

CLEARWATER

GROUP, INC.

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Environmental Services

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FAX #: 3379335
FROM: HEIDI BAUER

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CLEARWATER
GROUP, INC.
Environmental Services

May 24, 1999


Ms. Madulla Logan
Alameda County DHS
1131 Harbor Bay Parkway
Alameda, CA 94502

Re: Former E-Z Serve Station No. 100877 - Hayward
Addendum to January 29, 1999 Workplan for Additional Site Assessment

Dear Ms. Logan,

This addendum is written in accordance with our conversation regarding the additional work you requested be added to Clearwater's *Workplan for Additional Site Assessment* dated January 29, 1999. In addition to the site assessment work specified in the workplan Clearwater will provide a revised Risk Assessment which will elaborate on the one already submitted by Brown and Caldwell dated May 9, 1995. The revised Risk Assessment will include a determination of risk from exposure pathways from the hydrocarbon impacted soil and groundwater to indoor structures located above the impacted areas using a vapor migration model. Also included in the study will be a determination of clean-up levels for soil and groundwater at this site and a comparative analysis to current soil and groundwater quality conditions. The risk assessment study will be performed in accordance with ASTM RBCA guidelines. If you have any questions or comments regarding our proposed scope, or if I may be of any additional assistance, please do not hesitate to call.

Sincerely,
Clearwater Group, Inc.


Heidi M. Bauer
Project Geologist



FILE COPY

**WORKPLAN FOR
ADDITIONAL SITE ASSESSMENT**

**Former EZ Serve Site #100877
525 West A Street
Hayward, California**

Prepared for:
Restructure Petroleum Marketing Services, Inc.
205 South Hoover Boulevard
Suite 101
Tampa, Florida 33609

Prepared by:
Clearwater Group, Inc.
520 Third Street, Suite 104
Oakland, California 94607
Clearwater Job No. EZ100877

January 29, 1999



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Figure 1: Site Location Map

Figure 2: Site Plan

Figure 3A: Proposed Soil Boring Location Plan (pg 1 of 2)

Figure 3B: Proposed Soil Boring Location Plan (pg 2 of 2)

APPENDICES

Appendix A - Clearwater Drilling, Well Installation and Development and Groundwater Sampling Field Procedures.



1.0 INTRODUCTION

Clearwater Group, Inc. (Clearwater) has prepared this report on behalf of Restructure Petroleum Marketing Company, Inc. (RPMS) to provide a detailed description of proposed additional site assessment work for the Former EZ Serve Site #100877, located in Hayward, California. The primary purpose of the additional site assessment work is to delineate the extent of petroleum hydrocarbon impacted soil and groundwater at the subject site and determine current soil and groundwater conditions surrounding the former source area.

2.0 BACKGROUND

2.1 Site Description

The site is located at 525 West A Street in Hayward, California. It is situated on the northwest corner of West A Street and Garden Avenue in the City of Hayward, County of Alameda, State of California's Township 3 South Range, Range 2 West, Mount Diablo Base and Meridian (Figure 1). The Assessor's Parcel Number (APN) for the site is 432-0016-026-03. The site is not in use currently, and is secured by a chained link fence and a locked gate. The site was previously occupied by a gasoline service station. Remaining on the site is only the former dispenser island canopy and some lighting fixtures.

2.2 Project History

The site operated as a service station from 1966 until 1990. While operating the site contained one 10,000-gallon diesel and three 10,000-gallon gasoline underground storage tanks (USTs). In November 1986 results of tank tightness tests and discrepancies in inventory records resulted in the investigation of soil and groundwater beneath the site.

In December 1986, Converse conducted an initial Phase II Site Assessment which included the drilling of three soil borings (B-1 through B-3), which were subsequently converted into groundwater monitoring wells (MW-1 through MW-3). Results from soil and groundwater sampling from this investigation confirmed the presence of petroleum related hydrocarbons in the soil and groundwater. In June 1987, Converse implemented the second phase of the Phase II site assessment. This included the drilling and installation of three additional groundwater monitoring wells (MW-4 through MW-6). Wells MW-1 through MW-6 were constructed to depths of approximately 30 feet below ground surface (bgs). Results of this phase of work indicated that petroleum related hydrocarbons had impacted the soil and groundwater beneath the site to the property boundary.

In June 1990, the USTs, dispenser islands, and associated piping were removed from the site. During this phase of work monitoring wells MW-3, MW-5 and MW-6 were destroyed and MW-1, MW-2 and MW-4 were damaged.

After a round of project bidding and contractor selection, Associated Soils Analysis (ASA) replaced Converse as the project contractor. As documented in their March 2, 1992 report, ASA abandoned two of the original Converse wells (MW-2 and MW-4) that had been damaged following the UST removal project, repaired a third (MW-1), and constructed four new monitoring wells on the subject property. Groundwater was encountered at approximately 21 feet below grade; the wells were finished at 30 feet. Significant soil and groundwater contamination was encountered in most areas explored, thereby not defining the lateral extent of impact by petroleum related hydrocarbons to the soil and groundwater. A quarterly groundwater program was initiated.

In order to satisfy agency requirements for additional plume delineation, a workplan for further assessment was prepared by E-Z Serve staff on September 21, 1992. Proposals for the implementation of the contemplated work were solicited, and as a result of the competitive bidding process, ASA was again selected to continue the subsurface assessment. The next phase of work completed by ASA included extensive off-site permitting, drilling and sampling four borings to 30 feet, and the construction of four additional monitoring wells (MW-7 through MW-10) in these borings. The results of this effort were documented in the ASA report dated July 20, 1993, and concluded in the report that the lateral extent of the petroleum hydrocarbons affected groundwater still remained undefined.

The Alameda County DEH responded to ASA's July 1993 report and requested that E-Z Serve continue efforts to determine the extent of the impacted area and begin to contemplate measures for interim remedial action. In response to County directives E-Z Serve retained Hydro-Environmental Technologies, Inc. (HETI), who prepared technical submittals to address the County requests. As one of their first tasks, HETI prepared a workplan describing measures necessary for the implementation of feasibility testing for the evaluation of the most appropriate interim remedial measure. The workplan was approved by Alameda County and results of testing were reported by HETI in a submittal dated March 1, 1994. In an effort to satisfy the Alameda County request to define the lateral and downgradient extent of contamination HETI prepared a workplan for additional investigative activities. File material indicates that the recommended assessment and

mitigative activity proposed by HETI were not implemented by E-Z Serve. File correspondence shows a request by the RWQCB to attend to the County concerns, and on September 29, 1994 a technical proposal to satisfy the stated County objectives was submitted by (B&C). The B&C letter report outlined a series of subsurface tests that were similar to those previously proposed by HETI.

Results of B & C discrete sampling and monitoring well installation program were reported in a series of letter reports submitted in early to mid-1995. Four additional off-site monitoring wells (MW-11 through MW-14) were installed by B&C in February 1995 to further define the lateral extent of impacted groundwater. A comprehensive report was transmitted to the County in March, 1995. The conclusions and recommendations in this report indicated that the level of risk posed to the residents of the area impacted by the subgrade contamination had not yet been evaluated, and that with the County's permission, a comprehensive risk assessment would be completed. The report indicated that a workplan for the completion of this risk assessment would be completed and provided to the County, and that upon receipt of their approval the assessment would proceed.

The *Risk Assessment* was prepared by B&C and submitted to the County on May 9, 1995. In a letter dated May 23, 1995, apparently responding to a verbal request for progress clarification by the County, B&C staff indicated that the preparation of a Corrective Action Plan (CAP) would commence following review and revision of the submitted risk assessment by the County, as a thorough CAP would not be possible without established remedial endpoints. The County requested clarification to the Risk Assessment in a letter dated August 3, 1995. B&C staff responded to the County queries in a letter dated September 12, 1995.

2.3 Analysis Of Investigative Activities To Date

Groundwater sampling to date has shown the continued presence of hydrocarbon contaminants in groundwater extending radially from the former tank excavation. Groundwater monitoring data evidences that contaminant concentrations have stabilized (neither significantly increasing nor decreasing), suggesting the presence of a continued source for longer term, though non-migrating, groundwater contamination. This source area may be in soil that is present beneath the former USTs, or it may be associated with historic releases from dispensers and piping.

Results of recent sampling events (June 1998) indicate concentrations of total petroleum hydrocarbons as gasoline (TPGgas) ranging from not detected (<50ug/l) in MW-14 to 33,000 ug/l



in MW-2 and MW-4. Results from the same sampling event show benzene concentrations ranging from not detected (<0.5ug/l) in MW-14 to 6,100 ug/l in MW-1. The fuel oxygenate, MTBE, was also detected in eight of the nine well sampled with concentrations not exceeding 720 ug/l.

2.4 Geology And Hydrogeology

According to B&C in their May, 1995 *Risk Assessment* the site lies within the San Leandro cone, a low gradient alluvial fan which originates at the mouth of Castro Valley and spreads westward onto the Bay Plain. This cone consists of alluvial sediments which overlie marine clay, terrigenous sand and silt of intertidal provenance's. The sediments directly under the site consist primarily of silty- and clayey-sands with occasional sandy-silt or sandy-clay layers. Groundwater is generally encountered between 13 and 17 feet bgs.

Also according to B&C in their May 1995 *Risk Assessment* for the subject site the shallowest regional aquifer in the area is the Newark Aquifer. The Newark is a permeable, water-bearing alluvial sand aquifer, which is composed of a series of laterally discontinuous saturated lenses of course to fine sediments 10 to 100 feet thick at depths less than 200 feet bgs. The regional hydraulic gradient is westward, from the mouth of the Castro Valley towards the San Francisco Bay. Groundwater directly under the site flows towards the west under an average hydraulic gradient of 0.005 feet per foot. The nearest point of release for the shallow aquifer to the surface water in the westerly direction is the San Francisco Bay, which is located approximately three miles from the subject site.

3.0 COUNTY REQUEST FOR ADDITIONAL ASSESSMENT

A meeting between the County and Clearwater took place in September, 1998 to discuss future requirements for additional site work and potential remedial alternatives for this site. During the meeting and review of historical data it became apparent that several areas on-site and off-site showed significant voids in soil and groundwater quality data. It was agreed upon by the County and Clearwater that data in these areas are needed for the determination of future remedial alternatives and the most appropriate locations for additional groundwater monitoring wells.



During the meeting the County specifically requested a well to be located in the area between MW-11 and MW-9, because the quality of the subsurface is not well established between MW-9 and MW-11, which lie approximately 660 feet apart.

It was also proposed during the meeting between Clearwater and the County that limited removal of source area soil would be a useful remedial measure in mitigating the extent of contamination at the site. However, a review of the soil and groundwater quality data at the site indicate that the area surrounding the former UST source is not well established. The assessment of the soil and groundwater quality in this area would be used to evaluate the feasibility of performing source removal at this site. The installation of discrete sampling points surrounding the source area would therefore yield invaluable information regarding the current soil and groundwater conditions in this immediate area.

During a subsequent conversation with the County, it was decided that additional investigation in the down gradient direction, west of MW-11 and the former UST source, is warranted. Historical data indicates that the down gradient extent of petroleum related hydrocarbon contamination remains undefined west of MW-11 and west of the former UST source. Therefore, it was agreed upon by the County and Clearwater that the soil and groundwater quality would be tested in these areas, in addition to those mentioned above.

4.0 OBJECTIVES OF RECOMMENDED ADDITIONAL ASSESSMENT

The objectives of this phase of proposed site assessment are primarily associated with the collection of data required to complete the subsurface investigation. A secondary objective is the evaluation of subsurface characterization relative to natural attenuation processes, one of the several remedial alternatives to be considered for future mitigative actions. The recommended tasks to be employed are as follows:

- Assessment of current soil and groundwater quality conditions surrounding source area using discrete sampling (Geoprobe®) methods.
- Evaluation of the lateral extent of soil and groundwater contamination using discrete sampling (Geoprobe®) methods.



- As per the County's request, install an additional monitoring well between MW-9 and MW-11 to provide a sampling point for the longer term monitoring of groundwater quality in this area. The exact location of the well will be determined based on the results from the installation of the discrete sampling points mentioned above.
- Recent field activity indicate that MW-11 has been paved over or destroyed. To remedy this a magnetometer will be used to locate this well during the next phase of field work. If MW-11 can not be relocated a replacement well will be installed.
- Install one permanent monitoring well on West A street, downgradient of MW-11. This will be done to obtain soil and groundwater quality data in the downgradient direction, as MW-11 has shown historically elevated levels of contaminants. The exact location of the well will be determined based on the results from the installation of the discrete sampling points mentioned above.
- Conduct one round of groundwater sampling in all wells, including the newly installed wells. The groundwater will also be tested for natural attenuation parameters and a remediation by natural attenuation (RNA) assessment conducted. If results from the RNA assessment indicate conditions receptive to natural attenuation, then the feasibility of using an oxygen releasing compound (ORC) to stimulate or accelerate bioremediation processes will be explored.

5.0 SCOPE OF RECOMMENDED ADDITIONAL ASSESSMENT

5.1 Discrete Soil and Groundwater Sampling

Based on project information collected to date, the initial installation of temporary discrete sampling points is the most appropriate and cost effective way to achieve the above stated goals. Discrete sampling should be completed as an initial screening measure in areas not previously explored, with the results of this initial screening used to establish the most appropriate location for the installation of the additional wells, or to establish current soil and groundwater conditions. Installation of the additional well without the intermediate screening step will likely guarantee future well installations, or the installation of a greater number of wells than necessary, as the locations for these wells will be selected "blind".



To accomplish the goal specified above Clearwater proposes that 12-14 discrete sampling borings be introduced in the areas shown on Figure 3A and 3B. Soil samples shall be collected from all of the borings at five foot intervals to their completed depth of approximately 15 feet below ground surface (bgs). Soil borings shall be advanced by the Geoprobe® direct push technique. The borings shall be grouted to grade with a Portland cement/bentonite slurry following completion.

Soil samples will be selected for lab analysis based on their proximity to significant changes in sedimentologic characteristics as determined in the field (i. e. presence of relatively impermeable layers, zones of significant porosity, etc.) or upon the detection of organic vapors by a field screening instrument. At a minimum, one soil sample collected from the vadose zone and one collected within the water-bearing or capillary fringe zone shall be submitted to the project lab for analysis (2 week turn-around) of the following chemical constituents:

- TPH as gasoline by modified EPAM 8015M
- BTEX by EPAM 8020
- MTBE by EPAM 8020

Groundwater samples shall also be collected from each boring using hydropunch methods. The selection of the actual groundwater sample depth will be made in the field based on the observation of sedimentologic characteristics (occurrence of relatively dense fine-grained layers, zones of greater transmissivity, etc.). Groundwater samples shall be forwarded to the selected project lab for analysis of the same chemical parameters as the soil samples.

5.2 Groundwater Monitoring Well Installation

As mentioned above Clearwater proposes that two borings be drilled and converted into groundwater monitoring wells (PMW-15 and PMW-16). PMW-15 will be placed between MW-11 and MW-9 and PMW-16 will be located down gradient (west) from MW-11. For reasons mentioned earlier the exact location of these wells will be determined by the results of the discrete sampling event in that vicinity. Once the exact location of PMW-15 and PMW-16 is determined Clearwater will submit the proposed location to the County for concurrence.

The borings for PMW-15 and PMW-16 shall be drilled from grade to 25 feet bgs. Soil samples shall be collected from the borings at five foot intervals to its completed depth. The soil borings



shall be advanced by a hollow stem auger drill rig. Soil samples will be selected for lab analysis based on their proximity to significant changes in sedimentologic characteristics as determined in the field (i. e. presence of relatively impermeable layers, zones of significant porosity, etc.) or upon the detection of organic vapors by a field screening instrument. At a minimum, two soil samples collected at the stated five foot intervals in the vadose zone and two from the saturated zone shall be submitted to the project lab for analysis (2 week turn-around) of the following chemical constituents:

- TPH as gasoline by modified EPAM 8015M
- BTEX by EPAM 8020
- MTBE by EPAM 8020

The wells shall be constructed of two-inch diameter materials, completed at 25 feet bgs and screened from the completed depth to 5 feet bgs to allow for water table fluctuation. The perforated section of each monitoring well shall be constructed of 0.020 inch slotted well screen.

5.3 Groundwater Sampling and RNA Assessment

Groundwater samples shall be collected from each newly installed and each existing monitoring well following development of the new well. Groundwater sampling shall be conducted in accordance with the attached protocols (Appendix A). Samples shall be analyzed by the previously stated EPA Methods for concentrations of TPH-G, BTEX and MTBE. Should MTBE be detected by EPA Method 8020, a confirmation sample shall be analyzed by EPA Method 8260.

Groundwater samples collected during this sampling event would also be tested for natural attenuation factors. In addition to the above analytes the samples would also be analyzed for ferrous iron, nitrates, sulfates, aerobic and anaerobic bacteria and hydrocarbon degrading bacteria. In the field the samples will be tested for dissolved oxygen and Eh. The results will be compiled, interpreted and included in the report generated.

If the results of the RNA assessment indicate that ongoing aerobic activity is taking place and the conditions are receptive to natural attenuation processes then the use of an oxygen releasing compound (ORC) to accelerate bioremediation will be investigated. Conclusions and recommendations will be included in the RNA assessment report indicating the viability of using ORC at this site.



6.0 REPORTING

Following completion of the investigative activities specified above, Clearwater will prepare a comprehensive Additional Site Assessment Report describing the results of discrete soil and groundwater sampling and monitoring well installation. The report shall contain a tabular and graphic presentation of all data collected during the proposed phase of site characterization, accompanied by text describing employed investigative methods and an interpretation of testing results. Based on initial assessment results, recommendations for the removal of source area soil or other remedial options, if found to be appropriate, will be made as needed. The report will be reviewed and signed by a California Registered Geologist.



7.0 CERTIFICATION

This workplan was prepared under the supervision of a professional Registered Geologist in the state of California. All statements, conclusions and recommendations are based solely upon published results from previous consultants, field observations by Clearwater Group, Inc. and laboratory analysis performed by a California DHS-certified laboratory related to the work performed by Clearwater Group, Inc.

Information and interpretation presented herein are for the sole use of the client and regulating agency. The information and interpretation contained in this document should not be relied upon by a third party.

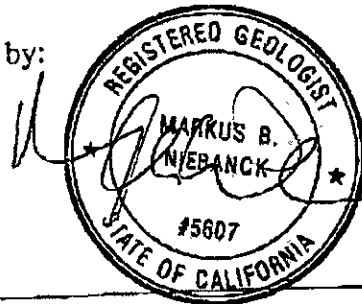
The service provided by Clearwater Group, Inc. has been conducted in a manner consistent with the level of care and skill ordinarily exercised by members of our profession currently practicing under similar conditions in the area of the site. No other warranty, expressed or implied, is made.

Clearwater Group, Inc.

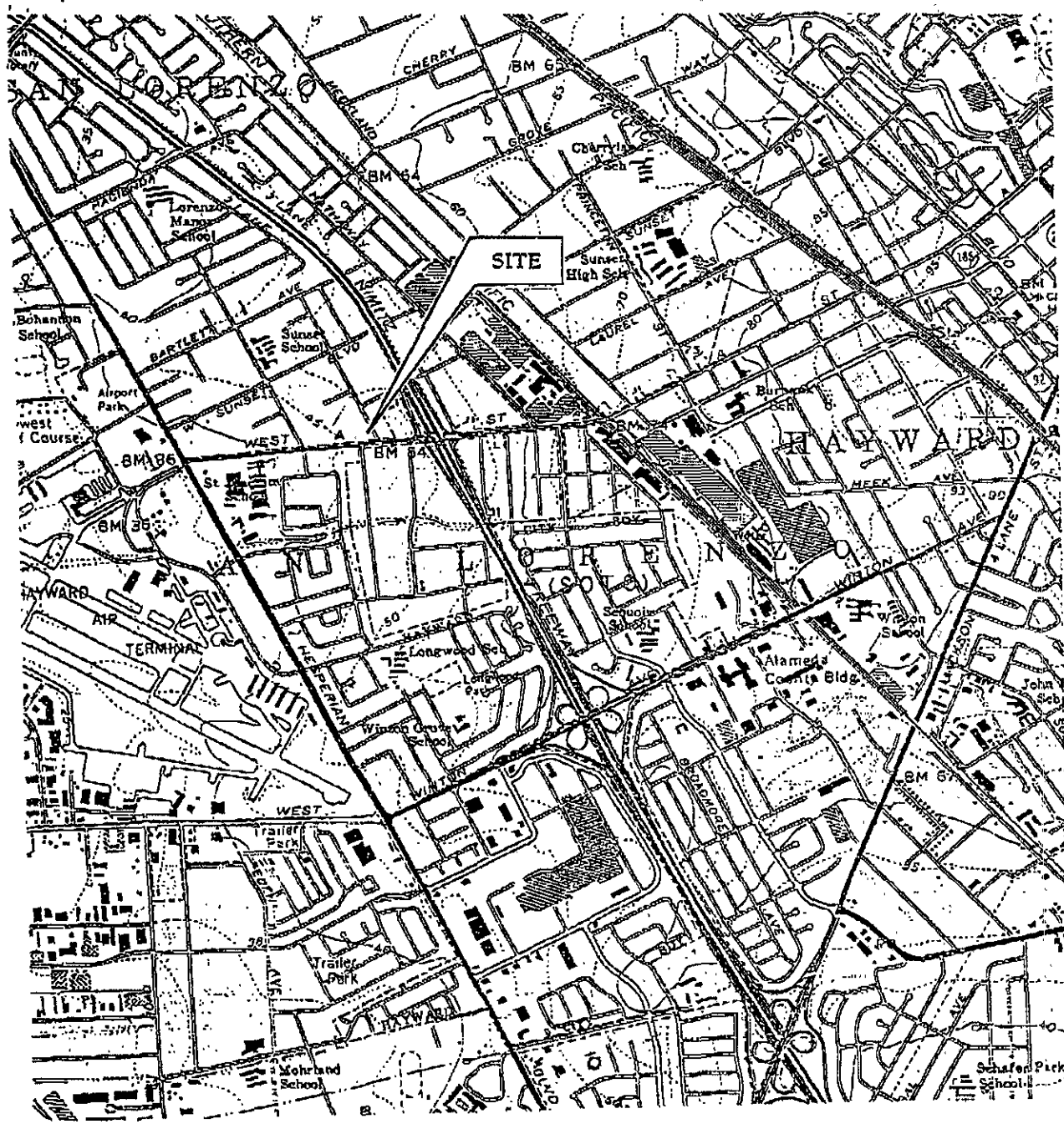
Prepared by:

Heidi M. Bauer
Project Geologist

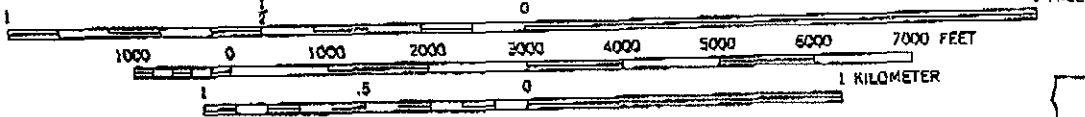
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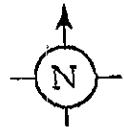
Markus Niebanck, R.G.
Operations Manager



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CONTOUR INTERVAL 20 FEET
 DOTTED LINES REPRESENT 5-FOOT CONTOURS
 NATIONAL GEODEIC VERTICAL DATUM OF 1929



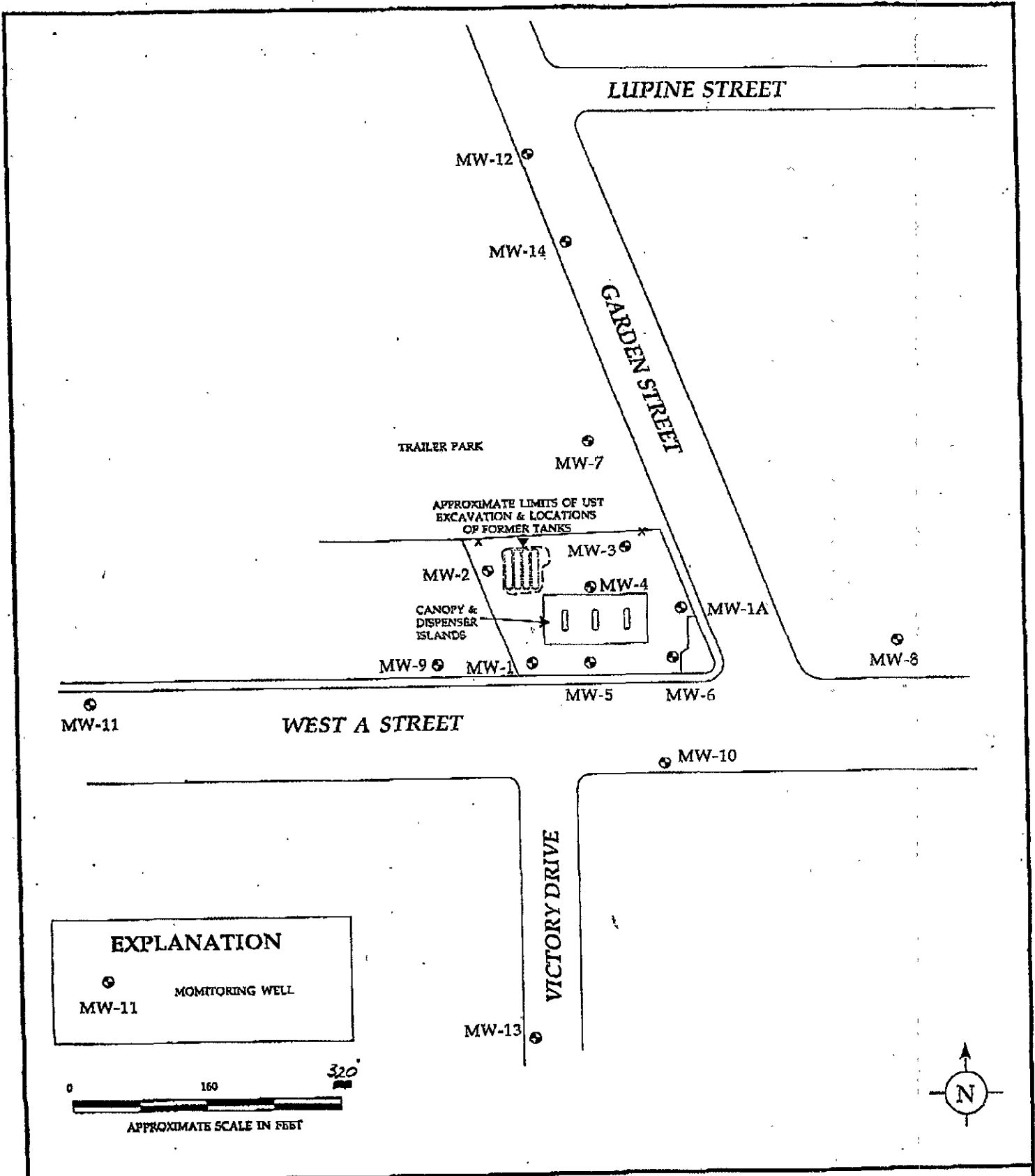
SOURCE: USGS 7.5 MINUTE QUADRANGLE MAP
 TITLED: HAYWARD, DATED: 1969, PHOTOREVISED: 1980

QUADRANGLE LOCATION

SITE LOCATION MAP
 E-Z Serve #100877
 525 West A Street
 Hayward, California

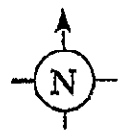
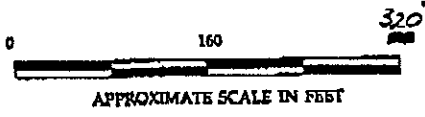
CLEARWATER GROUP, INC.

Project No 100877	Figure Date 8/98	Figure No. 1
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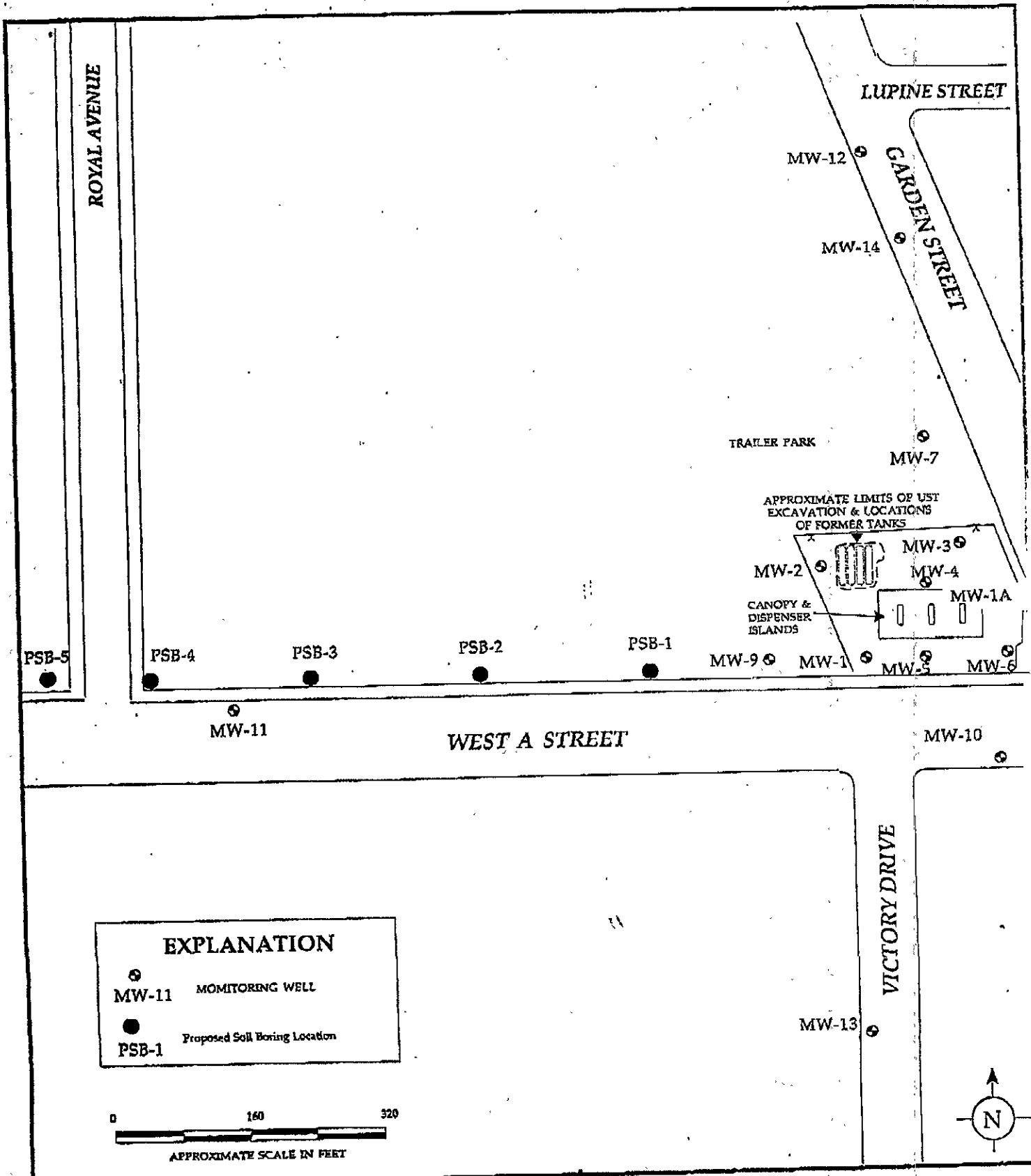


EXPLANATION

○ MW-11 MONITORING WELL



SITE VICINITY MAP E-Z Serve No. 100877 525 West A Street Hayward, California	CLEARWATER GROUP, INC.		
	Project No. EZ 100877	Figure Date 12/98	Figure 2



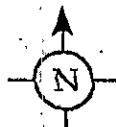
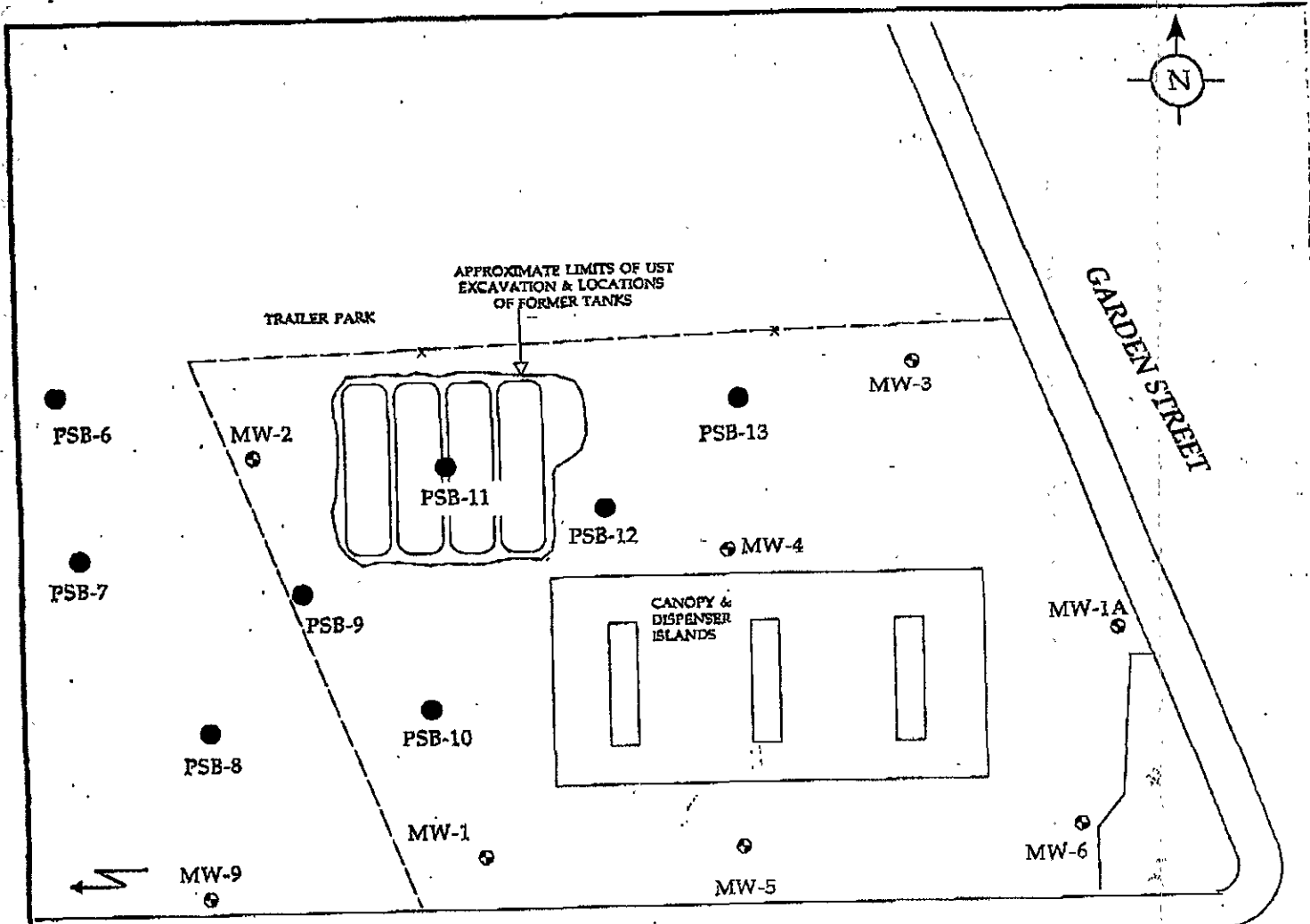
Proposed Soil Boring Location Plan (Pg1of2)
 E-Z Serve No. 100877
 525 West A Street
 Hayward, California

CLEARWATER GROUP, INC.

Project No.
EZ 100877

Figure Date
1/99

Figure
3A



EXPLANATION	
	MONITORING WELL
MW-10	
	PROPOSED SOIL BORING LOCATION
PSB-9	

PROPOSED SOIL BORING LOCATION PLAN (Pg 2of 2)
 E-Z Serve Station #100877
 525 West A Street, Hayward, California

CLEARWATER GROUP, INC.		
Project No. EZ 100877	Figure Date 1/99	Figure 3B

CLEARWATER GROUP, INC.**Soil Borehole Drilling, Monitoring Well Installation and Development,
and Groundwater Sampling Field Procedures****Drilling and Soil Sampling****Permits, Site Safety Plan, Utility Clearance**

Clearwater Group, Inc. (CGI) obtains all the required permits, unless otherwise contractually directed. CGI prepares a site specific Site Safety Plan detailing site hazards, site safety and control, decontamination procedures, and emergency response procedures to be employed throughout the defined phase of work. At least 48 hours prior to drilling, Underground Service Alert (USA) or an equivalent agency is notified of the planned work. CGI, attempts to locate all underground and above ground utilities by site inspection (in conjunction with its' subcontractors and knowledgeable site managers, if available), and review of site as-built drawings. CGI may employ a private, professional utility locator to refine the site utility inspection.

Drilling Equipment

All soil borings are drilled using a truck-mounted hollow-stem auger drill rig, unless site conditions warrant a different drilling method. Subsurface conditions permitting, the first five feet of each boring is advanced using a hand-auger or post-hole digger. All drilling equipment is inspected daily and maintained in safe working condition by the operator. All down-hole drilling equipment is steam cleaned prior to arriving on site. Working components of the drill rig near the borehole, as well as augers and drill rods are thoroughly steam cleaned between each boring location. All CGI drilling and sampling methods are consistent with ASTM Method D-1452-80, and local, state and federal regulations.

Soil Sampling and Lithologic Description

Whenever possible, the first Clearwater boring to be drilled at a site is continuously cored to obtain a complete lithologic description. Otherwise, soil samples are typically collected every 5 feet to the total depth explored, using brass tubes fitted in a California-modified split spoon sampler. If copper or zinc contamination is the subject of the investigation, stainless steel liners are used instead of brass. Additional soil samples may be collected based upon significant changes in lithology or in areas of obvious soil contamination. During soil sample collection, the split spoon sampler is driven 18 to 24 inches past the lead auger by a 140-pound hammer falling a minimum of 30 inches. The number of blows necessary to drive the sampler and the amount of soil recovered is recorded on the Field Exploratory Soil Boring Log. The soil sampler and liners are cleaned with an Alconox® solution and rinsed with tap water prior to each sampling event. New liners are used whenever a soil sample may be retained for laboratory analysis.

Soil samples selected for laboratory analysis are sealed on both ends with teflon tape and plastic end caps. The samples are labeled, documented on a chain-of-custody form and placed in a cooler for transport to a state certified analytical laboratory. Soil contained in remaining liners is removed for lithologic descriptions (according to the Unified Soil Classification System). Additional soil is screened for organic vapors by placing approximately 30 grams of soil in a sealed plastic bag or a glass jar sealed with aluminum foil. The bag or jar is left undisturbed for approximately 15 minutes, in the sun if possible. The head space in the bag is accessed in a manner to minimize entry of outside air, and is tested for total organic vapor using a calibrated organic vapor meter (OVM). The results of the field screening are noted with the lithologic descriptions on the Field Exploratory Soil Boring Log.

On encountering an impermeable (clayey) layer three feet or more in thickness below a saturated permeable layer, where the impermeable layer is considered to be a possible confining layer for an underlying aquifer, drilling is halted until a decision to proceed is obtained from the project manager. This process minimizes the chance of introducing contamination to an underlying, clean aquifer.

Soil Waste Management

Soil cuttings are stockpiled on and covered with plastic sheeting to control runoff, or contained in 55-gallon D.O.T.-approved drums on site. Waste soil is sampled to chemically profile it for disposable, and hauled by a licensed waste hauler to an appropriate landfill. All waste stored on site is properly labeled at the time of production.

Soil Boring Abandonment

Soil borings which are not to be converted into monitoring wells are sealed to the ground surface using neat cement or sand-cement slurry in accordance with federal, state and local regulations. Native soil may be used to fill the top two to three feet for cosmetic purposes, as permitted.

Monitoring Well Installation

Well Casing, Screen and Filter Pack Construction

All well construction is performed in accordance with Department of Water Resources "California Well Standards" and all requirements of local oversight agencies. Soil borings to be converted into single-cased monitoring wells are a minimum of eight inches in diameter for 2-inch diameter wells and a minimum of ten inches in diameter for 4-inch diameter wells. Monitoring wells are constructed with schedule 40, threaded, polyvinyl chloride (PVC) casing unless site geochemistry or contamination necessitates an alternative material. The wells are constructed with factory-slotted screen and threaded end caps.

The screened interval is placed such that it extends approximately ten feet into the water-bearing zone, and at least five feet above the expected maximum water level. The screened interval may extend less than five feet above the maximum water level, only to prevent intersection of the screened interval with the top of the confining layer of a confined aquifer, or where the water table is too shallow to allow this construction.

A graded sand filter pack is placed in the annular space across the screened interval and extended approximately one to two feet above the screen, as site conditions permit, so as to prevent extension of the sand pack into an overlying water-bearing unit. The well screen slot size is the maximum size capable of retaining 90% of the filter pack. Typically, 0.010-inch screen is used where the formation is predominantly clay and/or silt or poorly-graded fine sand. 0.020-inch screen is used where the formation is predominantly well-graded or medium to coarse sand and/or gravel.

The filter pack grade (mean grain size) is selected according to native sediment type as follows: a) for poorly graded fine sand or silt/clay - 4 times the 70% retained grain size of the formation b) for medium to coarse sand, gravel or well graded sediments - 6 times the 70% retained grain size. Since results of particle size analysis are not always available, Clearwater often selects screen size and filter pack on the basis of general site stratigraphy, and specifically the finest significantly thick layer of sediment to be screened. Commonly selected grades are Lone Star® 3, 2/12 or 2/16 (or equivalent) with 0.020-inch slotted screen and Lone Star® 1/20 with 0.010-inch slotted screen.

Well Seal and Completion

A minimum two foot seal of bentonite is placed above the sand pack. The bentonite seal is hydrated by either formation water or potable water. Neat cement or a cement/bentonite grout mixture seals the remaining annular space to the surface. If bentonite is used in the grout mixture, it does not exceed 5% by weight. The grout is placed using a tremie pipe, if the top of the bentonite is more than 20 feet below grade, or if water is present in the boring above the bentonite seal. A watertight locking cap and protective traffic-rated vault box is installed on top of each well. Well construction details are presented on the Field Exploratory Soil Boring Log. Following completion of a well, Clearwater completes and submits, or ensures that the driller has sufficient information to complete and submit, the state-required Well Completion Report or equivalent document.

Well Development

All newly installed wells are developed prior to sampling to remove fine grained sediments from the well and stabilize the filter pack and the disturbed aquifer materials. Development takes place prior to or at least 24 hours after setting the seal on the well, unless otherwise directed by a local oversight agency. Well development consists of surging with a surge block and removing water from the well with either a pump or bailer, until the well is free of sediment, or until at least 10 well casing volumes have been removed. Depth to bottom is measured to determine casing volume. If the well is sampled immediately following development, temperature, pH, specific conductance and turbidity (qualitative) are monitored during well development (see section "Groundwater Sampling"). All development equipment is cleaned prior to use and between wells with an Alconox® solution, then rinsed in potable water. All data collected during development are recorded on the Well Development Data Sheet and, if necessary, the Purging Data Sheet.

Well Surveying

All well elevations are surveyed at the north side of the top of casing to the nearest ± 0.01 foot. The exact survey point (at the center of the survey rod or, if the casing stub is uneven, the point of contact between casing and rod) is clearly marked and maintained on the casing rim. Elevations are referenced either to mean sea level or to a project datum. A project datum is typically chosen so as to minimize the possibility of its later disturbance. For instance, fire hydrants are commonly selected. Where required, the wells are surveyed by a licensed land surveyor, relative to mean sea level.

Groundwater Sampling

Groundwater Monitoring

Prior to beginning, a decontamination area is established. Decontamination procedures consist of scrubbing downhole equipment in an Alconox® solution wash (wash solution is pumped through any purging pumps used), and rinsing in a first rinse of potable water and a second rinse of potable water or deionized water if the latter is required. Any non-dedicated down hole equipment is decontaminated prior to use.

Prior to purging and sampling a well, the static water level is measured to the nearest 0.01 feet with an electronic water sounder. Depth to bottom is typically measured once per year, at the request of the project manager, and during Clearwater's first visit to a site. If historical analytical data are not available, with which to establish a reliable order of increasing well contamination, the water sounder and tape will be decontaminated between each well. If floating separate-phase hydrocarbons (SPH) are suspected or observed, SPH is collected using a clear, open-ended product bailer, and the thickness is measured to the nearest 0.01 feet in the bailer. SPH may alternatively be measured with an electronic interface probe. Any monitoring well containing a measurable thickness of SPH before or during purging is not additionally purged and no sample is collected from that well. Wells containing a hydrocarbon sheen are sampled unless otherwise specified by the project manager. Field observations such as well integrity as well as water level measurements and floating product thicknesses are noted on the Gauging Data/Purge Calculations form.

Well Purging

Each monitoring well to be sampled is purged using either a PVC bailer or a submersible pump. Physical parameters (pH, temperature and conductivity) of the purge water are monitored during purging activities to assess if the water sample collected is representative of the aquifer. If required, parameters such as dissolved oxygen, turbidity, salinity etc. are also measured. Samples are considered representative if parameter stability is achieved. Stability is defined as a change of less than 0.25 pH units, less than 10% change in conductivity in micro mhos, and less than 1.0 degree centigrade (1.8 degrees Fahrenheit) change in temperature. Parameters are measured in a discreet sample decanted from the bailer separately from the rest of the purge water. Parameters are measured at least four times during purging; initially, and at volume intervals of one well volume. Purging continues until three well casing volumes have been removed or until the well completely dewateres. Wells which dewater or demonstrate a slow recharge, may be sampled after fewer than three well volumes have been removed. Well purging information is recorded on the Purge Data sheet. All meters used to measure parameters are calibrated daily. Purge water is sealed, labeled, and stored on site in D.O.T.-approved 55-gallon drums. After being chemically profiled, the water is removed to an appropriate disposal facility by a licensed waste hauler.

Groundwater Sample Collection

Groundwater samples are collected immediately after purging or, if purging rate exceeds well recharge rate, when the well has recharged to at least 80% of its static water level. If recharge is extremely slow, the well is allowed to recharge for at least two hours, if practicable, or until sufficient volume has accumulated for sampling. The well is sampled within 24 hours of purging or repurged. Samples are collected using polyethylene bailers, either disposable or dedicated to the well. Samples being analyzed for compounds most sensitive to volatilization are collected first. Water samples are placed in appropriate laboratory-supplied containers, labeled, documented on a chain of custody form and placed on ice in a cooler for transport to a state-certified analytical laboratory. Analytical detection limits match or surpass standards required by relevant local or regional guidelines.

Quality Assurance Procedures

To prevent contamination of the samples, CGI personnel adhere to the following procedures in the field:

- A new, clean pair of latex gloves are put on prior to sampling each well.
- Wells are gauged, purged and groundwater samples are collected in the expected order of increasing degree of contamination based on historical analytical results.
- All purging equipment will be thoroughly decontaminated between each well, using the procedures previously described at the beginning of this section.
- During sample collection for volatile organic analysis, the amount of air passing through the sample is minimized. This helps prevent the air from stripping the volatiles from the water. Sample bottles are filled by slowly running the sample down the side of the bottle until there is a convex meniscus over the mouth of the bottle. The lid is carefully screwed onto the bottle such that no air bubbles are present within the bottle. If a bubble is present, the cap is removed and additional water is added to the sample container. After resealing the sample container, if bubbles still are present inside, the sample container is discarded and the procedure is repeated with a new container.

Laboratory and field handling procedures may be monitored, if required by the client or regulators, by including quality control (QC) samples for analysis with the groundwater samples. Examples of different types of QC samples are as follows:

- Trip blanks are prepared at the analytical laboratory by laboratory personnel to check field handling procedures. Trip blanks are transported to the project site in the same manner as the laboratory-supplied sample containers to be filled. They are not opened, and are returned to the laboratory with the samples collected. Trip blanks are analyzed for purgable organic compounds.
- Equipment blanks are prepared in the field to determine if decontamination of field sampling equipment has been effective. The sampling equipment used to collect the groundwater samples is rinsed with distilled water which is then decanted into laboratory-supplied containers. The equipment blanks are transported to the laboratory, and are analyzed for the same chemical constituents as the samples collected at the site.
- Duplicates are collected at the same time that the standard groundwater samples are being collected and are analyzed for the same compounds in order to check the reproducibility of laboratory data. They are typically only collected from one well per sampling event. The duplicate is assigned an identification number that will not associate it with the source well.

Generally, trip blanks and field blanks check field handling and transportation procedures. Duplicates check laboratory procedures. The configuration of QC samples is determined by CGI depending on site conditions and regulatory requirements.

CLEARWATER GROUP, INC.

Natural Attenuation Processes and Recommended Monitoring Guidelines

The following document details the processes involved in the natural attenuation of petroleum hydrocarbons in soil and groundwater and presents recommendations for monitoring and confirming these processes. By confirming natural attenuation, a conceptual basis is provided for regulatory site closure.

Natural Attenuation Processes

The predominant attenuation process is intrinsic biodegradation (aerobic and anaerobic) mediated by hydrocarbon degrading bacteria. Other factors in natural attenuation include physical and chemical processes such as volatilization, dispersion, sorption and hydrolysis. Unless otherwise referenced, the following information was derived from McAllister and Chiang (1994).

Aerobic degradation.

The aerobic process is the most important form of biodegradation wherever DO concentrations exceed 1 to 2 mg/L. Under hypoxic conditions (0.1 to 2 mg/L DO), aerobic degradation may occur along the edges of the plume while anaerobic degradation predominates in the center of the plume.

In aerobic respiration, microbes utilize dissolved oxygen (DO) as an electron acceptor during hydrocarbon oxidation (degradation), producing carbon dioxide, water, and microbial biomass. The electron acceptor is a substance that facilitates the reaction by taking up the electrons released by oxidation; the electron acceptor then becomes reduced during the process of biodegradation.

Anaerobic degradation.

Microbes may also degrade hydrocarbons via anaerobic processes by utilizing alternate biochemical pathways when DO concentrations are insufficient for aerobic degradation. Anaerobic degradation is much slower than the aerobic process and not all BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) are consistently degraded. Some studies indicate benzene is recalcitrant to anaerobic degradation while others have demonstrated limited degradation (Rifai et al, 1995). Anaerobic degradation generally occurs in the center of the plume where DO has been depleted by aerobic degradation. Research into the efficacy of anaerobic processes is ongoing.

Anaerobic electron acceptors include [in order of sequential use and decreasing redox potential (Eh)]:

- nitrate (NO_3^-),
- oxides of ferric iron (Fe^{3+}),
- sulfate (SO_4^{2-}),
- water.

The associated biochemical processes are: denitrification (or nitrate reduction), iron reduction, sulfate reduction, and methanogenesis. Manganese (Mn^{4+}) may also function as an electron acceptor. Nitrate and sulfate reduction do not degrade alkanes such as methane, propane, and butane.

Volatilization

Dissolved plume mass can be reduced by volatilization of contaminants to the vapor phase in the unsaturated zone. Normally volatilization is a negligible component of natural attenuation, however, it may contribute 5% or more of total mass loss in shallow (<15 feet), warm and/or fluctuating water table conditions in permeable soils (Rifai et al, 1995).

Dispersion

Mechanical/molecular mixing reduces dissolved concentrations, substantially by lateral spread. No dissolved contaminant mass is removed from the system by this process. Dispersion (D) is generally modeled based on the length of the plume (x). Conservative practice calls for dispersion in the downgradient direction (longitudinal dispersivity, D_x) to be equal to 0.1 times the plume length (x). Dispersion in the transverse direction (transverse dispersivity, D_y) is equal to 0.33 times D_x ; dispersion in the vertical direction (vertical dispersivity, D_z) is equal to 0.05 times D_x (Connor, et al., 1995).

Sorption

Contaminants partition between the aqueous phase and the soil matrix. Adsorption onto the soil surface significantly retards migration but does not permanently remove BTEX which may desorb later. Carbon is the most effective sorption material in soils, and although clay minerals and amorphous minerals such as iron hydroxides also have some influence, only sorption to carbon in soil is included in most contaminant fate and transport computer models.

Sorption is controlled by the organic carbon content of soil (f_{OC}), the chemical specific organic carbon partition coefficient (K_{OC}), the soil bulk density (ρ_s), and the water content of the soil (θ_s) (Table 1). K_{OC} is a measure of the affinity of a given chemical to sorb from water onto solid organic material. Once the porosity, bulk density, K_{OC} , and f_{OC} have been established, the retardation factor (R) for the site can be calculated as follows:

$$R = (1 + k_s * \rho_s / \theta_s) \quad \text{where: } k_s = f_{OC} * K_{OC}$$

The retardation factor is used in transport models (discussed below) as a measure of the degree to which the rate of plume migration is reduced by sorption processes.

Hydrolysis etc.

Other chemical reactions such as hydrolysis may reduce contaminant mass without microbial mediation. Hydrolysis occurs when an organic molecule reacts with water or a component ion of water. Unlike biodegradation, hydrolysis is not catalyzed by microorganisms. Hydrolysis has not been observed to reduce BTEX concentrations, but is significant for halogenated volatile organics (solvents, etc.).

Monitoring Groundwater For Natural Attenuation

Assessment and monitoring of natural attenuation should be performed to confirm that intrinsic bioremediation and other forms of natural attenuation are occurring in the subsurface and are sufficient to limit plume migration by achieving an equilibrium between hydraulic transport (advection) and removal/degradation/reduction of mobile contaminants. To confirm natural attenuation, it needs to be demonstrated that intrinsic factors are limiting migration, and that they will continue to do so until the plume has degraded to acceptable levels.

Natural attenuation can be evaluated by monitoring specific indicator parameters over a given period of time. As further confirmation, simple fate and transport models can be applied to the site using the site-specific information obtained. Several lines of evidence will generally need to be combined to provide a convincing case of natural attenuation. First, it is necessary to establish that the plume is stable or being reduced in terms of size and concentrations, by review of historical data, possibly including statistical analysis. At least one year of monitoring data utilizing an adequate distribution of wells should be sufficient. For all chemical parameters, background concentrations need to be established by sampling one or more clean wells. In addition to plume concentrations, Rifai et al., (1995), recommends, at a minimum, monitoring the following parameters:

- Microbial enumeration [total heterotrophic bacteria (plate count), and total hydrocarbon using bacteria (ASTM method G-2)].
- Temperature (field measurement)
- pH (field measurement)
- Dissolved Oxygen (field measurement or EPA Method 360.1)

If DO is depleted relative to background concentrations, additional monitoring for anaerobic processes may be considered and should include the following:

- Eh (field measurement)
- Sulfate (EPA method 300 or 375.4)
- Nitrate/nitrite (EPA method 300, 353.1 or 353.2)
- Dissolved iron (EPA method 200.7)
- Total iron (EPA Method 236.1 or 6010)
- Methane (field measurement)
- Alkalinity (EPA method 310.1)
- Dissolved carbon dioxide (with alkalinity or method SM406C)

Certain parameters, notably DO and Eh, may be measured in the field using downhole meters. Most of the other parameters require laboratory analysis of a groundwater sample for accurate quantification. Trends in methane concentrations may be identified using an organic vapor meter fitted with an appropriate filter at the wellhead.

The combination of parameters that Clearwater will monitor at a particular site will depend on site-specific conditions and previous site investigation. The minimum set of parameters as defined by Rifai will always be included for at least one clean (background) well and at least one well representative of mid-plume conditions.

The following sections provide a detailed description of monitoring methods and anticipated results for indicator parameters outlined above.

Microbial Populations

Hydrocarbon degrading bacteria are generally ubiquitous; however, the total population of microbes (measured in counts per liter) is dependent on the available energy source (i.e., hydrocarbons). To evaluate natural attenuation, microbial counts should include separate enumerations for hydrocarbon degrading bacteria and for total heterotrophic bacteria, both normally obtained from cultured plate counts. The ratio of hydrocarbon degraders to total heterotrophs is the most useful in assessing natural attenuation. This ratio should be relatively large in samples from contaminated wells, compared to the ratio in samples from clean wells, indicating a proliferation of the indicator species in contaminated areas, independent of overall microbial population variations. Such a distribution of bacteria may require 1 to 2 years to become established once hydrocarbon contamination is present. As further confirmation, it may be useful to establish that sufficient concentrations of microbial nutrients such as nitrogen and phosphorus are present in the subsurface.

Groundwater typically contains total microbial counts of 10^3 to 10^8 counts per liter. Lower counts in contaminated areas may indicate toxic conditions. In sites with organic rich soils, microbial populations may be high but hydrocarbon degradation may be inhibited because the microbes preferentially degrade the naturally occurring carbon compounds found in the soils (Cookson, 1995).

pH

pH is best measured with a meter or by collecting a sample for laboratory analysis. The probe portion of pH meters must be regularly cleaned and periodically soaked in solutions designed to remove oil and protein build up. Lowered pH corresponding spatially to the plume may be indicative of the production of organic acid metabolic end-products of aerobic hydrocarbon degradation. Uncontaminated groundwater is commonly slightly alkaline, but pH varies widely depending on many natural and human influenced factors. pH between 6 and 8 is optimal for BTEX degradation.

Redox Potential (Eh)

Eh is a measure of electron activity within a solution. Each pathway of degradation is generally restricted to a prescribed range of Eh values. Hydrocarbon degradation reduces the Eh of the system in which it occurs, unless the groundwater recharge rate exceeds the utilization rate of the electron acceptor (this is normally not the case since mixing is limited). Once an electron acceptor has been utilized and thereby depleted in the system, Eh conditions determine which next electron acceptor in the sequence will become predominant.

The utility of Eh measurement is as an adjunct to electron acceptor concentration measurements (discussed below). Eh must be measured in situ to avoid atmospheric influence as described in the section on DO sampling. Eh units are millivolts (mV). Decreased Eh should coincide with elevated contaminant concentrations, and depleted DO. Very low Eh (reducing conditions: <0 mV) should coincide with depleted anaerobic electron acceptors. Table 2 presents Eh values typical of each biodegradation pathway.

Dissolved Oxygen (DO)

DO is best measured with a downhole meter measuring in mg/L. Some meters also read DO as a percentage of saturation at a given temperature, however, the volumetric concentration has more utility in fate and transport models. Measurement of DO and Eh are both sensitive to several factors associated with field methodologies, particularly exposure to atmospheric oxygen; hence the preferred use of a downhole meter. It is necessary to strictly adhere to instructions provided with a given model of instrument. DO meters function by permitting a small quantity of oxygen to diffuse across a porous membrane. Consequently, it is necessary to keep water moving in the vicinity of the membrane to prevent a depletion of DO immediately adjacent to the membrane. This can be achieved

manually, by a gentle raising and lowering of the meter in the well. The membrane is delicate and must be carefully maintained.

A negative correlation should occur between DO concentrations and hydrocarbon concentrations. Background concentrations should exceed 1 to 2 mg/L for effective aerobic degradation. DO in groundwater is derived from the atmosphere at the recharge area or the vadose zone. Surface water saturated with oxygen by contact with atmospheric air will contain between approximately 7.5 mg/L at 5°C and 12.75 mg/L at 30°C, though these figures may vary somewhat depending on other chemical parameters. DO concentrations in groundwater are generally less than those for surface water by an amount dependent on the quantity of oxidizable materials (e.g. sulfides) in contact with the groundwater, and the length of time the groundwater has been stored in the aquifer. Background groundwater DO concentrations in shallow aquifers can be as high as 12 mg/L in warm conditions or as low as 1 mg/L in cool conditions. (Hem, 1985). DO may be increased by local groundwater recharge (e.g. irrigation). Aerobic degradation typically occurs when Eh is approximately +800 mV (discussed below).

Anaerobic Electron Acceptors

Analysis of water samples for nitrate, dissolved iron, and/or sulfate can provide data indicative of intrinsic bioremediation. The higher the background concentrations the better, unless they are so high as to create toxicity for the microbes or exceed water quality standards. Depleted dissolved electron acceptor concentrations (except iron, see below) in areas of high hydrocarbon concentration are indicative of microbial degradation.

Nitrate. Nitrate concentrations may be derived by analyzing nitrate plus nitrite as N (EPA Method 353.2). This laboratory method calculates total nitrate, since nitrite is metastable in groundwater and seldom present in sufficient quantities to affect the ionic balance (Wiedemeier et al, 1995). The bulk of nitrates in groundwater are derived from human contamination (e.g., agricultural runoff/septic systems). Background concentrations vary widely with human activity in the site vicinity, and would otherwise be commonly less than 1 mg/L. Concentrations considered indicative of a significant biodegradation capacity might be those in excess of 20 mg/L. Denitrification/nitrate reduction typically occur when Eh is approximately +750 mV (but more than 0 mV).

Iron. Laboratory analysis of iron concentration may be accomplished by collecting an unfiltered groundwater sample to obtain the total iron content (precipitated and dissolved), or by passing the sample through a 0.45 micron filter immediately after collection to obtain the dissolved iron concentration. Iron in groundwater is derived primarily from soil minerals. Dissolved iron concentrations are very sensitive to changes in pH and redox potential (Eh). Free dissolved ferric iron can only exist stably under extremely acidic conditions (pH<2) (Hem, 1985). Ferric iron reduction to ferrous iron occurs at intermediate Eh values. Under aerobic, moderately acidic or alkaline conditions, dissolved iron is typically present as a hydroxide; the ferric species is ferric orthohydroxide (Wiedemeier et al, 1995). Dissolved ferric iron is usually rapidly reprecipitated as a sulfide, oxide or hydroxide. Since microbes utilize insoluble sedimentary ferric iron-oxides as their energy source, producing more soluble ferrous iron, an increase in total dissolved iron is indicative of microbial hydrocarbon degradation.

The solubility of ferrous iron is significantly reduced by the presence of sulfides; the end-product of sulfate reduction (Barker et al, 1995). Analytical results of dissolved ferrous iron concentration will likely be an underestimate, since it is not based on the actual amount of ferric hydroxide (the electron acceptor) present in the aquifer, but the amount of reduced ferrous iron (the end-product) remaining in solution at the time of sampling.

Typical background concentrations of total dissolved iron in groundwater are below 1.0 mg/L. Results in excess of 1.0 mg/L indicate iron-reducing conditions (Cookson, 1995) which may have resulted from anaerobic hydrocarbon degradation. High dissolved iron concentrations may also indicate the presence of very fine particulates, low pH, or high organic content. High organic content induces stability of soluble iron complexes (Hem, 1985). Measurement of the total iron content of a sample is useful as a background datum against which to compare changes in the dissolved concentration.

Sulfate. Sulfate is derived primarily from soil minerals. The occurrence of sulfate reduction may be inferred from the presence of black acid volatile sulfide deposits on materials in long-term contact with contaminated groundwater (Barker et al, 1995). Pyrite may be precipitated in the soil. Sulfate concentrations in groundwater are naturally higher than those for nitrate. Sulfate concentrations of 100 mg/L might be considered moderate and several hundred mg/L is not uncommon. Concentrations below 40 mg/L are indicative of methanogenic conditions (Cookson, 1995). Sulfate reduction typically occurs when Eh is approximately -200 mV.

Methanogenesis. Under methanogenic conditions (Eh of approximately -250 mV), carbon dioxide and methane are both produced by hydrocarbon oxidation. The utility of measurement of these compounds is discussed below (metabolic end-products).

Carbonate/Hardness/Total alkalinity

One of these associated analyses is typically conducted at the laboratory on collected water samples. Increased carbonate concentration will commonly occur where acidity dissolves carbonates from the soil. Sufficient concentrations of carbonate will buffer the pH and prevent acid toxicity that may result from hydrocarbon degradation. Total alkalinity (as carbonate) concentrations exceeding 100 mg/L may be considered conducive to effective buffering. Dissolved carbon dioxide may be assessed in conjunction with total alkalinity analysis.

Metabolic end-products

Metabolic end-products of hydrocarbon biodegradation include carbon dioxide, water, nitrogen, nitrites, ferrous iron, sulfites, sulfides, hydrogen sulfide, and methane. Carbon dioxide, hydrogen sulfide and methane may be measured with a gas meter at the wellhead. Reduced ferrous iron, sulfite and sulfide may be analyzed in water samples. Sulfides may precipitate into the soil and be under-represented in groundwater samples. Nitrite is metastable and therefore nitrite detection (generally <0.1 mg/L) is indicative of ongoing denitrification. Ammonium ions in excess of 1.0 mg/L may also be indicative of anaerobic conditions. Elevated concentrations of all metabolic end-products should correlate positively with elevated hydrocarbons.

Field measurement of dissolved carbon dioxide (DCD) is of secondary importance but may provide useful data. Dissolved carbon dioxide is derived primarily from the atmosphere. Elevated DCD spatially correlated with decreased DO concentration, may be indicative of aerobic microbial hydrocarbon degradation as DCD is a metabolic end-product. Elevated DCD may also result from anaerobic degradation. High background DCD is a desirable feature in terms of the capacity of the groundwater to buffer decreases in pH produced by microbial hydrocarbon degradation which may otherwise limit biological activity. Carbon dioxide is more soluble than oxygen and average concentrations are around an order of magnitude higher.

Contaminant Fate and Transport Modeling

Plume transport can be modeled using simple analytical equations. Transport assuming no attenuation can be modeled and the results compared with field data to provide a preliminary indication of the extent of natural attenuation. Transport models can be modified to include various natural attenuation factors based on actual site data. Comparison of these modeling results to actual field results can be used to confirm natural attenuation.

To model plume transport, the following basic site characteristics need to be determined:

- Historical dissolved hydrocarbon distribution
- Hydraulic conductivity
- Soil density/porosity
- Aquifer thickness
- Groundwater gradient/depth fluctuations
- Possible preferential migration pathways
- Organic content of the soil, f_{oc} .

Laboratory analysis of soil samples may be necessary to establish f_{oc} , which is useful for modeling sorption. Hydraulic conductivity may be obtained as an estimate from the literature based on soil type (for homogenous lithologies), or by performing an aquifer test (slug or pump).

For plumes under steady-state conditions, contaminant transport models such as the Domenico Transport Equation (Appendix A) can be modified to include the processes of dispersion and sorption to predict contaminant concentrations at a given distance from the source (Connor et al, 1995). In addition, biological and chemical degradation may be collectively modeled by a first-order decay function requiring assignment of a literature-based decay half-life value (in days) for each contaminant. Conservative decay half-life default values from Connor et al (1995) are provided on Table 1. Alternatively, for most realistic results, biodegradation may be modeled based on actual concentrations of electron acceptors, by determining the biodegradation capacity for each electron acceptor and contaminant concentration (Connor et al, 1995).

The biodegradation capacity is a measure of the actual potential of an electron acceptor (n) to remove contaminant mass. The BC_n is calculated for each contaminant and electron acceptor by dividing the concentration of the acceptor in the groundwater by its utilization factor (UF_n). The UF_n can be easily derived from the stoichiometric equation for the particular degradation reaction and represents the ratio of mass of electron acceptor utilized to the mass of hydrocarbon degraded (Wiedemeier, 1995). Values of UF_n for benzene for each pathway are presented in Table 2. The sum of the BC_n values obtained for the principal electron acceptors is the total biodegradation capacity of the groundwater (BC_t) (Connor et al, 1995). This datum is necessary in contaminant fate and transport models to realistically evaluate the potential for plume attenuation resulting from intrinsic biodegradation.

MTBE is almost completely recalcitrant to biological degradation and does not sorb onto the soil. Due to these properties, MTBE concentrations generally mimic non-attenuated plume transport. Therefore, MTBE may be used as a conservative tracer or "internal standard" for modeling plume transport with no attenuation.

Confirming Natural Attenuation

To best confirm natural attenuation in anticipation of site closure, the assessment and monitoring activities should confirm the following plume characteristics:

- 1) Fieldscale contaminant mass has been reduced (based on historical groundwater analyses)
- 2) Microbial activity is occurring in the plume (based on microbial counts)
- 3) The less recalcitrant compounds are reduced in concentration and extent relative to the more recalcitrant compounds. The approximate order of increasing recalcitrance for BTEX aromatics is: toluene, o-xylene, m- and p- xylene, benzene, ethylbenzene i.e. toluene concentrations should be most attenuated; ethylbenzene least attenuated.
- 3) Electron acceptors such as DO, nitrate and sulfate are depleted within the plume
- 4) Metabolic end-products such as carbon dioxide, hydrogen sulfide and methane have accumulated within the plume relative to outside of the plume.

References

- Arulanantham, R. and Salhotra, A., 1996. Risk and Decision Making at Petroleum Contaminated Sites. University of California Extension, Programs in Environmental Management.
- Barker, G. et al, 1995. "Assessment of Natural Hydrocarbon Bioremediation at Two Gas Condensate Production Sites." In R. E. Hinchee, J. T. Wilson, and D. C. Downey (Eds.), *Intrinsic Bioremediation*, pp. 181-188. Battelle Press, Columbus, OH.
- Cookson, J.T., Jr., 1995. Bioremediation Engineering: Design and Application: (Ed. Nalven, G.). McGraw-Hill, Inc., New York, NY.
- Connor, J., Nevin, P.J., Fisher, R.T., Bowers, R.L., and Newell, C.J., 1995. Tier 2 Guidance Manual for Risk-Based Corrective Action, Appendix A. Groundwater Services, Inc., Houston, TX.
- Hem, J., 1985. *Study and Interpretation of the Chemical Characteristics of Natural Water*. U.S. Geological Survey Water - Supply Paper 2254. U.S. Government Printing Office.
- McAllister, P.M. and Chiang, C.Y., 1994. "A Practical Approach to Evaluating Natural Attenuation of Contaminants in Ground Water." In *Ground Water Monitoring and Remediation*, Spring 1994.
- Rifai, H.S. et al, 1995. "Intrinsic Bioattenuation for Subsurface Restoration." In R. E. Hinchee, J. T. Wilson, and D. C. Downey (Eds.), *Intrinsic Bioremediation*, pp. 1 - 25. Battelle Press, Columbus, OH.
- Wiedemeier, T.H., 1995. "Patterns of Intrinsic Bioremediation at Two U.S. Air Force Bases." In R. E. Hinchee, J. T. Wilson, and D. C. Downey (Eds.), *Intrinsic Bioremediation*, pp. 31 - 50. Battelle Press, Columbus, OH.

Table 1
SELECTED PHYSICAL PARAMETERS OF CONTAMINANTS

	Molecular Weight (g/mole)	FOD Coefficient (Days)	Partition Coefficient (Koc) (mL/g)	Solubility (mg/L)	Henry's Constant (H) (H2O/L-air)	Vapor Pressure (20°C) (atm)	Diffusion Coefficient (H2O) (cm²/s)
Benzene	78	720	3.8	1800	0.22	0.125	1.10E-05
Toluene	92	28	135	524	0.26	0.037	9.40E-06
Ethylbenzene	106	228	1290	206	0.32	0.0125	8.50E-06
Xylenes (total)	106	360	240	200	0.29	0.0087	8.50E-06
MTBE	88.15	360	1.15	48000	0.024		8.71E-06

Explanation

g/mole grams per mole
 mL/g milliliters per gram
 mg/L milligrams per liter
 atm atmospheres
 cm²/s square centimeters per second
 MTBE Methyl tertiary butyl ether
 FOD First order decay

Data after Aruntham and Salhotra, 1996.

**Table 2
ELECTRON ACCEPTOR DATA**

Electron Acceptor	Process	Utilization Factor (UF) (1) (g/g)	Redox Potential (2) (mV)	Chemical parameters indicating conducive biodegradation conditions (3) (mg/l)	Metabolic Products	Typical Background Concentrations in Groundwater (4) (mg/L)
Oxygen	Aerobic Respir'n	3.14	+800	DO>1.0	CO ₂ , H ₂ O	1 to 12
Nitrate	Denitrification Nitrate Reduction	4.90	+750	DO<1.0 (for all anaerobic) High nitrate/nitrite (<0.2)	CO ₂ , N ₂ or NO ₂	<1 to 100 (>1 or 2 mg/L is likely due to human activity)
Iron	Iron Reduction	41.10	Intermediate (5)	Fe ²⁺ >1.5 Nitrate<0.2 NH ₃ >1.0	CO ₂ , Fe ²⁺	<1 to 10
Sulfate	Sulfate Reduction	4.60	-220	Nitrate<0.2 Sulfite>0.2 NH ₃ >1.0	CO ₂ , H ₂ S, SO ₃ HS	1 to several hundred (rarely several thousand)
Methane (for water) (6)	Methanogenesis	0.78	-240	Methane>1.0 Sulfate<40 Sulfite>0.2 NH ₃ >1.0	CO ₂ , CH ₄	0 to >1 (7)

Explanation

- DO Dissolved oxygen
- mV millivolts
- g/g grams of electron acceptor reduced per gram of benzene oxidized
- mg/L milligrams per liter
- (1) Calculated for benzene after Wiedemeyer et al, 1995.
- (2) Cookson, 1995
- (3) Values are as a guideline only, after Cookson, 1995.
- (4) Hem, 1985
- (5) Conditions for manganese reduction are slightly more aerobic than those for iron.
Dissolved Mn>0.2 mg/L indicative of Mn reduction.
- (6) Methane is the utilizable indicator of methanogenesis but is an end-product. For methanogenesis, the UF is the ratio of product produced (methane) to benzene degraded.
- (7) Best assessed by wellhead gas measurement.

**Table 3
ANALYTICAL / FIELD MEASUREMENT METHODS**

Analyte	Method	Technique	Sample Container	Sample Preservation	Hold time, approx. price misc.
Oxygen	Field reading	Downhole meter			Provide consistent stirring
Nitrate	Field reading	Downhole meter			
Nitrate	EPA 300 or 352.1	lab	250 mL plastic or glass	4°C	48 hour hold, \$15
Nitrite	EPA 300 or 354.1	lab	250 mL plastic or glass	4°C	48 hour hold, \$25
Nitrate/nitrite	EPA 353.1	Colorimetric	500mL plastic	4°C, H2SO4	14 day hold, \$20
Iron, total	EPA 200.7 or SW 6010	ICP	100mL plastic	4°C, HNO3	unfiltered
Iron, dissolved	EPA 200.7 or SW 6010	ICP	100mL plastic	4°C, HNO3	0.45 micron filter in field
Sulfate	EPA 300 or 375.4	lab	250 mL plastic or glass	4°C	28 day hold, \$20
Sulfide	SW 9030 or EPA 376.1	Titrimetric	250mL glass or plastic	4°C, Zn acetate + NaOH	7 day hold, \$25
Redox	Field reading	Downhole meter			Minimize atm. exposure
pH	Field reading	Downhole meter			
Temperature	Field reading	Downhole meter			
Conductivity	Field reading	Downhole meter			
Total heterotrophs	Plate Count	Proprietary			\$45
Total H ₂ O using bacteria	Plate Count	Proprietary			\$60
Chloride/Sulfate/Nitrate	EPA 300.0	IC	500mL plastic	NA	28 day hold
Hydrogen Sulfide	Gas meter	Purged soil gas sample			
Carbon Dioxide	Gas meter	Purged soil gas sample			
Methane	Gas meter	Purged soil gas sample			
Total Organic Content	EPA 415.1	Oxidation/NDIR	500mL plastic	4°C, H2SO4	28 day hold, \$30
Alkalinity	EPA 310.1	Colorimetric	100mL plastic or glass	4°C	14 day hold, \$16
Hardness, total CaCO ₃	EPA 130.2	lab	250mL glass or plastic	4°C, H2SO4 or HNO3	6 month hold, \$20
Ammonium	EPA 350.3	lab	500mL plastic	4°C, H2SO4	
Phosphorous	EPA 365.1	lab	100ml plastic	4°C, H2SO4	28 day hold