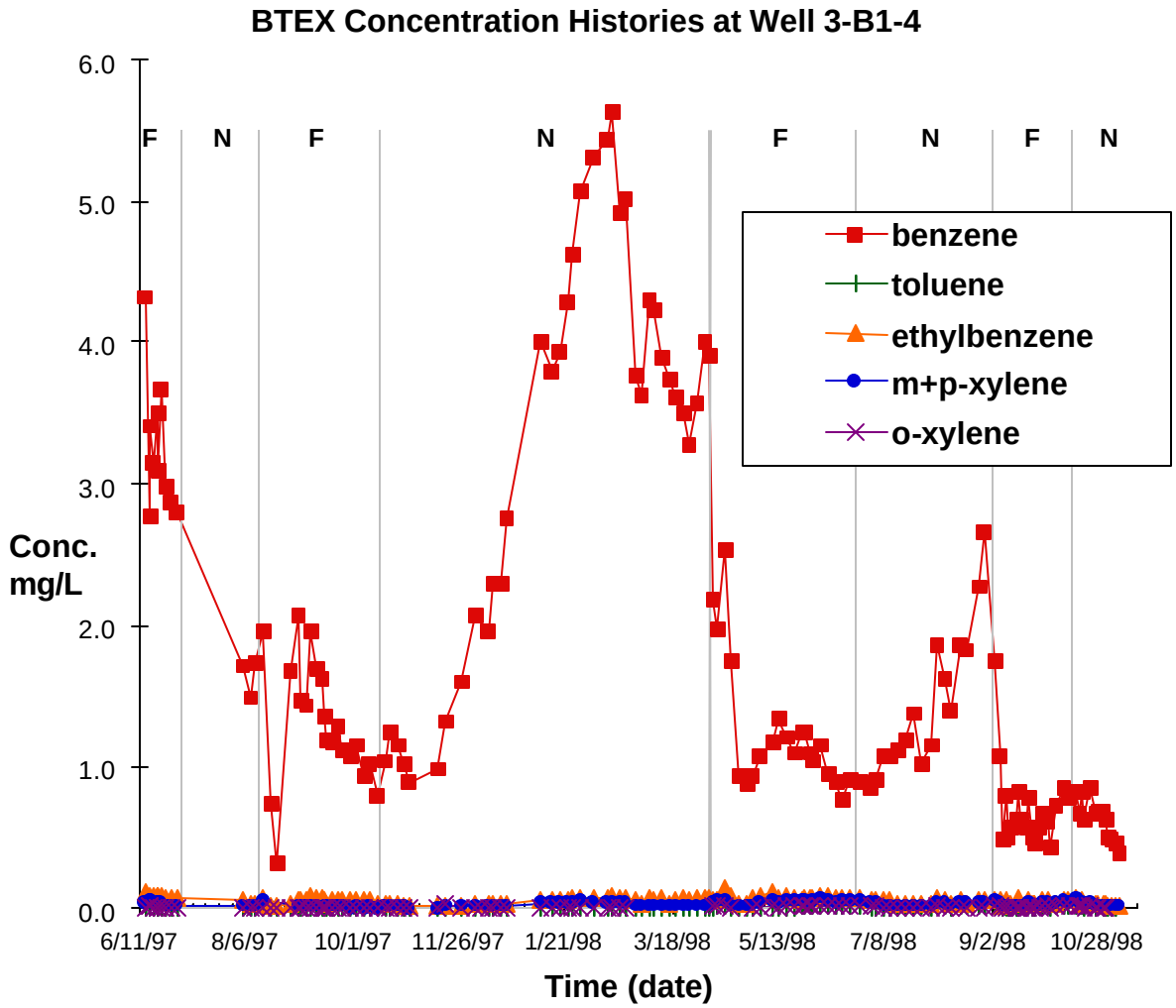

Figure 7: BTEX concentration histories in Zone 3.

Figure 8 shows the BTEX concentration histories in Zone 4, which was augmented with both sulfate and nitrate. As in Zone 3, the benzene concentration in Zone 4 decreased during flushing and augmentation stages, but rebounded during no-flow stages. However, the toluene, ethylbenzene, and xylene concentrations did not exhibit the same rebound behavior as benzene. Notably, ethylbenzene and m+p-xylene were removed much more quickly in Zone 4 than in Zone 2, which received sulfate only. It appears that nitrate augmentation is capable of stimulating biodegradation of ethylbenzene and of m+p-xylene. The toluene and o-xylene concentrations were very low even at the beginning of the demonstration, making it difficult to assess the effects of nitrate augmentation on the biodegradation of these two compounds.

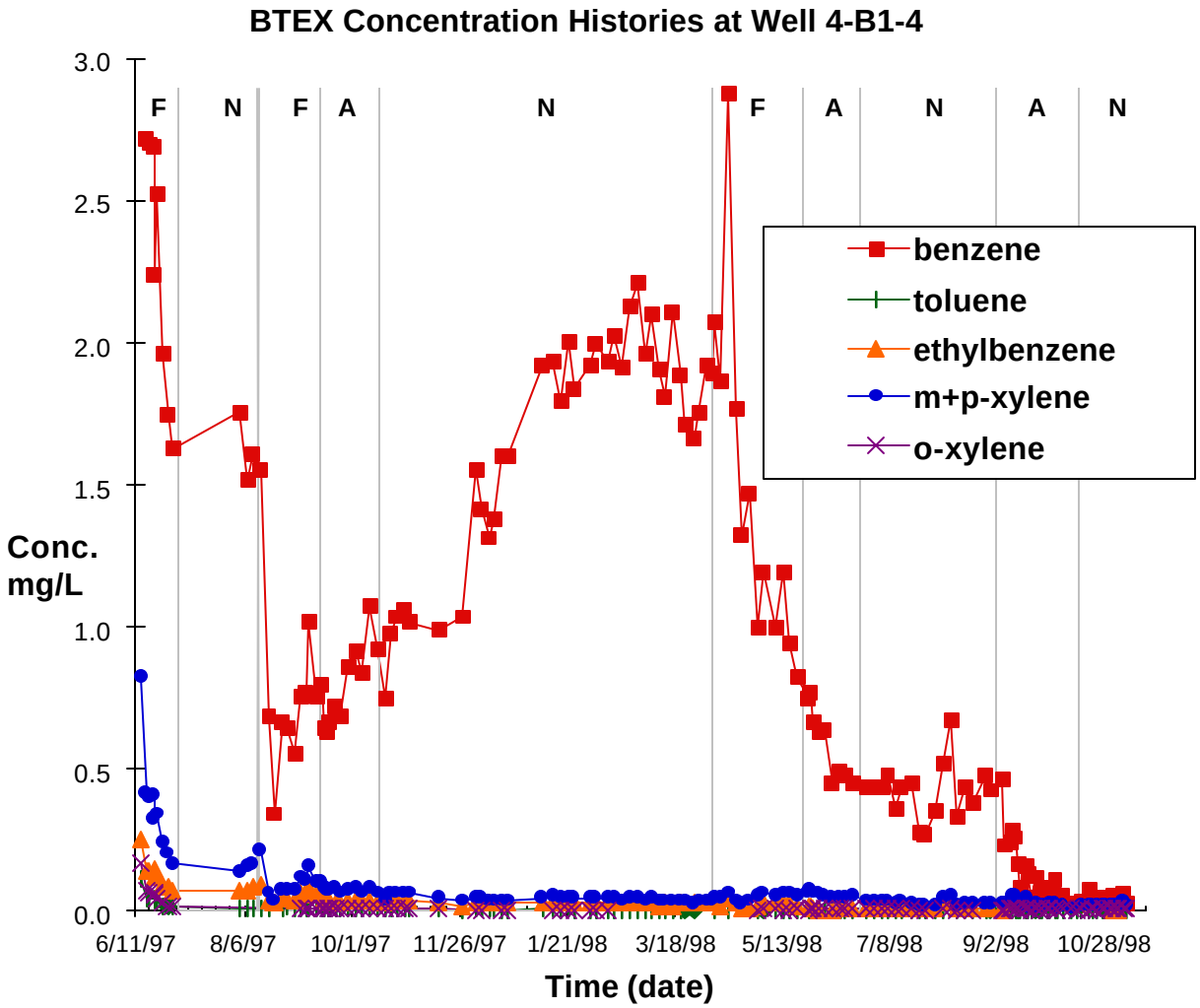

Figure 8: BTEX concentration histories in Zone 4.

Because it is impossible to perform a quantitative mass balance on the BTEX degradation, a secondary performance metric for this demonstration was the response of the injected sulfate and nitrate electron acceptors. Figure 9 compares the injected sulfate and nitrate concentrations at injection well I4 to the measured concentrations at monitoring well 4-B1-4. As expected, all three augmentations exhibited similar behavior: the sulfate broke through at nearly 100% of the injected concentration, then disappeared slowly, whereas the nitrate broke through at less than 100% and disappeared quickly. Nitrate was used preferentially over sulfate, and was quickly consumed by the microorganisms present during oxidation of petroleum hydrocarbons. Sulfate is used secondarily when nitrate is present. In Zone 2, where sulfate was injected without nitrate, sulfate utilization occurred more rapidly (data not shown). The use of the injected electron acceptors was good evidence that petroleum hydrocarbons were being degraded at this site; however, it is impossible to determine which hydrocarbons in particular were degraded most rapidly.

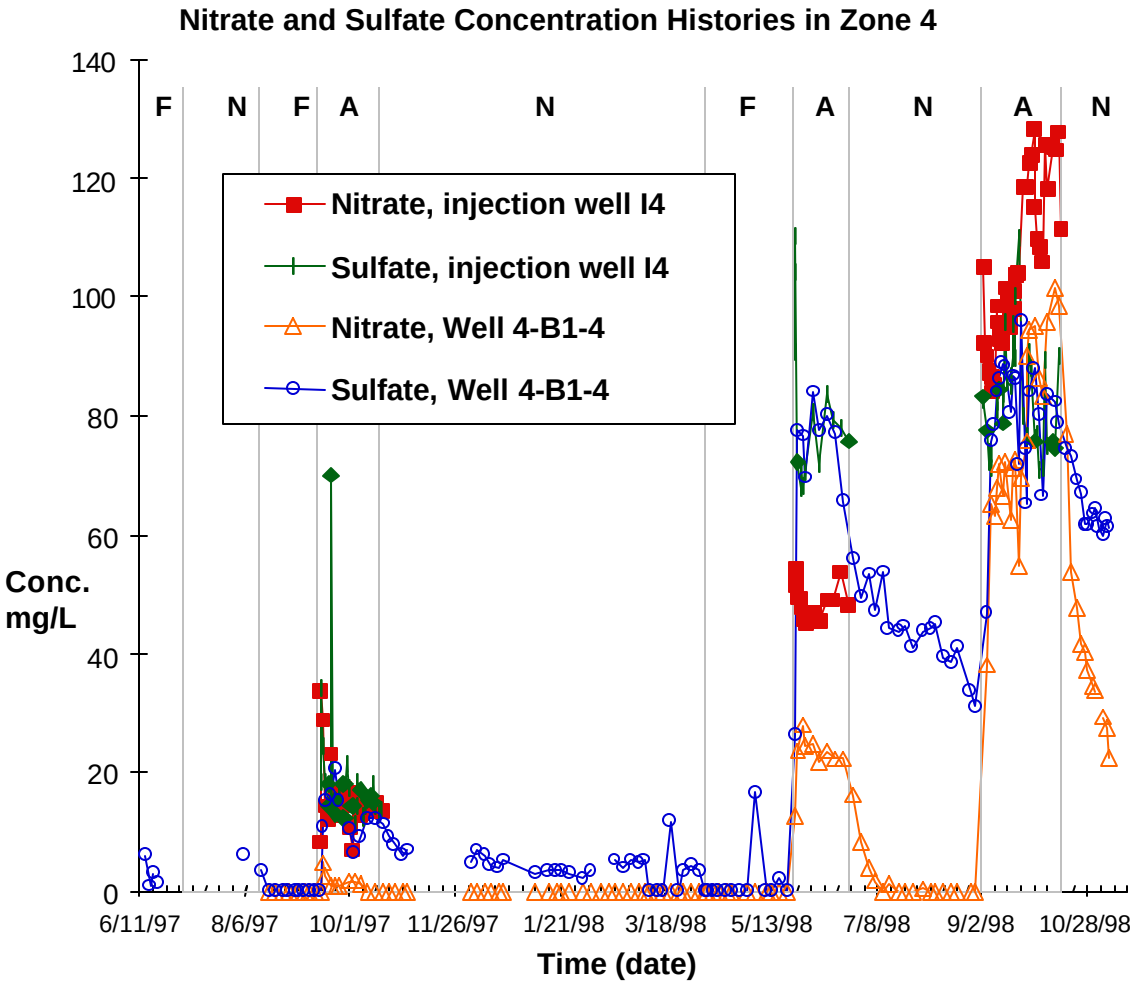

Figure 9: Concentration histories of sulfate and nitrate at injection well I4 and at monitoring well 4-B1-4.

4.2. Data Assessment

In general, we believe the reported data to be of high quality and to allow assessment of the demonstration's objectives. The Automated Sampling and Analysis Platform (ASAP) enabled us to compile a very large database of concentration histories at 105 different sampling point locations throughout the contaminated site. Altogether, the ASAP analyzed over 9000 samples for the 15 analytes listed in Table 4, as well as some analytes not listed in Table 4. As a result, we have a very complete picture of how particular compounds responded to the treatment in time and in space. Furthermore, the large database allows us to compare particular recorded measurements in order to provide an internal check on the consistency of the data. For instance, the BTEX concentrations were measured using gas chromatography with detection via photo-ionization (PID) and flame ionization (FID) detectors. The concentrations reported in this report are those that were measured via PID, which is believed to be more reliable for aromatic hydrocarbons; however, the FID measurements are available as a qualitative cross-check that the PID measurements are reasonable.

Also, the availability of seven sampling points spaced vertically at each monitoring well allows for another useful internal check on the data. We would not expect two different sampling points in the same well bundle to record exactly the same concentrations of a particular compound, but because there is not extreme physical heterogeneity at this site, we would expect the two sampling points to record similar trends. For example, a comparison of benzene concentrations measured at sampling points 2-B1-4 and 2-B1-6 shows that the two monitoring points seldom produced identical concentration measurements, but that the two monitoring points were qualitatively in agreement with each other (data not shown). This is precisely what we would expect from different points along the same vertical sampler.

We observed that different monitoring wells often produced very different measurements. For instance, wells 2-B1 and 2-B2 produced very different measurements for sulfate concentration (data not shown). However, we do not believe this to be an indication of poor data quality; rather, we believe that it indicates the spatial variability present at most field sites.
Despite our general confidence in the quality of the data, it is not possible to compute a mass balance on the BTEX compounds. At the Seal Beach site, non-aqueous-phase liquids (NAPLs) were present, and are believed to have acted as a source of BTEX throughout the duration of the demonstration. Other field processes also confound a quantitative analysis of the mass of BTEX degraded. Desorption of BTEX from aquifer solids into the aqueous phase, diffusion of BTEX from regions of high concentration into the treatment zones, and slow encroachment of native ground water can all lead to the introduction of additional BTEX into the aqueous phase of the treatment zones. Quantification of these sources is infeasible.

4.3. Comparison of Actual Performance Results to Expected Performance

As expected, sulfate and nitrate were used for the oxidation of fuel hydrocarbons, with nitrate used preferentially over sulfate. Augmentation of the ground water with nitrate and sulfate was able to reduce the concentrations of toluene, ethylbenzene, and xylenes to very low levels, far below the maximum contaminant levels (MCLs). Consistent with previous findings were the observations that toluene was degraded preferentially among BTEX compounds, and that ethylbenzene degradation occurs under nitrate-reducing conditions but not under sulfate-reducing conditions. The behavior of the xylene compounds was slightly different than anticipated: o-xylene was rapidly removed under sulfate-reducing conditions, m+p-xylenes were more effectively removed under nitrate-reducing conditions.

Over the time span of this demonstration, benzene concentrations were not reduced to below the benzene MCL of 5 µg/L. Because the benzene concentration was reduced over time in all three treatment zones (Figures 6–8), we suspect that continued operation of this technology would be able to reduce the benzene concentration in ground water to below the MCL. However, it appears that much of the benzene removal is due to flushing by the extraction well, not due to biodegradation.

Operation of the technology proceeded as anticipated. Some routine maintenance was required for the above-ground water treatment system was required.

4.4. Performance Conclusions

We found that this treatment technology was effective at removing all BTEX compounds from the ground water. Specifically:

- Toluene appeared to be preferentially degraded, and was rapidly degraded even without augmentation of the electron acceptors. A few feet below the water table, toluene concentration was typically below 10 µg/L.
- Biodegradation of ethylbenzene appeared to be stimulated by the introduction of nitrate. In Zone 4, where nitrate was introduced, ethylbenzene concentration was reduced from 250 µg/L to less than 10 µg/L.
- Biodegradation of ortho-xylene appeared to be stimulated by the introduction of sulfate. In Zone 2, where only sulfate was introduced, the o-xylene concentration was quickly reduced from over 400 µg/L to less than 10 µg/L.
- Biodegradation of meta- and para-xylene appeared to be stimulated by the introduction of nitrate. In Zone 4, where nitrate was introduced, the combined m+p-xylene concentration was reduced from 500 µg/L to less than 20 µg/L.
- Benzene was effectively removed from the ground water, but it appears that most of the removal was due to flushing by the extraction well, with a small contribution from biodegradation. In Zone 4, which was augmented with nitrate and sulfate, benzene concentration was reduced from 3 mg/L to about 50 µg/L, but removal was slow. In the zone that received neither nitrate nor sulfate (i.e., methanogenic conditions), benzene concentration was reduced from 4 mg/L to about 0.4 mg/L, and also was slow. Benzene concentrations often rebounded when pumps were temporarily shut off.

5. Cost Assessment

5.1. Summary of Demonstration Costs

The total cost for this project was approximately $875,000. Table 5, below, provides estimates for the specific items that contributed to this total cost. However, Table 5 does not include some costs incurred by the Department of Defense (DoD) and the Naval Facilities Engineering Service Center (NFESC), including some costs for personnel salaries, project management, site support, and travel.

Table 5: Approximate Costs for Technology Demonstration

Cost Element	Cost	Sub-Cost
Fabrication and installation of wells and treatment system:	$47,000	
Labor:	$361,000	
Project staff salaries and benefits:		$355,000
Other student support:		$6,000
Sub-contractor expenses:	$24,600	
Injection well and extraction well installation:		$13,100
Monitoring well installation:		$10,100
Asphalt excavation and replacement:		$1,400
Expendable materials and services:	$92,400	
Laboratory supplies and expenses:		$73,800
Chemicals and compressed gas:		$8,200
Other expendable materials and services:		$10,400
Travel:	$55,000	
Overhead and indirect costs:	$295,000	
Total Cost:	**$875,000**	

The $361,000 labor cost includes partial support of two professors, one senior engineering associate, one post-doctoral research associate, one staff research assistant, and several graduate student research assistants over the course of the three-year project. The $73,800 cost for laboratory supplies and expenses includes costs for analysis of all samples collected by the Automated Sampling and Analysis Platform (ASAP). Over the duration of the demonstration, the ASAP collected and analyzed more than 9000 samples for the 15 different analytes listed in Table 4. The travel cost of $55,000 is relatively large because many of the project personnel traveled regularly between Stanford University and the demonstration site at NWS Seal Beach.

5.2. Projected Cost of Full-Scale Field Application

Tables 6, 7a, and 7b provide an assessment of the expected operational costs for the technology when implemented. The tables do not necessarily represent the actual cost of the particular demonstration described in this report; rather, they are a prediction of how much it should cost to implement this technology at a typical site. An example of typical site conditions is given below. For the cost assessment, we make the following assumptions, which are all reasonable for a typical fuel-contaminated site:

- About 5000 gallons of fuel leaked from an underground storage tank, contaminating the soil and shallow ground water. About 95% of the fuel (4750 gallons) was recovered via

excavating the vadose zone down to the water table, or via some other removal mechanism. The remaining 250 gallons are present below the water table in three forms: as globules of non-aqueous phase liquid, dissolved in the ground water, and sorbed to aquifer solids.

- Five treatment zones are developed at the contaminated site, each consisting of an injection well and an extraction well. The injection rate and extraction rate in each zone are 4.6 L/min.
- A treatment cycle consists of a 1 month flushing period, a 1 month augmentation period, and a 1 month no-flow period. Four treatment cycles are performed per year. Based on these parameters, about 200,000 L water are injected into each of the 5 treatment zones during the augmentation stage, for a total of 1,000,000 L injected during each augmentation stage.
- During the augmentation stages, nitrate is injected at 80 mg/L, sulfate at 80 mg/L, and oxygen at 9 mg/L. Stoichiometrically, the injection of 320 kg/year nitrate, 320 kg/year sulfate, and 36 kg/year oxygen degrades 145 kg/year fuel hydrocarbons (as toluene). This is equivalent to about 44 gallons/year.
- The above-ground treatment system for extracted water consists of granular activated carbon for hydrocarbon removal, followed by aeration for the removal of nitrogen gas (via stripping) and sulfide (via oxidation to sulfate). The treatment system operates 8 months out of each year, i.e., during the flushing stages and during the augmentation stages, but not during the no-flow stages. Treated water is augmented with electron acceptors and is re-injected into the aquifer.
- The hydrocarbon concentration in extracted ground water averages 3 mg/L, and is effectively removed by the granular activated carbon. This is consistent with observations from the NWS Seal Beach demonstration. Therefore, about 24 kg/year hydrocarbons are removed via adsorption onto activated carbon, which is equivalent to about 7.2 gallons/year.
- The activated carbon system has an empty-bed volume of 230 L and an empty-bed contact time of 10 minutes. The system is loaded with 92 kg activated carbon (400 kg/m^3). During each treatment cycle, about 6 kg hydrocarbons are removed, such that the loading at the end of the treatment cycle is 65 g hydrocarbon per kg activated carbon. The activated carbon is replaced after each treatment cycle, i.e., four times annually.
- The overall hydrocarbon removal rate is 169 kg/year, equivalent to 51 gallons/year. About 85% of the removal is from in situ biodegradation, and about 15% is from activated carbon adsorption. The projected clean-up time is 4.9 years.

Under these conditions, Table 6 summarizes the anticipated capital costs, while Tables 7a and 7b summarize the present value of the operating and maintenance (O&M) costs. The estimated capital cost is $470,000. The estimated present value of the O&M costs is $615,000 over 5 years. The total present value of the clean-up costs is $1,085,000, or $4,340 per gallon of fuel hydrocarbon recovered.

Table 6: Capital Cost for Enhanced In Situ Bioremediation Technology Capital Cost

Capital Cost Element	Cost	Sub-Cost
Site Characterization:		
Hydrogeologic characterization:	$100,000	
Wells for estimating hydraulic head and gradient:		$60,000
Pump tests to estimate hydraulic conductivity:		$20,000
Cores and core analysis to estimate hydraulic conductivity:		$20,000
Microcosm studies to test biological activity:	$10,000	
Technology mobilization, set-up, and demobilization:		
Transportation/delivery of equipment, facilities, and personnel:	$20,000	
Set-up of temporary facilities (e.g., trailer) and utilities:	$20,000	
Demobilization:	$10,000	
Planning and preparation:		
Engineering design and modeling:	$50,000	
Permits and licenses, including air emission and water discharge:	$20,000	
License fees associated with use of a technology:	$0	
Regulatory interaction:	$5,000	
Written plans:	$35,000	
Work plans:		$10,000
Sampling and analysis plans:		$10,000
Health and safety plans:		$5,000
Community relations plans:		$5,000
Site management plans:		$5,000
Site work:		
Establish physical infrastructure for technology application:	$15,000	
Activities necessary to restore site to pre-remediation conditions:	$15,000	
Activities necessary to meet specifications of site restoration plan:	$15,000	
Preparing specific site of the technology:	$15,000	
Clearing and grubbing:		$5,000
Earthwork:		$5,000
Construction of utilities, culverts, treatment pads, foundations, etc.:		$5,000
Installation of treatment system (equipment and appurtenances):		
Extraction wells (5 wells, $5000 each):	$25,000	
Injection wells for augmentation (5 wells, $5000 each):	$25,000	
Monitoring wells (10 multi-level samplers, $5000 each):	$50,000	
Above-ground water treatment system:	$10,000	
Activated Carbon column (1 m length, 0.5 m diameter):		$2,000
Trickling Filter for aeration:		$6,000
Chemical Injection System:		$2,000
Startup and testing:		
Establishment of operating conditions:	$5,000	
Shakedown:	$5,000	
Training of O&M personnel:	$5,000	
Other capital costs:		
Data processing and computer equipment:	$5,000	
Safety equipment:	$5,000	
Vehicles:	$5,000	
Total Capital Cost:	**$470,000**	

Table 7a: Annual Operating and Maintenance (O&M) Costs for Technology

O&M Cost Element	Cost	Sub-Cost
Labor:		
Maintenance of technology and associated equipment:	$25,000	
Labor supervision:	$5,000	
Payroll expenses:	$5,000	
Materials:		
Consumable supplies:	$5,000	
Activated carbon (replaced quarterly; includes disposal):		$5,000
Process materials:	$0	
Bulk chemicals:	$13,000	
Nitrate (320 kg/year):		$7,000
Sulfate (320 kg/year):		$6,000
Raw materials:	$0	
Utilities and Fuel		
Fuel:	$500	
Electricity: (primarily for running pumps)	$1,000	
Natural gas:	$0	
Water:	$500	
Equipment ownership, rental, or lease:	$0	
Performance testing and analysis:		
Monitoring, sampling, analysis ($1000 per well per round):	see Table 7b	
Other O&M Costs:		
Maintenance and repair of office/administrative equipment:	$5,000	
Health and safety costs:	$5,000	
Personal protective equipment:		$2,000
Monitoring of personnel for health and safety:		$3,000
Total Annual O&M Costs (not including monitoring):	**$65,000**	
Total Annual O&M Costs (including monitoring):	**see Table 7b**	

Table 7b: Present Value of O&M Costs, Including Monitoring Enhanced In Situ Anaerobic Bioremediation Method

Year	Sampling Frequency	Monitoring Cost (Unadjusted)	Total O&M Cost (Unadjusted)	O&M Cost (with inflation)	O&M Cost (present value)
1	Monthly	$120,000	$185,000	$185,000	$185,000
2	Bi-Monthly	$60,000	$125,000	$131,250	$121,528
3	Bi-Monthly	$60,000	$125,000	$137,813	$118,152
4	Quarterly	$40,000	$105,000	$121,551	$96,491
5	Quarterly	$40,000	$105,000	$127,628	$93,811
Total O&M Cost, Present Value					**$615,000**

Notes: Sampling frequency is assumed to follow the schedule above
Costs based on assumption of 10 monitoring wells and cost of $1000 per well per round of sampling/analysis
Inflation rate assumed 5% annually, discount rate assumed 8%
Clean-up time for this method estimated to be 5 years
Other site characteristics described in Section 5.2

For comparison, we estimated the cost of applying the conventional pump-and-treat method to the "typical" spill described above. Details of this cost estimation are provided in the project Final Report. For the pump-and-treat remediation, the estimated capital cost is $397,000. The estimated present value of the O&M costs is $1,143,000 over 15 years. The total present value of the clean-up costs is $1,530,000, or $6,120 per gallon of fuel hydrocarbon recovered.

Based on this analysis, the proposed technology, enhanced in situ bioremediation, is preferable to conventional pump-and-treat remediation. Although there are some additional costs associated with implementing a relatively new technology, the overall cost is lower, and the associated clean-up time is much shorter (about 5 years instead of about 15 years). However, it is important to note that the extent of biodegradation for the conventional pump-and-treat remediation is extremely uncertain. If the actual rate is much faster or much slower than the assumed rate, then the cost for the pump-and-treat remediation could be affected significantly.

6. Implementation Issues

6.1. Cost Observations

One of the major costs for this demonstration was the cost for monitoring, sampling, and analysis. This cost was approximately $74,000, as shown in Table 5 (laboratory supplies and expenses). This cost was relatively large because the Automated Sampling and Analysis Platform (ASAP) collected and analyzed more than 9000 samples over the course of the demonstration. Labor costs were also increased as a result of the intense sampling and analysis effort, because personnel were required to maintain the equipment and verify the analyses. In future applications of this technology, where a less rigorous monitoring program would be sufficient, we would expect both laboratory costs and labor costs to decrease.

The cost of this project was also affected by the fact that the demonstration site was far away from Stanford University, where many of the project personnel were located.

6.2. Performance Observations

Overall, the performance of the demonstration was similar to what had been expected at the project inception. The target contaminants (BTEX) and the injected electron acceptors (nitrate and sulfate) behaved in a manner that qualitatively agrees with what had been expected from previous studies [e.g., Reinhard, et. al., 1997].

The issue that most affected the demonstration performance was the presence of BTEX compounds in a non-aqueous liquid phase. Gasoline is less dense than water, so most of the non-aqueous-phase liquid (NAPL) was located near the top of the saturated zone (i.e., near the water table), but there may have been some residual NAPL present below the water table as well. The presence of BTEX in a non-aqueous phase affected the performance primarily in two ways:

1. Because it was impossible to determine the mass of BTEX present in the non-aqueous phase, we were unable to perform a quantitative mass balance or to quantify the amount of BTEX removed via biodegradation over the course of the demonstration.
2. During no-flow periods of the demonstration, the BTEX concentrations (particularly that of benzene) in the monitoring wells rebounded to high levels.

Therefore, in moving this technology to a full-scale application, we suggest that the presence of non-aqueous-phase liquids is liable to significantly extend the required time for clean-up. Nevertheless, this technology is one that may be relatively successful at treating sites where residual NAPL is present, because the treatment zones are established in situ at the same location where the contamination is present. Therefore, if a sufficient level of electron acceptors can be maintained, then as the NAPL dissolves, it will be degraded biologically.

6.3. Regulatory Issues

There are three main regulatory issues with regard to the implementation of the technology described in this report:

1. Nitrate, which has a drinking water maximum contaminant level (MCL) of 45 mg/L, is injected into the ground water as an electron acceptor. In order for the technology to operate at maximum efficiency, nitrate should be injected at a concentration higher than its MCL. Although nitrate is consumed rapidly after its injection, and therefore does not represent a significant contamination risk, regulatory approval is required for injection of nitrate at high concentrations.
2. Contaminated ground water is extracted, treated, augmented with electron acceptors, and then re-injected into the aquifer. The re-injection of treated ground water requires regulatory approval.
3. It must be satisfactorily demonstrated that sufficient hydraulic control is established, so that the plume can be contained if any problem arises during implementation of the remediation technology.

For the demonstration at NWS Seal Beach, we first injected nitrate at low concentrations and monitored the subsequent biological utilization of nitrate. When we had demonstrated that nitrate was biologically degraded very rapidly, regulators were amenable to the injection of higher concentrations of nitrate.

We found regulators to be concerned with the re-injection of treated ground water into the aquifer. Demonstration of hydraulic control of the site and formulation of appropriate contingency plans are helpful aides in obtaining regulatory approval for re-injection.

6.4. Lessons Learned

Some of the most important findings from this demonstration project are the following.

- Ground water contaminated from gasoline contains not only BTEX compounds, but many other gasoline components as well. At the Seal Beach site, much of the injected nitrate and sulfate was used by bacteria to degrade non-BTEX hydrocarbons. This makes it difficult to predict the amount of electron acceptor(s) that will be needed for complete BTEX removal.
- At the Seal Beach site, nitrate utilization was fast. Most or all of the injected nitrate was consumed within 30 days after injection ceased for the third augmentation, and even faster for the first and second augmentations. Sulfate utilization was also relatively fast in the region where sulfate was the only electron acceptor injected. In the region where both sulfate and nitrate were injected, the sulfate utilization was much slower.

- Injection of nitrate at very high concentrations (greater than 100 mg/L) might lead to the formation of nitrogen gas bubbles, which alters the hydraulic character of the aquifer.
- Methanogenesis was observed in all three treatment zones during the demonstration, but was most apparent in the zone where neither nitrate nor sulfate was added. In two of the zones, several mg/L methane were generated (5–6 mg/L in Zone 3, and 3–5 mg/L in Zone 4), which might correspond to the degradation of several mg/L fuel hydrocarbons. However, it did not appear that benzene was effectively removed via methanogenesis.
- The removal rate and the removal sequence for BTEX compounds depends on a number of factors, including the terminal electron acceptor. Toluene concentrations were very low even at the onset of the demonstration, consistent with previously-observed preferential toluene degradation under sulfate-reducing, denitrifying, and methanogenic conditions. Augmentation with nitrate was effective for the removal of all BTEX compounds except benzene. Augmentation with sulfate accelerated the removal of xylenes, particularly o-xylene, but not the other BTEX compounds.
- Benzene was effectively removed via flushing, in part because it does not sorb strongly to aquifer materials. However, benzene biodegradation was slow if it occurred at all. Some previous studies have shown that benzene biodegradation occurs only when no other BTEX compounds are present, indicating a preferential removal sequence.
- During periods when the injection and extraction wells were not operated, a rebound in the BTEX concentrations was observed, especially for benzene. This probably indicates the presence of a residual non-aqueous liquid (NAPL) phase, but it might also indicate the desorption of BTEX compounds from aquifer solids, the diffusion of BTEX from highly contaminated areas that are not effectively flushed, and/or slow encroachment of highly contaminated ground water.
- Many of the design parameters for this system depend on site-specific contamination and hydrogeologic conditions. Some of these design parameters include: the number and location of extraction and injection wells; the injection and extraction flow rates; the method of above-ground treatment for extracted water; the choice of electron acceptors injected; the concentrations of electron acceptors injected; and the duration of flushing, augmentation, and no-flow periods.

7. References

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Appendix A
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