### **RECEIVED**

MR. ROBERT FLORY AEI CONSULTANTS 2500 CAMINO DIABLO WALNUT CREEK, CA. 94597 2:53 pm, Sep 25, 2007

Alameda County **Environmental Health** 

"I DECLARE, UNDER PENALTY OF PERJURY, THAT THE INFORMATION AND/OR RECOMMENDATIONS CONTAINED IN THE ATTACHED DOCUMENT OR REPORT IS TRUE AND CORRECT TO THE BEST OF MY KNOWLEDGE."

NAT AND DARLENE PIAZZA tele Trayga rlene Ti

7613 PEPPERTREE ROAD DUBLIN, CALIF. 94568-2243



September 21, 2007 Mr. Steven Plunkett Environmental Health Services – Environmental Protection 1131 Harbor Bay Parkway, Suite 250 Alameda, CA 94502-6577

Subject: **Revised Work Plan** 20957 Baker Road Castro Valley, California 94546 Leak Case RO0002739 AEI Project # 273928

Dear Mr. Plunkett:

In your letter of September 6, 2007, you requested that AEI Work Plan for Soil and Groundwater Investigation and Interim Source Removal dated May 14, 2007, which was a revision of the original AEI Work Plan for Soil and Groundwater Investigation, dated February 3, 2006 issued following the letter dated January 24, 2007 reviewing the original work plan. Attached is the revised work plan requested you requested.

I believe this work plan revision incorporates the previously submitted information requested by Ms. Dona Drogos during the meeting with Supervisor Scott Haggerty and in the subsequent telephone conversation with Ms. Drogos, as well as the additional items requested in your letter dated September 6, 2007, which reviewed the AEI work plan dated May 17, 2007.

I am trying to re-schedule the drilling the week of October 8, 2007. Please let me know if this is not acceptable as soon as possible.

Sincerely, **AEI** Consultants

Robert F. Flory, P.G

September 20, 2007

### **REVISED WORKPLAN FOR SOIL AND GROUNDWATER INVESTIGATION AND INTERIM SOURCE REMOVAL PILOT**

20957 Baker Road Castro Valley, California 94546

Leak Case RO0002739 AEI Project # 273926

Prepared For

Nat and Darleen Piazza 7613 Peppertree Road Dublin, California 94568-3343

Prepared By

**AEI Consultants**  2500 Camino Diablo Blvd. Walnut Creek, CA 94597 (800) 801-3224



September 20, 2007

Nat and Darlene Piazza 7613 Peppertree Road Dublin, California 94568-3343

**Re: Workplan for Soil and Groundwater Investigation and Interim Source Removal**  20957 Baker Road Castro Valley, California 94546 Leak Case RO0002739 AEI Project # 273928

Dear Mr. and Mrs. Piazza,

The following workplan has been prepared on behalf of Mr. and Mrs. Nat Piazza (client), owners of the above referenced property. AEI Consultants (AEI) has been retained by the client to provide environmental engineering and consulting services associated with releases from two previously removed underground storage tank (USTs) on the property. This workplan has been prepared in response to a request from the Alameda County Environmental Health Services (ACEHS) for preparation of a work plan for a soil and groundwater investigation to determine the horizontal and vertical extent of impacted groundwater resulting from the hydrocarbon release from the former USTs.

### **SITE DESCRIPTION AND BACKGROUND**

The subject property (hereafter referred to as the "site" or "property") is located at 20957 Baker Road in Castro Valley, California (Figure 1: Site Location Map). The site is located in a mixed residential and commercial/light-industrial area of Castro Valley. The site is approximately 160 feet by 300 feet in area and is currently undeveloped and not in use. The site is partially covered with asphalt surfacing and concrete slabs with the remainder of the site graveled.

Baker Road makes up the east boundary of the site with residential property to the east of the road. Rutledge Road bounds the property to the west with commercial and residential property west of the road. The property is bounded to the north by a partially vacant, which contains two residential buildings in its northeast quadrant. The east half of the property is bounded to the south by an apartment complex and the west half to the south by a plumbing contractor. The locations of these buildings relative to the subject site and locations of the former UST are shown

on Figure 2, "Site Map". A copy of the Assessors parcel map and several aerial photo of the area are attached in Appendix A.

### **TANK REMOVAL**

On April 21, 2004, AEI removed two 1,000-gallon USTs from the site (Figure 2). The removal was performed under permit from the ACEHS. Robert Weston, Inspector for the ACEHS, observed the tank removal. Two soil samples were collected from underneath each UST and analyzed for Total Petroleum Hydrocarbons as gasoline (TPH-g), benzene, toluene, ethylbenzene, xylenes (BTEX) and Methyl tertiary butyl ether (MTBE) by EPA Method 8021B/8015Cm. Fuel oxygenates and 1,2 Dibromoethane (EDB) and 1,2 Dichloroethane (1,2 DCA) were analyzed by EPA Method 8260. Total Petroleum Hydrocarbons as diesel (TPH-d) was analyzed by EPA Method 8015C and total lead by EPA method 7010.

Hydrocarbons were detected in all the soil samples, TPH-g at concentrations ranging from 160 milligrams per kilogram (mg/kg) (T1W-EB8') to 1,400 mg/kg (T2W-EB8') and TPH-d at concentrations ranging from 1,400 mg/kg (T2E-EB8') to 10,000 mg/kg (T1E-EB8'). Total xylenes were reported in two samples at 8.4 mg/kg (T2W-E8') and 0.25 mg/kg (T2E-EB8'). No fuel oxygenates, EDB, or DCA were detected in the samples. Total lead was reported at concentrations ranging from 6.1 mg/kg to 24 mg/kg (stockpile sample STKP1-4). The results of chemical analyses on soil samples collected from the tank removal are included in Table 1.

### **PRELIMINARY SITE ASSESSMENT**

AEI performed a subsurface investigation at the property on May 18, 2005. Eight (8) soil borings (SB-1 through SB-8) were advanced to depths ranging from 14 ft. to 18 ft. below ground surface (bgs) using a Geoprobe<sup>®</sup> Model 5410 direct-push drilling rig. The locations of the soil borings are shown on Figure 2, Site Map and Figure 3, Detailed Site Map.

Detectable concentrations of TPH-g, TPH-d, TPH-mo, MTBE or BTEX, were not reported in any of the soil samples from depths of 7.5 to 11 feet bgs above detection limits of 1.0 mg/kg, 1.0 mg/kg, 5.0 mg/kg, 0.05 mg/kg, and 0.005 mg/kg, respectively.

TPH-g was reported at a concentration of 7,300 micrograms per liter  $(\mu g/L)$  in SB-2 (SB-2W). No TPH-g was reported in groundwater samples from any other borings at or above a detection limit of 50  $\mu$ g/L.

The maximum concentration of TPH-d was reported in the groundwater sample from boring SB-2 at a concentration of 23,000  $\mu$ g/L. LNAPL was observed in the field and reported by the laboratory in the groundwater sample from SB-2. TPH-d was reported in the other seven borings at concentrations ranging from ND<50  $\mu$ g/L (SB-7) to 670  $\mu$ g/L (SB-5).

TPH-mo was not reported in groundwater samples from borings SB-3, SB-4 and SB-7 at or above a detection limit of 250 µg/L. TPH-mo was reported in groundwater samples from borings SB-1, SB-2, SB-5, SB-6 and SB-8 at concentrations ranging from 300 µg/L (SB-6) to 1400 µg/L (SB-1 and SB-5).

MTBE was not reported by EPA Method 8021B in groundwater samples from any of the eight soil borings at or above a detection limit of 5.0 µg/L.

The results of the groundwater analyses are summarized in Table 2 (Groundwater Sample Analytical Data) and shown on Figures 5 through 8.

### **GEOLOGICAL SETTING**

The site is located at approximately 180 feet above mean sea level (msl). The site is relatively flat and the local topography slopes very gently to south-southwest toward an unnamed stream (Figure 1).

The lithology observed in the borings drilled to date typically consists of 1 to 2 feet of gravelly clay – clayey gravel (Fill). The fill is underlain by silty clay, which becomes clayey silt downward to a depth of 6 to 8 feet bgs. The silt and clay are underlain by silty and gravelly sands to the top of the bedrock at depths of 13 to 17 feet bgs (Figure 9). In several borings saprolitic clay is present between the sandy sediments and the claystone (shale) bedrock. Groundwater, where present, was encountered at depths of 9 to 11 feet bgs in May 2005. During the later part of the dry season groundwater may be not be present above the top of the bedrock. The overall northward slope to the bedrock surface and the local low in the area of SB-2 may result in hydrocarbon up or across the normal groundwater gradient if the groundwater level drops below the top of the bedrock. The relationships of the sediments that underlie the site are shown on cross sections A-A' and B-B' (Figure 11), copies of the boring logs are included in Appendix B, Soil Boring Logs

No groundwater monitoring wells are present on the site and no historical hydraulic gradient data is available. The regional gradient is west toward the San Francisco Bay. Reported flow directions at near by monitoring sites is highly variable. Groundwater flow has been reported as toward the four cardinal points of the compass and points in between. Several sites have reported gradient direction changes up to 180 degrees within several years time (Well Survey table, Appendix C, Preferential Pathway Survey). Based on the geometry of the groundwater contaminant plume, the groundwater gradient on the site is to the south or southwest.

Depth to groundwater reported in the area ranges from 2 feet bgs to more than 50 feet bgs. Variation reported in depth to groundwater in the area over several year periods ranges from less than two (2) feet to more than six (6) feet.

The nearest surface water body to the site is a small unnamed creek, located approximately 500 feet southwest of the site that drains into San Lorenzo Creek.

### **PREFERENTIAL PATHWAY SURVEY**

### **Lateral pathways – Underground Utilities**

A survey of underground utilities was performed to determine if utilities onsite or beneath the adjacent street intersected the groundwater or the hydrocarbon plume originating from the former USTs. No known underground utilities are present under the parcel identified as 20957 Baker Road. The locations of the utilities under the adjacent streets are shown on the Utility Map as part of Appendix C, Preferential Pathway Survey). Based on available data, the only utilities intersecting the groundwater in the vicinity of the site are the sanitary sewers in both Baker and Rutledge Roads, which are, located approximately 175 feet to the east and 100 feet to the west, respectively. Underground utilities do no appear to be located in positions to affect the migration of the groundwater in the immediate vicinity of the former USTs.

The underlying bedrock is mapped as Joaquin Miller formation (R.W. Graymer, OFR 96-252) and consists of shale with thin-bedded sandstones, which are not like to contain sufficient water for drinking water purposes. The Joaquin Miller Formation is not likely to contain primary porosity pathways that would facilitate downward migration of contaminants. The bedrock is likely fractured and these fractures could act as conduits for vertical and lateral migration. However, during much of the year the topographically higher areas to the north and south would like act as re-charge areas with net groundwater flow through the fractured rock being from the topographically high areas toward San Lorenzo Creek.

### **Vertical pathways – Wells**

California Department of Water Resources, Geotracker and the ACEHS Online Database were searched for wells located with a one-half radius of the site. The identified wells are listed on the Well Survey table attached in Appendix B. Seventeen sites were located with in the one half mile radius. The majority of the wells are shallow groundwater monitoring wells with total depths of less than 30 feet bgs. Several wells located north of the site, which range in depth from 50 to 250 feet deep, appear to be irrigation wells. These wells, which are located to the north, are topographically higher than the subject site and up the local gradient, as indicated by the apparent contaminant plume in the groundwater at the site. One well 50 feet deep is located to the south on Tyee Court. No groundwater gradient direction is available for that site, but groundwater at the adjacent SBC site is two the northeast toward the creek that flow between the subject site and the SBC site. None of the identified well appear to be located within the apparent flow path of groundwater underlying the subject site

### **ENVIRONMENTAL CONCERNS**

Analysis of soil samples collected from beneath the two previously removed 1000-gallon fuel USTs reported maximum TPH-g and TPH-d concentrations of 1,400 mg/kg and 10,000 mg/kg, respectively from a depth of 8.0 bgs. No soil samples the collected during the 2005 PSA reported any detectable concentrations of TPH or MBTEX, however obviously impacted greenish gray sand was observed below the groundwater in boring SB-2. Based on the available data, impacted soil is limited to an area approximately 10 feet by 40 feet, essentially the footprint of the previous tank hold and the low in the bedrock surface around boring SB-2.

The reported concentration of TPH-g exceeded the detection limit of 50  $\mu$ g/L only in SB-2 where TPH-g was reported at a concentration of 7,300 µg/L. The reported concentrations of BTEX exceeded the detection limit of 0.5 µg/L only SB-2 where toluene and total xylenes were reported at concentrations of 11 µg/L and 27 µg/L, respectively.

TPH-d was reported at concentrations up to 23,000  $\mu$ g/L (SB-2). TPH-mo was reported at concentrations of up to 1,400 µg/L (SB-1, SB-5). The results of the groundwater analyses are summarized on Figure 5. The distribution of TPH-g, TPH-d, and TPH-mo are show in Figure 6 through Figure 8

In addition to direct chemical oxidation of hydrocarbons in the source area, hydrogen peroxide produces an oxygenated environment which results in an increase in the natural biomass and accelerates the natural bio-degradation of hydrocarbons in the surrounding soil and groundwater.

### **MONITORING WELL INSTALLATION**

AEI proposes to install four groundwater monitoring wells (MW-1 through MW-4) and one injection well (IN-5) at the subject site.

The locations of the wells are shown on Figure 10 (Proposed well Locations and TPH-d Isopleths). The locations of Wells MW-1, MW-2, and MW-3 are twins to soil borings SB-5, SB-2, and SB-6, respectively. Contaminant concentrations in grab water samples from soil borings are commonly higher than concentrations in subsequent wells due to cross contamination or mixing of contaminated soil from adjacent zones with the groundwater during drilling of the soil borings. The locations of these wells are designed to confirm the contaminant levels reported in the groundwater and determine the lateral and down gradient extent of the hydrocarbons plume in the groundwater. As the actual groundwater flow direction is not known, well MW-4 has been located west of MW-3 in case the groundwater gradient is more toward to the southwest.

A 4-inch diameter well (IN-5), will be located in the center of the UST excavation. The location of injection well IN-5 was selected to optimize the ability to inject peroxide into and under the impacted soil beneath the backfilled excavation. This well will be used for a pilot test of the

feasibility of injecting a chemical oxidant, hydrogen peroxide to be injected into the impacted soil and groundwater beneath the former tank hold. This location will allow peroxide and/or oxygen migration along the same natural pathways followed by the hydrocarbons as they leaked from the former tank pit.

Prior to the initiation of field activities a drilling permit will be obtained from Alameda County Public Works Department (ACPWA) and notification will be made to Underground Service Alert (USA. North). All drilling will be carried out by an appropriately licensed driller (CA C-57). The borings will be drilled using nominal 8-inch diameter hollow stem augers. An experienced AEI professional geologist will be onsite for all drilling and sampling activities. The soil borings will be logged by the AEI geologist using the Unified Soil Classification System (USCS).

Soil samples will be collected at a minimum of 5 foot intervals with a split spoon sampler advanced ahead of the auger bit. Additional soil samples will be collected within the capillary fringe and within the water bearing sediments to determine the amount of hydrocarbons present in these intervals. Well IN-5 will be continuously cored from a depth of 8 feet bgs to allow determination of the optimum screen interval for injection of fluids into the well. Samples will be utilized to characterize the sediments beneath the site and for chemical analyses. Soil samples will be sealed in brass liners with Teflon tape and plastic end caps. All samples will be stored on ice and transported under appropriate chain-of-custody protocols to a California certified laboratory for analysis. Selected samples will be sent out for sieve analysis to determine their grain size distributions.

### **Field Screening and Sample Analysis**

Soil samples will be field screened using a Photo Ionization Detector (PID). Based on the results of field screening, samples will be selected for chemical analyses. A minimum of one soil sample will be selected for analysis from each boring, typically from the capillary fringe. Additional soil samples may be retained at the AEI professional geologist's discretion. All samples selected for laboratory analysis will be analyzed for TPH-g, TPH-d, TPH-mo and MBTEX by method 8015/8021. Two representative soil samples will be analyzed for CAM-17 metals, hexavalent chromium and sieve analyses. The purposes of CAM 17 metals and hexavalent chromium is present in the soil and to allow determination if insitu chemical oxidation (ISCO) affects concentrations of CAM 17 metals and hexavalent chromium.

### **Well Completion**

Wells MW-1 through MW-4 will be competed with 2-inch diameter schedule 40 PVC casing with 0.020 slotted casing with appropriately sized sand pack. Well IN-5 will be completed with 4-inch diameter schedule 40 PVC casing with 0.020 slotted casing and will be screened across permeable zones within the UST excavation backfill and impacted permeable zones between the base of the fill and the top of the bedrock. As illustrated by cross sections A-A" and B-B',

groundwater is present in a single aquifer typically consisting of an upper unit of silt to silty clayey sand and a more lower unit consisting of cleaner sand. Depth to standing water levels measured in the borings was commonly greater that the depth to first wet appearing sediment. Water level fluctuations of over 6 feet have been reported in nearby site. As the range of fluctuation in depth to water at the side, to avoid the drowning of well screens or dry wells due to water level changes, a 10-foot screen interval will be used. To concerns of biased sampling results, samples will be collected from various depths in the well using standard EPA low flow sampling protocols with draw tubes at varying depths to determine the optimum depth for sample collection. A traffic-rated, flush-mounted well box will be installed at the surface.

The wells will be developed no sooner than 72 hours after seal placement by surging, bailing, and purging to remove accumulated fines from the casing and sand pack.

### **XYZ Survey**

The newly installed wells will be surveyed to meet GeoTracker requirements by a California licensed land surveyor. The survey data will be utilized to calculate groundwater flow direction and hydraulic gradient.

### **Initial Groundwater Sampling**

The initial groundwater monitoring event will occur within 7 days following well development. All the wells on site including injection well IN-5 will be sampled. Ongoing monitoring and sampling of well MW-1 through MW-4 will continue on a quarterly basis.

Water sampling will be done with a peristaltic pump as follows:

- 1 During purging the pump rate will be maintained at less than 0.5 liter per minute with the draw tube at a depth of approximately 10 feet bgs or 18" below the top of standing water in the well. During the initial sampling additional water samples will be collected from MW-2 at depths of 12, 14 and 16 feet bgs.
- 2 The standard groundwater parameters of pH, temperature, conductivity, dissolved oxygen (DO) and oxidation-reduction potential (ORP) will be measured.
- 3 Groundwater sampled will be collected when the groundwater parameters stabilize.
- 4 Stabilization will be defined as follows:  $pH \pm 0.1$  units, conductivity  $\pm 3\%$  µs/cm,  $DO \pm 0.3$  milligrams per liter, and  $ORP \pm 10$  millivolts.

The groundwater samples will be analyzed for TPH-g, BTEX, TPH-d, TPH-mo by method 8015/8012. The groundwater samples from well MW-1 and MW-5 will be analyzed for dissolved metals, CAM-17 and hexavalent chromium to determine if ISCO is precipitating or mobilizing metals.

### **Well Vapor Analysis**

During the first groundwater monitoring event the soil vapors present in the vadose zone of each well will be measured using a RKI Eagle gas analyzer. The Eagle measures hydrocarbon,  $oxygen, CO<sub>2</sub>$ , and methane concentrations. The relative presence of these gasses can be used to determine the amount and type of biodegradation taking place in the subsurface.

### **Waste Storage**

Drill cuttings will be stored in DOT approved 55-gallon drums in a secure location onsite, pending the results of sample analyses. Upon receipt of analytical data, drill cutting and waste liquid disposal will be arranged with a properly licensed waste hauler and disposal facility(s).

### **Decontamination**

Sampling equipment will be decontaminated between samples using a triple rinse system containing Alconox ™ or similar detergent. Rinse water will be contained in sealed labeled DOT approved 55-gallon drums in a secure location onsite pending proper disposal.

### **INTERIM SOURCE REMOVAL**

AEI recommends infusion of a 1.0 to 2.5 % hydrogen peroxide  $(H_2O_2)$  into the base of the UST tank sediment underlying the UST. Injection of  $H_2O_2$  has been shown to be an effective way to directly oxidize hydrocarbons and to enhance biodegradation by ubiquitous and naturally occurring bacteria and other organisms present in the soil and groundwater. The work demonstrating the presence of naturally occurring microorganisms within hydrocarbon plumes is voluminous. A simple internet search for the terms *hydrocarbon + natural biodegradation* returns 583,000 hits and a search for *hydrogen peroxide and bioremediation* returned 1,730,000 hits. The activity of the contamination biomass can be easily demonstrated my measurements of the relative presence of  $CO<sub>2</sub>$  and other gasses in the wells that will be installed.

Numerous studies have indicated that low concentrations of  $H_2O_2$  negative effects are limited to a few feet of the injection well and biomass recover within that zone is rapid.. The  $H_2O_2$  infusion pilot would demonstrate the effectiveness and feasibility of the method. Summaries of several peroxide cases and methods are included in Appendix D.

### *H2O2 Infusion Pilot Test*

 $H<sub>2</sub>O<sub>2</sub>$  will be injected into well IN-5 using a double diaphragm pump. The procedures during injection will be as follows:

- 1 Depth to water (DTW) in wells MW-1 through MW-4 will be measured prior to adding the fluid. DTW will be measured periodically in the wells throughout the injection to determine any effect in that well.
- 2 1.0 % to 2.5%  $H_2O_2$  solution will be made up by adding sufficient 35%  $H_2O_2$  solution to water in a poly tank. The poly drum will be equipped with a bottom drain.
- 3 Approximately 1000 2000 gallons of 1.0 % to 2.5%  $H_2O_2$  solution will be gravity infused into the pea gravel that makes up the basal backfill in tank excavation through well IN-5, located within the former tank excavation.
- 4 It is expected that one to three days will be required to complete injection of the  $H_2O_2$ .

### **Water Sampling**

Groundwater samples will be collected from each of the five (5) wells described above at twoweek intervals for one month, then monthly until the next quarterly monitoring event. All groundwater samples will be analyzed TPH-d and TPH-mo by EPA method 8015.

### **Data Analysis**

The results of groundwater analyses will be evaluated as they are received. Following the second sampling, a decision will be made after consultation with the client whether or not additional injection of  $H_2O_2$  is warranted.

### **SITE SAFETY**

Prior to commencement of field activities, a site specific Health and Safety Plan conforming to Part 1910.120 (i) (2) of 29 CFR will be prepared. A copy of site safety plan to will be on site at all times during the project. A site safety meeting will be held at a designated command post near the working area. Emergency procedures will be outlined at this meeting, including an explanation of the hazards of the known or suspected chemicals of interest. All site personnel will be in modified Level D personal protection equipment, which is the anticipated maximum amount of protection needed. A working area will be established with barricades and warning tape to delineate the zone where hard hats and steel-toed shoes must be worn, and where unauthorized personnel will not be allowed. During  $H_2O_2$  injection, waterproof Tyvex and eye protection in the form of either a faceplate or goggles will be required of all personnel in the work area.

### **REPORTING**

Upon installation of the monitoring wells, receipt of the results of the initial groundwatermonitoring event, and receipt of all analytical and well survey data, a *Soil and Groundwater* 

Investigation Report will be prepared. The report will detail the methods and findings of the installation and sampling of the wells. This report will include figures, data tables, cross sections, logs of borings, well construction details, and interpretation of the contaminant distributions. Ouarterly monitoring reports will be submitted within approximately one month of monitoring and sample collection activities. Following the second quarterly groundwatermonitoring event an Interim Source Remediation and Groundwater Monitoring report will be prepared. This report will include figures, data tables, cross sections, logs of borings, well construction details, a summary of  $H_2O_2$  injection activities and interpretation of the results with recommendations for closure or additional follow-up actions if deemed necessary.

#### **ESTIMATED SCHEDULE**

Once the scope of work has been approved by the ACHCSA, project permitting will begin. Drilling will be scheduled upon approval of permits. Reports will be available within approximately 1 month of receipt of all necessary data.

AEI requests your comments and approval to proceed with this project. Please contact me at (925) 944-2899, extension 122, if you have any questions or need any additional information.

Sincerely,

**AEI** Consultants

Adrian Angel Project Geologist ROBERT **IPROF** No. 5825 Robert F. Flory, P.G. Senior Project Manager

### **REFERENCED REPORTS**

- 1. *Geotechnical Exploration and Engineering Study, Proposed Baker Road Apartments*, December 3, 1986, prepared by JMK Environmental Solutions, Inc.
- 2. *Underground Storage Tank removal Final Report*, May 19, 2004, prepared by AEI **Consultants**
- 3. *Preliminary Site Investigation Report*, June 5, 2005, prepared by AEI Consultants
- 4. Preliminary Geologic Map Emphasizing Bedrock Formations in Alameda County, California, 1996, R.W. Graymer, et al., U.S.G.S. Open File Report 96-252
- *5.* Enhanced Bioremediation Utilizing Hydrogen Peroxide As A Supplemental Source Of Oxygen: A Laboratory And Field Study, 1990, U.S. Environmental Protection Agency, Washington, D.C., EPA/600/2-90/006 (NTIS PB90183435)
- *6. In situ Aeration: Air Sparging, Bioventing, and Related Remedial Processes, 1995, Hinchee, R.E,* Battelle Memorial Institute
- **Figure 1**  Site Location Map
- **Figure 2** Site Map
- **Figure 3** Detailed Site Plan
- **Figure 4** Tank Excavation Sampling
- **Figure 5** Groundwater Analytical Results (5/18/05)
- **Figure 6** TPH-g Isopleths
- **Figure 7** TPH-d Isopleths
- **Figure 8** TPH-mo Isopleths
- **Figure 9** Depth to Bedrock
- **Figure 10** Proposed Well Locations with TPH-d Isopleths
- **Figure 11** Cross Sections A-A' and B-B"
- **Table 1**  Soil Analytical Data
- **Table 2**  Groundwater Analytical Data
- **Appendix A MISC. Photos and Maps**
- **Appendix B Soil Boring Logs**
- **Appendix C Preferential Pathway Survey**
- **Appendix D MISC. Materials**

Distribution:

File

Nat Piazza, 7613 Pepper Tree Road, Dublin, California, 94568-3343 -2 copies

Steven Plunkett, Alameda County Environmental Health Services, 1131 Harbor Bay parkway, Suite 250, Alameda, California 94502-6577

Donna Drogos

Scott Haggerty

Geotracker

**FIGURES** 



















![](_page_25_Figure_0.jpeg)

![](_page_26_Figure_0.jpeg)

![](_page_27_Figure_0.jpeg)

**TABLES** 

![](_page_29_Picture_359.jpeg)

### **Table 1, Soil Analytical Data, 20957 Baker Road, Castro Valley, California**

Notes

TPH-g = total petroleum hydrocarbons as gasoline

TPH-d = total petroleum hydrocarbons as diesel

TPH-mo = total petroleum hydrocarbons as motor oil

MTBE = methyl tert-butyl ether

mg/kg = micrograms per liter (parts per billion)

![](_page_30_Picture_312.jpeg)

### **Table 2, Groundwater Analytical Data, 20957 Baker Road, Castro Valley, California**

#### Notes

2 = diesel range compounds are significant, no recognizable pattern TPH-d = total petroleum hydrocarbons as diesel

4 = lighter than water immiscible sheen/product is present MTBE = methyl tert-butyl ether

 $5 =$  gasoline range compounds are significant

1 - oil range compounds are significant TPH-g = total petroleum hydrocarbons as gasoline

3 = no recognizable pattern TPH-mo = total petroleum hydrocarbons as motor oil

 $\mu$ g/l = micrograms per liter (parts per billion)

### **APPENDIX A**

### **MISC. Photos and Maps**

![](_page_32_Picture_0.jpeg)

58933 usas 8-27-98 1-700ft  $5893329$ 

![](_page_33_Picture_0.jpeg)

Subject Site<br>20957 Baker Road CastroValley CA CastroValley, CA

![](_page_34_Picture_0.jpeg)

Subject site and adjacent Area<br>20957 Baker Road Castro Valley CA Castro Valley, CA

### **APPENDIX B**

**Soil Boring Logs** 

### **Log of Boring SB-1**

Sheet 1 of 1

![](_page_36_Picture_242.jpeg)

![](_page_36_Picture_243.jpeg)

ENVIRONMENTAL & CML ENGINEERING

### **Log of Boring SB-2**

Sheet 1 of 1

![](_page_37_Picture_241.jpeg)

![](_page_37_Picture_242.jpeg)

### **Log of Boring SB-3**

Sheet 1 of 1

![](_page_38_Picture_239.jpeg)

![](_page_38_Picture_240.jpeg)

### **Log of Boring SB-4**

Sheet 1 of 1

![](_page_39_Picture_255.jpeg)

![](_page_39_Picture_256.jpeg)

ENVIRONMENTAL & CML ENGINEERING

X:PROJECTS\CHARACTERIZATION & REMEDIATION\CHARACTERIZATION\10509 PH II (Piazza) Castro Valley\Prelim Inv\Borings 1-8.bgs [DP Boring 20.tpl] X:\PROJECTS\CHARACTERIZATION & REMEDIATION\CHARACTERIZATION\10509 PH II (Piazza) Castro Valley\Prelim Inv\Borings 1-8.bgs [DP Boring 20.tpl]

### **Log of Boring SB-5**

Sheet 1 of 1

![](_page_40_Picture_252.jpeg)

![](_page_40_Picture_253.jpeg)

ENVIRONMENTAL & CML ENGINEERING

### **Log of Boring SB-6**

Sheet 1 of 1

![](_page_41_Picture_245.jpeg)

![](_page_41_Picture_246.jpeg)

### **Log of Boring SB-7**

Sheet 1 of 1

![](_page_42_Picture_246.jpeg)

![](_page_42_Picture_247.jpeg)

### **Project: Piazza**

### **Project Location: 20957 Baker Road, Castro Valley, CA Project Number: 10509**

### **Log of Boring SB-8**

Sheet 1 of 1

![](_page_43_Picture_266.jpeg)

**CONSULTANTS** ENVIRONMENTAL & CML ENGINEERING

X:PROJECTS\CHARACTERIZATION & REMEDIATION\CHARACTERIZATION\273928 WI (Piazza) Castro Valley - (RFF)\10509 PH II (Piazza) Castro Valley/Prelim Inv\Borings 1-8.bgs [DP Boring 20.tpl] X:\PROJECTS\CHARACTERIZATION & REMEDIATION\CHARACTERIZATION\273928 WI (Piazza) Castro Valley - (RFF)\10509 PH II (Piazza) Castro Valley\Prelim Inv\Borings 1-8.bgs [DP Boring 20.tpl]

### **APPENDIX C**

**Preferential Pathway Survey**

![](_page_45_Figure_0.jpeg)

![](_page_46_Figure_0.jpeg)

### **WELLS LOCATED WITHIN 1/2 MILE OF SUBJECT SITE**

**Piazza Property, 20957 Baker Road, Castro Valley, CA**

![](_page_47_Picture_432.jpeg)

### **WELLS LOCATED WITHIN 1/2 MILE OF SUBJECT SITE**

![](_page_48_Picture_410.jpeg)

**Piazza Property, 20957 Baker Road, Castro Valley, CA**

### **WELLS LOCATED WITHIN 1/2 MILE OF SUBJECT SITE**

**Piazza Property, 20957 Baker Road, Castro Valley, CA**

![](_page_49_Picture_428.jpeg)

BR = Depth to Bedrock

Var = Variation in depth to water

### **APPENDIX D**

**MISC. Materials** 

### In Situ Bioventing at a Natural Gas Dehydrator Site: **Field Demonstration**

Alonzo W. Lawrence, Daniel L. Miller, Jeffrey A. Miller, Robin L. Weightman, Richard M. Raetz, and Thomas D. Hayes

#### **ABSTRACT .**

This paper describes a bioventing/biosparging field demonstration that was conducted over a 10-month period at a former glycol dehydrator site located near Traverse City, Michigan. The goal of the project was to determine the feasibility of this technology for dehydrator site remediation and to develop engineering design concepts for applying bioventing/ biosparging at similar sites. The chemicals of interest are benzene, toluene, ethylbenzene, and xylenes (BTEX) and alkanes (C<sub>4</sub> through C<sub>10</sub>). Soil sampling indicated that the capillary fringe and saturated zones were heavily contaminated, but that the unsaturated zone was relatively free of the contaminants. A pump-and-treat system has operated since 1991 to treat the groundwater BTEX plume. Bioventing/biosparging was installed in September 1993 to treat the contaminant source area. Three different air sparging operating modes (pulse, continuous, and vapor recycle) were tested to determine an optimal process configuration for site remediation. These operational modes were compared through in situ respirometry studies. Respirometry measurements were used to estimate biodegradation rates. Dissolved oxygen and carbon dioxide were monitored in the groundwater. A hydrocarbon mass balance based on soil and groundwater sampling was compared to the estimate of hydrocarbons biologically degraded based on the respiration studies. Gaseous-phase nutrients, nitrous oxide, and triethyl phosphate (TEP) were added to stimulate the rates of biodegradation. The results of the study suggest that bioventing/biosparging is a feasible technology for in situ remediation of soil and groundwater at gas industry glycol dehydrator sites.

### **INTRODUCTION**

This Gas Research Institute (GRI) field experiment at a member company's site was performed to investigate the feasibility of using bioventing/biosparging for

### Oxygen-Enhanced In Situ Bioremediation in a Sand and Gravel Aquifer

Sean R. Carter and James E. Clark

### **ABSTRACT\_**

In situ bioremediation was chosen to remediate shallow oxygen-limited groundwater contaminated with volatile and semivolatile aromatic hydrocarbons from a fuel release. The remediation system included groundwater recovery at rates up to 100 L/min and treatment with a packed-tower air stripper to remove volatiles and increase dissolved oxygen levels. Dissolved oxygen was further increased using a pressureswing adsorption (PSA) oxygen generator and hollow-fiber oxygen dissolution membranes. This oxygenated water was injected back to the subsurface through two horizontal injection galleries. Prior to startup of the remediation system, groundwater in contaminated wells was oxygen-limited, with levels from 0 to less than 1 mg/L. After several months of groundwater injection, dissolved oxygen levels began to increase in contaminated wells by 1 to 2 mg/L. A significant decrease in dissolved-phase hydrocarbons was observed in a well nearest an injection gallery once dissolved oxygen was increased to background levels (>5 mg/L). A decrease in nitrogen was also observed, suggesting that aerobic biodegradation was a significant factor in the hydrocarbon decrease.

### **INTRODUCTION**

In situ bioremediation can be an efficient, cost-effective means of degrading volatile and semivolatile organic compounds in groundwater (Brubaker and Stroo 1992 and Anid et al. 1993). Sufficient oxygen and nutrient levels must be established for indigenous microorganisms to be effective in this process (Madsen 1991). However, aquifers contaminated with these compounds will generally exhibit anoxic conditions within the plume, inhibiting the degradation process. The described adaptation of enhancing dissolved oxygen levels in the affected area of the aquifer was used to promote bioremediation at this site. This method of remediation is becoming a widely used technique for removing petroleum hydrocarbons from groundwater (Nelson et al. 1994 and Norris et al. 1994).

### Pilot-Scale Feasibility of Petroleum Hydrocarbon-Contaminated Soil In Situ Bioremediation

Joseph F. Walker, Jr., and Angela B. Walker

#### **ABSTRACT.**

An environmental project was conducted to evaluate in situ bioremediation of petroleum hydrocarbon-contaminated soils on Kwajalein Island, a U.S. Army Kwajalein Atoll base in the Republic of the Marshall Islands. Results of laboratory column studies determined that nutrient loadings stimulated biodegradation rates and that bioremediation of hydrocarbon-contaminated soils at Kwajalein was possible using indigenous microbes. The column studies were followed by an ~10-month on-site demonstration at Kwajalein to further evaluate in situ bioremediation and to determine design and operating conditions necessary to optimize the process. The demonstration site contained low levels of total petroleum hydrocarbons (diesel fuel) in the soil near the ground surface, with concentrations increasing to  $\sim$ 10,000 mg/kg in the soil near the groundwater. The demonstration utilized 12 in situ plots to evaluate the effects of various combinations of water, air, and nutrient additions on both the microbial population and the hydrocarbon concentration within the treatment plots as a function of depth from the ground surface.

### **INTRODUCTION**

The U.S. Army Kwajalein Atoll (USAKA) base is located within the Republic of the Marshall Islands in the west-central Pacific Ocean. The Kwajalein Atoll consists of ~100 small islands and forms the largest enclosed lagoon in the world. Kwajalein Island, with a land surface area of  $\sim$ 1.2 mi<sup>2</sup> (3.1 km<sup>2</sup>), is the largest island within the atoll. It is located  $\sim$ 2,100 mi ( $\sim$ 3,380 km) southwest of Honolulu, Hawaii, and 700 mi (1,127 km) north of the equator.

USAKA has significant petroleum hydrocarbon contamination resulting from years of military activities. Given the remoteness of the site, the lack of sophisticated on-site remediation or waste disposal facilities, and the amenability of petroleum hydrocarbons to biodegradation, USAKA requested, through the

### In Situ Diesel Fuel Bioremediation: A Case History

Derek K. Rhodes, George K. Burke, Nancy Smith, and David Clark

#### **ABSTRACT.**

As a result of a ruptured fuel line, the study site had diesel fuel soil contamination and free product more than 2 ft (0.75 m) thick on the groundwater surface. Diesel fuel, which is composed of a high percentage of nonvolatile compounds, has proven difficult to remediate using conventional extraction remediation techniques. A number of remedial alternatives were reviewed, and the patented in situ biodegradation BioSparge<sup>SM</sup> technology was selected for the site and performed under license by a specialty contractor. BioSparge<sup>SM</sup> is a field-proven closedloop (no vapor emissions) system that supplies a continuous, steady supply of oxygen, moisture, and additional heat to enhance microorganism activity. The system injects an enriched airstream beneath the groundwater surface elevation and/or within the contaminant plume and removes residual vapors from vadose zone soil within and above the contaminant plume. The technology has no air discharge, which is critical in areas where strict air discharge regulations apply. The focus of this paper is the viability of in situ biodegradation as an effective remediation alternative for reducing nonvolatile petroleum products.

### **INTRODUCTION**

The BioSparge<sup>SM</sup> system is a closed-loop in situ remediation technology that uses a designed system of gas injection sparge/purge wells combined with surrounding vapor extraction wells. A mobile surface treatment system provides injection, capture, and treatment without gas venting and emissions (Figure 1).

The technology has been applied to a select number of petroleum hydrocarbon sites in the southwestern United States and in Wisconsin. The site presented is a unique and difficult in situ remediation problem which demonstrates the effectiveness of biosparging technology to remediate nonvolatile, free product compounds.

### **Membrane Oxygen Dissolution** at the Libby, Montana, Superfund Site

Charles J. Gantzer and David Cosgriff

### **ABSTRACT.**

The creosote- and pentachlorophenol-contaminated aquifer at the Libby Superfund Site is being bioremediated using naturally occurring aerobic microorganisms. Water is injected into the aquifer downgradient from the major contaminant source area. Between January 1991 and May 1993, the injection water was amended with hydrogen peroxide at a delivered concentration of approximately 100 mg/L. Theoretically, this hydrogen peroxide decomposed in the aquifer to produce approximately 50 mg/L of biologically available dissolved oxygen. The use of hydrogen peroxide was successful in making portions of the aquifer aerobic, which reduced water-phase contaminant concentrations. In May 1993, the hydrogen peroxide system was replaced by an oxygen generation/ dissolution system that reduced the operating costs for oxygenating the aquifer by about \$35,000 annually. Oxygen is now generated on site by a pressure-swing absorption oxygen generator and is dissolved by four membrane oxygen dissolution devices. The membrane oxygen dissolution system has operated at the Libby Superfund site for more than 26 months with no loss in performance due to membrane fouling or membrane fatigue.

### **INTRODUCTION**

The Libby Superfund Site is located in northwestern Montana and is an active lumber-production facility. Wood-treating operations were conducted on the site from 1946 through 1969. Uncontrolled releases of creosote and pentachlorophenol (PCP) occurred in a waste pit. In addition to contaminating the soils adjacent to the source, the groundwater beneath the site is contaminated with polycyclic aromatic hydrocarbons (PAHs) and PCP. Remedial efforts have centered on the shallowest aquifer, because of its potential use as a domestic water supply. This aquifer is located at depths of 18 to 70 ft (5.5 to 21.3 m) below ground surface. The contaminant plume is nearly 1 mile (1.6 km) in length. To promote the aerobic in situ bioremediation of the shallowest aquifer, oxygenated water and nutrients are added to the aquifer at two locations: the

### $H_2O_2$  Enhancement of Microbial Removal of Ethylene Glycol Contamination

Paul E. Flathman, Mary L. Laski, John H. Carson, Jr., Kathleen S. Leis, Douglas E. Jerger, and Paul R. Lear

### **ABSTRACT.**

1

The objectives of the laboratory study were (1) to evaluate the benefit of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as a source of molecular oxygen for enhanced biological treatment of ethylene glycol in a simulated groundwater environment, (2) to assess the tolerance of the ethylene glycol-adapted indigenous microflora to  $H_2O_2$ , and (3) to determine the magnitude of the nonenzymatic decomposition of  $H_2O_2$  in the subsurface soil used for the study. Test  $(n = 3)$  and control  $(n = 3)$  upflow soil columns containing sandy soil from a site previously contaminated with ethylene glycol were used for the study. This soil exhibited extremely low activity in nonenzymatically catalyzing the breakdown of  $H_2O_2$ . Test and control columns received an influent ethylene glycol concentration of  $2,000$  mg/L in Dworkin-Foster medium. Influent  $H_2O_2$  concentration in the test columns was incrementally increased to 5,400 mg/L. With greater than an 80% reduction in influent total organic carbon (TOC) in the test columns in excess of the control, the benefit of  $H_2O_2$  addition was demonstrated. At an influent  $H_2O_2$  concentration of 5,400 mg/L, a toxic effect for treatment of the influent TOC was not demonstrated, and a significant increase in bacterial population density in the test columns over the controls was observed.

#### **INTRODUCTION**

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### **EIMS Metadata Report - Document**

**Entry ID:** 50761 **Title:** ENHANCED BIOREMEDIATION UTILIZING HYDROGEN PEROXIDE AS A SUPPLEMENTAL SOURCE OF OXYGEN: A LABORATORY AND FIELD STUDY

**Version:** 1.0

#### **Abstract**

**Abstract:** Laboratory and field scale studies were conducted to investigate the feasibility of using hydrogen peroxide as a supplemental source of oxygen for bioremediation of an aviation gasoline fuel spill. Field samples of aviation gasoline contaminated aquifer material were artificially enhanced with nutrients to promote microbiological degradation of fuel carbon in a laboratory column experiment. The rapid rate of hydrogen peroxide decomposition at 100.0 mg/l resulted in the production of oxygen gas. n oxygen mass balance indicated that approximately 44.0% and 45.0% of the influent oxygen was recovered in aqueous and gaseous phases respectively. Reduced rates of oxygen consumption during this period indicated that microbial inhibition may have occurred. A mass balance of the fuel carbon indicated that approximately 36% of the initial mass leached out in the aqueous phase, 10.0% remained, and 54.0% degraded. The ratio of oxygen consumed to aviation gasoline degraded was greater than that predicted by the ideal stoichiometric conversion. Hydrogen peroxide breakthrough in the column effluent never exceeded 11.0% of the influent concentration. Ground-water data from the enhanced in-situ bioremediation pilot field study indicates that hydrogen peroxide successfully increased the concentration of available oxygen down-gradient. In this study, however, it was observed that there was a measurable increase of oxygen in the soil gas area where hydrogen peroxide was injected. This indicated that a significant fraction of hydrogen peroxide rapidly decomposed to oxygen gas and escaped into the unsaturated zone.

### Citation up<del><sub>1</sub></del> (1)

**Citation:** Huling, S., B. Bledsoe, AND M. White. ENHANCED BIOREMEDIATION UTILIZING HYDROGEN PEROXIDE AS A SUPPLEMENTAL SOURCE OF OXYGEN: A LABORATORY AND FIELD STUDY. U.S. Environmental Protection Agency, Washington, D.C., EPA/600/2-90/006 (NTIS PB90183435), 1990.

United States **Solid Waste and State Account States** EPA 542-F-96-007 Environmental Protection Emergency Response April 1996 Agency (5102G)

# **&EPA** A Citizen's Guide to **Bioremediation**

Technology Innovation Office Technology Fact Sheet

### **What is bioremediation?**

Bioremediation is a treatment process that uses naturally occurring microorganisms (yeast, fungi, or bacteria) to break down, or *degrade*, hazardous substances into less toxic or nontoxic substances. Microorganisms, just like humans, eat and digest organic substances for nutrients and energy. In chemical terms, "organic" compounds are those that contain carbon and hydrogen atoms. Certain microorganisms can digest organic substances such as fuels or solvents that are hazardous to humans. The microorganisms break down the organic contaminants into harmless products—mainly carbon dioxide and water (Figure 1). Once the contaminants are degraded, the microorganism population is reduced because they have used all of their food source. Dead microorganisms or small populations in the absence of food pose no contamination risk.

### **How does it work?**

Microorganisms must be active and healthy in order for bioremediation to take place. Bioremediation technologies assist microorganisms' growth and increase microbial populations by creating optimum environmental conditions for them to detoxify the maximum amount of contaminants. The specific bioremediation technology used is determined by several factors, for instance, the type of microorganisms present, the site conditions, and the quantity and toxicity of contaminant chemicals. Different microorganisms degrade different types of compounds and survive under different conditions.

*Indigenous* microorganisms are those microorganisms that are found already living at a given site. To stimulate the

growth of these indigenous microorganisms, the proper soil temperature, oxygen, and nutrient content may need to be provided.

If the biological activity needed to degrade a particular contaminant is *not* present in the soil at the site, microorganisms from other locations, whose effectiveness has been tested, can be added to the contaminated soil. These are called *exogenous* microorganisms. The soil conditions at the new site may need to be adjusted to ensure that the exogenous microorganisms will thrive.

Bioremediation can take place under *aerobic* and *anaerobic* conditions. In aerobic conditions, microorganisms use available atmospheric oxygen in order to function. With sufficient oxygen, microorganisms will convert many organic contaminants to carbon dioxide and water. *Anaerobic* conditions support biological activity in which no oxygen is present so the microorganisms break down chemical compounds in the soil to release the energy they need. Sometimes, during aerobic and anaerobic processes of breaking down the original contaminants, intermediate products that are less, equally, or more toxic than the original contaminants are created.

Bioremediation can be used as a cleanup method for contaminated soil and water. Bioremediation applications fall into two broad categories: *in situ* or *ex situ*. In situ bioremediation treats the contaminated soil or groundwater in the location in which it was found. Ex situ bioremediation processes require excavation of contaminated soil or pumping of groundwater before they can be treated.

#### **A Quick Look at Bioremediation**

- Uses naturally occurring microorganisms to break down hazardous substances into less toxic or nontoxic substances.
- A cost effective, natural process applicable to many common organic wastes.
- Many techniques can be conducted on-site.

![](_page_58_Picture_19.jpeg)

#### **In Situ Bioremediation of Soil**

In situ techniques do not require excavation of the contaminated soils so may be less expensive, create less dust, and cause less release of contaminants than ex situ techniques. Also, it is possible to treat a large volume of soil at once. In situ techniques, however, may be slower than ex situ techniques, may be difficult to manage, and are most effective at sites with *permeable* (sandy or uncompacted) soil.

The goal of aerobic in situ bioremediation is to supply oxygen and nutrients to the microorganisms in the soil. Aerobic in situ techniques can vary in the way they supply oxygen to the organisms that degrade the contaminants. Two such methods are **bioventing** and **injection of hydrogen peroxide.** Oxygen can be provided by pumping air into the soil above the water table (bioventing) or by delivering the oxygen in liquid form as hydrogen peroxide. In situ bioremediation may not work well in clays or in highly layered subsurface environments because oxygen cannot be evenly distributed throughout the treatment area. In situ remediation often requires years to reach cleanup goals, depending mainly on how biodegradable specific contaminants are. Less time may be required with easily degraded contaminants.

*Bioventing***.** Bioventing systems deliver air from the atmosphere into the soil above the water table through injection wells placed in the ground where the contamination exists. The number, location, and depth of the wells depend on many geological factors and engineering considerations.

An air blower may be used to push or pull air into the soil through the injection wells. Air flows through the soil and the oxygen in it is used by the microorganisms. Nutrients may be pumped into the soil through the injection wells. Nitrogen and phosphorous may be added to increase the growth rate of the microorganisms.

*Injection of Hydrogen Peroxide.* This process delivers oxygen to stimulate the activity of naturally occurring microorganisms by circulating hydrogen peroxide through contaminated soils to speed the bioremediation of organic contaminants. Since it involves putting a chemical (hydrogen peroxide) into the ground (which may eventually seep into the groundwater), this process is used only at sites where the groundwater is already contaminated.

#### **What Is An Innovative Treatment Technology?**

Treatment technologies are processes applied to the treatment of hazardous waste or contaminated materials to permanently alter their condition through chemical, biological, or physical means. Innovative treatment technologies are those that have been tested, selected or used for treatment of hazardous waste or contaminated materials but lack welldocumented cost and performance data under a variety of operating conditions.

A system of pipes or a sprinkler system is typically used to deliver hydrogen peroxide to shallow contaminated soils. Injection wells are used for deeper contaminated soils.

#### **In Situ Bioremediation of Groundwater**

In situ bioremediation of groundwater speeds the natural biodegradation processes that take place in the watersoaked underground region that lies below the water table. For sites at which both the soil and groundwater are contaminated, this single technology is effective at treating both.

Generally, an in situ groundwater bioremediation system consists of an extraction well to remove groundwater from the ground, an above-ground water treatment system where nutrients and an oxygen source may be added to the contaminated groundwater, and injection wells to return the "conditioned" groundwater to the subsurface where the microorganisms degrade the contaminants.

One limitation of this technology is that differences in underground soil layering and density may cause reinjected conditioned groundwater to follow certain preferred flow paths. Consequently, the conditioned water may not reach some areas of contamination.

Another frequently used method of in situ groundwater treatment is *air sparging,* which means pumping air into the groundwater to help flush out contaminants. Air sparging is used in conjunction with a technology called soil vapor extraction and is described in detail in the document entitled *A Citizen's Guide to Soil Vapor Extraction and Air Sparging* (see page 4).

#### **Ex Situ Bioremediation of Soil**

Ex situ techniques can be faster, easier to control, and used to treat a wider range of contaminants and soil types than in situ techniques. However, they require excavation and treatment of the contaminated soil before and, sometimes, after the actual bioremediation step. Ex situ techniques include **slurry-phase bioremediation** and **solidphase bioremediation.**

*Slurry-phase bioremediation.* Contaminated soil is combined with water and other additives in a large tank called a "bioreactor" and mixed to keep the microorganisms which are already present in the soil—in contact with the contaminants in the soil. Nutrients and oxygen are added, and conditions in the bioreactor are controlled to create the optimum environment for the microorganisms to degrade the contaminants. Upon completion of the treatment, the water is removed from the solids, which are disposed of or treated further if they still contain pollutants.

Slurry-phase biological treatment can be a relatively rapid process compared to other biological treatment processes, particularly for contaminated clays. The success of the process is highly dependent on the specific soil and chemical properties of the contaminated material. This technology is particularly useful where rapid remediation is a high priority.

**Figure 1 Schematic Diagram of Aerobic Biodegradation in Soil**

![](_page_60_Figure_1.jpeg)

*Solid-phase bioremediation.* Solid-phase bioremediation is a process that treats soils in above-ground treatment areas equipped with collection systems to prevent any contaminant from escaping the treatment. Moisture, heat, nutrients, or oxygen are controlled to enhance biodegradation for the application of this treatment. Solid-phase systems are relatively simple to operate and maintain, require a large amount of space, and cleanups require more time to complete than with slurry-phase processes. Solid-phase soil treatment processes include *landfarming, soil biopiles,* and *composting.*

*Landfarming.* In this relatively simple treatment method, contaminated soils are excavated and spread on a pad with a built-in system to collect any "leachate" or contaminated liquids that seep out of contaminant-soaked soil. The soils are periodically turned over to mix air into the waste. Moisture and nutrients are controlled to enhance bioremediation. The length of time for bioremediation to occur will be longer if nutrients, oxygen or temperature are not properly controlled. In some cases, reduction of contaminant concentrations actually may be attributed more to volatilization than biodegradation. When the process is conducted in enclosures controlling escaping volatile contaminants, volatilization losses are minimized.

*Soil biopiles.* Contaminated soil is piled in heaps several meters high over an air distribution system. Aeration is provided by pulling air through the heap with a vacuum pump. Moisture and nutrient levels are maintained at levels that maximize bioremediation. The soil heaps can be placed in enclosures. Volatile contaminants are easily controlled since they are usually part of the air stream being pulled through the pile.

*Composting.* Biodegradable waste is mixed with a bulking agent such as straw, hay, or corn cobs to make it easier to deliver the optimum levels of air and water to the microorganisms. Three common designs are *static pile composting* (compost is formed into piles and aerated with blowers or vacuum pumps), *mechanically agitated in-vessel*

*composting* (compost is placed in a treatment vessel where it is mixed and aerated), and *windrow composting* (compost is placed in long piles known as windrows and periodically mixed by tractors or similar equipment).

### **Will it work at every site?**

Biodegradation is useful for many types of organic wastes and is a cost-effective, natural process. Many techniques can be conducted on-site, eliminating the need to transport hazardous materials.

The extent of biodegradation is highly dependent on the toxicity and initial concentrations of the contaminants, their biodegradability, the properties of the contaminated soil, and the particular treatment system selected.

Contaminants targeted for biodegradation treatment are non-halogenated volatile and semi-volatile organics and fuels. The effectiveness of bioremediation is limited at sites with high concentrations of metals, highly chlorinated organics, or inorganic salts because these compounds are toxic to the microorganisms.

### **Where has it been used?**

At the Scott Lumber Company Superfund site in Missouri, 16,000 tons of soils contaminated with polyaromatic hydrocarbons (PAHs) were biologically treated using land treatment application. PAH concentrations were reduced by 70%.

At the French Ltd. Superfund site in Texas, slurry-phase bioremediation was used to treat 300,000 tons of lagoon sediment and tar-like sludge contaminated with volatile organic compounds, semi-volatile organic compounds, metals, and pentachlorophenol. Over a period of 11 months, the treatment system was able to meet the cleanup goals set by EPA.

Some additional examples of Superfund sites where different types of bioremediation have been selected as a treatment method are listed in Table 1 on page 4.

#### **Table 1 Examples of Superfund Sites Using Bioremediation Technologies\***

![](_page_61_Picture_158.jpeg)

For a listing of Superfund sites at which innovative treatment technologies have been used or selected for use, contact NCEPI at the address in the box below for a copy of the document entitled **Innovative Treatment Technologies: Annual Status Report (7th Ed.), EPA 542-R-95-008.** Additional information about the sites listed in the Annual Status Report is available in database format. The database can be downloaded free of charge from EPA's Cleanup Information bulletin board (CLU-IN). Call CLU-IN at 301-589-8366 (modem). CLU-IN's help line is 301-589-8368. The database also is available for purchase on diskettes. Contact NCEPI for details.

\* Not all waste types and site conditions are comparable. Each site must be individually investigated and tested. Engineering and scientific judgment must be used to determine if a technology is appropriate for a site.

### **For More Information** The publications listed below can be ordered free of charge by calling NCEPI at 513-489-8190 or faxing your request to 513-489-8695. If NCEPI is out of stock of a document, you may be directed to other sources. Write to NCEPI at: National Center for Environmental Publications and Information (NCEPI) P.O. Box 42419 Cincinnati, OH 45242 • Selected Alternative and Innovative Treatment Technologies for Corrective Action and Site Remediation: A Bibliography of EPA Information Sources, January 1995, EPA 542-B-95-001. **A bibliography of EPA publications about innovative treatment technologies.** • Bioremediation Resource Guide, September 1993, EPA 542-B-93-004. **A bibliography of publications and other sources of information about bioremediation technologies.** • A Citizen's Guide to Soil Vapor Extraction and Air Sparging, EPA 542-F-96-008 • Engineering Bulletin: In Situ Biodegradation Treatment, April 1994, EPA 540-S-94-502. • Engineering Bulletin: Slurry Biodegradation, September 1990, EPA 540-2-90-016. • Abstracts of Remediation Case Studies, March 1995, EPA 542-R-95-001. • WASTECH® Monograph on Bioremediation, ISBN #1-883767-01-6. Available for \$49.95 from the American Academy of Environmental Engineers, 130 Holiday Court, Annapolis, MD 21401. Telephone 410-266-3311.

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http://www.frtr.gov/matrix2/section4/4-31.html

#### Ground Water, Surface Water, and Leachate

3.9 In Situ Biological Treatment

#### 4.29 Enhanced Bioremediation

The rate of bioremediation of organic contaminants by microbes is enhanced by increasing the concentration of electron acceptors and nutrients in ground water, surface water, and leachate. Oxygen is the main electron acceptor for aerobic bioremediation. Nitrate serves as an alternative electron acceptor under anoxic conditions.

Bioremediation is a process in which indigenous or inoculated micro-organisms (i.e., fungi, bacteria, and other microbes) degrade (metabolize) organic contaminants found in soil and/or ground water.

Bioremediation is a process that attempts to accelerate the natural biodegradation process by providing nutrients, electron acceptors, and competent degrading microorganisms that may otherwise be limiting the rapid conversion of contamination organics to innocuous end products.

Oxygen enhancement can be achieved by either sparging air below the water table or circulating hydrogen peroxide  $(H_2O_2)$  throughout the contaminated ground water zone. Under anaerobic conditions, nitrate is circulated throughout the ground water contamination zone to enhance bioremediation. Additionally, solidphase peroxide products (e.g., oxygen releasing compound (ORC)) can also be used for oxygen enhancement and to increase the rate of biodegradation.

#### *Oxygen Enhancement with Air Sparging*

Air sparging below the water table increases ground water oxygen concentration and enhances the rate of biological degradation of organic contaminants by naturally occurring microbes. (VOC stripping enhanced by air sparging is addressed in Technology Profile 4.34). Air sparging also increases mixing in the saturated zone, which increases the contact between ground water and soil. The ease and low cost of installing small-diameter air injection points allows considerable flexibility in the design and construction of a remediation system. Oxygen enhancement with air sparging is typically used in conjunction with SVE or bioventing to enhance removal of the volatile component under consideration.

#### *Oxygen Enhancement with Hydrogen Peroxide*

During hydrogen peroxide enhancement, a dilute solution of hydrogen peroxide is circulated through the contaminated ground water zone to increase the oxygen content of ground water and enhance the rate of aerobic biodegradation of organic contaminants by naturally occurring microbes.

#### *Nitrate Enhancement*

Solubilized nitrate is circulated throughout ground water contamination zones to provide an alternative electron acceptor for biological activity and enhance the rate of degradation of organic contaminants. Development of nitrate enhancement is still at the pilot scale. This technology enhances the anaerobic biodegradation through the addition of nitrate.

Fuel has been shown to degrade rapidly under aerobic conditions, but success often is limited by the inability to provide sufficient oxygen to the contaminated zones as a result of the low water solubility of oxygen and because oxygen is rapidly consumed by aerobic microbes. Nitrate also can serve as an electron acceptor and is more soluble in water than oxygen. The addition of nitrate to an aquifer results in the anaerobic biodegradation of toluene, ethylbenzene, and xylenes. The benzene component of fuel has been found to biodegrade slower under strictly anaerobic conditions. A mixed oxygen/nitrate system would prove advantageous in that the addition of nitrate would supplement the demand for oxygen rather than replace it, allowing for benzene to be biodegraded under microaerophilic conditions.

These technologies may be classified as long-term technologies, which may take several years for plume clean-up.

Use of hydrogen peroxide for subsurface remediation: Microbial responses and their implications.

Fiorenza, Stephanie, Rice University Dissertation

Bioremediation uses microorganisms to degrade chemicals of interest and can be limited by mineral nutrients and terminal electron acceptors, especially oxygen. This research investigated in situ bioremediation with hydrogen peroxide  $(H_2O_2)$  as a supplemental oxygen source, added in increasing concentration, and addressed the microbial responses to  $H_2O_2$ . The microbial responses studied were changes in microbial numbers, population structure, degradative ability, and adaptation by induction of catalase and superoxide dismutase. Several assays were developed for this work.

Batch experiments, using microcosms of aquifer material from two sites, Traverse City, MI (TCM) and Granger, IN (GI), contaminated with gasoline, determined mineralization of toluene. Aquifer material treated with  $H_2O_2$  in situ in GI mineralized more toluene than untreated contaminated material; when supplemented with  $H_2O_2$ , it had a greater rate of mineralization.

These results indicated that subsurface microorganisms had adapted to the  $H_2O_2$  applied in GI. At a field demonstration in TCM, heterotrophs and hydrocarbon degraders declined in deep, uncontaminated subsurface cores and deep level cluster wells 7 feet and 31 feet from the H<sub>2</sub>O<sub>2</sub>injection wells, demonstrating toxicity. Microbial numbers were elevated and soil catalase activity was induced in shallow, contaminated cores at 31 and 62 foot distances after the addition of  $H_2O_2$ , indicating adaptation.

Columns filled with slightly contaminated aquifer material from TCM were perfused with benzene, toluene, ethylbenzene, and o- and m- xylene (BTEX) and increasing concentrations of H<sub>2</sub>O<sub>2</sub>. Catalase and superoxide dismutase were induced, especially at the column inlets. Microbial numbers were higher at the column inlets. Abiotic  $H_2O_2$  decomposition was observed in a sterile column; at a feed concentration of 500 mg/l, gas production impeded flow. The biologically active columns required increases in the BTEX concentration to eliminate plugging caused by oxygen gas evolution from catalase activity. The oxygen:BTEX mass ratio was 0.3 before  $H_2O_2$  addition. These results showed that subsurface microorganisms could, if a carbon source was available, adapt to a continuous input of  $H_2O_2$ . The low O:BTEX mass ratio and the requirement for an increase in BTEX when the  $H_2O_2$  concentration was increased demonstrated that supplemental  $H_2O_2$  was unnecessary in these column studies.

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**THE PROBLEM:** Volatile organic compounds (VOCs), include petroleum hydrocarbons and chlorinated solvents. Petroleum hydrocarbons, commonly associated with refueling and maintenance facilities, include chemicals such as gasoline, diesel, jet fuel, motor oil, and benzene, toluene, ethylbenzene and toluene (BTEX). Chlorinated solvents, commonly associated with electrical manufacturing and degreasing operations, include chemicals such as tetrachlorethylene (PCE), trichloroethylene (TCE) and dichloroethylene (DCE).

**THE SOLUTION TO VOC DESTRUCTION**: VOCs can be destroyed using chemical oxidizers such as ozone, hydrogen peroxide and potassium permanganate. The complete oxidation of VOCs produces carbon dioxide and water.

![](_page_65_Picture_195.jpeg)

In-situ oxidation uses contact chemistry of the oxidizing agent to react with VOCs, munitions, certain pesticides and wood preservatives. The most common oxidizers used in soil and groundwater remediation are hydrogen peroxide (and the hydroxyl radical) and potassium permanganate, and ozone, which are non-selective oxidizers. Other oxidants are available, but are used less due to cost, time or potential toxic by-products.

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Hydrogen peroxide when in contact with a metal catalyst such as iron (II), which is commonly known as Fenton's reagent, forms the more powerful oxidizer, the hydroxyl radical. The metal catalyst can be usually provided by iron oxides within the soil or fill, or added separately as iron sulfate. Fenton's reagent has been well documented for over 100 years and has been in use in water treatment plants for well over 50 years (Barb et al., 1950; Stanton et al., 1996). The chemistry is well documented (Watts, et al, 1991, 1992 and 1994) to destroy petroleum hydrocarbons and other volatile organic compounds. Hydrogen peroxide arrives in the field as a liquid stored in poly drums. When chemical oxidant hydrogen peroxide  $(H_2O_2)$  is injected into the subsurface, it decomposes readily into reactive hydroxyl radicals (OH<sup>\*</sup>), hydroxyl ions (OH<sup>\*</sup>) and water  $(H<sub>2</sub>O)$ . The oxidation of a contaminant by hydrogen peroxide involves complex reactions influenced by a number of variables, including pH, reaction time, temperature, catalysts, and hydrogen peroxide dosage. In subsurface environments having pH of 8.0 or greater, strong or weak acids can be used to lower pH and optimize the oxidation process, as determined by a laboratory bench test. Hydrogen peroxide works best in acidic environments with low alkalinity. Chemical oxidant delivery systems have been described (Jacobs, 2000a, 2000b and 2001).

There are also a large number of competing reactions including the free radical scavengers, most importantly, carbonate and bicarbonate alkalinity that will greatly affect the overall reaction scheme. Although handling hydrogen peroxide and other oxidants requires significant safety training and planning, the oxidant is effective at remediation and relatively inexpensive. Forensic chemical analysis from various sites have shown that the hydrogen peroxide reaction tends to work first on the longer chain carbon sources, including total organic carbon (TOC), rootlets, heavier-end hydrocarbons, prior to oxidizing the lighter hydrocarbons.

Potassium permanganate  $(2KMnO<sub>4</sub>)$  lasts longer and can react in an environment with much higher pH than hydrogen peroxide. For field use, potassium permanganate is shipped as a powder and is mixed with water creating a deep purple liquid. The solubility of potassium permanganate is strongly influenced by temperature and at 30  $^{\circ}C$ , the solution has slightly over an 8% concentration of potassium permanganate. The pH range is critical in being able to determine whether the oxidation reaction will be fast or slow. If trivalent chromium Cr (III) is present in the soil, adding potassium permanganate will oxidize the Cr (III) to Cr (VI). Field conditions indicate that once the oxidant is consumed, the Cr (VI) will revert back to Cr (III).

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Ozone  $(O_3)$  is a powerful gas phase oxidizer that can be used to treat VOCs. It must be generated on-site and the gas cannot be stored; therefore all the ozone gas that is generated must be injected into the subsurface or destroyed using an ozone destruction unit on the ozone generator. The ozone gas can be bubbled into closely spaced injection ports that release the bubbles into the aquifer for remediation. The smaller the bubbles, the more surface area and the faster they can travel through small pore spaces. Pushing the ozone gas through a diffusion pipes can produce micro-bubbles.

For all types of in-situ chemical oxidation methods, chemical compatibility of the injection equipment, personal protective equipment and safety procedures become critical with the injection of potentially dangerous chemicals including oxidizers, acids, bases, and other chemicals.

**BIOREMEDIATION:** Chemical oxidants can also serve as an oxygen source for microbes in the subsurface to enhance biodegradation of contaminants. Therefore, many in-situ chemical oxidation projects are designed to move into a second, longer-term bioremediation phase due to all the newly available oxygen in the subsurface. Potassium and sodium permanganate do not kill microbes. Hydrogen peroxide and ozone at higher concentrations will kill microbes, however, the oxygen rich treatment area will be attractive to indigenous populations in adjacent zones.

**RECOMMENDED PLAN:** ENVIRONMENTAL BIO-SYSTEMS recommends a review of the existing physical and chemical data, including pH, permeability, lithology, and water depth, concentrations of VOCs, alkalinity, and other data. A simple laboratory bench test (5 to 10 working days) is recommended to optimize the pH, and dosage of the hydrogen peroxide, as well as evaluate the addition of iron or acids. A pilot-scale in-situ remediation project can occur within a few days after the bench test results are available. After a pilot-scale project is performed, a large-scale full remediation program can be developed. In some cases, the pilotscale size project may be enough to treat a lingering hot spot. For hydrocarbon-impacted sites, the hydrogen peroxide reaction will liberate large amount of free oxygen, allowing for a second treatment phase using aerobic bioremediation of the contaminants.

**SUMMARY:** Chemical oxidants hydrogen peroxide, potassium permanganate and ozone can be injected into soil and groundwater impacted by VOCs. The remediation injection process is

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rapid, precise, less disruptive and generally lower cost than most of the alternative remediation methods.

**COMPANY BACKGROUND:** Since 1990, ENVIRONMENTAL BIO-SYSTEMS has been a leader in in-situ remediation. The company has developed proprietary injection remediation technologies.

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Preferential Pathway Survey

![](_page_70_Picture_5.jpeg)

### **A Novel, In-Situ Delivery Method for Peroxide for Remediation of Organically Contaminated Soils**

**EPA Contract Number:** 68D98121 **Title:** A Novel, In-Situ Delivery Method for Peroxide for Remediation of Organically Contaminated Soils **Investigators:** Inman, Maria E. **Small Business : Faraday Technology, Inc. EPA Contact :** Manager, SBIR Program **Phase:** I **Project Period:** September 1, 1998 through March 1, 1999 **Project Amount:** \$69,338 **RFA:** SBIR - Phase I (1998) **Research Category:** Hazardous Waste/Remediation , SBIR - Remediation **Description:** 

There is a critical need to develop and implement effective in-situ treatment methods for organically contaminated groundwater. This SBIR Phase I project focuses on an innovative, in-situ method for remediating organically contaminated soils, sludges, and sediments, by in-situ generation of peroxide, which acts as either an oxidant for destruction of organic contaminants or as an oxygen supply in bioremediation schemes. This method is cost effective and suitable for large-scale field applications. The proposed method: (a) generates the peroxide ions in-situ, in the subsurface layers, thus avoiding the transport of large volumes of oxidant to contaminated sites, (b) transports the peroxide ion in the contaminated groundwater under the application of applied electric fields, for uniform in-situ chemical oxidation, and (c) avoids extensive soil mixing for in-situ application. The use of an electrochemical method allows metering of the peroxide production rate, which prevents overdosing of the system. Additionally, peroxide does not persist in the environment; therefore, there is no possibility of further contamination of the site. **Supplemental Keywords:**

*small business, SBIR, remediation, groundwater, chemistry, EPA.* , Economic, Social, & Behavioral Science Research Program, Water, Scientific Discipline, Waste, Remediation, Engineering, Chemistry, & Physics, Chemistry, Environmental Engineering, Environmental Chemistry, Contaminated Sediments, Groundwater remediation, Bioremediation, Market mechanisms, organic pollutants, groundwater, oxidation, contaminated sediment, in-situ bioremediation, contaminants in soil, cost effective, groundwater contamination, bioremediation of soils, electrochemical methods, organic contaminants, sediment treatment, treatment technology, sediments, soil sediment, electrochemical technology, in situ remediation