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SOURCE ZONE REMEDIATION PLAN

VALLEY GAS (FORMERLY B&C MINIMART)
2008 1ST STREET
LIVERMORE, CALIFORNIA
(APN 097-0001-24-01)

Submitted to:

Ms. Chris Davidson
City of Livermore
1052 S. Livermore Avenue
Livermore, California 94550-4899

Submitted by:

Golder Associates Inc.
2580 Wyandotte Street
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August 11, 2006 053-7020

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This material and data in this report were prepared under the supervision and direction of the undersigned. This report was prepared consistent with current and generally accepted geologic and environmental Consulting principles and practices that are within the limitation provided

Golder Associates Inc.

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August 11, 2006

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SOURCE ZONE REMEDIATION PLAN

1.0 INTRODUCTION

Golder Associates Inc. (Golder) has prepared this source zone remediation plan for the Valley Gas site (formerly B&C Mini Mart) at the request of our client, Mr. Balaji Angle, and consistent with Golder's February 3, 2006, *Revised Work Plan for Corrective Action* (Work Plan). The revised Work Plan was prepared in response to the letter dated August 25, 2005 from the City of Livermore requesting a cleanup plan for the former B & C Mini Mart (now Valley Gas) station located at 2008 1st Street, Livermore, California (Figure 1).

The purpose of this remediation plan is to evaluate remedial alternatives for treating benzene in groundwater and non-aqueous phase liquids (NAPL) potentially present near the water table within the source zone that extends from the site to approximately 250 feet downgradient (west-northwest) of the site beneath the Groth Brothers property (see Figure 2). The source zone was assessed and delineated in Golder's June 6, 2006, *Field Investigation for Source Zone Remediation*. The field investigation report included a *Screening Vapor Intrusion Risk Assessment*[1] that indicated unacceptable risks may be posed by benzene in water above 418 micrograms per liter (µg/L) or the potential future exposure to soil vapor of currently submerged NAPL (in the case that the water table drops in the future). In addition to the alternatives evaluation, this remediation plan includes a description of the rationale for selecting the preferred alternative (ozone/air sparging) and provides a plan for implementing interim and full scale remediation.

Consistent with Golder's revised Work Plan[2], Golder's subconsultant, PRIMA Environmental (PRIMA) performed a bench-scale test to evaluate activated persulfate as an in situ chemical oxidation (ISCO) agent for interim and/or final remediation of the petroleum hydrocarbons in the source zone. The soil and groundwater samples for the bench-scale test were acquired during the field investigation referenced above. The results of the bench study are in PRIMA's June 14, 2006 *Draft Evaluation of Activated Persulfate for the Destruction of Petroleum Hydrocarbons* (Appendix A). The test results demonstrated that activated persulfate was ineffective at treating the petroleum hydrocarbons at this site. The bench test indicated that after 29 days activated persulfate reduced petroleum hydrocarbon concentrations in soil and groundwater by less than 13 to 15%. The ineffectiveness of activated persulfate may have been related to oxidant demand of the site soil and

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[1] *Screening Vapor Intrusion Risk Assessment*, Golder Associates Inc., May 31, 2006, included as Appendix E in the *Field Investigation for Source Zone Remediation*, Golder Associates, Inc., June 6, 2006.
[2] *Revised Work Plan for Corrective Action*, Golder Associates, Inc., February 3, 2006.

groundwater and the dosage of activated persulfate during the test. Therefore, Golder is currently expanding the scope of remedial investigation at this site to include a bench study to evaluate oxidation of site soil and groundwater using ozone and proposing the installation of wells and equipment for an extended pilot study and interim remediation.

This remediation plan includes the following sections:

- Summary of Source Zone Conditions
- Remedial Objectives;
- Remedial Alternatives Evaluation; and,
- Remedial Implementation Work Plan.

2.0 SUMMARY OF SOURCE ZONE CONDITIONS

Golder performed a source zone soil and groundwater investigation during the weeks of March 22 and March 29, 2006 and performed soil vapor sampling on April 25, 2006.[3] The following sections summarize the findings of that investigation. The soil, groundwater, and soil vapor sampling locations are shown on Figure 2.

2.1 Geology and Hydrogeology

The data collected with the Membrane Interface Probe (MIP) indicates three stratigraphic units can be identified within the alluvial sediments in the vicinity of the source zone: (1) an upper coarse-grained unit, (2) a fine-grained deposit interpreted as floodplain deposit, and (3) a coarse-grained unit extending from 36 feet to the base of the depth explored (52 feet).

The flood plain deposit is encountered in borings southwest of a line extending approximately from the southwest corner of the Valley Gas Site (MIP-14) to the northwest corner of Groth Brothers (MIP-11). To the northeast of this line, including at the B&C Site proper, the floodplain deposit is either absent, or is intermittent, and is interpreted to have been eroded by stream flow processes associated with deposition of the coarser channel deposits. This stratigraphic boundary appears to correlate well with the known distribution of the dissolved contaminant phase, which in turn, is likely controlled by the relatively higher transmissivity of the channel feature defined by the MIP. Furthermore, where the floodplain deposit is present, it serves as a cap to trap the source zone NAPL below in the coarse grained deposits.

Depths to groundwater in the source zone have ranged from approximately 18 to 37 feet bgs since March 1995. The groundwater flow direction is slightly north of west and the hydraulic gradient is typically approximately 0.014 foot per foot. Groundwater velocity is estimated to be from 2 to 4 feet per day[4].

2.2 Petroleum Hydrocarbon Impact to Soil and Groundwater

The largest photo-ionization detector (PID) and flame-ionization detector (FID) responses were measured within select intervals of MIP borings MIP-3, MIP-8, MIP-13 and MIP-14. PID and FID

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[3] *Field Investigation for Source Zone Remediation*, Golder Associates Inc., June 6, 2006.

[4] Conor Pacific. Revised Site Conceptual Model (Revision 1.1), B&C Gas Mini Mart/Desert Petroleum Retail Station, Livermore, California. March 24, 2004.

detectors respond strongly to compounds such as total petroleum hydrocarbons as gasoline (TPHg) and benzene, toluene, ethylbenzene, and xylenes (BTEX). Based on the confirmation laboratory analytical results MIP-8, MIP-13 and MIP-14 were confirmed as being located within the source zone of potential NAPL in soil. MIP-3 appears to be located downgradient of the source zone based on soil confirmation data. and groundwater. The estimated extent of the source zone is shown on Figure 2.

Based on this information, the source zone area is estimated to be approximately 250 feet long, extending to the northwest from the tank pit toward and under the Groth Brothers showroom. The source zone is estimated to be approximately 80 to 120 feet wide. The zone of NAPL is generally confined to the lower coarse grained unit with the majority of the impacted sediment from 36 to 48 feet bgs.

TPHg was detected in all groundwater confirmation samples at concentrations ranging from 4,800 µg/L (CB-10) to 82,000 µg/L (CB-8) (Figure 2). Benzene and methyl tertiary butyl ether (MTBE) were detected in all but one sample (CB-12). Toluene, ethylbenzene, and xylenes were detected in all six sample locations. The concentrations of dissolved hydrocarbons in groundwater are generally consistent with existing information regarding the known extent and concentration of the contaminant plume. However, the concentration of benzene at CB-8 confirms the presence of relatively high levels of dissolved petroleum hydrocarbons along the eastern margin of the Groth property in the area of the showroom.

2.3 Vapor Intrusion Assessment and Evaluation

Comparisons of soil vapor data obtained during the April 2006 soil vapor sampling to the California Environmental Protection Agency's (Cal EPA's) Human Health Screening Levels (CHHSLs) and the San Francisco Bay Regional Water Quality Control Board's (RWQCB's) Environmental Screening Levels (ESLs) indicate that the concentrations of BTEX and TPHg were below the screening levels for soil vapor samples collected from 5 feet below grade.

Golder performed a screening-level vapor intrusion risk assessment (risk assessment) using soil vapor data acquired during the source zone investigation in April 2006[5]. The modeling study involved several different scenarios to estimate potential indoor vapor concentrations for a future building.

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[5] *Screening Vapor Intrusion Risk Assessment*, Golder Associates Inc., May 31, 2006, included as Appendix E in the *Field Investigation for Source Zone Remediation*, Golder Associates, Inc., June 6, 2006.

The predicted indoor air concentrations were less than the CHHSLs and ESLs for the soil vapor-to-indoor air scenario modeled using the Johnson and Ettinger model. However, when a groundwater-to-indoor air scenario is modeled assuming a two-layer soil moisture model and 10X empirical reduction factor, the predicted indoor benzene concentration exceeds the indoor air ESL.

Modeling the NAPL-to-indoor air scenario resulted in a prediction that much higher and unacceptable indoor air concentrations and associated health risks were possible. However, this scenario is very conservative in that it is assumed that NAPL is fully exposed to soil vapor by a significant drop in groundwater table elevation and that there is no biodegradation of vapor as it moves through the vadose zone to the ground surface.

At the Groth Brothers site there is a relatively thick unsaturated zone and slab-on-grade building construction is proposed for the future site development. Provided that the NAPL stays submerged, the measured soil vapor concentrations and modeling results suggest that there is relatively low potential for soil vapor intrusion into site buildings that would result in indoor vapor concentrations above acceptable risk levels. If the water table elevation drops to below the top of the NAPL zone, the soil vapor concentrations would be expected to increase. While bioattenuation of hydrocarbon vapors would be expected, it is not certain whether significant vapor intrusion (i.e., unacceptable risk levels) can be excluded for this scenario.

3.0 REMEDIAL ACTION OBJECTIVES

Based on the results of the risk assessment, Golder recommends that remedial measures be implemented to reduce the dissolved benzene concentration in groundwater to below 418 µg/L beneath the Groth Brothers site.[6] This target concentration is the back-calculated groundwater concentration obtained using the site-specific Johnson and Ettinger model.

Since there is some uncertainty in soil vapor intrusion for a NAPL scenario, it is recommended that NAPL source mitigation be implemented focusing on shallow NAPL near the water table. In addition, supplemental soil vapor monitoring is recommended to evaluate temporal variability. This vapor monitoring could be completed during and after remediation to evaluate the influence of source zone treatment on vapor concentrations.

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[6] *Field Investigation for Source Zone Remediation*, Golder Associates, Inc., June 6, 2006.

4.0 REMEDIAL ALTERNATIVES EVALUATION

In this section, remedial alternatives are described and screened based on identified evaluation criteria, site constraints, and the results of remedial investigation activities performed to date. This section concludes with an explanation of the rationale for the selection of the preferred alternative.

4.1 Identification of Remedial Alternatives

Remedial alternatives under consideration were listed in the February 2006 Work Plan. These alternatives included monitored natural attenuation (MNA), enhanced aerobic bioremediation, bioventing, dual-phase extraction, and in-situ chemical oxidation (ISCO). MNA includes monitoring groundwater and possibly soil vapor as the petroleum hydrocarbons in soil and groundwater naturally attenuate. Enhanced aerobic bioremediation includes subsurface delivery of nutrients and electron donors (e.g., oxygen) needed to enhance biodegradation. Bioventing includes injecting oxygen through venting wells installed in the vadose zone and/or low-flow soil vapor extraction (SVE). The increased oxygen levels increase biodegradation rates. Dual-phase extraction involves extracting groundwater and soil vapor from a single well. Extracting groundwater and soil vapor can be accomplished in shallow groundwater using high-vacuum extraction or in deeper groundwater using a combination of SVE and groundwater pumping. ISCO involves injecting chemical oxidants and other amendments as needed to destroy (oxidize) contaminants, in this case, petroleum hydrocarbons, and in particular, benzene. Typical oxidants successfully used for ISCO of petroleum hydrocarbons include Fenton’s Reagent, persulfate, and ozone.

4.2 Evaluation of Remedial Alternatives

The evaluation criteria described in Golder’s February 2, 2006 work plan include 1) regulatory agency acceptance, 2) reduction of toxicity, mobility, or volume, 3) technical feasibility, 4) schedule, and 5) cost. The remedial objectives described in Section 3.0 include reducing benzene concentrations in groundwater beneath the Groth Brothers site to less than 418 μg/L and mitigation of potentially remaining non-aqueous phase liquids (NAPL) in the source area. Therefore, this evaluation focuses on the criteria described above and the ability of the remedial alternatives to meet the remedial objectives.

4.2.1 MNA

MNA could be effective at this site based on attenuation monitoring performed by Golder. The results of monitoring indicates attenuation is occurring.[7] However, the remediation time frame required to meet the remedial objectives (Section 3.0) is likely unacceptable. In order for NAPL to attenuate, it will need to volatilize, or, dissolve into groundwater. Since NAPL is suspected to be trapped within saturated soils in the source zone, MNA could potentially take decades to meet the remedial objectives. If groundwater levels were to decline exposing NAPL during this timeframe, vapor intrusion at unacceptable risk levels may occur.

4.2.2 Enhanced Aerobic Bioremediation/Bioventing

Similar to MNA, bioremediation is limited by the bioavailability of the contaminants which could be trapped in small pores that are inaccessible to microbes and present as NAPL. The microbes cannot consume NAPL directly, but will degrade hydrocarbons dissolved in groundwater and adsorbed on soil particles. Therefore, the NAPL removal rate is limited by both the biodegradation rate and the desorption and solubilization rate of the NAPL. Even though this alternative has the potential to be faster than MNA, the bioavailability of the petroleum hydrocarbons would limit it's effectiveness within the available time frame. Bioventing would also be ineffective due to the bioavailability of dissolved and trapped contaminants.

4.2.3 Dual-phase Extraction

Dual-phase extraction involves more equipment installation than the other alternatives and generates relatively large quantities of waste products that need to be treated before discharge or disposal. The equipment, and operation and maintenance costs for this alternative are higher than ISCO.

4.2.4 ISCO

ISCO technologies have two main advantages compared to conventional treatment technologies: large volumes of waste material are not generated and treatment is commonly implemented over a much shorter time frame.[8] For these reasons ISCO is the preferred alternative for this site.

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[7] *Field Investigation for Source Zone Remediation*, Golder Associates, Inc., June 6, 2006.

8 *Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater*, Second Edition, the Interstate Technology & Regulatory Council In Situ Oxidation Team, January 2005.

Oxidants applicable to petroleum hydrocarbon-impacted sites include Fenton's Reagent, activated persulfate, ozone, and ozone with peroxide (peroxone). The oxidation potential of activated persulfate is as high as the potential for ozone, but reacts much slower than ozone such that the radius of influence is increased because the oxidant is not as quickly consumed after injection. Fenton's reagent, ozone, and peroxone react quickly with organics present in the subsurface, which may limit the size of the treatment zone for each injection well or point.

Due to the access constraints at this site, Groth Brothers showroom and South L Street, Golder selected persulfate as the preferred oxidant due to its potentially larger radius of influence and relative permanence. PRIMA performed a bench study on site soils with persulfate (Appendix A), and concluded that persulfate was ineffective at treating the petroleum hydrocarbons at this site. Even though the bench test indicated that persulfate is ineffective, ISCO remains the preferred alternative due to the benefits described above. The ineffectiveness of persulfate indicated in the bench test may have been a dosage issue in comparison to site soil and groundwater oxidant demand. Since ozone is applied as a gas through wells or sparge points, it can be continuously supplied compared to the batch application approach for persulfate or Fenton's reagent. The continuous application of ozone will have a better likelihood of overcoming the soil oxidant demand at a lower cost than the batch injection approaches.[9]

Golder recommends implementing interim remediation and evaluating the use of ISCO with ozone at this site. Ozone is the preferred oxidant for the following reasons:

- Ozone is a strong oxidant and its effectiveness has been demonstrated at numerous petroleum hydrocarbon sites[7];
- No storage or handling of hazardous materials is required;
- Ozone can be generated on site at relatively low costs;
- Since ozone can be applied through sparge wells, there is less site disruption and injection can occur over a longer time frame compared to other oxidants; and

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[9] *Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater*, Second Edition, the Interstate Technology & Regulatory Council In Situ Oxidation Team, January 2005.

- Sparge wells can be installed beneath the street.

4.3 Preferred Alternative Description

Ozone is an oxidant that, in contrast to the other ISCO processes, can be applied as a gas to remediate the vadose zone via injection, as well as the saturated zone via sparging. Ozone can be applied on its own or in combination with peroxide (peroxone)[10]. Ozone is a more powerful oxidant than hydrogen peroxide, but less powerful than sulfate or hydroxyl radicals. Ozone can directly oxidize a contaminant or can indirectly oxidize a contaminant via the production of hydroxyl radicals. Oxidation by hydroxyl radicals is a faster reaction than direct oxidation by the ozone itself. Hydroxyl radicals can be formed when ozone reacts with hydroxide ions in a neutral to basic pH range. Elevated pH conditions result in increasing hydroxyl radical production, and oxidizing power, but also the production of hydroxide precipitates. In addition to producing radicals, a chain reaction is also initiated that typically causes the formation of new radicals. As a secondary benefit, ozone provides oxygen to the subsurface when it decomposes, which facilitates bioremediation.

Ozone is three times more soluble in water than oxygen. When typical ozonated feed gases are sparged into clean water, the aqueous equilibrium ozone concentrations can theoretically reach 30 milligrams per liter (mg/L), but the mass transfer of ozone into water is limited[11]. The half-life of ozone in water is typically 30 minutes at standard temperatures and pressures, but it can be longer in subsurface environments because of natural deviations from standard temperatures and pressures[12]. Because the mass transfer of ozone to groundwater is limited, ozonation is applied over a longer time period than other ISCO processes. To maximize mass transfer to groundwater, ozone is commonly delivered via microporous sparge points with very small orifices that form fine bubbles. If applied at too great a rate, there is potential for uncontrolled migration of ozone gas and volatile contaminants.

Ozone–hydrogen peroxide (peroxone) injection has been used to treat contaminants in water ex situ for several years. Peroxone injection is more aggressive than ozonation or Fenton’s reagent because of its high yield of hydroxyl radicals. Excess peroxide can consume hydroxyl radicals as well, so it is important to inject the appropriate volume of reactants in order to have an efficient process.

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[10] U.S. Environmental Protection Agency. *Alternative Disinfectants and Oxidants Guidance Manual*. Office of Water (4607) EPA 815-R-99-014. April 1999.

11 U.S. Environmental Protection Agency. *Alternative Disinfectants and Oxidants Guidance Manual*. Office of Water (4607) EPA 815-R-99-014. April 1999.

12 *Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater*, Second Edition, the Interstate Technology & Regulatory Council In Situ Oxidation Team, January 2005.

A key difference between ozone and peroxone is that ozone relies heavily on direct ozone oxidation while peroxone relies on hydroxyl radical oxidation. In the peroxone process, the ozone residual is short lived because the added peroxide greatly accelerates the ozone decomposition. The net result is that oxidation is more reactive and much faster in the peroxone process compared to the ozone molecular process. However, the peroxone process is more difficult to implement due to the sensitivity of the process to peroxide concentrations and requires the storage and handling of concentrated peroxide on site.

Oxidant scavengers (e.g., carbonate, non-target organics) can limit the effectiveness of ozone and peroxone (as well as other oxidants) due to consumption of the radicals produced by the oxidant. Thus, pH and bicarbonate alkalinity play a major role in effectiveness due to bicarbonate and carbonate competition for hydroxyl radicals at high alkalinity and carbonate competition for hydroxyl radical at high pH levels. During the fourth quarter 2005 natural attenuation parameters monitoring, total alkalinity ranged from 280 to 350 mg/L (relatively high) and pH ranged from 7.69 to 7.85 (slightly basic).[13]

Golder recommends performing a pilot study and interim remediation with ozone sparging. If monitoring data indicate that more oxidative power is warranted, peroxide addition will be evaluated. The following section describes the proposed implementation of the preferred remedy.

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[13] Fourth Quarter 2005 Groundwater Monitoring Results, Golder Associates Inc., January 31, 2006.

5.0 REMEDIAL IMPLEMENTATION

In order to design a full-scale system to meet the remedial objectives for the source zone, Golder recommends performing a bench scale test and an extended pilot study while performing interim remediation. These activities are summarized in the following sections.

5.1 Ozone Bench Scale Test

The bench scale test will include analyses to assess the ozone dose requirements and the natural buffering capacity of the soil. To confirm the effectiveness of ozone as an oxidant and to assess whether ozone sparging will generate chemical species that are deleterious to groundwater quality, bench-scale testing will be performed using representative aquifer materials and groundwater. The aquifer materials and groundwater for the bench-scale testing will be collected during the installation of the sparge wells described in Section 5.2. The bench test apparatus will provide a continuous source of ozone to representative soil and groundwater from the site by sparging in a manner consistent the sparging that will be performed on site. The bench scale testing will assess the following:

- The effectiveness of ozonation and the extent to which removal is due to destruction or volatilization;
- The ozone demand of soil and water;
- The effect of ozonation on secondary groundwater quality parameters; and
- The potential for the formation of hexavalent chromium and/or bromate and the attenuation of these species, if formed.

Details regarding the proposed bench-scale testing are included in **Appendix B**. The results of the bench study will be used to develop the sampling and analysis plan for the ozone sparging pilot test and allow modification of the pilot test approach if necessary (such as a larger ozone generator if necessary).

5.2 Ozone/Air Sparge Well Installation

Three double-nested ozone/air sparge wells (SP-1 through SP-3) will be installed at the approximate locations shown on Figure 3. A schematic of the sparge well construction is shown on Figure 4. The sparge wells will be installed using hollow-stem auger drilling methods. Continuous soil samples will be collected from 36 to 48 feet bgs. Soil samples will be logged by a geologist or engineer working under the direct supervision of a California-registered geologist. Soil and groundwater samples will be collected during the installation of the SPs for the bench scale testing. One soil sample will also be collected for chemical analysis as discussed in Section 5.3.3.

The sparge wells will be constructed from 1.5-foot long, 25-micron, porous, polyvinylidene fluoride (PVDF) sparge points connected to schedule 80 polyvinyl chloride or PVDF well casing (Figure 4). The sparge points will be set within higher permeability zones at approximately 40.5 to 42 feet and 46.5 to 48 feet below surface grade (bgs). A filter pack consisting of No. 8/30 sand (or equivalent) will be installed to one foot above each sparge point, and the sparge points will be separated by a continuous bentonite seal approximately 3.0 to 3.5 feet thick. Approximately one to two gallons of clean potable water will be placed on top of the well seals to hydrate the bentonite. The bentonite will be allowed to hydrate a minimum of 30 minutes prior to constructing the upper sparge point or grouting the remaining well annulus. The remaining well bore will be sealed to within eight inches of surface grade with bentonite grout and capped at grade with concrete. The sparge wells will be completed in an 18-inch traffic-rated well boxes installed in concrete. A four-inch diameter sweep elbow will be installed beneath the skirt of the vault boxes to allow future routing of conveyance tubing or flexible piping.

5.3 Ozone Pilot Test/Interim Remediation

The primary goal of the pilot test is to confirm the effectiveness of ozone sparging and provide data to formulate the design basis for the full scale implementation. The pilot test will be performed to evaluate the following:

- The gas entry pressure of the course-grained unit within the source zone;
- The potential radius of influence;
- The relationship between pressure and flow rate during sparging;
- If petroleum hydrocarbons are off-gasing to the vadose zone;
- The contaminant removal rates from groundwater;
- If oxidation by-products accumulate (in conjunction with the bench study); and,
- The potential effects on the water table and the capillary fringe induced by gas injection.

5.3.1 System Components

The primary components anticipated for the sparging pilot test include:

- Power supply;
- Dual completion ozone/air sparge well (SP-1)
- Ozone sparging equipment package to include:
    - oxygen enriched inlet air,
    - programmable operation with actuated valves and manifold;
    - capability to produce up to 2 pounds per day ozone;
    - capablility of 2 standard cubic feet per minute (SCFM);
    - capability of up to 20 pounds per square inch (psi).
- Pressure gauges on injection and monitoring wells
- Helium delivery system with flow meter, pressure gauge/regulator.
- Helium detector;
- Ozone detector (optional);
- Miscellaneous soil vapor and groundwater sampling equipment; and
- Photo-ionization detector (PID).

5.3.2 Testing Procedures

Golder proposes to conduct two types of performance tests including:

- Variable pressure/flow rate tests for estimating sparge cycle durations and gas injection system equipment requirements.
- Constant-rate tests for evaluating sparge areas of influence and contaminant removal effectiveness.

The variable pressure/flow rate tests will be conducted first to evaluate the gas entry pressure and determine the time required to generate the maximum effective zone of sparging. These results will also be used to plan the injection configuration and flow rates for the constant-rate test. The constant-rate test will be conducted following the variable pressure/flow rate test to evaluate the area of influence and efficiency of contaminant removal from groundwater and effects on soil vapor petroleum hydrocarbon concentrations. Testing will be performed on SP-1 initially and after operating parameters are established, the other sparge points (SP-2 and SP-3) will also be operated. The constant-rate test will be performed as interim remediation over a period of months until the system modifications for full-scale implementation can be completed for the full-scale system.

5.3.3 Baseline Sampling

Prior to starting the pilot test, a sampling pump will be used to obtain baseline vapor samples for field screening of VOCs, ozone (optional), helium, carbon dioxide, and oxygen. Vapor samples will be collected from the upper screen of CMT-4 that is not below water level and head space from either monitoring well MW-2 or MW-6, or both using a drop tube.

Groundwater samples will be collected from the sparge wells (SP-1 through SP-3), MW-2, and MW-6 according to procedures in Appendix C. Groundwater samples will be collected for chemical analysis using disposable polyethylene bailers or inertial pumps. Groundwater samples will be analyzed for total petroleum hydrocarbons as gasoline (TPHg); benzene, toluene, ethylbenzene, and total xylenes (BTEX); and fuel oxygenates by US EPA Method 8260B. Other parameters will be added based on the results of the bench scale study.

5.3.4 Variable Pressure/Flow Rate Test

This part of the pilot test will be performed by injecting air into each of the shallow (SP-1A) and deep (SP-1B) sparge points separately. The shallow sparge point will be tested first since it will disturb less groundwater than the deeper sparge point and the time required for re-stabilization after the test will be less for the shallow sparge point.

The variable pressure/flow rate test will consist of applying air pressure to a sparge point and recording the resulting air flow. The air flow will be zero until the break-out pressure is reached. Groundwater is pushed out of the sparge point until the hydrostatic pressure (height of the water column) is equalized. The pressure will continue to increase until the air-entry pressure is overcome. The air-entry pressure is the pressure necessary to push the air out of the porous sparge screen, through the filter pack, and into the aquifer materials. The sum of the hydrostatic pressure and the air-entry pressure is the break-out pressure.

Once air begins to flow, pressure and flow rates will be increased incrementally and recorded. Helium tracer gas will be added to the injected air to aid in assessment of the radius of influence (ROI) at each pressure/flow. The pressure will be increased to a maximum of 25 to 50% above the break-out pressure (and within the limitations of the pilot test equipment). This data will be used to develop a relationship between pressure, flow, and ROI necessary for full-scale system design and selection of operating parameters for the remainder of the pilot test and interim remediation. During this testing, soil vapor will be monitored as described in Section 5.3.3 at CMT-4 and MW-2 or MW-6, or both. In addition, water levels will be recorded periodically to assess upwelling. The deeper sparge point (SP-1B) will be tested after the water level in SP-1A is within 10% of its baseline measurement (water column height).

5.3.5 Constant–Rate Injection Test Procedures

Based on the data acquired during the variable pressure/flow rate testing, ozone will be injected at the assumed optimal flow rates and monitoring will be performed to assess the area of effectiveness and confirm the optimal flow rate for each sparge point. The optimal flow rate will be the flow rate that maximizes the injection of ozone with minimal liberation of petroleum hydrocarbons to the vadose zone. The pilot test system will be operated manually at first and then programmed for continuous operation at all three sparge wells as the optimal operating parameters are identified. Continuous operation will likely involve sparging into one or two sparge points at a time and rotating from point to point in a programmed sequence.

Soil vapor monitoring will be performed as described in Section 5.3.3 frequently (e.g. hourly) during the first day of this testing and within 2 to 3 days after continuous operation commences. Groundwater sampling will be performed as described in Section 5.3.3 within 2 to 3 days after continuous operation commences and approximately one week later. The frequency of future monitoring will depend on the results of this data and the results of the bench study.

5.3.6 Rebound Testing

Within the first one to two months of operation, the system will be shut down for approximately two weeks. At the beginning and at the end of this stabilization period, soil vapor and groundwater monitoring will be performed as described in Section 5.3.3 to assess rebound. Rebound can be caused by migration from higher-concentration areas, desorption from saturated soils, or solubilization of NAPL. The occurrence and magnitude of rebound can indicate the potential time to remediate, whether or not sufficient ozone is being applied, and whether augmentation such as the addition of peroxide should be conducted. Note that it is normal for ISCO to cause temporary increases in dissolved-phase concentrations as organic carbon in the soil is oxidized causing a reduction in the adsorptive capacity of the soil and the adsorbed mass is desorbed by the physical agitation of sparging. The presence of NAPL within the area of ozone sparging will also cause temporary increases in dissolved-phase concentrations due to agitation and changes in the equilibrium conditions in the subsurface.

5.4 Pilot Test Data Analysis and Reporting

VOC removal rates will be calculated for the detected constituents according to the field and laboratory data for VOC concentrations from the monitoring wells. The data will be presented in terms of VOC removal percentages. The changes in VOC concentrations over time will be reviewed together in order to establish a general rate of decline towards clean-up goals. This data will serve as a baseline for estimating the duration of full-scale ozone treatment (with consideration of rebound). Secondary chemical effects of injection will be performed as indicated by the bench study.

Wellhead vapor measurements will be summarized in tables and graphs of concentrations versus time. In addition, the ratio of the ozone to helium tracer gas will be calculated at each well over time to determine the breakthrough periods for both gases (ozone may not be measured). Helium breakthrough time will be used along with gas injection rates to estimate the volume of aquifer contacted by the injected gases. The changes in vadose zone vapor concentrations will be used to asses the relative effects of volatilization versus oxidation.

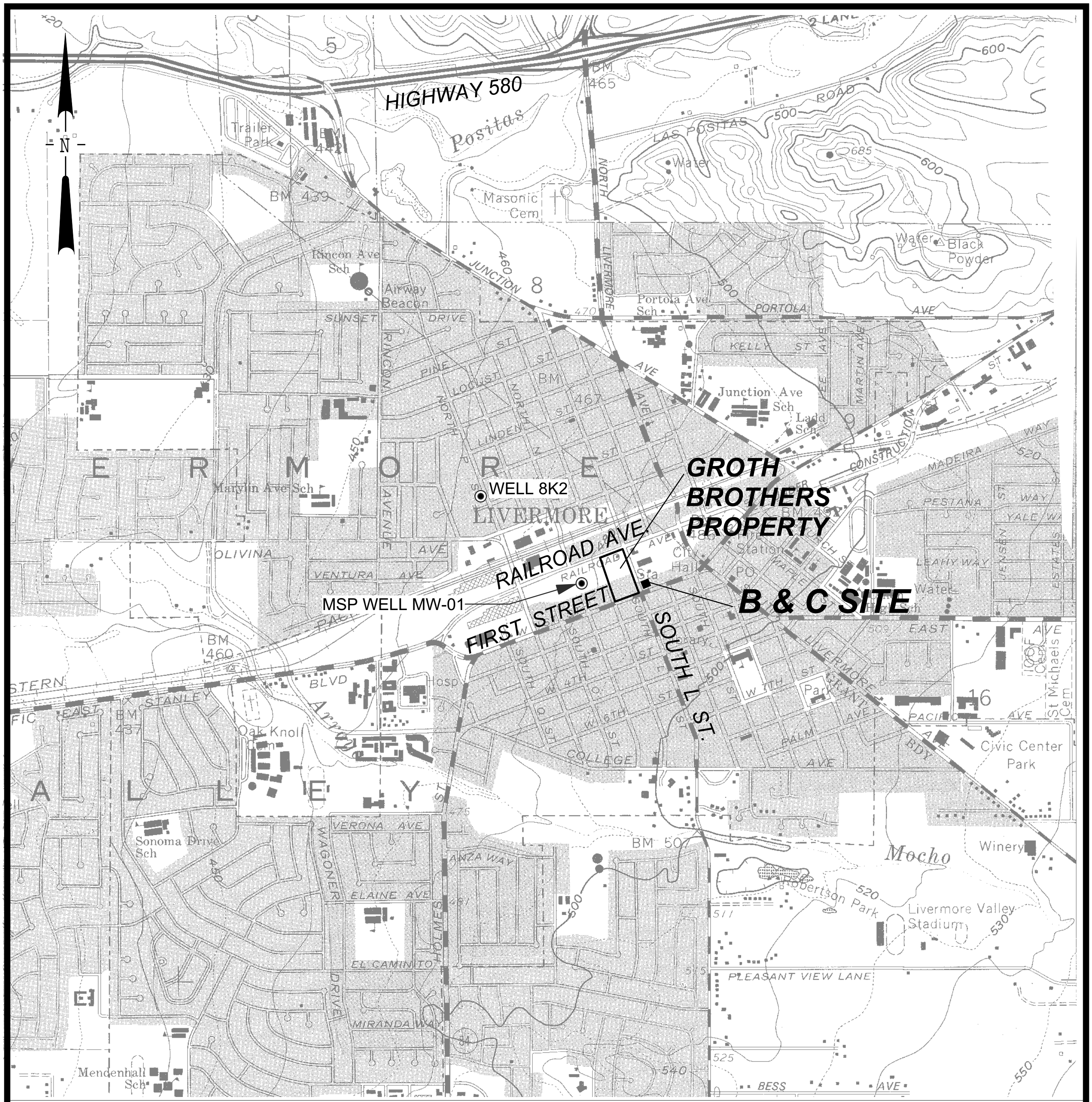
5.5 Reporting

A report will be prepared to summarize the results of the sparge well installation, bench study, and pilot test. The report will be prepared after the rebound check; approximately 1 to 2 months after the start of the test. The technical report will include design basis and remedial implementation plan for ozone/air sparging in the source zone.

6.0 SCHEDULE

After receiving approval from Alameda County Environmental Health Services to implement this source zone remediation plan, Golder will begin permitting and coordinating the installation of the ozone/air sparge wells (SP-1 through SP-3). These prefield activities should be completed in about one month. The pilot test will be scheduled for approximately one month after the installation of the sparge wells (dependent on electrical service availability). The pilot test will be conducted over approximately one to two months and the Source Zone Remediation Plan Addendum including the full-scale implementation layout with the results of the bench and pilot test will be available before this Remediation Plan is submitted to the Regional Water Quality Control Board for approval. During the preparation of the Source Zone Remediation Plan Addendum, negotiations with the City and adjacent property owners will be performed to establish sparge well, trenching, and equipment installation locations for the full-scale implementation plan.

FIGURES



Base map: USGS 7.5' topography, Livermore, California (1961; photorevised 1980)

SCALE: 0 2,000 4,000 FEET

G:\053-7020\FIGURES\SITELOC-mn.DSF 8/11/06

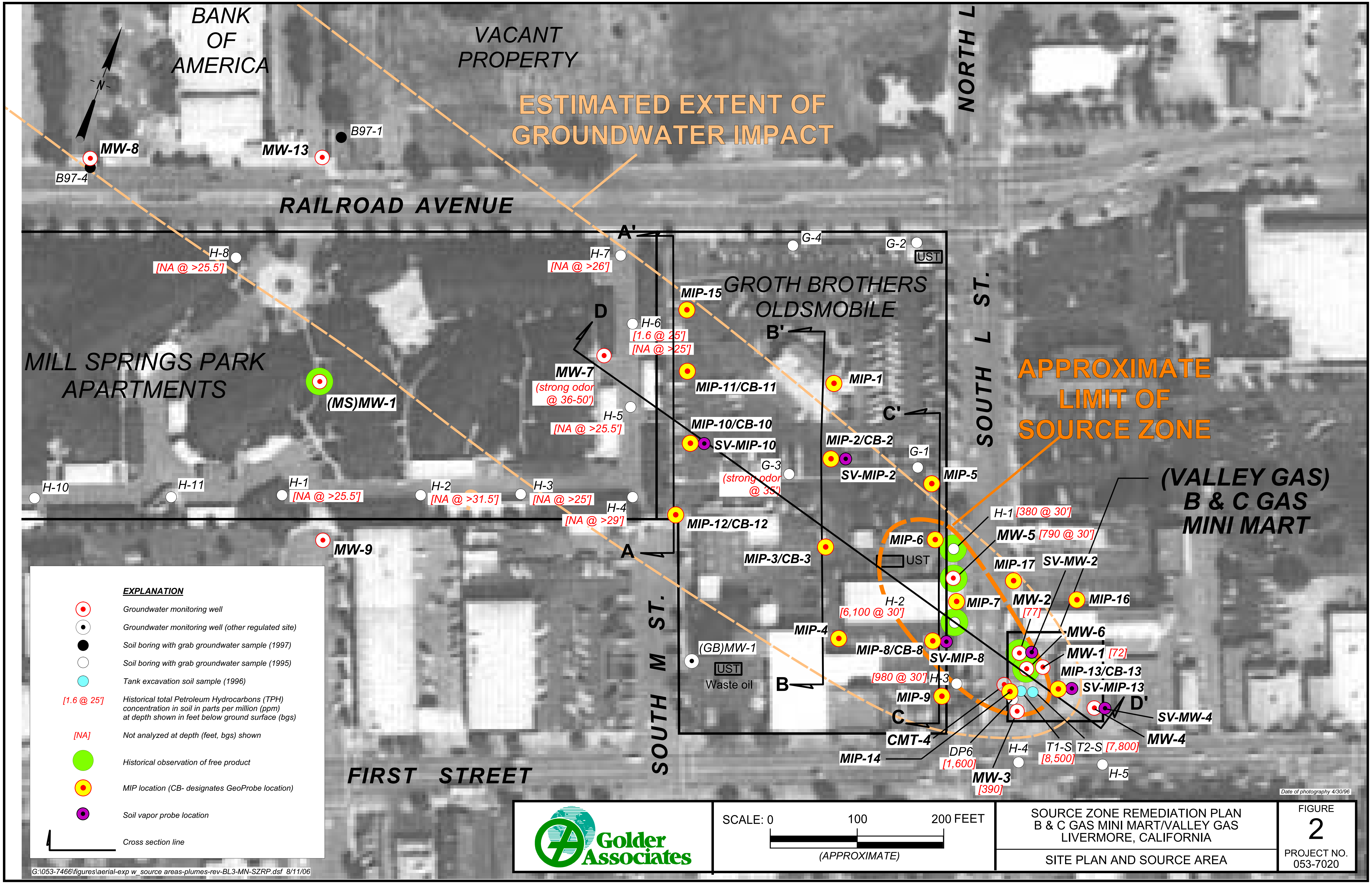
Golder Associates

SOURCE ZONE REMEDIATION PLAN
B & C GAS MINI MART/VALLEY GAS
LIVERMORE, CALIFORNIA

SITE LOCATION MAP

FIGURE
1

PROJECT NO.
053-7020



EXPLANATION

⊙	*Groundwater monitoring well*
⊙	*Groundwater monitoring well (other regulated site)*
●	*Soil boring with grab groundwater sample (1997)*
○	*Soil boring with grab groundwater sample (1995)*
●	*Tank excavation soil sample (1996)*
[1.6 @ 25']	*Historical total Petroleum Hydrocarbons (TPH) concentration in soil in parts per million (ppm) at depth shown in feet below ground surface (bgs)*
[NA]	*Not analyzed at depth (feet, bgs) shown*
🟢	*Historical observation of free product*
⊙	*MIP location (CB- designates GeoProbe location)*
⊙	*Soil vapor probe location*
└	*Cross section line*

G:\053-7466\figures\aerial-exp w_source areas-plumes-rev-BL3-MN-SZRP.dsf 8/11/06

Golder Associates

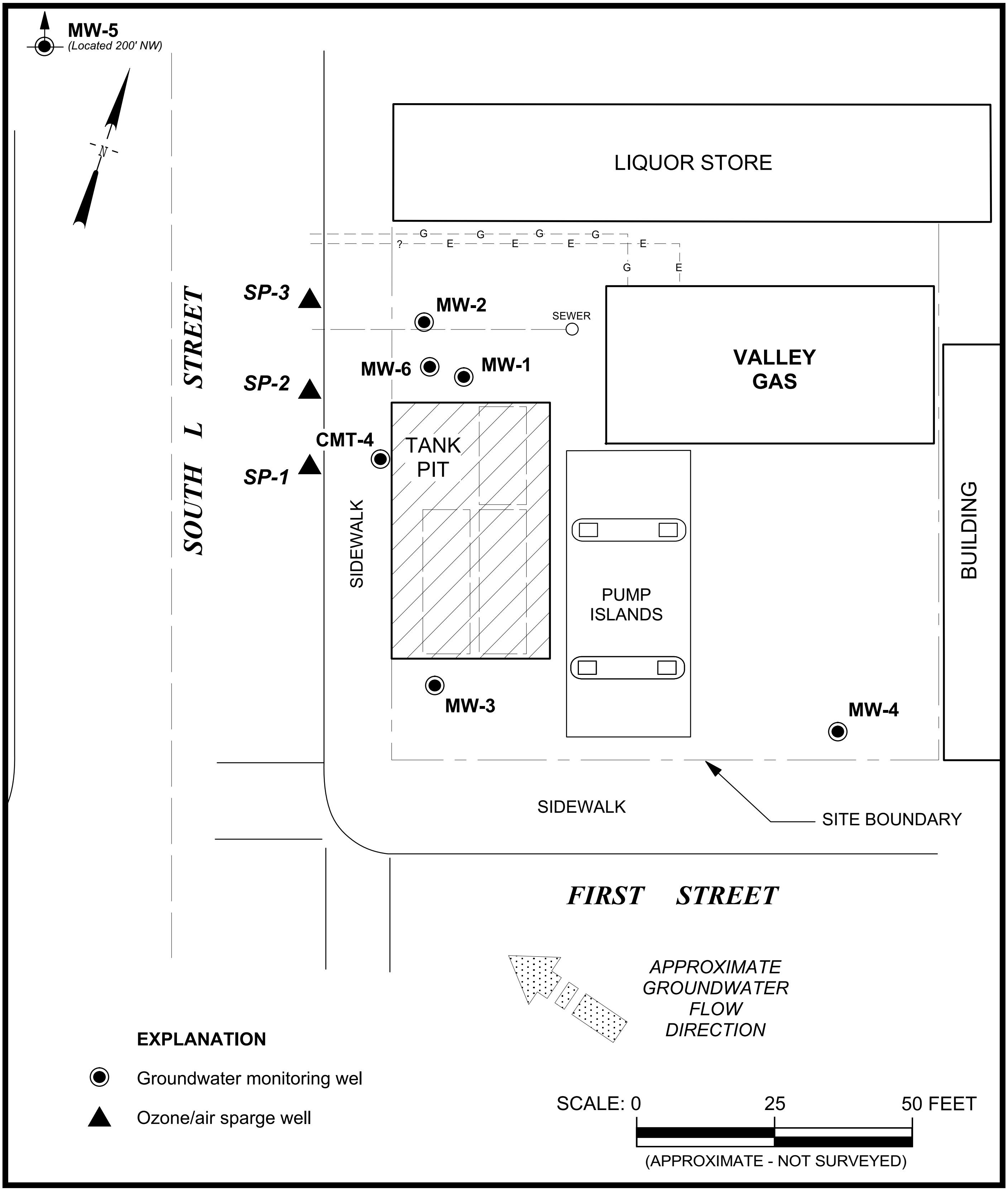
SCALE: 0 100 200 FEET
(APPROXIMATE)

SOURCE ZONE REMEDIATION PLAN
B & C GAS MINI MART/VALLEY GAS
LIVERMORE, CALIFORNIA

SITE PLAN AND SOURCE AREA

FIGURE
2

PROJECT NO.
053-7020



Golder Associates

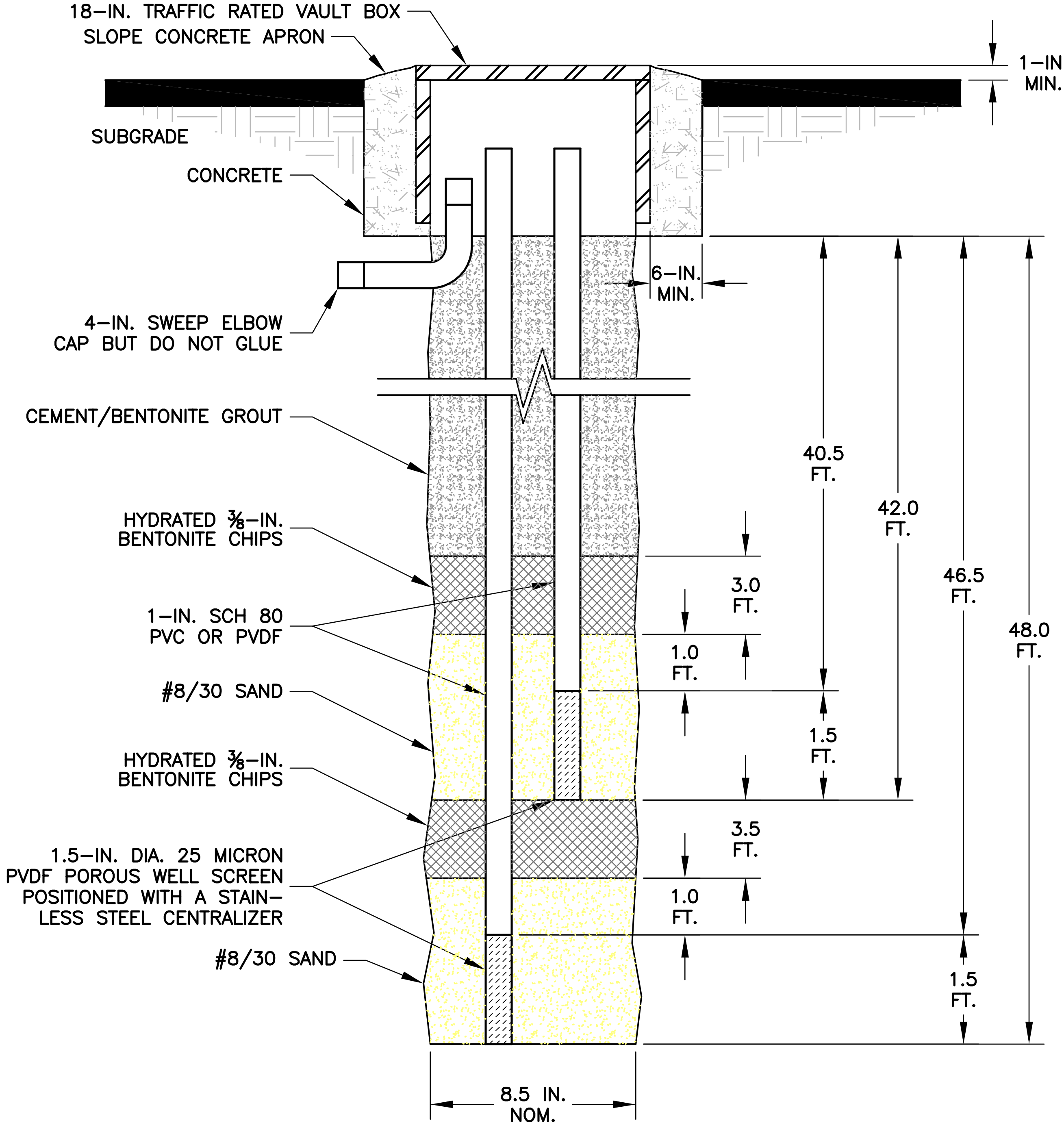
SOURCE ZONE REMEDIATION PLAN
B & C GAS MINI MART
LIVERMORE, CALIFORINA

OZONE/AIR SPARGE WELL LOCATIONS

FIGURE
3
PROJECT NO.
053-7020

G:\053-7020\FIGURES\MN AIR SPARGE-SITE PLAN-FIG3-rev.DSF 8/10/06

(NOT TO SCALE)



LEGEND

IN.	INCH
FT	FEET
MIN.	MINMUM
NOM.	NOMINAL
PVDF	POLYVINYLIDENE FLUORIDE (KYNAR ®)

OZONE/AIR SPARGE WELL SCHEMATIC

Golder Associates
Sacramento, CA

FIGURE 4

PROJECT No. 053–7020 FILE No. Fig 4 – Air CADD JDR DATE 08/10/06

Drawing file: Fig 4 – Air Sparge Well.dwg Aug 10, 2006 – 4:58pm

APPENDIX A
Activated Persulfate Bench Study Results Report

PRIMA
ENVIRONMENTAL

June 14, 2006

William Fowler, P.G.
Golder Associates
2580 Wyandotte Street, Suite G
Mountain View, CA 94043

RE: Draft Report of Findings, laboratory testing of activated persulfate, B&C Gas Mart, Livermore, CA

Dear Bill:

Enclosed is the draft report of findings “Evaluation of Activated Persulfate for the Destruction of Petroleum Hydrocarbons” that describes bench testing conducted on soil and groundwater from the B&C Gas Mart site located in Livermore, California. Please review the report at your earliest convenience. I will finalize the report upon receipt of your comments. If you have any questions, please give me a call at 916-363-8798.

Sincerely,
PRIMA Environmental

Cindy G Schreier, Ph.D.
Principal

10265 Old Placerville Road, Suite 15, Sacramento, CA 95827-3042 • Ph (916) 363-8798 • Fax (916) 363-8829
www.primaenvironmental.com

DRAFT

Report of Findings

Evaluation of Activated Persulfate for the Destruction of Petroleum Hydrocarbons

B&C Gas Mart
Livermore, California

June 14, 2006

Submitted to

William Fowler, P.G.
Golder Associates
2580 Wyandotte Street, Suite G
Mountain View, CA 94043

Submitted by
Cindy G. Schreier, Ph.D.
PRIMA Environmental
10265 Old Placerville Road, Suite 15
Sacramento, CA 95827

Cindy G. Schreier, Ph.D., Principal
Date

EXECUTIVE SUMMARY

Bench-scale treatability testing was conducted on soil (CB-3, CB-8, CB-10, and CB-13) and groundwater (MW-5) from the B&C Gas Mart site in Livermore, California to evaluate the ability of activated persulfate to destroy petroleum hydrocarbons. Specific petroleum hydrocarbons at this site were gasoline range total petroleum hydrocarbons (TPH-g), BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), and fuel oxygenates (MTBE, DIPE, ETBE, TAME, TBA, methanol, and ethanol). Batch tests in which soil, groundwater and activated persulfate were combined, were conducted to evaluate removal of contaminants of concern (COCs), assess the effect of activated persulfate on secondary water quality.

Treatment of site soil and groundwater with up to 6 g/L sodium persulfate activated with 500 mg/L of iron-EDTA (chelated iron) was ineffective at treating COCs in this laboratory test. Up to 2.5 g/L of $Na_2S_2O_8$ was present after 29 days, yet benzene was still present and concentrations of TPH-g and MTBE had only decreased marginally. The formation of TBA, acetone—potential intermediates of MTBE and TPH-g degradation—increased in the persulfate tests, implying that some oxidation was occurring. It is unknown whether improved removal could be achieved with a different activator, such as high pH.

Treatment with persulfate activated with iron-EDTA increased the concentration of several dissolved metals, including Cr(VI), copper and lead. These changes may or may not be activator-specific. Iron, pH, ORP, and sulfate changed as expected.

The soil oxidant demand for the composite soil was 1.7-3.1 g $Na_2S_2O_8$ /kg soil and was independent of the initial concentration of $Na_2S_2O_8$.

Site soil easily buffered 10 mmol H^+/kg soil.

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1.0 INTRODUCTION

Bench-scale treatability testing was conducted on soil (CB-3, CB-8, CB-10, and CB-13) and groundwater (MW-5) from the B&C Gas Mart site in Livermore, California to evaluate the ability of activated persulfate to destroy petroleum hydrocarbons. Specific petroleum hydrocarbons at this site were gasoline range total petroleum hydrocarbons (TPH-g), BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), and fuel oxygenates (MTBE, DIPE, ETBE, TAME, TBA, methanol, and ethanol).

1.1 Technology Background

Activated persulfate is an emerging technology for the oxidation of organic compounds, including chlorinated solvents, BTEX, and petroleum hydrocarbons. Persulfate alone is a relatively strong oxidant, but activation (Eqn. 1) generates the sulfate radical ($SO_4^{-\bullet}$), an even stronger oxidant that enables treatment of an even greater range of compounds. Common activators include heat, divalent metals, chelated metals, hydrogen peroxide, and high pH.

$$\underset{\textit{persulfate}}{S_2O_8^{2-}} + \text{activator} \rightarrow \underset{\textit{sulfate radical}}{2SO_4^{-\bullet}} \qquad \text{Eqn. 1}$$

Oxidation using activated persulfate is often much slower than oxidation using reagents such as Fenton's reagent or ozone. It also reacts typically reacts slowly with soil. These factors potentially make activated persulfate an excellent option for treatment of SPH, since the persulfate may persist in the subsurface, reacting with hydrocarbons as they dissolve into the groundwater.

The sulfate radical decomposes to sulfate (Eqn. 2), while persulfate may decompose to sulfuric acid and oxygen (Eqn. 3) under near-neutral conditions. The change in sulfate concentration and the effect on pH after in situ application of activated persulfate will depend upon the amount of persulfate used, the rate at which it decomposes, the presence of cations that can precipitate sulfate, and the buffering ability of site soil and groundwater. The amount of oxygen gas that can be formed is small (at most about 60 mL O_2 per gram $S_2O_8^{2-}$), and is not expected to cause significant off-gassing under most conditions.

$$SO_4^{-\bullet} + e^- \rightarrow \underset{\textit{sulfate}}{SO_4^{2-}} \qquad \text{Eqn. 2}$$

$$S_2O_8^{2-} + H_2O \rightarrow \underset{\textit{sulfuric acid}}{2HSO_4^-} + \underset{\textit{oxygen}}{\tfrac{1}{2} O_2} \qquad \text{Eqn. 3}$$

As with all strong oxidants, persulfate may have secondary affects such as oxidation of soil-bound chromium to Cr(VI) and mobilization of metals (due to changes in pH and or the presence of a chelating agent as activator). The magnitude of any such affects is site specific and presumably depends upon the concentration of reagents used.

1.2 Study Objectives

The objectives of this bench test were to

- assess COC removal
- evaluate the effect of treatment on secondary water quality parameters
- measure soil oxidant demand for activated persulfate
- generate soil buffering curves

Batch tests to achieve these goals were conducted and the results presented herein.

2.0 MATERIALS and METHODS

Batch tests were conducted to achieve the goals listed in Section 1.2. Sodium persulfate (NaS_2O_8) was the source of persulfate in all tests. The activator chelated iron (GrowMore™ agricultural iron, which is a iron-EDTA that is 13% iron by weight).

2.1 Materials

Sodium persulfate ($Na_2S_2O_8$): $Na_2S_2O_8$ was obtained from FMC (Philadelphia, Pennsylvania). Persulfate solutions were prepared by dissolving $Na_2S_2O_8$ in deionized (DI) water.

Chelated Iron: the chelated iron used in this study as an activator for persulfate was GrowMore™ agricultural iron (Gardenia, California), an iron-EDTA product that is 13% iron by weight. Solutions of chelated iron were prepared by dissolving GrowMore™ iron in DI water.

2.2 Soil and Groundwater Preparation and Characterization

Soil (CB-3, CB-8, CB-10, and CB-13) was received on March 30, 2006. Prior to testing, soil was sieved to remove particles > 4 mesh, then composited. Composited soil was analyzed for

- COCs (TPH-g, BTEX, fuel oxygenates)
- Acetone (a potential oxidation by-product)
- Cr(VI)
- Total metals (arsenic, barium, cadmium, chromium, copper, iron, lead, selenium)

Five (5) 1-gallon glass containers of groundwater (MW-5) were received on April 14, 2006. The groundwater was composited prior to testing, then analyzed for composited, then analyzed for

- COCs
- acetone
- Cr(VI)
- dissolved metals (arsenic, barium, cadmium, chromium, copper, iron, lead, selenium)
- Oxidation reduction potential (ORP)
- pH
- sulfate

2.3 Persulfate Soil Oxidant Demand

The persulfate soil oxidant demand was measured by preparing 3 series of 4 replicates. Each replicate contained 75 g of composited soil, 65 mL of composited groundwater and 10 mL of activated persulfate solution. The intitial persulfate and activator concentrations are shown in Table 1. The replicates were capped and stored in the dark. Once per day, the replicates were shaken by hand. At 7, 14 and 31 days, one replicate from each series was destructively sampled and analyzed for residual persulfate using the ferrous iron/permanganate method. SOD was calculated according to

$$SOD = \left([Na_2S_2O_8]_{init} - [Na_2S_2O_8]_t\right) \times \frac{V}{M} \qquad \text{Eqn. 4}$$

where

SOD = sodium persulfate soil oxidant demand, in g $Na_2S_2O_8$/kg soil
$[Na_2S_2O_8]_{init}$ = the initial concentration of sodium persulfate (in g/L)
$[Na_2S_2O_8]_t$ = the concentration of sodium persulfate at time, t (in g/L)
V = total volume of the aqueous phase, in L
M = mass of soil, in kg

Table 1. Initial Conditions for SOD Tests.

Test	Initial $Na_2S_2O_8$, g/L	Initial Iron*, mg/L
Low Dose	2	500
Medium Dose	5	500
High Dose	10	500

* Iron added as iron-EDTA

2.4 COC Removal

To determine whether activated persulfate can destroy the contaminants and estimate dose requirements, batch tests were conducted. Three series of replicates were prepared. For each replicate, concentrated solutions of persulfate and chelated iron activator were added to 800 mL site groundwater and 450 g soil in a glass bottle with < 10 mL headspace such that the initial concentrations were as listed in Table 2. DI water was added as needed to bring the total aqueous phase to 900 mL. The bottles were capped and stored upside down in the dark. Approximately once per day, each bottle was shaken by hand to mix. Periodically, one replicate from each series was destructively sampled and the aqueous phases analyzed for COCs and acetone. The sampling schedule was 7 days, 14 days, and 29 days. Note that soil will not be analyzed and that the Time 0 sample from the control will serve as the Time 0 conditions for all tests.

Table 2. Estimated Initial Conditions for Dissolved Phase COCs Tests

Test	# Reps	$Na_2S_2O_8$ g/L soln	Activator*, mg Fe/L soln.	Sampling times
Control	4	0	0	0, 7, 14, 29 days
Low	3	3	500	7, 14, 29 days
High	3	6	500	7, 14, 29 days

* iron-EDTA

2.5 Effect on Secondary Water Quality

To assess the effect of activated persulfate on secondary water quality, the aqueous phases from the COC Removal test (Section 2.3) were analyzed for various water quality parameters.

All reactors were analyzed for ORP, pH, residual persulfate, and sulfate. The reactors sampled at Time 0, 7 days and 29 days were also analyzed for Cr(VI) and dissolved metals (arsenic, barium, cadmium, chromium, copper, iron, lead, selenium).

2.6 Buffering Curves

Because persulfate decomposes to form sulfuric acid, buffering curves were developed in order to determine the maximum amount of persulfate that can be added without inducing a long-term decrease in pH. Soil (100 g) and dilute sulfuric acid (100 mL) were combined. Three concentrations of acid were used: pH 1, pH 2, and pH 3. The pH was measured periodically for 15 days.

2.7 Analytical Procedures

The analytical procedures used in this study and the laboratory performing the tests are summarized n Table 3.

Table 3. Analytical Methods.

Analyte	Method	Laboratory Performing Test*
COCs (TPHg, BTEX, fuel oxygenates)	EPA 8260B	Kiff Analytical
Acetone	EPA 8260 B	Kiff Analytical
Cr(VI)	EPA 7199	Excelchem
Metals (As, Ba, Cd, Cr, Cu, Fe, Pb, Se)	EPA 6010B	Excelchem
ORP	Probe	PRIMA
pH	Probe	PRIMA
Residual persulfate	Ferrous iron/ permanganate titration	PRIMA
Sulfate	Turbidimetric**	PRIMA

* Kiff Analytical (Davis, CA), Excelchem (Rocklin, CA)
** Hach DR2010 Spectrophotometer and appropriate Hach test reagents

3.0 RESULTS AND DISCUSSION

3.1 Untreated Soil and Groundwater

The concentrations of COCs and acetone in composited, untreated soil and groundwater are shown in Table 4. Inorganic parameters are shown in Table 5. None of the COCs nor acetone were detected in soil. However, groundwater contained 760 μg/L TPH-g and approximately 13 μg/L total BTEX compounds. The only oxygenates detected were MTBE (63 μg/L) and TAME (2.6 μg/L). Acetone was present at 9.9 μg/L. Several of the metals tested for were detected in both soil and groundwater, including barium, total chromium, copper, iron, and selenium. Arsenic and lead were detected in soil, but not in groundwater. Cadmium was not detected in either matrix. Although total chromium was present in both soil and groundwater, Cr(VI) was not detected in either matrix above the 1 ppb detection limit.

3.2 COC Removal

The results of the COC removal test are shown in Table 6. “AP-3” refers to the activated persulfate test using an initial $Na_2S_2O_8$ concentration of 3 g/L, while “AP-6” refers to the activated persulfate test using an initial $Na_2S_2O_8$ concentration of 6 g/L. Only detected compounds are included. DIPE and ETBE were not detected in any test. Full analytical reports are provided in the Appendix.

Treatment of site soil and groundwater with persulfate activated with chelated iron had little effect on the concentration of most COCs in this study. Total xylenes were completely removed (from 9.5 μg/L to < 0.5 μg/L) in both persulfate tests, but complete removal was also seen in the control test. TPH-g decreased from 400 μg/L to 340-350 μg/L and MTBE decreased from 56 μg/L to 50-52 μg/L in the persulfate tests, but better removal of both compounds was seen in the controls. Similarly, benzene was completely removed in the control test, but increased slightly (to 0.8-1.1 μg/L) I the persulfate tests. TBA, methanol, ethanol, and acetone all increased in the persulfate tests, but not in the controls.

The losses in the control tests are presumably due to biodegradation that was enhanced by the introduction of oxygen into the reactors during set-up. The losses are most likely not due to volatilization because i) the concentration of MTBE—a non-volatile compound—decreased by about 46% in the control test, ii) all reactors were stored upside down, and iii) similar degrees of removal were not seen in the persulfate tests.

The poor performance of activated persulfate in this study was unexpected since persulfate was still present in both tests by Day 29 (see Section 3.3) and is generally considered effective toward these COCs, especially BTEX and MTBE. The increase in TBA and acetone indicate that activated persulfate reacted with some compounds because TBA is a potential intermediate of MTBE oxidation and acetone is often a by-product of oxidation of MTBE and TPH.

Table 4. Concentrations of Organic Compounds in Untreated Materials.

Analyte	Units	Untreated Soil	Untreated Groundwater
TPH-g	ppb	< 5	790
Benzene	ppb	< 5	0.95
Toluene	ppb	< 5	< 0.5
Ethylbenzene	ppb	< 5	< 0.5
Total xylenes	ppb	< 5	12
MTBE	ppb	< 5	63
DIPE	ppb	< 5	< 0.5
ETBE	ppb	< 5	< 0.5
TAME	ppb	< 5	2.6
TBA	ppb	< 5	< 5
Methanol	ppb	< 200	< 5
Ethanol	ppb	< 10	< 5
Acetone	ppb	< 5	9.9

"ppb" = µg/kg for soil and µg/L for water

Table 5. Inorganic Parameters of Untreated Materials.

Analyte	Units	Untreated Soil	Untreated Groundwater
Cr(VI)	ppb	< 1	< 1
Metals			
Arsenic	ppb	1900	< 10
Barium	ppb	9700	382
Cadmium	ppb	< 500	< 5
Chromium (total)	ppb	7500	54.7
Copper	ppb	24900	268
Iron	ppb	7650000	2800
Lead	ppb	2600	< 10
Selenium	ppb	< 2000	22.5
ORP	mV	n.m.	-171
pH	--	n.m.	7.37
Sulfate	mg/L	n.m.	32

"ppb" = µg/kg for soil and µg/L for water

Table 6. COC Concentrations after Treatment with Activated Persulfate

Time, Days	**Analyte Concentration, ppb**		
	Control	**AP - 3**	**AP - 6**
	TPH-g		
0	400	400	400
7	270	270	190
14	220	410	290
29	180	350	340
	Benzene		
0	0.68	0.68	0.68
7	< 0.5	0.81	0.63
14	< 0.5	1.1	0.72
29	< 0.5	1.1	0.8
	Toluene		
0	< 0.5	< 0.5	< 0.5
7	3.6	< 0.5	< 0.5
14	< 0.5	< 0.5	< 0.5
29	< 0.5	< 0.5	< 0.5
	Ethylbenzene		
0	< 0.5	< 0.5	< 0.5
7	< 0.5	< 0.5	< 0.5
14	< 0.5	0.84	< 0.5
29	< 0.5	< 0.5	< 0.5
	Total Xylenes		
0	9.5	9.5	9.5
7	< 0.5	< 0.5	< 0.5
14	< 0.5	1.3	< 0.5
29	< 0.5	< 0.5	< 0.5
	MTBE		
0	56	56	56
7	28	51	44
14	26	51	50
29	30	52	50
	TAME		
0	2.3	2.3	2.3
7	1.2	2.1	2.1
14	n.m.	n.m.	n.m.
29	1.2	2	2
	TBA		
0	< 5	< 5	< 5
7	< 5	6.1	6.1
14	n.m.	n.m.	n.m.
29	< 5.0	7	8.6
	Methanol		
0	< 50	< 50	< 50
7	< 50	< 100	320
14	n.m.	n.m.	n.m.
29	< 50	230	390
	Ethanol		
0	< 5	< 5	< 5
7	< 5	< 20	< 20
14	n.m.	n.m.	n.m.
29	< 5	13	23
	Acetone		
0	8.3	8.3	8.3
7	< 0.5	43	43
14	n.m.	n.m.	n.m.
29	< 5	47	59

Notes:
“AP-3” = activated persulfate test with 3 g/L initial $Na_2S_2O_8$
“AP-6” = activated persulfate test with 6 g/L initial $Na_2S_2O_8$.
“n.m.” = not measured

3.4 Effect on Secondary Water Quality

The effect of activated persulfate treatment on secondary water quality parameters is shown in Tables 7 (total dissolved metals) and 8 (other inorganic parameters). Treatment with activated persulfate decreased the concentrations of arsenic (from 41.9 µg/L to < 10 µg/L), barium (from 180 µg/L to 98-106 µg/L), and selenium (form 28.4 µg/L to < 20 µg/L), while increasing the concentrations of total chromium (from 34 µg/L to 303-314 µg/L), Cr(VI) (from < 1 µg/L to 40-48 µg/L), copper (from 480 µg/L to 2,400 µg/L), iron (from 2,100 µg/L to 416,000-425,000 µg/L), lead (from < 10 µg/L to 70.7-139 µg/L) and sulfate (from 54 mg/L to 940-1,200 mg/L). pH decreased from 7.82 to 6.02 in the AP-6 test and to 6.36 in the AP-3 test. ORP increased from 65 mV to up to 497 mV.

The changes in iron, pH, ORP and sulfate were expected due to the nature of persulfate activated with chelated iron. The decrease in barium was probably due to precipitation of barium sulfate, while the increases in total chromium, copper and lead were most likely due to dissolution of these metals from soil caused by the decrease in pH and/or to chelation of these metals by activator.

The concentration of persulfate over time is also shown in Table 8. In both tests, the concentration of persulfate decreased within the first 7 days, then stabilized. At least 50% of the initial persulfate was present at the end test.

The amount of sulfate formed (886-1,146 mg/L) was lower than expected (1,200-2,000 mg/L) based on the amount of persulfate that was degraded. However, some sulfate may be removed via precipitation with barium or calcium and/or sorption onto soil.

Table 7. Effect of Activated Persulfate on Selected Metals.

Time, Days	Analyte Concentration, ppb		
	Control	AP - 3	AP - 6
	Arsenic, μg/L		
0	41.9	41.9	41.9
7	< 10	< 10	< 10
14	n.m.	n.m.	n.m.
29	22.5	< 10	< 10
	Barium, μg/L		
0	180	180	180
7	212	204	172
14	n.m.	n.m.	n.m.
29	269	106	98.1
	Cadmium, μg/L		
0	22.7	22.7	22.7
7	< 5	< 5	< 5
14	n.m.	n.m.	n.m.
29	22.1	21.9	20.7
	Chromium (total), μg/L		
0	34.1	34.1	34.1
7	10.8	187	170
14	n.m.	n.m.	n.m.
29	34	303	314
	Copper, μg/L		
0	480	480	480
7	151	1530	1660
14	n.m.	n.m.	n.m.
29	378	2420	2400
	Lead, μg/L		
0	< 10	< 10	< 10
7	< 10	149	110
14	n.m.	n.m.	n.m.
29	28.2	139	70.7
	Iron, μg/L		
0	2100	2100	2100
7	2020	426000	423000
14			
29	3760	416000	425000
	Selenium, μg/L		
0	28.4	28.4	28.4
7	< 20	< 20	< 20
14	n.m.	n.m.	n.m.
29	< 20	< 20	< 20

Table 8. Effect of Activated Persulfate on Other Inorganic Parameters

Time, Days	Analyte Concentration		
	Control	**AP - 3**	**AP - 6**
	Cr(VI), µg/L		
0	< 1	< 1	< 1
7	< 1	32.9	25.7
14	n.m.	n.m.	n.m.
29	< 1	39.8	48
	ORP, mV		
0	65	65	65
7	265	354	497
14	144	413	374
29	172	355	371
	pH		
0	7.82	7.82	7.82
7	7.83	6.88	6.83
14	7.8	6.84	6.66
29	7.65	6.36	6.02
	sulfate, mg/L		
0	54	54	54
7	61	520	680
14	62	590	820
29	35	940	1200
	residual sodium persulfate, g/L		
0	0	3	6
7	0	1.9	3.3
14	0	1.8	3.7
29	0	1.5	3.5

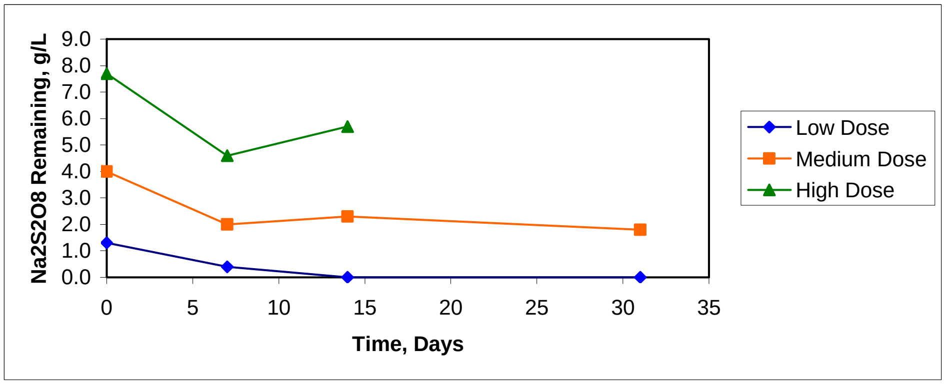
3.6 Activated Persulfate Soil Oxidant Demand

The concentration of $Na_2S_2O_8$ over time and the amount of $Na_2S_2O_8$ consumed by the soil in the SOD test are summarized in Figure 1. All of the persulfate was consumed within 14 days when the initial $Na_2S_2O_8$ was 2 g/L, but only 2-3 g/L were consumed when the initial concentration was 5 g/L or 10 g/L. This indicates an SOD of 1.7-3.1 g $Na_2S_2O_8$ / kg soil when persulfate is activated with 500 mg/L of iron-EDTA. It should be noted that unlike other oxidants, the persulfate SOD appears to be independent upon initial $Na_2S_2O_8$ concentration, at least for the ranges used in this study.

3.7 Buffering Curve

Buffering curves for the soil are shown in Figure 2. Addition of 1 mmol H^+/kg soil had little effect on the pH—by Day 15, the pH was < 0.2 pH units lower in the unacidified test. Addition of 10 mmol H^+/kg initially decreased the pH to 5.2, but the pH rebounded to pH 6.6 within 1 day, then stabilized. In contrast, addition of 100 mmol H^+/kg soil initially reduced the pH of the soil to 1.8, which rebounded to 3.5 by Day 15, but was still about 4 pH units lower than the unacidified soil.

	Na2S2O8 Remaining, g/L Soln.			Na2S2O8 Consumed, g/kg Soil		
Time, Days	Low Dose	Medium Dose	High Dose	Low Dose	Medium Dose	High Dose
0	1.3	4.0	7.7	0	0	0
7	0.4	2.0	4.6	0.9	2.0	3.1
14	0.0	2.3	5.7	1.3	1.7	2.0
31	0.0	1.8			2.2	



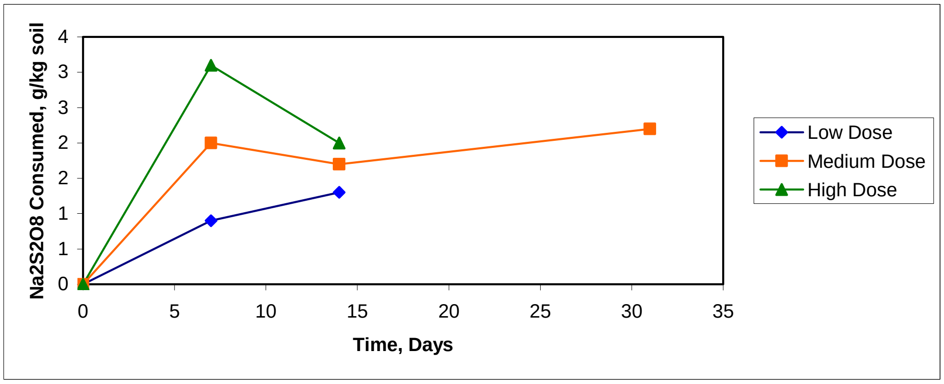


Figure 1. Persulfate Soil Oxidant Demand

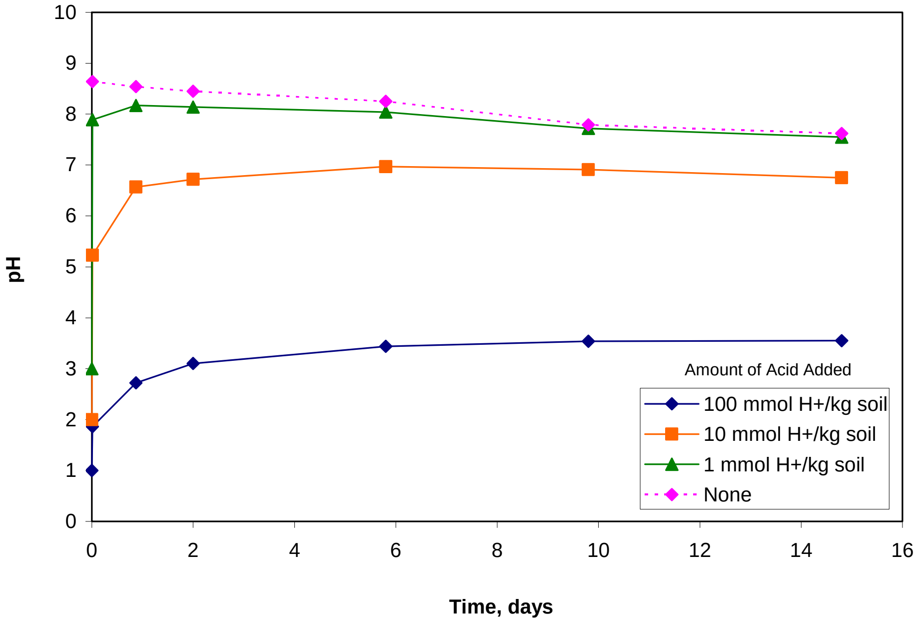


Figure 2. Soil Buffering Curves.

4.0 CONCLUSIONS

Treatment of site soil and groundwater with up to 6 g/L sodium persulfate activated with 500 mg/L of iron-EDTA (chelated iron) was ineffective at treating COCs at this site. Up to 2.5 g/L of $Na_2S_2O_8$ was present after 29 days, yet benzene was still present and concentrations of TPH-g and MTBE had only decreased marginally. The formation of TBA, acetone—potential intermediates of MTBE and TPH-g degradation—increased in the persulfate tests, implying that some oxidation was occurring. It is unknown whether improved removal could be achieved with a different activator, such as high pH.

Treatment with persulfate activated with iron-EDTA increased the concentration of several dissolved metals, including Cr(VI), copper and lead. These changes may or may not be activator-specific. Iron, pH, ORP, and sulfate changed as expected.

The soil oxidant demand for the composite soil was 1.7-3.1 g $Na_2S_2O_8$ /kg soil and was independent of the initial concentration of $Na_2S_2O_8$.

Site soil easily buffered 10 mmol H^+/kg soil.

APPENDIX B

Ozone Bench Study Example Scope of Work

August 9, 2006

Mark Naugle
Golder Associates
1009 Enterprise Way, Ste 350
Roseville, CA 95678

RE: Preliminary proposal for bench scale evaluation of ozone for destruction of petroleum hydrocarbons, Livermore site

Dear Mark:

Thank you for your interest in PRIMA Environmental's bench-scale testing services. Per your request, I am sending you a general Scope of Work to evaluate ozone for the destruction of petroleum hydrocarbons. This is a general scope and can be modified to fit the specific needs of your site. Costs assume that the chemicals of concern (COCs) are TPH-g, BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) and fuel oxygenates (MTBE, TBA, TAME, ETBE and DIPE).

BACKGROUND

Ozone gas is a strong oxidant that can destroy a wide range of organic compounds. Dissolved iron and other metal ions in soil and groundwater can increase the effectiveness of ozone by reacting with ozone to form hydroxyl radicals. The hydroxyl radical is an even stronger oxidant than ozone and may react more quickly and produce fewer intermediates than ozone itself. Equations 1-6 show the reactions for conversion of BTEX compounds and the fuel oxygenates to carbon dioxide (CO_2) and water (H_2O). The stoichiometric ozone requirements for the complete mineralization of each contaminant are given in Table 1. Chemical reactions cannot be written for TPH-g (and stoichiometric requirements cannot be pre-determined) because TPH-g is a complex mixture of chemicals. In practice, a greater-than-stoichiometric dose of O_3 will usually be required because O_3 is a non-selective oxidant that will react with natural organic matter and other non-target compounds, and because mass transfer of O_3 into the aqueous phase and/or COCs into the gas phase is inefficient.

$$15O_3 + \underset{\textit{benzene}}{C_6H_6} \rightarrow 6CO_2 + 15O_2 + 3H_2O \qquad \text{Eqn. 1}$$

$$18O_3 + \underset{\textit{toluene}}{C_7H_8} \rightarrow 7CO_2 + 18O_2 + 4H_2O \qquad \text{Eqn. 2}$$

$$21O_3 + \underset{\substack{\textit{ethylbenzene or}\\ \textit{xylene}}}{C_8H_{10}} \rightarrow 8CO_2 + 21O_2 + 5H_2O \qquad \text{Eqn. 3}$$

$$15O_3 + \underset{\textit{MTBE}}{C_5H_{12}O} \rightarrow 5CO_2 + 15O_2 + 6H_2O \qquad \text{Eqn. 4}$$

$$\underset{\text{TBA}}{12O_3 + C_4H_{10}O} \rightarrow 4CO_2 + 12O_2 + 5H_2O \qquad \text{Eqn. 5}$$

$$\underset{\text{ETBE/TAME/DIPE}}{18O_3 + C_6H_{14}O} \rightarrow 6CO_2 + 18O_2 + 7H_2O \qquad \text{Eqn. 6}$$

Table 1. Ozone Stoichiometry

Compound	g Ozone / g contaminant
Benzene	9.2
Toluene	9.5
Ethylbenzene	9.5
Xylenes	9.5
MTBE	8.2
TBA	8.5
ETBE	8.5
TAME	8.5
DIPE	8.5

Because ozone is a gas, *in situ* treatment of volatile compounds via injection of ozone into the sub-surface could result in removal of contaminants by stripping rather than oxidation. Lab testing will, therefore, address contaminant destruction versus volatilization.

As with all strong oxidants, ozone is a non-selective oxidizing agent and may react with soil and water constituents other than the target compounds. The most likely potential effects of ozone include oxidation and precipitation of dissolved iron, oxidation and dissolution of manganese oxides, oxidation of naturally-occurring bromide to bromate, oxidation of soil chromium to hexavalent chromium ([Cr(VI))] and oxidation of reduced nitrogen species to form nitrate. The magnitude of these changes is site specific and may or may not be of significance.

APPROACH

Batch tests will be conducted to evaluate each of the technologies. Specific goals are:

- Confirm COC removal for each ozone
- Evaluate the effect of treatment on secondary water quality parameters
- Measure soil oxidant demand for ozone
- If necessary, assess the potential for natural attenuation of Cr(VI)

Specific tests to achieve these goals are presented in the Scope of Work. PRIMA Environmental will evaluate the effectiveness of each oxidant based on the results of the bench tests and will present findings in a report to Golder. The report will include the results as well as any observations that PRIMA Environmental feels should be considered when evaluating field application of each technology. However, it is the responsibility of Golder to review the report and use its knowledge and expertise to determine which, if any, of the oxidants may be practically and cost-effectively applied at the site.

SCOPE OF WORK

Task 1. Soil and Groundwater Preparation and Characterization

Prior to testing, soil will be sieved to remove particles > 4 mesh, then homogenized. Groundwater will be used as received. Homogenized soil will be analyzed for

- TPH-g,
- BTEX,
- 5 oxygenates,
- acetone,
- Cr(VI), and
- metals (arsenic, chromium, iron, lead, molybdenum, selenium, uranium and vanadium).

Groundwater received in multiple containers will be composited prior ot testing. Composited groundwater will be analyzed for

- TPH-g,
- BTEX,
- 5 oxygenates,
- acetone,
- Cr(VI), and
- metals (arsenic, chromium, iron, lead, molybdenum, selenium, uranium and vanadium).
- oxidation reduction potential (ORP), and
- pH.

Task 2. Ozone Demand

The ozone demand of soil and groundwater will be estimated by adding a small amount of either material to ozone-saturated water, then measuring the concentration of ozone over time using the indigo method (SW 4500-O_3). A control in which no soil or groundwater is added will also be performed. Each test will be conducted in duplicate. The ozone demand is taken to be the difference in ozone consumption in the presence and absence of site material.

Task 3. COC Removal

To confirm that hydrocarbons are removed, determine the amount of removal due to destruction versus volatilization, and estimate the appropriate ozone dose, batch tests will be conducted. Five reactors containing site soil and groundwater will be prepared, then allowed to mix in a closed container for about 20 minutes. One of the reactors will then be destructively sampled and analyzed for GRO, BTEX, oxygenates, and acetone. This reactor is the “time 0” reactor. Two of the remaining reactors will be capped and mixed for the duration of the test. These reactors are the controls. The final two reactors will be sparged with ozone (~ 45 mg O3/L air) at a flowrate of 50 mL/min for up to 24 hours. Off-gases will be collected in Tedlar bags. Periodically, one control and one ozonated reactor will be destructively sampled and the off-gases and aqueous phases analyzed for GRO, BTEX, oxygenates and acetone. Soil will not be analyzed due to the difficulty of sampling soil without losing significant hydrocarbons to volatilization. The tests are summarized in Table 2.

Table 2. Tests to Evaluate Effect of Ozone on COC Removal

Test	# Replicates	Sparge Gas	Est. Sample Time
Time 0	1	None	0 hr
Control	2	None	4 hr, 24 hr
Ozone	2	Ozone	4 hr, 24 hr

Task 4. Secondary Effects

The effect of ozone on secondary water quality will be assessed by analyzing the aqueous phases of each test in Task 3 for the following parameters: bromide, bromate, Cr(VI), metals (arsenic, chromium, iron, lead, molybdenum, selenium, uranium and vanadium), ORP, and pH.

Task 5. Natural Attenuation of Cr(VI) or Bromate—*Optional*

If Cr(VI) or other parameters are formed during treatment with ozone, additional tests can be conducted to assess whether these parameters can naturally attenuate. Tests will simulate attenuation in the treatment zone as well as downgradient of the treatment zone. Cr(VI) will be measured colorimetrically by PRIMA Environmental using a Hach DR 2010 Spectrophotometer and appropriate test reagents.

The available Cr(VI) reducing capacity of soil, developed by Bartlett (Bartlett, R.J. **1991**. “Chromium Cycling in Soils and Water: Links, Gaps and Methods,” *Environmental Health Perspectives*, **92**, 17-24.), will be measured for treated soil and clean, untreated soil. This method is a first approximation of the amount of Cr(VI) that can be reduced under conditions somewhat similar to those in the sub-surface, but is probably high.

Tests will also be conducted to assess the ability of Cr(VI) and other parameters to naturally attenuate in the presence of soil and groundwater in the treatment zone and downgradient of the treatment zone. Two sets of tests will be conducted. The first set will comprise four replicates containing treated water and *untreated* site soil. The second set will consist of four replicates containing treated water and *treated* soil. Periodically, one replicate from each set will be sacrificed and the aqueous phase analyzed for appropriate parameters.

Task 6. Report Preparation

A report will be prepared that contains a complete description of the procedures used, observations, results, and evaluation of the data.

ANALYTICAL METHODS

The method for each analysis and the laboratory to perform the analysis are given in Table 3.

Table 3. Analytical Methods.

Analyte	Method	Lab performing test*
GRO, BTEX, MTBE, TBA, acetone	8015/8260B	Alpha Analytical
Metals (Cr, Fe, Mn)	ICP/MS	Alpha Analytical
Bromide and bromate	EPA 300	Columbia Analytical
Cr(VI)	7199 or Hach**	Excelchem/PRIMA
ORP	Probe	PRIMA
pH	Probe	PRIMA

* Alpha Analytical (Sparks, NV), CLS (Sacramento, CA), Columbia Analytical Serives (Kelso, WA), Excelchem (Roseville, CA),
** Hach DR 2010 Spectrophotometer and appropriate Hach kit reagents

SAMPLE REQUIREMENTS

- 8 x 1L of site groundwater, chilled, but otherwise unpreserved
- 2 kg of **IMPACTED** site soil (3-4 2” diameter by 6” cores or equivalent). If soil contains many large (> 1/4 ”) rocks, additional sample is needed since the large pieces will be removed prior to testing.
- 1 kg **CLEAN** site soil (1-2 2” diameter by 6” cores or equivalent)

SCHEDULE

It is anticipated that a draft report can be submitted within 45 days of receipt of samples and notice to proceed. Some Task 5 data may require additional time. This schedule should be confirmed with PRIMA Environmental 2 weeks prior to desired start date.

If you have any questions regarding this Scope of Work, please do not hesitate to call. I look forward to working with you on this project.

Sincerely,
PRIMA Environmental

Cindy G. Schreier, Ph.D.
Principal

APPENDIX C

Golder Associates Inc.

Standard Operating Procedures

Golder Associates

GROUNDWATER MONITORING PROCEDURES

The methods and procedures used by Golder Associates Inc. (Golder) for groundwater sampling are described below. These procedures for groundwater sampling are designed to provide consistent and reproducible results and ensure that the overall objectives of the monitoring program are achieved.

The following documents have been used as guidelines for the development of these procedures:

- *Leaking Underground Fuel Tank Field Manual*, State of California Leaking Underground Fuel Tank Task Force (revised 1989, as updated by memoranda)
- *Procedures Manual for Groundwater Monitoring at Solid Waste Disposal Facilities* (EPA-530/SW-611, August 1977)
- *RCRA Groundwater Monitoring Technical Enforcement Guidance Document* (OSWER 9950.1, September 1986)
- *Standard Guide for Sampling Groundwater Monitoring Wells* (ASTM, D 4448-85a)
- *Standard Practice for Decontamination of Field Equipment Used at Non-radioactive Waste Sites* (ASTM, D 5088-90)
- *Standard Test Method for Determining Subsurface Liquid Levels in a Borehole or Monitoring Well (Observation Well)* (ASTM, D 4750-87)
- *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods* (EPA SW-846, Base Manual [3rd edition, November 1986], through Update III [June 1997])

GROUNDWATER ELEVATION, FLOATING PRODUCT, AND TOTAL DEPTH SURVEY

Before the sampling event, the static water level is measured in appropriate monitoring wells and piezometers. The monitoring wells are purged and sampled for chemical constituents after measuring water levels.

The water level in the wells and piezometers is measured with an electric sounder with cable markings stamped at 0.01-foot increments. The water level is measured by lowering the sensor into the monitoring well. A low current circuit is completed when the sensor contacts the water, which serves as an electrolyte. The current is amplified which activates an indicator light and audible buzzer, thus signaling when water has been contacted. A sensitivity control compensates for very saline or conductive water. The electric sounder is decontaminated by rinsing with a detergent solution then deionized water after each use. Depth to water is recorded to the nearest 0.01 foot on a water level data sheet. The groundwater elevation at the monitoring well is calculated by subtracting the measured depth to water from the surveyed elevation of the top of the well casing.

The level and thickness of floating hydrocarbon product in a well is measured using an interface meter and/or a clear bailer. The interface meter works on a principal similar to the electric sounder, measuring both conductive and non-conductive liquid within the well. Floating product can also be measured using a clear, bottom-filling bailer. The bailer is lowered slowly into the well until the bailer is approximately half submerged. The bailer is then retrieved from the well and the thickness of floating product in the bailer is measured. The thickness of floating product is recorded to the nearest 0.01 foot on the water level data sheet.

Total well depth is measured in monitoring wells scheduled for sampling by lowering a probe to the bottom of the well and recording the depth. Total well depth, used to calculate purge volumes and to determine whether the well screen is partially obstructed by silt, is typically recorded to the nearest 0.1 foot on the water level data sheet.

SAMPLE COLLECTION

Sample collection procedures include equipment cleaning, well purging, and sampling.

Equipment Cleaning

Before the sampling event, all equipment that is placed in the well or comes in contact with groundwater is disassembled and cleaned thoroughly with detergent water, and then steam cleaned or rinsed with deionized water. Any parts that may absorb contaminants, such as plastic pump valves, bladders, etc., are cleaned or replaced.

For electric submersible pumps used for purging wells, all external pump surfaces and the discharge tube are steam cleaned prior to lowering the pump into the well casing. An aqueous solution of Liquinox (phosphate-free detergent), followed by deionized water, is then run through the pump and discharge tubing to clean internal surfaces. Water is prevented from draining back though the pump by an in-line check valve located immediately above the pump.

Well Purging

Before sampling, standing water in the casing and sand pack is purged from the monitoring well using either a positive displacement polyvinyl chloride (PVC) hand pump, a portable or dedicated electric submersible pump, a PVC or polyethylene bailer, a centrifugal pump, a dedicated pneumatic bladder pump, or a peristaltic pump. Field measurements for pH, specific conductance, turbidity, and temperature are recorded on water sample field data sheets at casing volume intervals during purging. The field measurements are used as indicator parameters to determine when a representative sample can be taken. Purging is generally performed until stabilization (± 10 percent variation) of the indicator parameters takes place. The amount of water purged before sampling is greater than or equal to three casing volumes, unless a well dries. If a well dries during purging, it will be allowed to recharge for up to 24 hours; samples will be collected as soon as sufficient volume is available. If a well does not recharge sufficiently within 24 hours, the well will be considered dry for that sampling event.

Well Sampling

Groundwater samples are collected using a Teflon bailer, an individually sealed disposable polyethylene bailer, a dedicated electric submersible or pneumatic bladder pump, or in-line through a peristaltic pump with clean tubing. Wells are sampled in progression from less impacted to more impacted. The purpose of this procedure is to reduce the potential for cross contamination of wells by purging or sampling equipment.

Clean glass bottles of at least 40 milliliters volume fitted with Teflon-lined septa are used to collect samples for volatile organic analyses. These bottles are completely filled to prevent air from remaining in the bottle. A positive meniscus forms when the bottle is completely full. A convex Teflon®-lined septum is placed over the positive meniscus to eliminate air. After capping, the bottles are inverted and tapped to verify that they do not contain air bubbles. The sample containers for other parameters are filled, filtered as required, and capped.

To determine dissolved concentrations of metals, appropriate field filtration techniques are used. When using a bailer for sampling, a transfer vessel is filled with sample and fitted with a disposable 0.45-micron acrylic copolymer filter. Air pressure is applied to the transfer vessel forcing the sample through the filter; the filtrate is then directed into the appropriate containers. If a pump is used for sampling, the filter is placed in-line at the end of the discharge tubing and the filtrate directed into the appropriate containers. Each filter is used once and discarded.

SAMPLE PRESERVATION AND HANDLING

The following section specifies sample containers, preservation methods, and sample handling procedures.

Sample Containers and Preservation

Sample containers and preservatives vary with each type of analytical parameter. Container types and materials are selected to be non-reactive with the particular analytical parameter tested. Sample preservatives used are consistent with regulatory guidelines and specified analytical methods.

Sample Handling

All sample containers are labeled immediately following collection. Samples are kept cool with ice until received by the laboratory. At the time of sampling, each sample is logged on a chain-of-custody record, which accompanies the samples to the laboratory. Water samples are transported from the site by the sampler.

Upon receipt of the samples by laboratory personnel, the chain-of-custody record is signed and released, and a unique sample identification number is assigned to each sample container. This number is recorded on the chain-of-custody record and is used to identify the sample in all subsequent internal chain-of-custody and analytical records. The manager of the subcontracted laboratory ensures that the holding times for requested analyses are not exceeded.

SAMPLE DOCUMENTATION

The following procedures are used during sampling and analysis to provide chain-of-custody control during sample handling from collection through storage. Sample documentation includes the use of the following:

- Water sample field data sheets to document sampling activities in the field
- Labels to identify individual samples
- Chain-of-custody record sheets for documenting possession and transfer of samples

Water Sample Field Data Sheets

In the field, the sampler records the following information on a water sample field data sheet:

- Location
- Project number
- Client name
- Sample ID
- Name of sampler
- Regulatory agency
- Date and time
- Pertinent well data (e.g., casing diameter, depth to water, well depth)
- Calculated and actual purge volumes
- Purging equipment used
- Sampling equipment used
- Appearance of sample (e.g., color, turbidity, sediment)
- Results of field analyses (e.g., temperature, pH, specific conductance)
- Purge water containment

- General remarks, including well accessibility and integrity

The sampler signs the field data sheets.

Labels

Sample labels contain the following information:

- Project number
- Sample ID (e.g., well designation)
- Sampler's initials
- Date and time of collection
- Type of preservative used

Sampling and Analysis Chain-of-Custody Record

The sampling and analysis chain-of-custody record, initiated at the time of sampling, contains, but is not limited to, the well number, sample type, analytical request, date of sampling, and the name of the sampler. The record sheet is signed and dated by the sampler when transferring the samples. Custody transfers are recorded for each individual sample. The number of custodians in the chain of possession is kept to a minimum. A copy of the sampling and analysis chain-of-custody record is returned to Golder for inclusion with analytical results.

FIELD QUALITY ASSURANCE PROCEDURES

Field quality assurance procedures are specified for each sampling event. Field quality assurance typically includes documenting field instrument calibration, and collecting and analyzing trip blanks, field blanks, equipment blanks, and duplicate samples.

The analysis of trip, field, and equipment blanks, prepared with organic-free water, are used to detect contamination introduced through sampling procedures, external field conditions, sample transportation, container preparation, sample storage, and the analytical process.

Trip blanks are prepared at the same time and location as the sample containers for a particular sampling event. Trip blanks accompany the containers to and from that event, but at no time are they opened or exposed to the atmosphere. Typically, one trip blank for volatile organic parameters will be included per sampling event.

Field blanks are prepared in the field so they are exposed to the ambient atmosphere at a specified monitoring point during sample collection to determine the influence of the external field conditions on sample integrity. Equipment blanks are prepared in the field to ensure that sampling equipment does not cross-contaminate water samples. Organic-free water is run through the properly cleaned or unused (if disposable) sampling equipment, collected and analyzed. One field blank or equipment blank for volatile organic parameters will typically be included per sampling event.

Duplicate samples are collected to assess sampling and analytical precision. For each sampling event including more than six wells, duplicate monitoring well samples will typically be collected at a frequency of 10 percent. Where possible, field duplicates are collected at sampling points known or suspected to contain chemical constituents of interest. Duplicates are packed and shipped blind to the laboratory for analysis with the samples from that particular event.

LOW-FLOW GROUNDWATER MONITORING PROCEDURES

The methods and procedures used by Golder Associates Inc. (Golder) for low-flow groundwater monitoring are described below. These procedures are designed to provide consistent and reproducible results and ensure that the overall objectives of the sampling program are achieved.

Monitoring well purging and sampling using low-flow procedures are intended to minimize potential bias in the analytical results. The U.S. Environmental Protection Agency (U.S. EPA) recognizes that mobile, suspended particles (colloids) may constitute an additional matrix capable of contaminant transport. Low-flow sampling procedures are intended to obtain representative samples of total contaminant loading in dissolved (groundwater) and naturally suspended (colloidal) matrices. High-flow procedures involving high-flow pumps or bailers can increase turbidity by mobilizing immobile particles, possibly resulting in biased results (i.e., higher concentrations). Filtration of samples collected using high-flow techniques removes particulates, including colloids, which also introduces bias (i.e., lower concentrations).

Low-flow groundwater sampling involves removal of water from the geologic formation immediately surrounding the screened interval of a monitoring well at velocities sufficiently low to minimize drawdown in the well. Minimizing drawdown minimizes mixing between the overlying stagnant casing water and water within the screened interval, which is more likely to be representative of formation water.

The Golder procedure for low-flow groundwater sampling is based on the following U.S. EPA technical publications from the Office of Solid Waste and Emergency Response.

- *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures* (EPA-540/S-95/504, April 1996)

- *Standard Practice for Decontamination of Field Equipment Used at Non-radioactive Waste Sites* (ASTM, D 5088-90)

- *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods* (EPA SW-846, 3rd edition, November 1986)

GROUNDWATER ELEVATION, FLOATING PRODUCT, AND TOTAL DEPTH SURVEY

If a groundwater elevation and floating product survey are to be conducted, they are to be completed prior to the sampling event. Static water level is measured in specified monitoring wells and piezometers. The monitoring wells are purged and sampled for chemical constituents after measuring water levels, in accordance with this procedure.

The water level in the wells and piezometers is measured with an electric sounder with cable markings stamped at 0.01-foot increments. The water level is measured by lowering the sensor into the monitoring well. A low current circuit is completed when the sensor contacts the water, which serves as an electrolyte. The current is amplified which activates an indicator light and audible buzzer, thus signaling when water has been contacted. A sensitivity control compensates for very saline or conductive water. The sensor is not to be lowered below the water surface more than is necessary to obtain a reading; water level measurements should minimize disturbance and mixing of casing water.

The electric sounder is decontaminated by rinsing with a detergent solution then distilled water after each use. Depth to water is recorded to the nearest 0.01 foot on a water sample field data sheet (field data sheet). The groundwater elevation at the monitoring well is calculated by subtracting the measured depth to water from the surveyed elevation of the top of the well casing.

The level and thickness of floating hydrocarbon product in a well is to be measured with an interface meter to avoid unnecessary agitation of the product/water interface. The interface meter works on a principal similar to the electric sounder, measuring both conductive and non-conductive liquid within the well. Floating product should not be measured using a bailer. The thickness of floating product is to be recorded to the nearest 0.01 foot on the field data sheet.

Well total depth is obtained after low-flow purging and sampling to minimize the disturbance of particulates within the well. Depths are to be measured and recorded to the nearest 0.1 foot.

SAMPLE COLLECTION

Sample collection procedures include equipment cleaning, well purging, and sampling.

Equipment Cleaning

Before the sampling event, all re-usable equipment that is placed in the well or comes in contact with groundwater is disassembled and cleaned thoroughly with detergent water, and then steam cleaned or rinsed with distilled water. Any parts that may absorb contaminants, such as plastic pump valves, bladders, etc., are cleaned or replaced.

Any disposable tubing used is to be tested for cleanliness before its use in the field.

For submersible pumps, all external pump surfaces and the discharge tube are steam cleaned prior to lowering the pump into the well casing. An aqueous solution of Liquinox (phosphate-free detergent) is run through the pump and discharge tubing, followed by distilled water, to clean the internal surfaces of the pump and discharge tubing. Water is prevented from draining though the pump by an in-line check valve located immediately above the pump.

Well Purging

Before sampling, low-flow purging shall be conducted to ensure the presence of formation water within the screened interval of the monitoring well. Purging is to be performed using peristaltic, bladder, or electric submersible pumps. Bailers are not to be used. Pumps may be either dedicated or portable (dedicated is recommended). Pumps shall be capable of consistent flow rates less than 0.5 liters per minute (lpm), and pumps shall be capable of consistent operation across low-flow pumping rates (i.e., between 0.1 and 0.5 lpm). If non-dedicated submersible pumps are to be used, they must be lowered slowly and carefully into place to minimize the mixing of stagnant water into the sampling zone and the re-suspension of particulates. The water column must then be allowed to re-equilibrate for at least two hours before purging to minimize the effects of placing the pump. If low permeability formations are to be sampled (< 0.1 lpm recharge) non-dedicated pumps must be set in place for 48 hours. Use of a peristaltic pump should be limited to shallow applications (less than 15 feet recommended, 25 feet maximum) because it may cause degassing, resulting in an alteration of pH and alkalinity, as well as some loss of volatiles.

The pump intake for low-flow purging must be set at a project-specific depth located above the bottom and below the top of the screened interval for the well. Placement of the intake too near the bottom of the well could result in entrainment of solids that have accumulated in the well. Placement of the pump intake too near the top of the screened interval could result in the collection of stagnant casing water. The pump intake location must be recorded for each well.

Purging a well using low-flow methods when floating product is present requires additional preparation of equipment. An ice coating and plug must be formed on the purging and sampling equipment that is to be inserted below the floating product layer using water and dry ice. The coating should cover the lower 0.2 meters (0.67 feet) of the equipment to be inserted (the length equal to or greater than 2 times the maximum allowable drawdown). After the equipment is emplaced, the ice coating is allowed to melt allowing product that may be coating the equipment to slough off.

During purging, flow rates are to be set according to the following requirements:

- Flow rates are to be selected such that drawdown in the well is minimized (i.e., observed drawdown is less than 0.1 meter [0.33 feet]).
- Initial flow rates during purging shall be no more than 0.5 lpm, and
- Flow rate shall be adjusted downward as required to minimize drawdown.

Monitoring of water quality parameters using a flow-through cell is to be used to determine when formation water has been drawn into the screened interval. Stabilization of water quality parameters is indicative of the presence of formation water. Field measurements for pH, specific conductance, dissolved oxygen (DO), oxidation-reduction potential (ORP), temperature, and turbidity are to be recorded during purging on field data sheets. In general, the order of stabilization is pH, temperature, and specific conductance, followed by ORP, DO, and turbidity. Temperature and pH are generally insensitive in distinguishing between formation water and stagnant casing water. Turbidity is a conservative parameter for assessing stabilization, and is usually the last parameter to stabilize.

In-line measurements of water quality parameters are to be taken every three to five minutes. Stabilization should be considered complete when readings for all parameters have stabilized after three successive readings. The three successive readings should be within the following limits:

- ± 0.1 for pH
- ± 3% for temperature and conductivity
- ±10 millivolts (mV) for ORP
- ± 10% for turbidity and DO. As noted, DO and turbidity require the longest time for stabilization.

Well Sampling

Low-flow groundwater sampling involves the same general operations that are used in standard groundwater sampling procedures, although there is no change of equipment between purging and sampling. The sample flow rate may remain at the established purge flow rate or lowered as needed to minimize aeration, bubble formation, or turbulent filling of sample containers.

Groundwater samples are to be collected in-line from the sampling pump from a point prior to the flow-through cell used to measure water quality parameters. Tubing shall be clean, and the length of tubing shall be minimized between the intake point and the sample container.

When non-dedicated pumps are used, wells are purged and sampled in progression from "clean wells" to wells yielding poorer-quality water. The purpose of this sampling sequence is to reduce the potential for cross contamination of wells by purging or sampling equipment.

In addition, gloves are to be changed between wells.

Sample bottles for VOC analyses are completely filled to prevent air from remaining in the bottle. A positive meniscus forms when the bottle is completely full. A convex Teflon septum cap is placed over the positive meniscus to eliminate air. After capping, the bottles are inverted and tapped to verify that they do not contain air bubbles.

The sample containers for other parameters are filled, filtered as required, and capped.

To sample for dissolved concentrations of metals, appropriate field filtration techniques are used. Filtration of samples is to be conducted only as part of the analytical program and not to reduce turbidity resulting from unacceptably high flow rates encountered during sampling. Should filtration be required, in-line filtration using a disposable 0.45-micron filter is used, unless otherwise specified. Each filter is to be used once and discarded. Any in-line device used during purging to measure water quality parameters (e.g., flow through cell) is to be bypassed or disconnected during sample collection.

SAMPLE PRESERVATION AND HANDLING

The following section specifies sample containers, preservation methods, and sample handling procedures.

Sample Containers and Preservation

Sample containers and preservatives vary with each type of analytical parameter. Container types and materials are selected to be nonreactive with the particular analytical parameter tested. Sample preservatives used are consistent with regulatory guidelines and specified analytical methods. Only clean, batch-tested containers are used.

Sample Handling

All sample containers are labeled immediately following collection. Samples are to be kept cool (approximately 4^{o}C) using blue ice and a cooler until received by the laboratory. At the time of sampling, each sample is logged on a chain-of-custody record that accompanies the samples to the laboratory. Water samples are transported from the site by the sampler.

Upon receipt of the samples by laboratory personnel, the chain-of-custody record is signed and released, and a unique sample identification number is assigned to each sample container. This number is recorded on the chain-of-custody record and is used to identify the sample in all subsequent internal chain-of-custody and analytical records. The subcontracted laboratory's manager ensures that the holding times for requested analyses are not exceeded.

SAMPLE DOCUMENTATION

The following procedures are used during sampling and analysis to provide chain-of-custody control during sample handling from collection through storage. Sample documentation includes the use of the following:

- Water sample field data sheets to document sampling activities in the field
- Labels to identify individual samples
- Chain-of-custody record sheets for documenting possession and transfer of samples

Water Sample Field Data Sheets

In the field, the sampler records the following information on a water sample field data sheet (attached):

- Location
- Project number
- Client name
- Sample ID
- Name of sampler
- Regulatory agency
- Sample Type
- Pertinent well data (e.g., casing diameter, depth to water, well depth)
- Purging/sampling equipment used and depth of intake from top of casing
- Purge water containment method
- QC samples
- Results of field analyses (pump rate, drawdown, temperature, pH, specific conductance, dissolved oxygen, turbidity, oxidation-reduction potential, and color/odor)
- Field devices
- General remarks, including well accessibility and integrity

The field data sheets are signed and dated by the sampler.

Labels

Sample labels contain the following information:

- Project number
- Sample ID (i.e., well designation)
- Sampler's initials
- Date and time of collection
- Type of preservative used

Sampling and Analysis Chain-of-Custody Record

The sampling and analysis chain-of-custody (COC) record, initiated at the time of sampling, contains, but is not limited to, the well number, sample type, number of bottles, analytical request, date of sampling, and the name of the sampler. The record sheet is signed and dated by the sampler when transferring the samples. Custody transfers are recorded for each individual sample. The number of custodians in the chain of possession is kept to a minimum. A copy of the completed COC is returned to Golder for inclusion with analytical results.

FIELD QUALITY ASSURANCE PROCEDURES

Field quality assurance procedures are included in each monitoring event. Field quality assurance typically includes documenting field instrument calibration, and collecting and analyzing trip blanks, field blanks, equipment blanks, and duplicate samples.

Trip, field, and equipment blanks, prepared with organic-free water, are used during the sampling events to detect contamination introduced through sampling procedures, external field conditions, sample transportation, container preparation, sample storage, and the analytical process.

Trip blanks are prepared at the same time and location as the sample containers for a particular sampling event. Trip blanks accompany the containers to and from that event, but at no time are they opened or exposed to the atmosphere. Field blanks are prepared in the field so they are exposed to the ambient atmosphere at a specified monitoring point during sample collection to determine the influence of the external field conditions on sample integrity. Typically, one trip blank or field blank for volatile organic parameters will be included per sampling event.

Equipment blanks are prepared in the field to ensure that non-dedicated sampling equipment does not cross-contaminate water samples. Organic-free water is run through sampling equipment after any necessary cleaning, before use. One equipment blank for each analytical parameter will typically be included per sampling event.

Duplicate samples are collected to assess sampling and analytical precision. For each sampling event including more than six wells, duplicate monitoring well samples will typically be collected at a frequency of 10%. Where possible, field duplicates are collected at sampling points known or suspected to contain chemical constituents of interest. Duplicates are packed and shipped to the laboratory for analysis with the samples from that particular event.