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September 29, 1994

Ms. Juliet Shin
Alameda County Department of
Environmental Health
Hazardous Materials Division
1131 Harbor Bay Parkway, 2nd Floor
Alameda, CA 94502-6577

Re: STID #3014
Shell Service Station
1601 Webster Street
Alameda, California
WA Job #81-0434-104

Dear Ms Shin:

Weiss Associates (WA), on behalf of Shell Oil Company (Shell), is submitting this work plan as you requested in your August 1, 1994 letter to Shell Environmental Engineer Dan Kirk for the above mentioned site (Figure 1). In your letter you discuss our request for sample frequency modification and further cross-gradient assessment of the extent of hydrocarbons in ground water. Presented below are a brief site summary, comments to your letter on sampling modifications and installing an additional well northeast of well MW-2, and our proposed scope of work.

SITE BACKGROUND

1987 Waste Oil Tank Removal: In June 1987, a 550-gallon underground waste oil tank originally installed in 1962 was removed (Figure 2). Blaine Tech Services (BTS) of San Jose, California reported that the tank contained numerous holes and that a hydrocarbon sheen was observed on the water in the excavation.[1] Soil sampled from 9.5 ft depth in the excavation contained 133 parts per million (ppm) petroleum oil and grease (POG), 14 ppm total

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[1] BTS, June 26, 1989, Consultant's letter-report presenting a summary of previously unpublished notes from the 1987 waste oil tank removal at the Shell service station at 1601 Webster Street in Alameda, California, prepared for Shell Oil Company, 19 pages.

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petroleum hydrocarbons (TPH) and 29 ppm 1,1,1-trichloroethane (TCA).[2] A grab water sample collected from the subsurface at about 12.5 ft depth contained 244 ppm POG, 132 ppm TPH, 11 ppm TCA and 59 ppm methylene chloride.

1987 Well Installation: In September 1987, Pacific Environmental Group (PEG) of Santa Clara, California installed ground water monitoring well S-1 (Figure 2) immediately downgradient of the former waste oil tank to assess the extent of hydrocarbons in ground water.[3] Soil from the boring for the well between 3.5 and 15.5 ft depth contained up to 130 ppm POG at about 5 ft depth. No halogenated volatile organic compounds (HVOCs) were detected.

1990 Well Installation: In April 1990, WA installed wells MW-1 and MW-2.[4] Up to 32 ppm TPH as gasoline (TPH-G) were detected in the boring for well MW-2, with the highest concentrations detected just below the water table. Unsaturated soil from the two borings contained less than 0.1 ppm benzene, ethylbenzene, toluene and/or xylenes (BETX). No POG or HVOCs were detected in soil from either boring.

1993 Borings and Wells: In October 12 and 22, 1992 and February 19, 1993, WA drilled borings BH-C through BH-J to assess the source and extent of hydrocarbons in soil and ground water. WA also installed well MW-3 at the downgradient property boundary to monitor hydrocarbon concentrations in ground water at this point. The investigation results indicated that hydrocarbons detected in ground water from well MW-2 apparently originated near the former pump islands at the south end of the site. Based on the soil and water samples collected during this investigation and in subsequent quarterly sampling, hydrocarbons are not migrating downgradient of well MW-3 (Figure 2).

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[2] BTS, July 16, 1987, Field Sampling at Shell Station, 1601 Webster Street, Alameda, California, consultant's letter-report prepared for Shell, 3 pages plus attachments.

[3] PEG, October 23, 1987, Consultant's letter-report regarding a well installation at the Shell service station at 1601 Webster Street in Alameda, California, prepared for Gettler-Ryan, Inc., 3 pages plus attachments.

[4] WA, July 6, 1990, Subsurface Investigation at Shell Service Station, 1601 Webster Street, Alameda, California, consultant's report prepared for Shell Oil Company, 17 pages and 3 appendices.

COMMENTS ON REDUCED SAMPLING AND ADDITIONAL WELL INSTALLATION

In your letter dated August 1, 1994 you said ,"due to the fact that ground water samples collected from well MW-1 have identified levels of cis-1,2-dichloroethene (1,2-DCE) exceeding CAL-EPA's Maximum Contaminant Levels in the past, quarterly sampling for chlorinated hydrocarbons must continue for well MW-1". However, based on our review of the analytic result, we found that cis 1,2-DCE has not exceeded it's MCL for the last three years and quarterly monitoring is unwarranted at this time. Therefore, we request that you reconsider our request to sample this well annually.

Also in your letter you requested that an additional monitoring well be installed northeast of well MW-2. We believe this request is not feasible because:

- Drilling in the western sidewalk along Webster Street, State Highway 61, (north-northeast of well MW-2) is too close to the existing well;
- Drilling in the northwest shoulder along Webster Street does not appear to be feasible due to the main gas and water lines in this area;
- Drilling and quarterly sampling of a well in the street is more hazardous than the contaminant we are trying to delineate and we are unlikely to obtain an Encroachment Permit from Caltrans; and
- Drilling across on the northeast side of Webster Street is too far away to accurately determine that if a plume is identified, that Shell is in fact the responsible party.

Therefore, because of the limited locations for an additional ground water monitoring well, Shell and WA are proposing to install a ground water remediation system in well MW-2 instead of installing an additional well. Our scope of work is described below.

SCOPE OF WORK

From the meeting on October 28, 1993 between you, Shell Oil Company and WA, three remedial alternatives were to be considered for the site. One alternative was investigating whether ground water oxygenation is a viable option by sampling the ground water for dissolved oxygen (DO) concentrations. Based on DO concentrations collected during quarterly monitoring, biodegradation is occurring onsite and may be further enhanced by installing a ground water oxygenation system. Therefore, we propose installing a ground water oxygenation system at the site. The scope of work for installing the system is to:

- Obtain any necessary permits;
- Procure and install equipment; and
- Monitor the effectiveness of the system.

GROUND WATER OXYGENATION (GO) SYSTEM

Shell is proposing to perform GO in well MW-2 to increase the availability of oxygen for biodegradation of hydrocarbons present in ground water beneath the site. A low volume of air (maximum of 1.0 cubic feet per minute) will be pumped into the ground water in the well through a diffuser. The flow rate will be sufficiently low to enable all of the air to dissolve in ground water. No off-gases will be generated. The solubility of oxygen in groundwater is temperature dependent. The lowest existing DO concentrations measured in site ground water are 3.2 mg/l in well MW-2. The solubility limit of oxygen at the groundwater temperature of 74 deg F is 8.7mg/L.

Per your request in your August 1st letter, we have included two papers written on the subject of biodegradation. The first paper suggests that the availability of DO is a "dominant control over BTX biodegradation." [5] The second paper states that "Each 1.0 milligram/liter (mg/L) of dissolved oxygen consumed by microbes will destroy approximately 0.29 mg/L of BTEX compounds."[6]

The GO system will consist of a 1/10-hp oil-less air pump operating at a maximum flow rate of 1.0 cfm. The system is planned to be installed approximately 20-feet or 120-feet from the well in a weatherproof box. The air will be pumped to existing monitoring well S-2 through buried tubing. A ceramic air diffuser will be installed approximately ten feet below the ground water surface to increase DO in ground water. The pressure

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[5] Barker, J.F., et al, *Natural Attenuation of Aromatic Hydrocarbons in a Shallow Sand Aquifer,* Ground Water Monitoring Review, Winter 1987.

[6] Wiedmeier, Todd. H., et al., "Proposed Air Force Guidelines for Successfully supporting the Intrinsic Remediation (Natural Attenuation) Option at Fuel Hydrocarbon Contaminated Sites."

will be approximately 5 pounds-per-square-inch (psig) to overcome the static head of the ground water, and the pressure will not exceed the estimated soil over burden pressure of 7.5 psi.

The effectiveness of the system will be evaluated through continued DO monitoring and TPH-G analysis in existing monitoring wells and will be reported to you in our quarterly monitoring reports. Once we obtain your authorization to proceed and we have obtained the permits, we can proceed with installing the system. We are very excited about the applicability of ground water oxygenation at this site and will await your response.

WA trusts that this submittal meets your needs. Please call Joyce Adams at (510) 450-6000 if you have any questions regarding this site or this letter.

Sincerely,
Weiss Associates

Joyce E. Adams

Joyce E. Adams
Senior Staff Geologist

JAMES W. CARMODY
No. EG 1576

James W. Carm

James W. Carmody, CEG
Senior Project Geologist

JEA/JWC:JEA

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cc: Dan Kirk, Shell Oil Company, P.O. Box 4023, Concord, California 94524
Lester Feldman, Regional Water Quality Control Board - San Francisco Bay, 2101 Webster Street, Suite 500, Oakland, California 94612

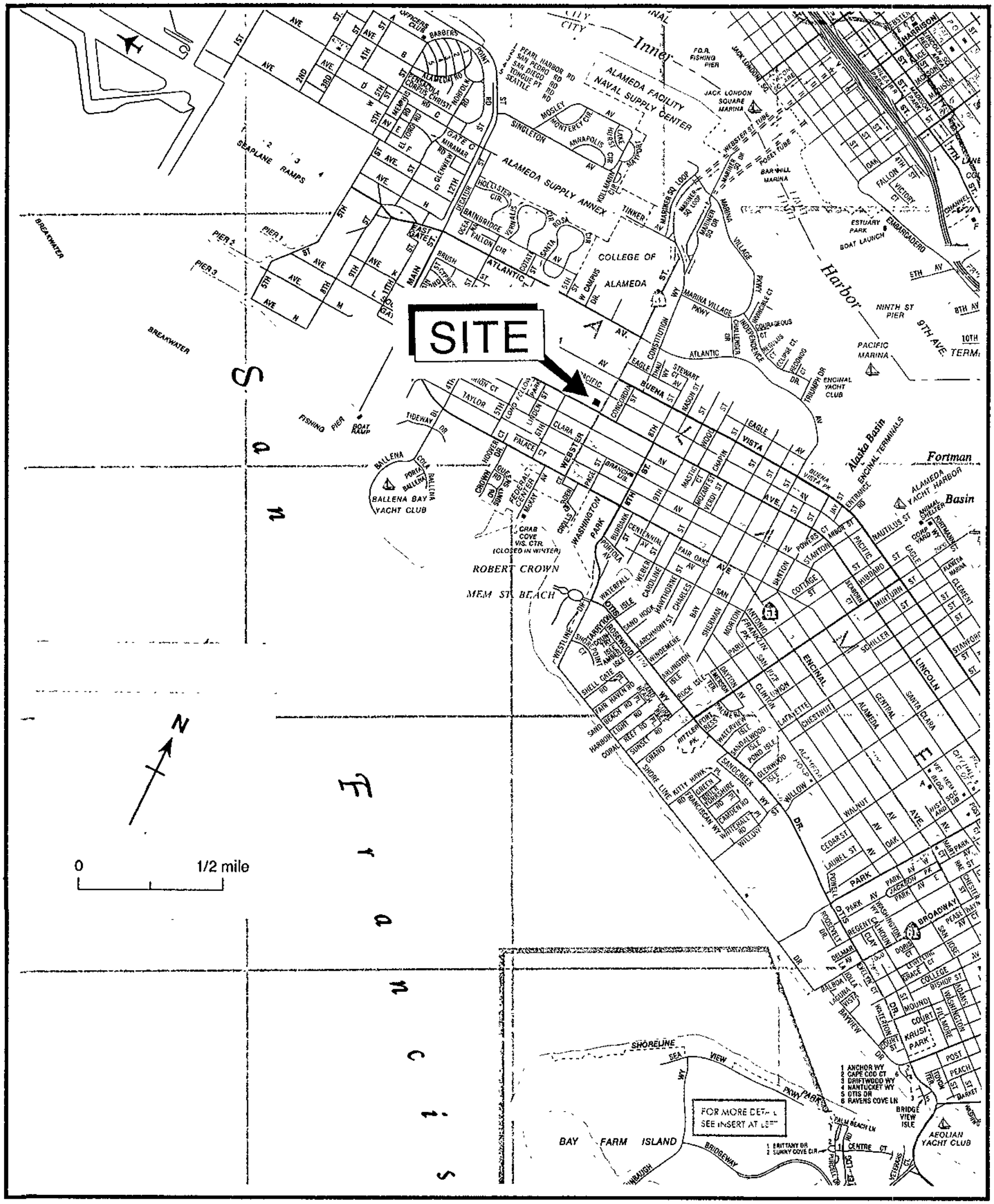

Figure 1. Site Location Map - Shell Service Station, WIC# 204-0072-0403, 1601 Webster Street, Alameda, CA

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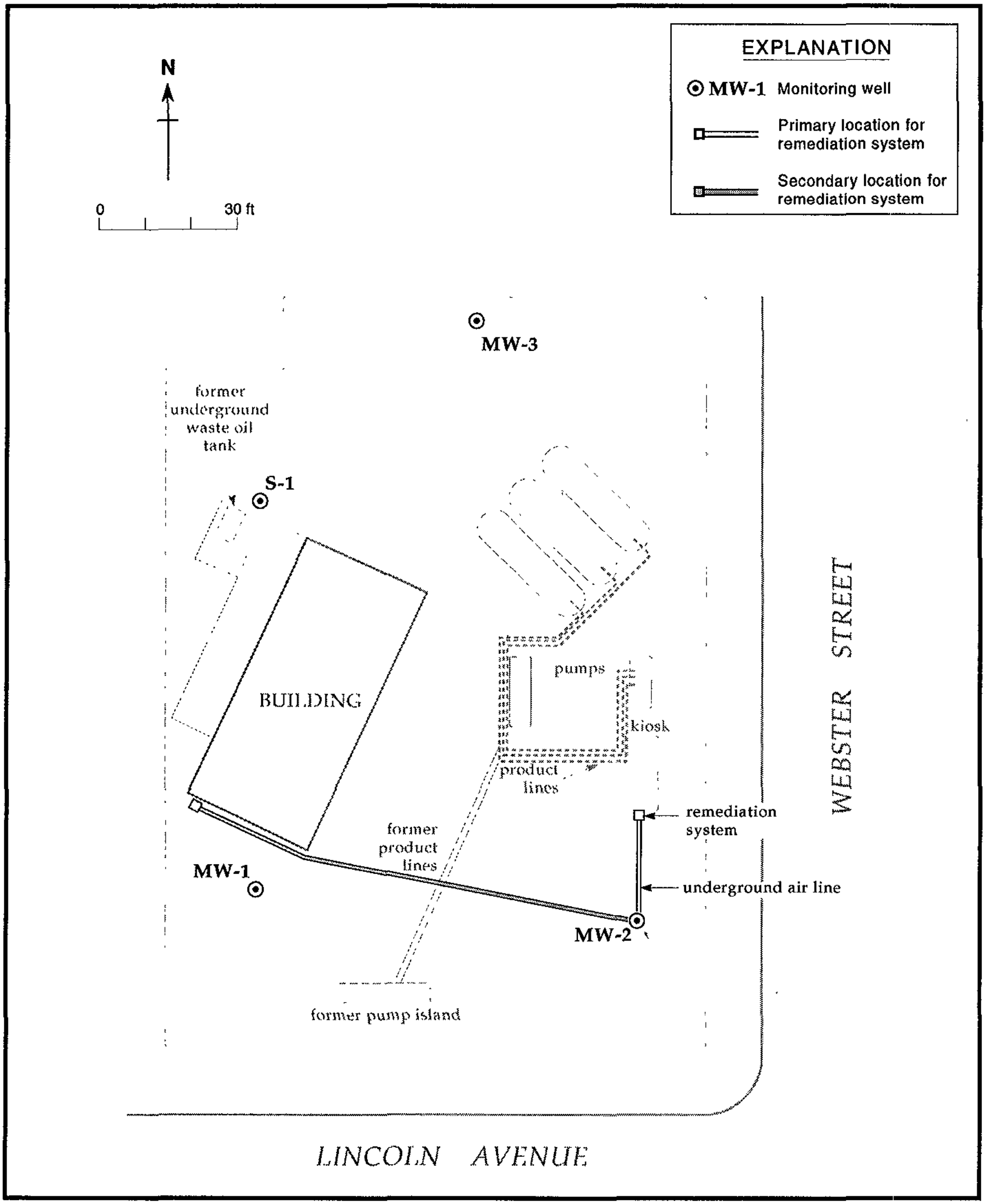

Figure 2. Monitoring Well Locations - Shell Service Station WIC #204-0072-0403, 1601 Webster Street, Alameda, California

Natural Attenuation of Aromatic Hydrocarbons in a Shallow Sand Aquifer

by J.F. Barker, G.C. Patrick and D. Major

Abstract

Inadvertent release of petroleum products such as gasoline into the subsurface can initiate ground water contamination, particularly by the toxic, water-soluble and mobile gasoline components: benzene, toluene and xylenes (BTX). This study was undertaken to examine the processes controlling the rate of movement and the persistence of dissolved BTX in ground water in a shallow, unconfined sand aquifer.

Water containing about 7.6 mg/L total BTX was introduced below the water table and the migration of contaminants through a sandy aquifer was monitored using a dense sampling network. BTX components migrated slightly slower than the ground water due to sorptive retardation. Essentially all the injected mass of BTX was lost within 434 days due to biodegradation. Rates of mass loss were similar for all monoaromatics; benzene was the only component to persist beyond 270 days. Laboratory biodegradation experiments produced similar rates, even when the initial BTX concentration varied.

A dominant control over BTX biodegradation was the availability of dissolved oxygen. BTX persisted at the field site in layers low in dissolved oxygen. Decreasing mass loss rates over time observed in the field experiment are not likely due to first-order degradation rates, but rather to the persistence of small fractions of BTX mass in anoxic layers.

Introduction

Although contamination by petroleum products commonly occurs at or above the water table, many components are sufficiently soluble in water to form a plume of contamination beneath the water table. Removal of the "floating" non-aqueous phase liquids by hydraulic means always leaves a residual fraction whose water-soluble components continue to contaminate subsurface waters.

In instances of gasoline spills, the monoaromatic hydrocarbons have relatively high pollution potentials based on their significant concentrations in gasoline, high aqueous solubilities and estimated toxicity or carcinogenicity. The monoaromatics of particular concern are benzene, toluene and the three xylene isomers, m-, p-, and o-xylene (collectively termed BTX). It is likely that gasoline spills will have the most serious and immediate impact upon highly permeable, shallow, water-table aquifers, which are also favored for private and municipal drinking water supplies. Thus, our research has concentrated upon the behavior of BTX in shallow sand aquifers.

The rate at which an organic contaminant migrates in ground water is determined by the processes of advection, dispersion, sorption, chemical and biological transformations, and perhaps by volatilization at the water table. All processes except advection can bring about lower aqueous concentrations and therefore can contribute to natural attenuation.

In response to the need for field evaluation of the transport and fate of these monoaromatics in shallow aquifers, a natural-gradient injection experiment was undertaken in 1984-85 at Canada Forces' Base Borden, Ontario. Such experiments provide the input control and sampling detail characteristic of laboratory studies and the realistic, natural hydrogeological and geochemical field setting. Similar studies had already been conducted in this unconfined sand aquifer. Sudicky et al. (1983) investigated dispersion of unreactive chloride; Sutton and Barker (1985) evaluated the transport of phenol, chlorophenol, phthalate and butyric acid; Mackay et al. (1983) reported on halogenated hydrocarbon migration.

This article emphasizes the biotransformation of BTX observed in the most recent experiment involving BTX. Advection and retardation aspects were emphasized by Patrick and Barker (1985), and Patrick et al. (1985).

Laboratory Biotransformation Experiments

The microbially mediated rate of BTX transformation was evaluated in three laboratory experiments. Experiment A was conducted using dissolved oxygen and BTX concentrations similar to the field injection solution and the natural microbiological community present in aquifer cores and ground water from the Borden site. A subsequent experiment (experiment B) also incorporated ranges of BTX and dissolved oxygen concentrations. A third experiment (experiment C) examined the biotransformation of BTX under anaerobic conditions. These experiments provided insight into the behavior of BTX in the field test, and identified potentially toxic intermediate breakdown products, which were monitored in the field. These experiments also provided predictions of biotransformation-rates that could be tested against the results of the field test.

Ground water was obtained aseptically from the same well that provided the injection water for the field experiment. Aquifer material was taken aseptically from a saturated core obtained at a depth of 1.9 to 2.1 m from an uncontaminated area of the aquifer near the injection well.

The initial experiment (A) utilized this ground water spiked with a methanol solution containing the monoaromatics. Initial concentrations were about 2.6 mg/L benzene, 2.5 mg/L toluene, 1.1 mg/L m-xylene and 20 mg/L o-xylene. Experiment B used similar ground water, either unaerated (2 to 3 mg O_2/L) or aerated (7 to 8 mg O_2/L), spiked with various amounts of a methanol stock solution containing BTX in the proportions injected at the field site. This produced solutions with total BTX ranging from 0.4 mg/L to 15 mg/L. Experiment C utilized 25g of sand and autoclaved, N_2-purged ground water to produce a very low initial dissolved oxygen concentration (less than 0.5 mg/L). The initial concentrations of benzene, toluene and o–, m-xylenes were 3 mg/L each in experiment C. The solutions were metered into 60 cm^3 hypovials already containing core material; the hypovials were then quickly capped using Teflon®-faced septa. Controls in which no significant microbial activity occurs for experiments A and B were obtained by injecting 0.4 cm^3 of a 10 percent sodium azide solution into some hypovials prior to capping. Controls for experiment C were prepared by autoclaving both ground water and soil. Each hypovial is assumed to be representative of the field situation and can be termed a microcosm (Pritchard and Bourquin 1984). The hypovials were incubated at 10 C, the average ground water temperature at Borden, for 0 to 80 days, either in the laboratory atmosphere (experiments A and B) or in a N_2-purged chamber (experiment C). At various times two or three hypovials, both unpoisoned and controls, were analyzed for BTX concentrations. Dissolved oxygen was determined in one or two other hypovials. Previously described gas chromatographic techniques and a modified Winkler titration technique for dissolved oxygen (D.O.) were employed for experiments A and B, while High Performance Liquid Chromatography using a concentrator column was employed for experiment C (Patrick et al. 1986).

In addition, one-liter microcosms, similar to those of experiment A, with total BTX of about 6500 μg/L and dissolved oxygen of about 2 mg/L, were incubated for up to 77 days and analyzed for possible acidic biotransformation products. The acidified aqueous phase was extracted with 200 cm^3 dichloromethane in a continuous liquid-liquid extractor, the solvent dried on an anhydrous sodium sulfate column and concentrated to 1 cm^3 with a Kuderna-Danish apparatus. An aliquot was analyzed by GC/MS (HP 5970 system). An aqueous standard was also processed in this manner, which permitted semi-quantitation of selected acidic organics assuming similar extraction efficiencies and mass-selective-detector responses were obtained. Although not all peaks in the chromatogram were identified by GC/MS, six significant compounds were found to occur in many samples: phenol, 2 methyl phenol isomers, 2 dimethyl phenol isomers, and 2-methyl benzoic acid (o-toluic acid).

The Field Injection Experiment

About 1800 L of ground water was obtained from the site and spiked to give average concentrations of 2360 μg/L benzene, 1750 μg/L toluene, 1080 μg/L p-xylene, 1090 μg/L m-xylene, 1290 μg/L o-xylene and 1280 mg/L chloride. The dissolved oxygen concentration was about 1 mg/L. This ground water was injected into the uncontaminated, unconfined sand aquifer via a single well screened at 1.4 to 2.0 m below the water table. Shortly after injection the ground water mound dissipated and the slug migrated under the natural ground water velocity of about 9 cm/d through a dense network of multilevel piezometers, most of which were installed for a previous experiment (Mackay et al. 1983). Piezometers were located on a 1 to 4 m grid and had sampling ports every 20 cm in depth (Figures 6 and 9).

Samples encompassing the total slug were collected three days after injection and at approximately monthly intervals thereafter for four months. Partial coverage was obtained about 270 days after injection and repeated sampling of the residual benzene plume was conducted 374 to 434 days after injection. In total, about 3000 samples have been collected and analyzed. Water samples for BTX analyses were retrieved in full, 19 mL hypovials using a sampling manifold system described by Mackay et al. (1983). Except for the first "snapshot" when no preservative was added, samples were preserved with 0.1 mL of 10 percent sodium azide, stored at 4 C and analyzed within 14 days. Chloride was determined colorimetrically.

BTX was determined by gas chromatography following a micro-solvent extraction described in detail by Patrick et al. (1985). The percent relative standard deviation for both laboratory standards (approximately 85 μg/L of each organic) and field replicates, excepting the first snapshot, was about 5 percent for each organic and chloride. The first snapshot samples were not preserved and biodegradation produced relative standard deviations from 7 percent to 81 percent. Biases of the laboratory standards from the true values were generally within 5 percent. A laboratory test of the peristaltic pump-manifold sampling technique indicated no significant bias was introduced by the sampling protocol (Patrick 1986).

Results — Laboratory Experiments

The temporal changes in BTX and dissolved oxygen concentrations in microcosms closely representing the field injection situation (experiment A) are shown in Figure 1. Organic concentrations shown are the average of analyses from three hypovials. Controls showed little variation over time. The BTX mass loss in active microcosms is dramatic — concentrations decreased to below detection limits (1 to 2 ppb) within 78 days. An initial lag phase when little mass loss occurred was evident (2 to 10 days), probably reflecting an acclimatization period for the microbial population.

The dissolved oxygen concentration generally increased from an initial 1 mg/L to a maximum of 3.3 mg/L and then generally declined. This was not expected — the initial dissolved oxygen should have been consumed during the aerobic biotransformation of BTX. This suggests that oxygen must have been leaking into the microcosms. A preliminary experiment has verified that the hypovial microcosms are penetrated by atmospheric oxygen, but the rate is yet to be established. The oxygen required for the aerobic biotransformation of BTX is considerable. Consider the mass-balanced equation for toluene transformation:

$$C_7H_8 + 9\ O_2 \rightarrow 7\ CO_2 + 4\ H_2O$$

For each 1 mg/L toluene (1.09×10^{-5} moles/1), 3.1 mg/L oxygen gas (9.8×10^{-5} moles/1 O_2) are required. In fact, the total biological oxygen demand for BTX biotransformation in experiment A is 23.2 mg/L O_2. This greatly exceeds the oxygen initially present and so must be supplied by diffusion or leakage into the hypovial. Although other oxidants could have been used, nitrate levels in the ground water are less than 0.05 mg/L (as NO_3^-) and sulfate, although present at about 130 mg/L (as SO_4^{2-}), does not appear to have been significantly reduced because no H_2S odor was found in acidified samples.

The decline of BTX masses or concentration was best represented as a zero-order reaction in which the decline is linear over time (Figure 1), indicating no dependence upon substrate (BTX) concentration. Zero-order biotransformation rates range from about 33 µg/L/d for benzene to about 37 µg/L/d for o-xylene. Most biotransformation processes are considered first-order, pseudo first-order or higher order (Lyman et al. 1982, Schmidt et al. 1985). While it is certainly possible to fit first-order kinetics to some of the data, such a fit is rarely better than the zero-order fit when all experiments are considered. It is probable that the observed rates of BTX loss are controlled, not by enzymatic processes, but by the rate of oxygen diffusion or leakage into the hypovials. The dissolved oxygen was never found to be less than 1 mg/L (Figure 1) and so it is likely that oxygen was always available.

In the 1 L microcosms, phenolic and acidic breakdown products were detected. The semiquantitative results are shown in Figure 2. The appearance of phenol is consistent with the common observation of phenol in gasoline-contaminated ground water. The classical microbial breakdown scheme for monoaromatics also includes catechols and cresols (methyl phenol), benzoic and various hydroxybenzoic acids and benzaldehyde as the benzene ring is prepared for fission and then a variety of easily metabolized compounds produced from ring fission (Gibson 1978). Methyl phenols or cresols and 2-methyl benzoic acid (o-toluic acid) were found in these experiments, but catechols and other products were not identified.

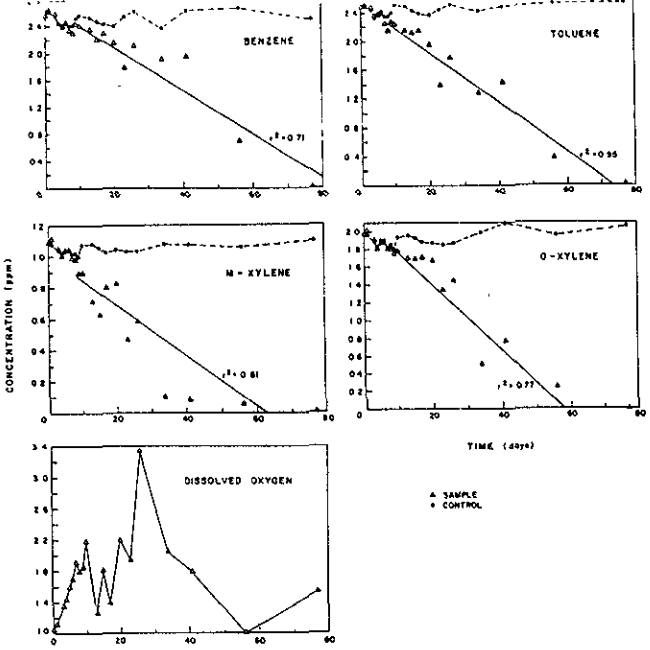

Figure 1. Observed concentrations in microcosms and controls — experiment A

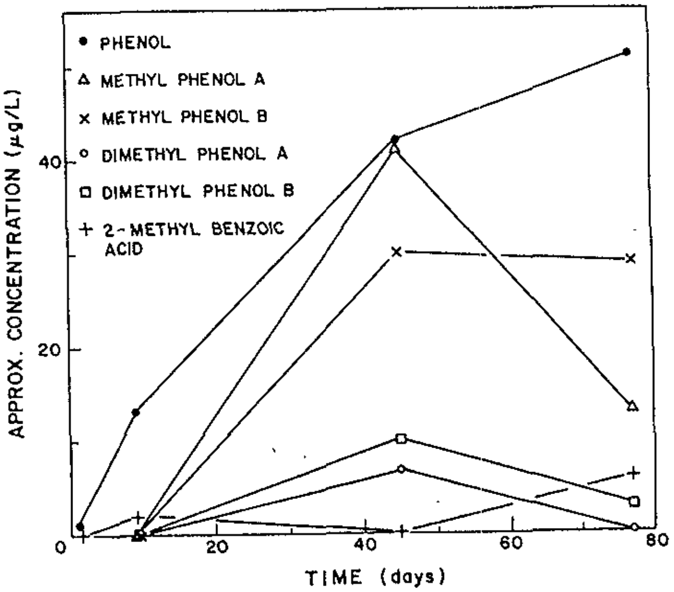

Figure 2. BTX breakdown products observed in large volume microcosms — experiment A

For experiment B, where the initial dissolved organic and BTX concentrations were varied, zero-order kinetics adequately represented most of the concentration decline curves (Figures 3 and 4).

The zero-order mass loss rates of all organics are similar, no matter what the initial BTX concentration. The individual zero-order mass loss rates are about 43 µg/L/d for each organic when the total initial BTX concentration is 5330 µg/L (Figure 3). The rates vary

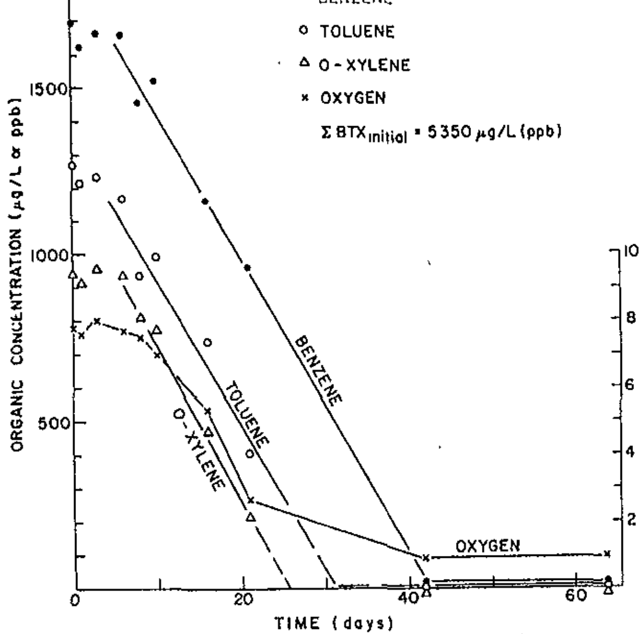

Figure 3. Observed concentrations of BTX and oxygen in microcosms —experiment B, initial BTX of 5350 µg/L

from about 27 to 52 when the total initial BTX concentration is 15.1 mg/L (Figure 4), with benzene exhibiting the slowest biotransformation. Although benzene is considered the most recalcitrant monoaromatic (Gibson 1978), it was biotransformed almost as rapidly as the others.

The similarity of biotransformation rates for all monoaromatics in experiments A and B indicates that the structural characteristics of the individual members are not a dominant control. This could indicate that the ring-cleavage reaction in the biotransformation pathway is the rate-controlling step and that the position of methyl groups on the ring is of minor importance. On the other hand, similar rates would also be observed if oxygen supply was the limiting factor with the biotransformation kinetics being relatively fast for all monoaromatics when oxygen was available.

The temporal changes of benzene and toluene over the 60 days of experiment C are shown in Figure 5. The initial decline in active hypovials beyond the decline in the controls is attributed to aerobic biotransformation. BTX loss was only about 20 percent because oxygen entry into the hypovials was prevented by incubation in an N_2 atmosphere. Typically, after this initial removal, no significant decrease in BTX concentrations occurred, so the effective rate of anaerobic biotransformation is taken as zero for the Borden sand. Although anaerobic biotransformation of monoaromatics in some ground water systems has been proposed (Barker et al. 1986, for example), rates appear to be extremely slow in the Borden Aquifer. Current studies indicate that simply the addition of an oxidant (NO_3 in this case), enhances BTX biotransformation. This suggests that only the oxidant is limiting biotransformation in experiment C.

Results of the Field Experiment

Aspects of advection, dispersion and sorptive retardation of BTX and Cl^- plumes are presented elsewhere (Patrick 1986, Patrick et al. 1985). This discussion will focus on the observed BTX mass losses.

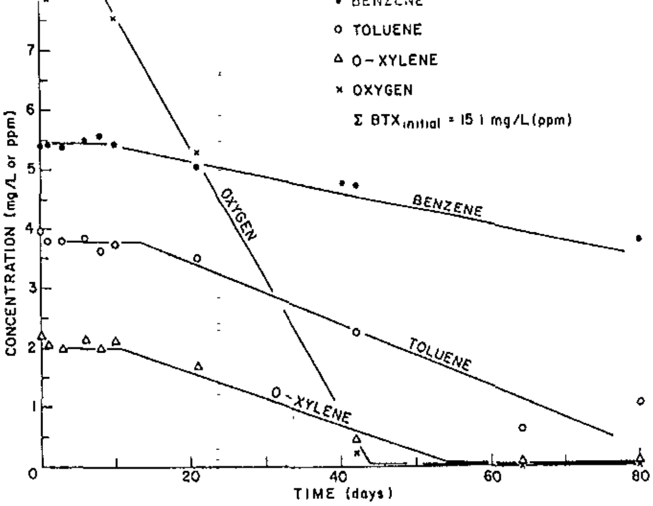

Figure 4. Observed concentrations of BTX and oxygen in microcosms —experiment B, initial BTX of 15.1 mg/L

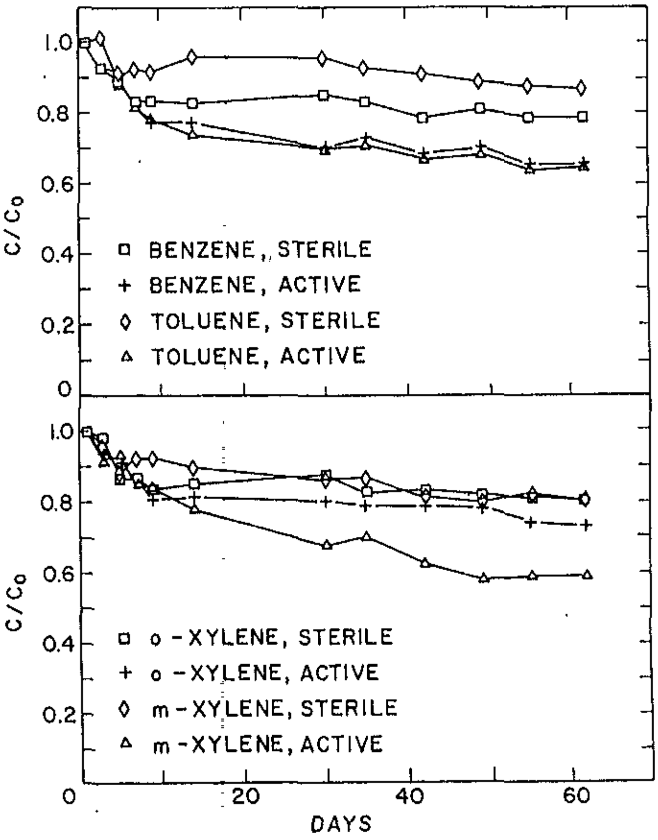

Figure 5. Changing concentrations of benzene, toluene, o- and m-xylene relative to the initial concentration. (C/C_0) of 3 mg/L for sterile and active microcosms under anaerobic conditions.

The horizontal aspect of the plume, produced by using vertically integrated concentrations of each constituent at each multilevel piezometer, displays the plume behavior (Figure 6). These contour plots were produced using the Surface II routines (Samson 1978) by interpolating the averaged concentration data to a regular dense grid. Details are provided in Patrick (1986).

Chloride behaves conservatively and illustrates only

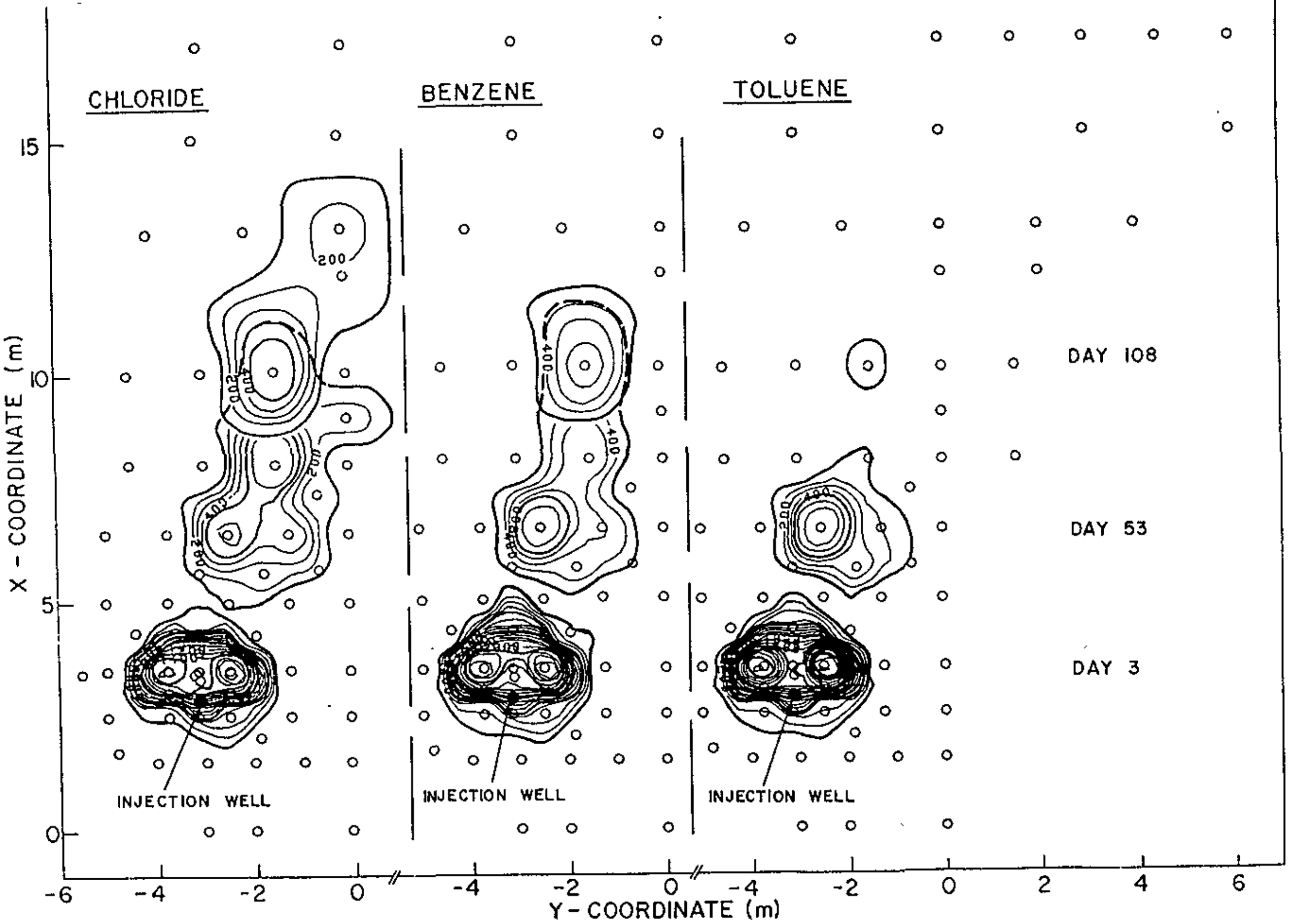

Figure 6. Contour plots of vertically integrated concentrations. Contour units are mg.m/L^{-1} for chloride and μg.m/L^{-1} for the organics.

the effects of advection and dispersion. Lateral spreading is small compared to longitudinal spreading (Figure 6), indicating much greater longitudinal dispersion than lateral dispersion in the Borden sand aquifer. Although the organics follow the same trajectory, their centers of mass move more slowly than that of chloride. This sorptive retardation is consistent with hydrophobic sorption theory (Karickhoff 1984) and is consistent with theoretical and laboratory predictions made by Ptacek et al. (in press). It is noteworthy that the sorptive retardation was not apparently affected by the mass losses.

The apparent decline in total mass of organics and chloride are shown in Figure 7. Mass calculations have been shown to underestimate the actual mass present in this situation (Patrick 1986). Calculated masses for the organics are probably underestimated slightly at day 3, and by up to 15 percent of the reported value by day 53. The chloride mass remains reasonably constant over time but the organics suffer almost complete mass loss within 410 days.

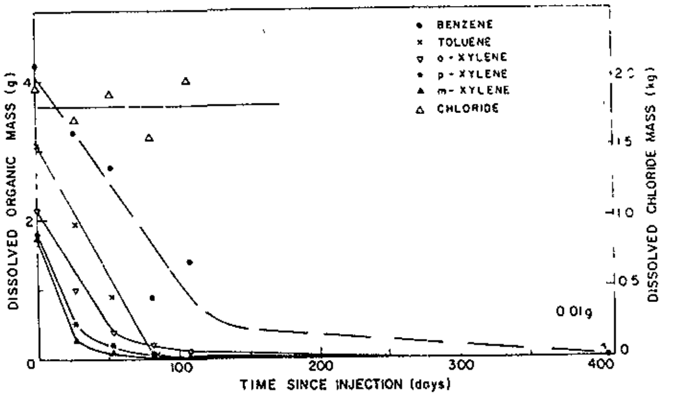

Figure 7. Masses of chloride and organics remaining in the ground water

Chloride was not determined on samples collected after day 108. Sampling on days 263, 271 and 286 revealed that only benzene persisted. Unfortunately, the density of sampling was insufficient to even estimate the mass of benzene present on these days. Sampling over days 374 to 426, revealed only occasional occurrences of detectable (>2 ppb) benzene. No benzene was found on day 434. The mass of benzene remaining at day 405 was estimated by projecting the observed benzene occurrences on days 374 to 426 to their position on day 405 by assuming a constant gradient and a benzene ground water velocity of 7 cm/d, the average over the initial 200 days of the experiment. Although far less reliable than data from earlier "snapshots," the estimated benzene mass at day 405 is 0.01 g and is inconsistent with a linear extrapolation of earlier benzene data (Figure 7). Given the lack of rapid abiological reactions, the lack of evidence for irreversible sorption and the results of the laboratory experiments, these mass losses are attributed to biotransformation.

The initial mass-loss rates for benzene, toluene and perhaps the xylenes appear to be linear. However, the mass-losses become non-linear: xylenes after 28 days and toluene and benzene after 81 and 108 days, respectively

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PROPOSED AIR FORCE GUIDELINES FOR SUCCESSFULLY SUPPORTING THE INTRINSIC REMEDIATION (NATURAL ATTENUATION) OPTION AT FUEL HYDROCARBON CONTAMINATED SITES[*]

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ABSTRACT

Based on work performed at 6 United States Air Force Bases and 35 industrial sites across the United States, a methodology and protocol for supporting and documenting intrinsic remediation of fuel hydrocarbons was developed. Intrinsic remediation, also known as natural attenuation, results in a reduction in the total contaminant mass in the subsurface through naturally occurring, *in situ* attenuation mechanisms, and results from both destructive and non-destructive processes. Non-destructive attenuation mechanisms include dilution (through recharge and dispersion) and sorption. Recharge generally results in an increased supply of dissolved oxygen to the plume. Dispersion causes the plume to spread out into more oxygenated areas of the aquifer. Sorption results in retardation of a compound so that oxygen and other electron acceptors flowing by advective processes can sweep across the plume. Destructive attenuation of fuel hydrocarbons is dominantly the result of biological processes. Biological attenuation mechanisms include aerobic and anaerobic biodegradation of contaminants by indigenous microorganisms. Abiotic processes such as hydrolysis generally are not important attenuation mechanisms for fuel hydrocarbon degradation.

This paper describes the activities and analytical protocol which should be implemented to scientifically support the intrinsic remediation option. Also discussed are the geochemical parameters indicative of aerobic and anaerobic biodegradation, the numerical fate and transport modeling of intrinsic remediation, and the documentation necessary to successfully support this remedial option.

1.0 INTRODUCTION

This document presents the technical protocol to be used for data collection, ground water modeling, and risk analysis in support of intrinsic remediation (natural attenuation) with long-term monitoring for restoration of petroleum hydrocarbon contaminated ground water. Intrinsic remediation is achieved when naturally occurring attenuation mechanisms, such as biodegradation (aerobic and anaerobic), bring about a reduction in the total mass of a contaminant dissolved in ground water. In some cases, it can be shown that intrinsic remediation will reduce dissolved-phase contaminant concentrations to below regulatory maximum contaminant levels (MCLs) before the contaminant plume reaches potential receptors, even if little or no source removal/reduction takes place. In situations where it cannot be shown that intrinsic remediation will reduce contaminant concentrations to below regulatory MCLs, less stringent cleanup goals may be implemented if it can be demonstrated that intrinsic remediation will result in a continual reduction in contaminant concentrations over a given period such that

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[*] Although this document was prepared in cooperation with United States Environmental Protection Agency (EPA) researchers, it is not an EPA document and does not represent EPA guidance.

calculated risk values are reduced. Advantages of intrinsic remediation include: 1) during intrinsic remediation, contaminants are transformed to innocuous byproducts, not just transferred to another phase or location within the environment; 2) current pump-and-treat technologies are slow, energy intensive, and generally are not capable of removing all contamination from the aquifer; 3) current remedial technologies can pose greater risk to potential receptors than intrinsic remediation because contaminants may be transferred into the atmosphere during remediation activities; and 4) intrinsic remediation is less costly than conventional remedial technologies.

This document describes intrinsic remediation processes, site characterization activities which may be performed to support the intrinsic remediation option, intrinsic remediation modeling using numerical fate and transport models such as Bioplume II®, and the post-modeling activities which should be completed to ensure successful support and verification of the intrinsic remediation option. The objective of the work described herein is to support the intrinsic remediation option at sites where naturally occurring subsurface attenuation processes are reducing dissolved-phase fuel hydrocarbon concentrations to acceptable levels. A recent comment made by a member of the regulatory community sums up what must be done to successfully implement intrinsic remediation.

> *A regulator looks for the data necessary to determine that a proposed treatment technology, if properly installed and operated, will reduce the contaminant concentrations in the soil and water to legally mandated limits. In this sense the use of biological treatment systems calls for the same level of investigation, demonstration of effectiveness, and monitoring as any conventional* [remediation] *system* (National Research Council, 1993).

To support implementation of intrinsic remediation, the property owner must scientifically demonstrate that degradation of site contaminants is occurring at rates sufficient to be protective of human health and the environment. This document presents a technical course of action which, if followed, should support intrinsic remediation at sites where natural processes are protective of the environmental quality of ground water.

Intrinsic remediation results from the integration of several subsurface attenuation mechanisms which may be classified as either destructive or nondestructive. Destructive processes include biodegradation, abiotic oxidation, and hydrolysis. Nondestructive attenuation mechanisms include sorption, dilution (caused by dispersion and infiltration), and volatilization.

Collection of all the necessary data during the site characterization phase of the remedial investigation is the most important step in the documentation of intrinsic remediation. At a minimum, site characterization activities should provide data on the location and extent of contaminant sources (oily-phase hydrocarbons present in both the free and residual phases); the location, extent, and concentration of dissolved-phase contamination; ground water geochemical data; geologic information on the type and distribution of subsurface materials; and hydrogeologic parameters such as hydraulic conductivity, hydraulic gradients, and potential contaminant migration pathways to human or ecological receptors.

After site characterization is complete, the data collected during the investigation should be used to model the fate and transport of contaminants in the subsurface so that predictions of the future extent and concentration of the dissolved-phase plume can be made. Several models, including Bioplume II® and BIO1D®, have been used successfully to model dissolved-phase contaminant transport and attenuation. Additionally, a new version of the Bioplume model, Bioplume III is under development. The intrinsic remediation modeling effort has three primary objectives: 1) to predict the future extent and concentration of a dissolved-phase contaminant plume by modeling the combined effects of advection, dispersion, sorption, and biodegradation; 2) to assess the possible risk to potential downgradient receptors; and 3) to provide technical support for the natural attenuation remedial option at post-modeling regulatory negotiations.

Upon completion of the fate and transport modeling effort, model predictions can be used in a risk analysis. The risk analysis phase of the intrinsic remediation investigation allows the proponent to attempt to show that potential exposure pathways will not be completed. If it can be shown that intrinsic remediation is sufficiently active to mitigate risks to potential receptors, the proponent of intrinsic remediation has a reasonable basis for negotiating this option with regulators.

The material presented herein was prepared through the joint effort of the Air Force Center for Environmental Excellence (AFCEE), the Bioremediation Research Team at the United States Environmental Protection Agency

Robert S. Kerr Research Laboratory (RSKERL) in Ada, Oklahoma, and Engineering-Science, Inc. (ES), to facilitate implementation of intrinsic remediation at fuel hydrocarbon contaminated sites owned by the United States Air Force. This document contains three sections, including this introduction. Section 2 presents the protocol to be used to obtain scientific data to support the intrinsic remediation option. Section 3 presents the references used in preparing this document.

2.0 PROTOCOL FOR IMPLEMENTING INTRINSIC REMEDIATION

The primary objective of the intrinsic remediation investigation is to show that natural processes of contaminant degradation will reduce contaminant concentrations to below regulatory standards before potential exposure pathways are completed. This requires that a projection of the potential extent and concentration of the contaminant plume be made based on historical variations in, and the current extent and concentration of, the contaminant plume as well as the measured rates of contaminant attenuation. Because of the inherent uncertainty associated with such predictions, it is the responsibility of the proponent of intrinsic remediation to provide sufficient evidence to demonstrate that the mechanisms of intrinsic remediation will reduce contaminant concentrations to acceptable levels before potential receptors are reached. This requires the use of conservative input parameters and numerous sensitivity analyses so that all plausible contaminant migration scenarios are considered. When possible, both historical data and modeling should be used to generate information that collectively and consistently supports the natural reduction and removal of the dissolved-phase contaminant plume. This section describes the steps which should be taken to gather the site-specific data necessary to predict the future extent of a contaminant plume and to successfully support the intrinsic remediation investigation.

Predicting the future extent of a contaminant plume requires the quantification of ground water flow and solute transport and transformation processes, including rates of natural attenuation. Quantification of contaminant migration and attenuation rates, and successful implementation of the intrinsic remediation option, require completion of the following steps, each of which is discussed in the following sections and outlined in Figure 1:

1) Review existing site data;
2) Develop preliminary conceptual model and assess potential significance of intrinsic remediation;
3) Perform site characterization in support of intrinsic remediation;
4) Refine conceptual model based on site characterization data, complete pre-modeling calculations, and document indicators of intrinsic remediation;
5) Model intrinsic remediation using numerical fate and transport models which allow incorporation of a biodegradation term (e.g., Bioplume II®, Bioplume III, or BIO1D®);
6) Conduct a risk analysis to determine if unacceptable risk to potential receptors exists;
7) Prepare long-term monitoring plan; and
8) Present findings to regulatory agencies and obtain approval for the intrinsic remediation with long-term monitoring option.

2.1 REVIEW EXISTING SITE DATA

The first step in the intrinsic remediation investigation is to review existing site-specific data to determine if intrinsic remediation is a viable remedial option. A thorough review of existing data also allows development of a preliminary conceptual model. The preliminary conceptual model will help identify any shortcomings in the data and will allow additional data collection points to be placed in the most scientifically advantageous and cost-effective manner possible.

When available, information to be obtained during data review includes:

- Soil and ground water quality data:
  - Three-dimensional distribution of residual-, free-, and dissolved-phase contaminants. The distribution of residual- and free-phase contaminants will be used to define the dissolved-phase plume source area.
  - Ground water and soil geochemical data.

  - Historical water quality data showing variations in contaminant concentrations through time.
  - Chemical and physical characteristics of the contaminants.
- Geologic and hydrogeologic data:
  - Lithology and stratigraphic relationships.
  - Grain-size distribution (sand vs. silt vs. clay).
  - Aquifer hydraulic conductivity.
  - Ground water flow gradients and potentiometric surface maps (over several seasons, if possible).
  - Preferential flow pathways.
  - Interactions between ground water and surface water.
- Location of potential receptors:
  - Ground water well locations.
  - Ground water discharge points downgradient of site.

In some cases, little or no site-specific data will be available. If this is the case, and if it can be shown that intrinsic remediation is a potential remedial option (Section 2.2), all future site characterization activities should be geared toward collecting the data necessary to support this remedial alternative. The additional costs incurred by such an investigation are greatly outweighed by the cost savings which will be realized if intrinsic remediation is selected as an alternative to active remediation. Even if not selected, many of the data collected in support of intrinsic remediation can be used to design and support more proactive remedial measures.

2.2 DEVELOP PRELIMINARY CONCEPTUAL MODEL AND ASSESS POTENTIAL FOR INTRINSIC REMEDIATION

After reviewing existing site characterization data, a conceptual model should be developed, and a preliminary assessment of the potential for intrinsic remediation should be made. The conceptual model is a three-dimensional representation of the ground water flow and solute transport system based on available geological, hydrological, climatological, and analytical data for the site. After development, the conceptual model can be used to determine optimal placement of additional data collection points as necessary to aid in the intrinsic remediation investigation and to develop the numerical ground water flow and solute transport model.

Successful conceptual model development involves:

- Definition of the problem to be solved (generally the unknown nature and extent of existing and future contamination).
- Integration of available data, including:
  - Local geologic and topographic maps,
  - Hydraulic data,
  - Site stratigraphy, and
  - Contaminant concentration and distribution data (isopleth and isopach maps).
- Design of the conceptual model.
- Selection of a numerical ground water model.
- Determination of additional data requirements, including:
  - Borehole locations and monitoring well spacing,
  - An approved sampling and analysis plan, and
  - Any data requirements listed in Section 2.1 which have not been adequately characterized.

After conceptual model development, an assessment of the potential for intrinsic remediation must be made. A stated previously, existing data can be useful in determining if intrinsic remediation will be sufficient to prevent dissolved-phase contaminant plume from completing exposure pathways to potential downgradient receptors (o from reaching a predetermined point of compliance located upgradient of potential receptors, such as monito wells located along a property boundary) in concentrations above applicable regulatory guidelines. Determining likelihood of pathway completion or predicting contaminant concentrations impacting a receptor if an expos pathway is completed, are the ultimate objectives of the intrinsic remediation investigation. This is achieved estimating the migration and future extent of the plume based on contaminant properties, aquifer properties, gro water velocity, and the location of the plume and contaminant source relative to the potential receptor (i.e.

distance between the leading edge of the plume and the potential receptor). Another important factor deserving consideration is the biodegradability of the contaminant(s) of interest.

If intrinsic remediation is a significant factor in contaminant reduction, then site characterization activities in support of this remedial option should be performed. If exposure pathways have already been completed and contaminants pose an unacceptable risk, or if such completion is imminent, then more active remedial measures should be considered. However, the collection of data in support of intrinsic remediation can be integrated into a comprehensive remedial plan and may help reduce the cost and duration of more active remedial measures such as intensive source removal operations or pump-and-treat technologies.

2.3 PERFORM SITE CHARACTERIZATION IN SUPPORT OF INTRINSIC REMEDIATION

Detailed site characterization is the single-most important consideration in the documentation of intrinsic remediation potential at a site. As discussed in Section 2.1, review of existing site characterization data is particularly useful before initiating site characterization activities. Such review will allow identification of data gaps and guide the most effective placement of additional data collection points.

There are two goals during the site characterization phase of the intrinsic remediation investigation. The first goal is to demonstrate that natural mechanisms of contaminant attenuation are occurring at rates sufficient to protect human health and the environment. The second goal is to provide sufficient site-specific data to allow prediction of the future extent and concentration of a contaminant plume through numerical ground water modeling. Because the burden of proof for intrinsic remediation is on the proponent, very detailed site-specific characterization is required to achieve these goals and to support this remedial option. Adequate site characterization in support of intrinsic remediation requires that the following site-specific parameters be determined:

- Extent and type of soil and ground water contamination.
- Location and extent of contaminant source area(s) (i.e., areas containing free- or residual-phase product).
- The potential for a continuing source due to leaking tanks or pipelines.
- Ground water geochemical parameters.
- Regional hydrogeology, including:
  - Drinking water aquifers, and
  - Regional confining units.
- Local and site-specific hydrogeology, including:
  - Local drinking water aquifers.
  - Lithology
  - Site stratigraphy, including identification of transmissive and non-transmissive units.
  - Grain-size distribution (sand vs. silt vs. clay).
  - Aquifer hydraulic conductivity.
  - Ground water hydraulic information.
  - Preferential flow pathways.
  - Location and type of surface water bodies.
  - Areas of local ground water recharge and discharge.
- Definition of potential exposure pathways and human and ecological receptors.

The following sections describe the methodologies which should be implemented to allow successful site characterization in support of intrinsic remediation.

2.3.1 Soil Characterization

In order to adequately define the subsurface hydrogeologic system and to determine the amount and three-dimensional distribution of free- and residual-phase contamination which can act as a continuing source of ground water contamination, extensive soil characterization must be completed. Depending on the status of the site, this work may have already been completed during previous remedial investigation work. The results of soils characterization will be used as input into a numerical model and to support the intrinsic remediation investigation.

2.3.1.1 Soil Sampling

The purpose of soil sampling is to determine the subsurface distribution of hydrostratigraphic units and the distribution of free- and residual-phase contaminants. These objectives can be achieved through the use of conventional soil borings or cone penetrometer testing. All soil samples should be collected, described, and analyzed using accepted procedures.

2.3.1.2 Soil Analytical Protocol

The analytical protocol to be used for soil sample analysis is presented in Table 1. This analytical protocol includes all of the parameters necessary to document intrinsic remediation of fuel hydrocarbons, including the effects of sorption and biodegradation (aerobic and anaerobic) of fuel hydrocarbons. The following paragraphs describe each soil analytical parameter and the use of each analyte in the intrinsic remediation investigation.

Total Petroleum Hydrocarbons: Knowledge of the location, distribution, concentration, and total mass of total petroleum hydrocarbons (TPH) sorbed to the aquifer matrix or present as free-phase product is required to calculate contaminant partitioning from the residual and free phases into the dissolved phase. The presence or absence of TPH is also used to define the edge of the oily-phase plume. Knowledge of the location of the leading edge of the oily-phase plume is important in proper model implementation.

Aromatic Hydrocarbons: Knowledge of the location, distribution, concentration, and total mass of individual aromatic hydrocarbons (especially BTEX) adsorbed to the aquifer matrix or present as free-phase product is required to calculate contaminant partitioning from the residual and free phases into the dissolved phase.

Total Organic Carbon: Knowledge of the total organic carbon (TOC) content of the aquifer matrix is important in sorption and solute-retardation calculations.

Soil Gas Analysis: The concentrations of soil gas oxygen, carbon dioxide, and total volatiles and BTEX are important in defining the extent of oily-phase contamination. This information can be used to define the edge of the oily phase plume and to estimate the potential for natural biodegradation of vadose zone fuel residuals. Depleted oxygen levels and elevated carbon dioxide levels in soil gas are indicative of aerobic biodegradation of fuel hydrocarbons in the unsaturated zone, which may be enhanced if additional oxygen is provided through bioventing

2.3.2 Ground Water Characterization

Biodegradation of fuel hydrocarbons brings about a measurable change in the chemistry of ground water in the affected area. By measuring these changes, the proponent of intrinsic remediation can document and quantitatively evaluate the importance of intrinsic remediation at a site. The following sections describe the characteristics of ground water chemistry most likely to be affected by the processes of intrinsic remediation and present a strategy for documenting these changes.

2.3.2.1 Ground Water Sampling

Ground water sampling must be conducted to determine the concentration and three-dimensional distribution of contaminants and ground water geochemical parameters. Ground water samples may be obtained from monitoring wells or point-source sampling devices such as the Geoprobe® or the Hydropunch®. All ground water samples should be collected using accepted procedures.

2.3.2.2 Ground Water Analytical Protocol

The analytical protocol to be used for ground water sample analysis is presented in Table 1. This analytical protocol includes all of the parameters necessary to document intrinsic remediation of fuel hydrocarbons, including the effects of sorption and aerobic and anaerobic biodegradation of fuel hydrocarbons.

The following paragraphs describe each ground water analytical parameter and the use of each analyte in the intrinsic remediation investigation.

Dissolved Oxygen: Dissolved oxygen is the most thermodynamically favored electron acceptor used in the biodegradation of fuel hydrocarbons. Measurements of dissolved oxygen concentrations are used to estimate the mass of contaminant which can be biodegraded by aerobic processes. Each 1.0 milligram/Liter (mg/L) of dissolved oxygen consumed by microbes will destroy approximately 0.29 mg/L of BTEX compounds. During aerobic biodegradation, dissolved oxygen levels are reduced to below background levels as aerobic respiration occurs. Anaerobic bacteria (obligate anaerobes) generally cannot function at dissolved oxygen levels greater than about 0.5 mg/L.

Carbon Dioxide: Metabolic processes operating during biodegradation of fuel hydrocarbons lead to the production of carbon dioxide (CO_2). Accurate measurement of CO_2 produced during biodegradation is difficult because carbonate in ground water (measured as alkalinity) serves as both a source and sink for free CO_2. If the CO_2 produced during metabolism is not removed by the natural carbonate buffering system of the aquifer, CO_2 levels higher than background may be observed. Comparison of empirical data to stoichiometric calculations can provide estimates of the degree of microbiological activity and the occurrence of *in situ* mineralization of contaminants.

Nitrate: After dissolved oxygen has been depleted in the microbiological treatment zone, nitrate may be used as an electron acceptor for anaerobic biodegradation. Nitrate concentrations will be a direct input parameter to the Bioplume III model currently under development by AFCEE. Measurements of nitrate concentrations are used to estimate the mass of contaminant which can be biodegraded by denitrification processes. Each 1.0 mg/L of nitrate-nitrogen consumed by microbes results in the destruction of approximately 0.9 mg/L of BTEX compounds. Each 1.0 mg/L of nitrate consumed by microbes results in the destruction of approximately 0.21 mg/L of BTEX compounds.

Sulfate: After dissolved oxygen and nitrate have been depleted in the microbiological treatment zone, sulfate may be used as an electron acceptor for anaerobic biodegradation. Sulfate concentrations are used as an indicator of anaerobic degradation of fuel compounds. Each 1.0 mg/L of sulfate consumed by microbes results in the destruction of approximately 0.22 mg/L of BTEX compounds. Sulfate concentrations will be used as a direct input parameter for Bioplume III.

Ferrous Iron (Iron II): In some cases ferric iron is used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons. During this process, ferric iron is reduced to the ferrous form which may be soluble in water. Ferrous iron concentrations are used as an indicator of anaerobic degradation of fuel compounds. Each 1.0 mg/L of ferrous iron produced during microbial iron oxidation results in the degradation of 0.047 mg/L of BTEX. Iron concentrations will be used as a direct input parameter to Bioplume III.

Methane: During methanogenesis (an anaerobic biodegradation process), CO_2 (or acetate) is used as an electron acceptor, and methane is produced. Methanogenesis generally occurs after oxygen, nitrate, and sulfate have been depleted in the treatment zone. The presence of methane in ground water is indicative of strongly reducing conditions. Because methane is not present in fuel, the presence of methane in ground water in contact with fuels is indicative of microbial degradation of fuel hydrocarbons. Methane concentrations can be used to estimate the amount of BTEX destroyed in an aquifer. Each 1.0 mg/L of methane produced by methanogenesis results in the degradation of approximately 1.3 mg/L of BTEX.

Alkalinity: The total alkalinity of a ground water system is indicative of a water's capacity to neutralize acid. Alkalinity results from the presence of hydroxides, carbonates, and bicarbonates of elements such as calcium, magnesium, sodium, potassium, or ammonia. Alkalinity is important in the maintenance of ground water pH.

Chloride: Chloride is used as a tracer to ensure that ground water samples collected at a site are representative of the water comprising the saturated zone in which the dissolved-phase contamination is present (i.e., to ensure that all samples are from the same ground water flow system). High chloride levels can inhibit the metabolic activity of contaminant-degrading bacteria.

Conductivity: Aqueous conductivity is a measure of the ability of a solution to conduct electricity. Like chloride, conductivity is used as a tracer to ensure that ground water samples collected at a site are representative of the water comprising the saturated zone in which the dissolved-phase contamination is present. The conductivity of ground water is directly related to the concentration of ions in solution; conductivity increases as ion concentration increases.

Oxidation/Reduction Potential (E_H): The oxidation/reduction (redox) potential of ground water (E_H) is a measure of electron activity and is an indicator of the relative tendency of a solution to accept or transfer electrons. Negative redox potentials are indicative of reducing conditions. Positive redox potentials are indicative of oxidizing conditions. Oxidation/reduction reactions in ground water are usually biologically mediated and therefore, the redox potential of a ground water system depends upon and influences rates of biodegradation. Knowledge of the redox potential of ground water is also important because some biological processes only operate within a prescribed range of redox conditions. Knowledge of the redox potential of ground water can be used as an indicator of certain geochemical activities such as sulfate reduction. The redox potential of ground water generally ranges from -400 millivolts (mV) to 200 mV.

Temperature: Ground water temperature directly affects the solubility of oxygen and other geochemical species. The solubility of dissolved oxygen is temperature dependent, being more soluble in cold water than in warm water. Ground water temperature also affects the metabolic activity of bacteria. Rates of hydrocarbon biodegradation roughly double for every 10-degree Celsius (°C) increase in temperature ("Q"$_{10}$ rule) over the temperature range between 5 and 25°C. Ground water temperatures less than about 5°C tend to inhibit biodegradation, and slow rates of biodegradation are generally observed in such waters.

pH: The pH of ground water has an effect on the presence and activity of microbial populations in ground water. This is especially true for methanogens. Microbes capable of degrading petroleum hydrocarbon compounds generally prefer pH values varying from 6 to 8 standard units.

Total Petroleum Hydrocarbons and Aromatic Hydrocarbons: These analytes are used to determine the type and distribution of fuel hydrocarbon in the aquifer. The combined concentrations of BTEX and the trimethylbenzenes (TMB) should not be greater than 50 percent of the TPH concentration. If these compounds are found in concentrations greater than 50 percent of the TPH concentration, sampling errors such as emulsification of product in the ground water sample should be investigated.

Data obtained from the analysis of ground water for these analytes will be used to scientifically document intrinsic remediation of fuel hydrocarbons and as input into a numerical ground water model.

2.3.3 Aquifer Parameter Estimation

Estimation of aquifer parameters such as hydraulic conductivity, hydraulic gradient, and hydrodynamic dispersion are important factors affecting solute transport. The determination of these parameters is discussed in the following sections.

2.3.3.1 Hydraulic Conductivity

Hydraulic conductivity is a measure of an aquifer's ability to transmit water and is perhaps the single-most important aquifer parameter governing fluid flow in the subsurface. The velocity of ground water and dissolved-phase contaminants is directly related to the hydraulic conductivity of the saturated zone. In addition, subsurface variations in hydraulic conductivity directly influence contaminant fate and transport by providing preferential pathways for contaminant migration. The most common methods used to quantify hydraulic conductivity in the subsurface are aquifer pumping tests and slug tests.

Pumping tests generally give the most reliable information on hydraulic conductivity but are difficult to conduct in contaminated areas because the water produced during the test generally must be contained and treated. In addition, a minimum 4-inch-diameter well is generally required to complete pumping tests in highly transmissive aquifers. In areas with fairly uniform aquifer materials, pumping tests can be completed in uncontaminated areas and the results used to predict hydraulic conductivity in the contaminated area.

Slug tests are a commonly used alternative to pumping tests. They are relatively easy to conduct and, in general, produce reliable information. One commonly cited drawback to slug testing is that this method generally gives hydraulic conductivity information only for the area immediately surrounding the monitoring well. Slug tests do, however, have two distinct advantages over pumping tests; they can be conducted in 2-inch monitoring wells, and they produce no water. If slug tests are going to be relied upon to provide information on the three-dimensional distribution of hydraulic conductivity in an aquifer, multiple slug tests must be performed; both within the same well and at several monitoring wells at the site. It is not advisable to rely on data from one slug test in one monitoring well.

2.3.3.2 Hydraulic Gradient

The hydraulic gradient is the change in hydraulic head (feet of water) divided by the length of ground water flow. To accurately determine the hydraulic gradient, it is necessary to measure ground water levels in all monitoring wells at the site. Because hydraulic gradients can change over a short distance within an aquifer, it is essential to have as much site-specific ground water elevation information as possible so that accurate hydraulic gradient calculations can be made. In addition, seasonal variations in ground water flow direction can have a profound influence on contaminant transport. To determine the effect of seasonal variations in ground water flow direction on contaminant transport, quarterly ground water level measurements should be taken over a period of at least one year.

2.3.3.3 Hydrodynamic Dispersion

The dispersion of organic solutes in an aquifer is an important consideration when modeling intrinsic remediation. The dispersion of a contaminant into relatively pristine portions of the aquifer allows the solute plume to admix with uncontaminated ground water containing higher concentrations of electron acceptors. Dispersion occurs both downgradient, and more importantly, crossgradient to the direction of ground water flow.

2.3.4 Microcosm Studies

Microcosm studies are necessary only when there is considerable skepticism about the biodegradation of fuel hydrocarbons. Skeptics should first be directed to the unequivocal evidence found in the literature that biodegradation of fuel hydrocarbons does occur under natural conditions.

If more evidence of intrinsic remediation of fuel hydrocarbons is required, then a microcosm study using site-specific aquifer materials and contaminants can be undertaken. The collection of material for the microcosm study, the procedures used to set up and analyze the microcosm study, and the interpretation of the results of the microcosm study, should be based on accepted procedures. It should be kept in mind that fuel hydrocarbon degradation rate constants are best determined by *in situ* field measurement.

2.4 REFINE CONCEPTUAL MODEL, COMPLETE PRE-MODELING CALCULATIONS, AND DOCUMENT INDICATORS OF INTRINSIC REMEDIATION

The data generated during the site investigation should first be used to refine the conceptual model, document the occurrence and rates of intrinsic remediation, and complete pre-modeling calculations. During this step of the intrinsic remediation investigation, site characterization data are used to refine the conceptual model and calculate rates of ground water flow, sorption, dilution, and biodegradation. The results of these calculations are then used to model intrinsic remediation and to provide scientific evidence that intrinsic remediation is occurring at a site. It is important to note that no single piece of data will be sufficient to successfully support the intrinsic remediation option at a given site. Additionally, it is important to remember that the burden of proof is on the proponent, and therefore, all available data must be integrated in such a way that the evidence in support of intrinsic remediation is sufficient and irrefutable.

2.4.1 Conceptual Model Refinement

Conceptual model refinement involves integrating newly gathered field data to refine the preliminary conceptual model which was developed based on previously existing site-specific data. During conceptual model refinement, all available site-specific data should be integrated to develop an accurate representation of the three-dimensional hydrogeologic contaminant transport system, which can be used for contaminant fate and transport modeling. Conceptual model refinement consists of several steps including boring log preparation, hydrogeologic section preparation, potentiometric surface map preparation, contaminant isopleth and isopach map preparation, and preparation of electron acceptor isopleth maps.

2.4.1.1 Geologic Boring Logs

Geologic boring logs of all subsurface materials encountered during the soil boring or cone penetrometer testing (CPT) phase of the field work should be constructed. Descriptions of the aquifer matrix should include relative density, color, major textural constituents, minor constituents, porosity, relative moisture content, plasticity of fines, cohesiveness, grain size, structure or stratification, relative permeability, and any other significant observations such as visible fuel. It is also important to correlate the results of volatiles screening using headspace vapor analysis with depth intervals of geologic materials. The depth of lithologic contacts and/or significant textural changes should be recorded to the nearest 0.1 foot. This resolution is necessary because preferential flow and contaminant transport pathways may be limited to a stratigraphic unit on the order of 6 inches thick.

2.4.1.2 Hydrogeologic Sections

Hydrogeologic sections should be prepared from boring logs or CPT data. A minimum of two hydrogeologic sections are required; one parallel to the direction of ground water flow and one perpendicular to the direction of ground water flow. These sections are useful in locating preferential contaminant migration pathways and in modeling the site using numerical models such as Bioplume II® or BIO1D®.

2.4.1.3 Potentiometric Surface Map(s)

A potentiometric surface map is a two-dimensional graphic representation of equipotential lines shown in plan view. A potentiometric surface map should be prepared from water level measurements and surveyor's data. These maps are used to estimate the probable direction of plume migration and to calculate hydraulic gradients. To document seasonal variations in ground water flow, separate potentiometric surface maps should be prepared for quarterly water level measurements taken over a period of at least 1 year. In areas with free-product, a correction must be made for the water-table deflection caused by the product.

2.4.1.4 Contaminant Isopleth Maps

Contaminant isopleth maps should be prepared for each of the BTEX compounds and for total BTEX. Isopleth maps allow interpretation of data on the distribution and the relative transport and degradation rates of contaminants in the subsurface. In addition, contaminant isopleth maps are necessary so that contaminant concentrations can be gridded and used for input into the Bioplume II® model.

2.4.1.5 Contaminant Isopach Maps

If residual- and free-phase product are present at the site, an isopach map showing the thickness and distribution of each phase should be prepared. These isopach maps will allow interpretation of the distribution and the relative transport rate of free product in the subsurface. In addition, these maps will aid in partitioning calculations and numerical model development. It is important to note that because of the differences between the magnitude of capillary suction in the aquifer matrix and the different surface tension properties of fuel and water, free-product thickness observations made in monitoring points are only an estimate of the actual volume of residual- and free-phase product in the aquifer. To accurately determine the distribution of residual- and free-phase product it is necessary to take continuous soil cores.

2.4.1.6 Electron Acceptor and Metabolic Byproduct Isopleth Maps

Isopleth maps should be prepared for the electron acceptors consumed (dissolved oxygen, nitrate, and sulfate), and metabolic byproducts produced (iron II, bicarbonate, and methane), during biodegradation. These maps will allow interpretation of data on the distribution of the electron acceptors and metabolic byproducts in the subsurface. Isopleth maps also provide a visual indication of the relationship between the contaminant plume and the various electron acceptors and metabolic byproducts. The electron acceptor and metabolic byproduct isopleth maps, used in conjunction with the contaminant isopleth maps and the statistical calculations discussed in Section 2.4.2.1, provide evidence of the occurrence of intrinsic remediation at a site.

Isopleth maps should be prepared for the following electron acceptors: dissolved oxygen, nitrate, and sulfate. During aerobic biodegradation, dissolved oxygen concentrations will decrease to levels below background. Similarly, during anaerobic degradation, the concentrations of nitrate and sulfate will be seen to decrease to levels below background. In addition, the dissolved oxygen isopleth map is used to grid dissolved oxygen concentrations for input into the Bioplume II® model. Isopleth maps should be prepared for the following metabolic byproducts:

iron II, bicarbonate, and methane. During anaerobic degradation, the concentrations of iron II, bicarbonate, and methane will be seen to increase to levels above background concentrations.

2.4.2 Pre-Modeling Calculations

Several calculations must be made prior to implementation of the numerical model. These calculations include sorption and retardation calculations, fuel/water partitioning calculations, ground water flow velocity calculations, and biodegradation rate constant calculations. Each of these calculations is discussed in the following sections.

2.4.2.1 Analysis of Contaminant, Electron Acceptor, and Metabolic Byproduct Data

The extent and distribution (vertical and horizontal) of the contamination and electron acceptor and metabolic byproduct concentrations and distributions are of paramount importance in documenting the occurrence of biodegradation of fuel hydrocarbons and in numerical model implementation. Because low concentrations of electron acceptors in areas with fuel hydrocarbon contamination generally indicate that an active zone of hydrocarbon biodegradation is present, plots of electron acceptor concentration vs. dissolved total BTEX concentration should be made and linear regression statistics performed on these plots. As dissolved oxygen decreases during aerobic biodegradation and nitrate and sulfate concentrations decrease during anaerobic degradation, BTEX concentrations should decrease. As iron II and methane concentrations increase during anaerobic degradation, BTEX concentrations should decrease. These relationships are important indicators of biodegradation and as such should be used as evidence that biodegradation of fuel hydrocarbons is occurring.

2.4.2.2 Sorption and Retardation Calculations

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The retardation of organic solutes caused by adsorption is an important consideration when modeling intrinsic remediation for two reasons: 1) adsorption of a contaminant to the aquifer matrix results in an apparent dilution which must be accounted for, and 2) dissolved oxygen and other electron acceptors present in the ground water are traveling at the advective transport velocity of the ground water and any slowing of the solute relative to the advective transport velocity of the ground water allows replenishment of electron acceptors into upgradient areas of the plume.

Contaminant sorption and retardation calculations should be made based on the TOC content of the aquifer matrix and the organic carbon partitioning coefficient (K_{OC}) of each contaminant. At a minimum, these calculations should be completed for each of the BTEX compounds.

2.4.2.3 Fuel/Water Partitioning Calculations

If free- or residual-phase product remains at the site, fuel/water partitioning calculations should be made to account for the partitioning from these phases into the dissolved phase in ground water. Several models for fuel/water partitioning have been proposed in recent years, including those by Hunt et al. (1988), Johnson and Pankow (1992), Cline et al. (1991) and Bruce et al. (1991). Because the models presented by Cline et al. (1991) and Bruce et al. (1991) represent equilibrium partitioning, they are generally the most conservative and should be used.

✓2.4.2.4 Ground Water Flow Velocity Calculations

[illegible]

The average ground water flow velocity should be calculated to check the accuracy of the numerical ground water model and to allow calculation of first-order biodegradation rate constants.

2.4.2.5 Anaerobic Biodegradation Rate Constant Calculation

Because aerobic degradation rates are calculated by both Bioplume II® and BIO1D®, calculation of aerobic biodegradation rates is not necessary. One of the limitations of both models is that they do not account for anaerobic degradation on a cell-by-cell basis, they only allow the modeler to input first order anaerobic decay constants for the model. Although not as concise as the aerobic degradation calculations produced by the models, using a first order rate constant is generally a good approximation because anaerobic biodegradation of fuel hydrocarbons can generally be approximated using first-order kinetics ($C=C_0e^{-kt}$). In order to calculate anaerobic rate constants for each chemical, the apparent degradation rate must be normalized for the effects of dilution, volatilization, and sorption. This is accomplished by normalizing the concentration of each contaminant to the concentration of a tracer which has similar sorptive properties, but which is recalcitrant. Two such chemicals found in fuel hydrocarbon plumes are trimethylbenzene and tetramethylbenzene. Bioplume III, now under development by AFCEE, will allow direct input of anaerobic electron acceptor data so that anaerobic degradation rates can be predicted using the model.

2.5 MODEL INTRINSIC REMEDIATION USING NUMERICAL MODELS

Modeling of intrinsic remediation allows projection of the migration and attenuation of the contaminant plume over time. The results of the modeling effort should be used to support the tenant that intrinsic remediation provides adequate protection of public health and the environment at the site. It is important to remember that intrinsic remediation modeling is a tool which allows site-specific data to be used to predict the fate and transport of solutes under governing physical, chemical, and biological processes. Hence, the results of the modeling effort are not in themselves sufficient proof that intrinsic remediation is occurring at a given site. The results of the modeling effort are only as good as the original data input into the model. In some cases, simple calculations of contaminant attenuation rates are all that is required to successfully support intrinsic remediation.

Only two well documented and widely accepted numerical models are available for modeling the fate and transport of fuel hydrocarbons under the influence of advection, dispersion, sorption, and biodegradation. These models are Bioplume II® and BIO1D®.

The Bioplume II® model is based upon the U.S. Geological Survey (USGS) two-dimensional (2-D) solute transport model of Konikow and Bredehoeft (1978). Bioplume II® includes a biodegradation component that is activated by a superimposed plume of dissolved oxygen (Rifai et al., 1988). The model solves the USGS 2-D solute transport equation twice, once for hydrocarbon concentrations in the aquifer and once for a dissolved oxygen plume. The two plumes are combined using superposition at every particle move to simulate the biological reaction between hydrocarbons and oxygen. The model incorporates modified Monod kinetics to simulate the degradation of hydrocarbon compounds and assumes that the hydrocarbons are directly mineralized to carbon dioxide and water through an instantaneous reaction. In recent years several studies have shown that Bioplume II® can be used to successfully support the intrinsic remediation option at fuel hydrocarbon contaminated sites (Downey and Gier, 1991; Wiedemeier et al., 1993).

BIO1D® is a one-dimensional, finite-difference numerical ground water flow and solute transport model. Like Bioplume II®, the BIO1D® model incorporates modified Monod kinetics to simulate the degradation of fuel hydrocarbons.

2.6 CONDUCT A RISK ANALYSIS

After the occurrence of, and rates of, intrinsic remediation have been documented, and predictions of the future extent and concentration of the plume have been made using the appropriate numerical solute fate and transport model, the proponent of intrinsic remediation should combine all available data and information to negotiate for implementation of the intrinsic remediation option. Supporting the intrinsic remediation option generally will involve implementation of a simplified risk analysis. The results of numerical fate and transport modeling are central to the simplified risk analysis process. If conservative model input parameters are used, the numerical fate and transport model should give conservative estimates of contaminant plume migration. From this information, the potential impacts to human health and the environment from contamination present at the site can be estimated.

2.7 PREPARE LONG-TERM MONITORING PLAN

The long-term monitoring plan consists of locating ground water monitoring wells and developing a ground water sampling and analysis plan. This plan is used to monitor plume migration over time and to ensure that intrinsic remediation is occurring at rates sufficient to protect potential downgradient receptors. The long-term monitoring plan should be developed based on the results of the modeling effort described in Section 2.5.

Long-term monitoring wells should be placed downgradient of the contaminant plume such that they are located approximately five years ahead of the current plume. The results of the numerical model should be used to help site these wells. Additional point-of-compliance monitoring wells should be located upgradient of potential receptors, generally along the property boundary. The final placement of these wells should be determined in collaboration with regulators.

2.8 CONDUCT REGULATORY NEGOTIATIONS

The purpose of regulatory negotiations is to provide scientific documentation that supports intrinsic remediation as the most appropriate remedial option for a given site. All available site-specific data and information developed during the site characterization, conceptual model development, pre-modeling calculations, biodegradation rate calculation, ground water modeling, model documentation, and long-term monitoring plan preparation phases of the intrinsic remediation investigation should be presented in a consistent and complementary manner at the regulatory negotiations. Of particular interest to the regulators will be proof that intrinsic remediation is occurring at rates sufficient to protect human health and the environment. The regulators must be presented with a "weight of evidence" argument in support of this remedial option. For this reason, all available evidence in support of intrinsic remediation must be presented at the regulatory negotiations. A comprehensive long-term monitoring plan should also be presented to demonstrate a commitment to proving the effectiveness of intrinsic remediation.

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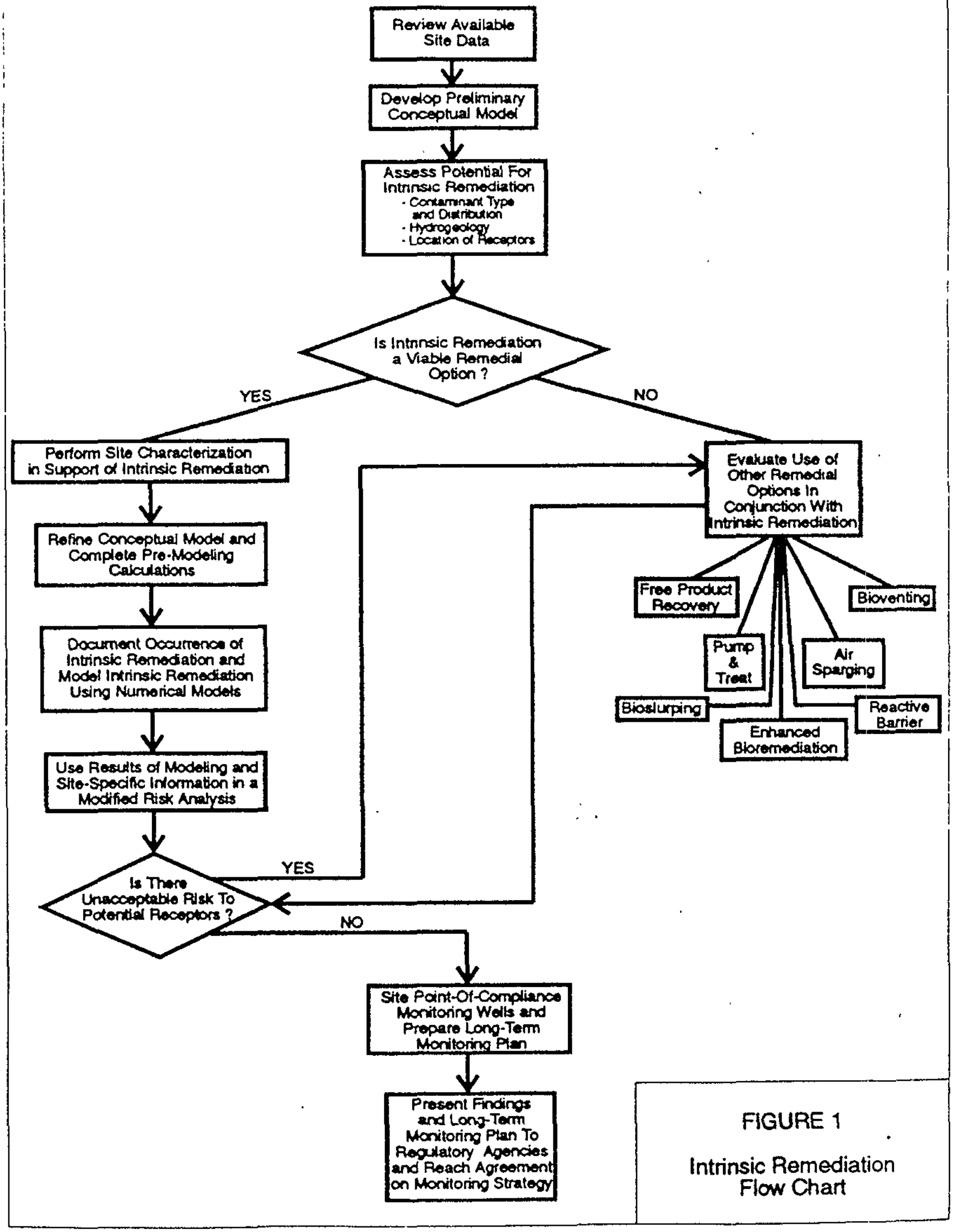

FIGURE 1

Intrinsic Remediation Flow Chart

Table 1 Laboratory Analytical Protocol for Ground Water and Soil

Analyte	Method	Sample Volume (ml)	Field (F) or Analytical Laboratory (L)
	Soil		
BTEX	SW 8020		L
Total Organic Carbon	Modified SW9060		L
Moisture	ASTM D-2216		L
Total Petroleum Hydrocarbons	Modified 8015		L
	Soil Gas		
Total Combustible Hydrocarbons	Direct reading meter		F
Carbon dioxide	Direct reading meter		F
Methane	Direct reading meter		F
Oxygen	Direct reading meter		F
	Water		
Alkalinity (Carbonate [CO_3^{2-}] and Bicarbonate [HCO_3^-])	E310.2	240	L
Aromatic hydrocarbons Must include, at a minimum, benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene, and *1,2,3*-, *1,2,4*-, and *1,3,5*-trimethylbenzene	SW8020	80	L
Total Petroleum Hydrocarbons	Modified 8015	80	L
Carbon dioxide (CO_2)	Titrimetric		F/L
Chloride	E300 or SW9056	240	L
Conductivity	Direct reading meter and E120.1	240	F/L
Total Dissolved Solids	E160.1		L
Ferrous Iron (Fe^{2+})	Colorimetric, HACH 25140-25	50	F
Methane	SW8020	120	L
Nitrate	Colorimetric or IC (E300 or SW9056)	120	F/L
Dissolved Oxygen	Direct reading meter	---	F
pH	Direct reading meter and E150.1/SW9040	200	F/L
Sulfate	Colorimetric or IC (E300 or SW9056)	240	F/L
Temperature	Direct reading meter	200	F
Total Organic Carbon	SW9060	120	L
Oxidation-Reduction Potential	Direct reading instrument	---	F
	Free-Phase Product		
BTEX (Mass Fraction)	SW8020		L

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Mr. Todd H. Wiedemeier[1] is a senior geologist with Engineering-Science, Inc. (ES). His responsibilities include design and installation of *in situ* remediation systems to perform light nonaqueous-phase liquid recovery, ground water pump-and-treat, air sparging, and vapor extraction. Mr. Wiedemeier's research and professional interests include contaminant transport modeling and *in situ* remediation methods for contaminated soils and ground water. He holds B.S. and M.S degrees in geology.

Dr. John T. Wilson[2] is a senior research microbiologist with the U.S. EPA in Ada, Oklahoma, at the R.S. Kerr Research Laboratory. Dr. Wilson's current research efforts involve the study of microbial processes that determine the fate and transport of organic contaminants in the subsurface environment. He has 10 years of extensive experience in site characterization, process definition, and modeling of intrinsic bioremediation. He received a Ph.D. in microbiology from Cornell University.

Dr. Donald Kampbell[3] is a senior research chemist with the U.S. EPA in Ada, Oklahoma, at the R.S. Kerr Research Laboratory. Dr. Kampbell's current research efforts involve field monitoring techniques and field bioremediation process performance He received a Ph.D. in Agricultural Chemistry from the University of Missouri. He is a licensed Professional Engineer.

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