"Value-Added Site Monitoring and Infrastructure Maintenance for In-Situ Bioremediation Technology Development"

A Final Report

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EXECUTIVE SUMMARY

This original project was funded in FY '98 and designed to achieve three main objectives. These are: 1) The continued serial monitoring of contaminant, geochemical constituents, and indicators of bioremediation at two actual sites of fuel and/or solvent contamination and during a BTEX-MTBE natural gradient tracer test conducted at the former Wurtsmith, AFB near Oscoda, MI, 2) The improvement and maintenance of the existing historical database on the progress of intrinsic (i.e. natural) bioremediation at these sites which extends from the late 1980's, and 3) Statistical analyses of the impact of observed spatial and temporal variability in contaminant source mass distributions on the reliability of estimates of rates of net mass removal (i.e. the progress of bioremediation), and projected timeframes for site closure. The project was subsequently amended after briefings to the SERDP Science Advisory Board in early 1998. The statistical analyses proposed in objective 3 above were then focused on the time series analyses of bioremediation performance indicators to test two hypotheses. The hypotheses were: Simple field measurements provide adequate reliability and confidence intervals on apparent bioremediation rate coefficients; and, semi-quantitative estimations of NAPL source strength terms favorably compare with those required by simple bioremediation fate and transport models. The project was terminated in FY '99.

The actual fuel (KC-135 crash site) and fuel/solvent (Fire Training Area-02) were monitored on a quarterly basis throughout the project period. A total of eighty-five wells were sampled for: field parameters (i.e. pH, conductance, O_2, temperature, redox potential and Fe^{2+}) and volatile organic compounds (EPA Method 8260). Most conventional wells had dedicated bladder pumps while multilevel installations were sampled with peristaltic pumps using low-flow (minimal-draw down) sampling techniques. During several sampling events total cation and anion determinations were made to calculate mass and charge balance on the inorganic constituents. Field spikes, standards and duplicate samples were used in addition to laboratory standards to insure acceptable levels of QA/QC throughout the project.

The results of this phase of the project disclosed that plumes from single contaminant releases (KC-135) showed indications of a decline in the overall extent of contamination and more stable

oxidation-reduction (redox) zones. At the FT-2 site, where fire-training had been conducted for over forty years, the overall contaminant plume extent declined somewhat, but both contaminant distributions and redox zones were quite variable in time and space. Individual contaminants at this site varied over a range of two to five times the annual mean on a quarterly basis. Analytical and sampling errors of the toxic, volatile fuel and solvent contaminants generally represented less than 20% of these variations. The remainder could be attributed to natural variability. The natural variability should be carefully considered in the uncertainty of fate and transport model predictions of the rates of natural attenuation, plume decay and eventual "cleanup".

The natural gradient reactive tracer test employing BTEX constituents and MTBE was staged to evaluate the performance of the Michigan Integrated Remediation Technology Laboratory (MIRTL), established in a previously uncontaminated area of the base. Initiated in October of 1998, the tracer solution was injected in a fully-instrumented test lane. It contained the BTEX compounds, MTBE as well as Br^-, SF_6 and perfluorinated benzene and toluene as non-degradable tracers. Migrating at a bulk ground-water flow rate of ~ 1.2 ft/d the plumes were tracked for over 200 days through successive transects of multilevel samplers. Over 10,000 samples were collected and analyzed during this experiment. The experiment verified the concept and performance of this in-situ facility and provided qualitative proof of the degradability of MTBE to tertiary butyl alcohol (TBA) under suboxic and highly oxidizing ORC® permeable reactive barrier conditions.

Evaluation of source stability at the KC-135 site begun in 1998 was ended in 1999 due to the termination of the project. A rapid field method (Petroflag®) for total petroleum hydrocarbon determinations was proven to correlate better with a compound specific gas-chromatography-mass spectrometric method than the time and labor intensive standard, EPA 418.1 method. Given the wide distribution of chlorinated solvents and fuel constituent related NAPL at the FT-2 site, the in-plume source areas were too scattered for accurate evaluation. The method was applied to two sites of fuel, petroleum product spills with success. Its use will significantly enhance source evaluation efforts at lower cost.

Apparent biodegradation rate constants for the BTEX constituents at the KC-135 site were found to vary by a factor of five over the course of four years. Values, by the method of Alcantar and Buscheck, varied from ~ 0.1 to 5.5 percent $.d^{-1}$. Apparent biodegradation rate constants in the reducing-suboxic source zone were consistently below those in the plume area which was in transition from suboxic to oxic due to the infiltration of oxygenated recharge water.

The results of this work will be made available on a continuing basis to a number of DoD-SERDP and other cooperating technology development groups. This will insure that the value-added benefits of the project continue to accrue for DoD's cleanup efforts.

INTRODUCTION

Currently available data on hydrogeologic, geochemical and microbial conditions in fuel and chlorinated solvent contaminated sites at DoD installations are normally limited to the results of short-term (i.e. < 1 year) remedial investigations followed by annual or biannual sampling and analysis of ground water from existing wells in support of feasibility studies for selection of remediation options. It is rare, in these instances, to obtain updated contaminant distribution data particularly on sorbed organic contaminants or free non-aqueous phase liquids. For sites where either intrinsic bioremediation or risk-cost-based corrective action (RBCA) is the remedy selected, long-term monitoring is limited to annual ground water sampling and analysis from compliance or sentry wells at the leading edge of the dissolved plume. These remedies are being proposed with increasing frequency as funds available for cleanup activities and must be focused on sites which pose actual risk to human or environmental health.

Intrinsic (i.e. natural) bioremediation and RBCA approaches assume that continued contaminant release from non-aqueous phase liquids and spatial variability in plume concentrations reflect steady-state or diminishing conditions. Implicit in these assumptions is that the dissolved contaminant plume is either stable or shrinking due to natural processes (e.g. dispersion, volatilization, sorption and biodegradation) which effectively offset any continued release (Chiang et al., 1989; McAllister and Chiang, 1994; Buscheck and Alcantar, 1995). Then simple (i.e. 1 or 2 dimensional) analytical fate and transport models are often used in order to estimate the rates of contaminant loss and the time frames for site closure (Domenico and Schwartz, 1990). This general approach has been proposed by a number of workers (Caldwell et al., 1992; Wiedemeier et al., 1995), the ASTM (ASTM E50.01) storage tank subcommittee, and the American Petroleum Institute (API, 1991).

The predicted rates and closure periods rarely include estimates of uncertainty because they are based on short-term datasets from a few monitoring wells along the axis of plume transport. It is recognized, however, that considerable uncertainty is associated with ground water contaminant concentration values due to: well construction details and sampling methods (Robbins et al., 1991; Martin-Hayden et al., 1991); spatial heterogeneity in aquifer transport properties (Garabedian et al., 1987; Sudicky, et al., 1983); and temporal variability in ground-water quality, flow gradient and magnitudes (Barcelona et al., 1989a,b, 1984; Stoline et al., 1993; Varljen et al., 1999). Concentration variations of 2 to 10 fold are common on a seasonal timeframe or at distances of sample separation of < 5m. Quantification of uncertainty in rates of contaminant loss and closure periods is critical to the design of post-closure monitoring networks at all sites (regardless of the remedy selected) as well as to realistically budget for operational costs in the out-years. Since intrinsic bioremediation and RBCA are essentially active monitoring approaches in lieu of active remedial operations (e.g. excavation, venting, sparging, etc.), it is important to have a defensible technical basis for their selection and estimates of their long-term reliability. This is not possible for datasets of one or two year duration.

An historical database is indeed the fundamental infrastructure for a test location focused on in-situ remediation. Data on existing conditions represent the benchmark for changes due to a natural mass removal processes. The uniquely rich database for the former Wurtsmith, AFB also contains QA/QC data (e.g. accuracy and precision for lab and field standards, matrix spikes, blanks) which permit one to independently distinguish analytical and sampling variability from natural variability in water quality (Barcelona et al., 1989a). In addition to the monitoring database, results from collaborating ground-water microbiologists, geologists and modelers enhance the record. The proposed project will document long term (i.e. approaching or exceeding 5 years) plume behavior at three actual sites of fuel and/or solvent contamination with existing, spatially dense networks of monitoring points which have been sampled on a quarterly frequency. The statistical analyses should: better quantify uncertainty in model inputs and outputs, explore the sensitivity of predictions to effective sample size (i.e. after effects of auto correlation and serial correlation are removed), and provide design guidelines to maximize monitoring network information value with minimum numbers of samples and analytical parameters. The project is unique and capitalizes on the considerable DoD investment at the site as well as others across the country.

EXPERIMENTAL

Routine Monitoring Methods

Methods used in the course of this project followed state-of-the-art recommendations for the practice of: ground-water and sediment sampling, and USEPA Level III QA/QC methods for analysis of geochemical and contaminant constituents. The primary references for these methods are included in: the NCIBRD-EGR field sampling plan (NICBRD-EGR, 1995) developed for the SERDP-NETTS test location (Wurtsmith AFB), Puls and Barcelona (1996), Wiedemeier, et al. (1995) and the laboratory's standard operating procedures (NCIBRD-EGR, 1999).

Field sampling and analysis operations were documented in hard-bound field notebooks which were verified and keyed to unique sample numbers and chain of custody (COC) records. The COC's accompanied samples in transport via courier to the laboratory and served to track sample results through the analytical reporting process. When complete, the results were verified on the laboratory data management system and later entered into the EGR relational database management system (RDBMS). This results' path was followed through successive refinements of the RDBMS.

Specialized Methods:

Total Petroleum Hydrocarbons (TPH)

TPH determinations of contaminated sediment and water samples were performed by three methods: EPA 418.1, Petroflag®and a specific compound gas-chromatography-mass spectrometry (GC-MS) method. (Xie, et al. 1999). This publication verified method performance and the validity of the rapid-field Petroflag® procedure for evaluations of TPH in hydrocarbon source areas. A complete description of the method and results is in Appendix 1.

MIRTL 2 Methods

Sampling during the course of the MIRTL 2 experiment was conducted from custom designed and emplaced stainless steel sampling points in transects at a vertical spacing of 1.0-1.5 feet and horizontal spacing of 1.5-2.5 feet. Samples were withdrawn via manual syringes, evacuating at least two sampling point volumes (50 mL) prior to sample collection. This method and associated procedures are described in detail in Barcelona and Jaglowski, 1999.

RDBMS Structure and Function.

Field and analytical data generated from project activities regardless of researcher, source of funding, primary research interest, or date, are incorporated into the RDBMS. Data that otherwise may never have been compared or considered jointly are now immediately available from a single source.

Due to multiple computing platforms in use (PC-Win, PC-NT, Mac, and UNIX) for data entry and retrieval, a browser-based user interface was developed. This browser-based user interface approach allows authorized users to enter data or query the RDBMS regardless of computing platform or physical location. Browser-based data entry forms are available for all data types from sample log-in at the EGR analytical laboratory to water level data entry at field locations. Once entered into the RDBMS, data is immediately available to all authorized users.

Presently, only EGR/NCIBRD staff members have access to the RDBMS. Authorized collaborators will have access through a public EGR/NCIBRD World Wide Web (WWW) home page.

The EGR/NCIBRD RDBMS is a uniquely powerful tool that facilitates immediate access to the body of data available (currently 162,000 unique records). Potential applications of this tool are virtually limitless.

RESULTS AND DISCUSSION

The results of the project are described in the papers referenced and discussion in the sections to follow. The sections correspond to the specific objectives of the project.

Quarterly Site Monitoring at KC-135 and FT-2.

Overview

The KC-135 and FT-2 sites have been monitored on a quarterly basis since 7/95 and 6/97 respectively, as a part of the overall NETTS program effort. From October of 1997 through September 1999 a total of sixteen quarterly sampling events were conducted at the sites (Figures 1a, 1b and 1c). Each conventional well or multilevel installation was inspected, a water-level was taken and in-well ground water temperatures were measured. Then, well-purging was conducted prior to field analysis and laboratory sample collection. More than 27,500 samples were collected. Table 1 and 2 detail the events, numbers of wells sampled and parameter groups determined during the project.

The results of the field and laboratory determinations documented in the RDBMS and can be accessed with password at the URL address: **https://www.umich.edu/ncibrd-bin/main.** Examples of the entry screens, query structure and results reports are shown in Figures 2, 3, 4, and 5. The results reports are indexed to the corresponding QA/QC data for each specific sample dataset. These data were used to conduct the overall assessment of: accuracy, precision and the nature of contaminant variability (i.e. field, analytical and natural) which follow.

Table 1. Site SS-51 sampling events

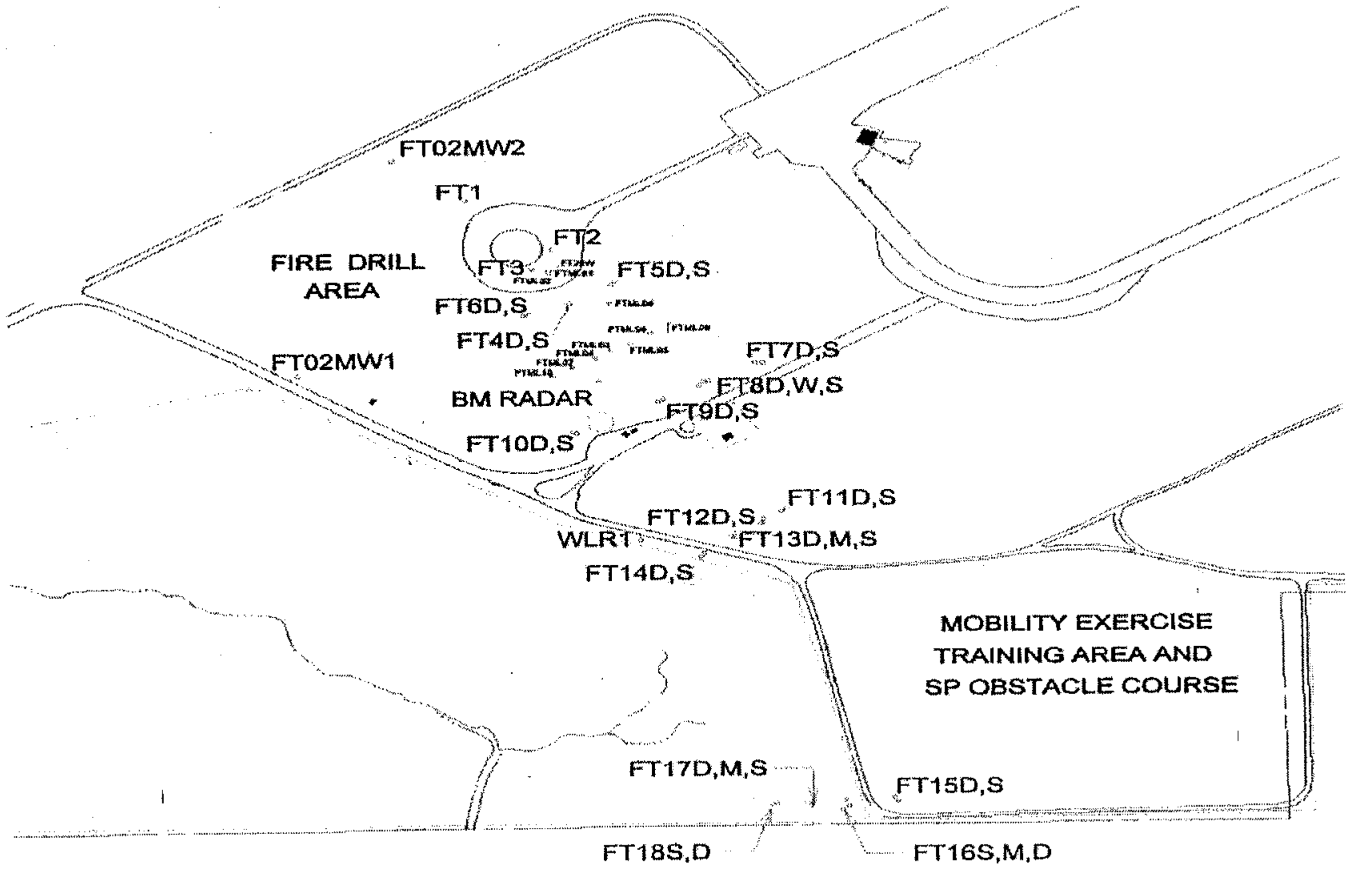
		PARAMETER SAMPLES								
DATE	# OF WELLS	VOC	IC	ISOTOPE	METHANE	METABOLITES	CATIONS	MICROTOX	PLFA	PURGE
Jul-95	11	▨								▨
Jan-96	25	▨								▨
Mar-96	30	▨								▨
Jun-96	38	▨	▨							▨
Nov-96	40	▨	▨		▨	▨				▨
Mar-97	30	▨	▨							▨
Jun-97	45	▨	▨							▨
Oct-97	41	▨	▨							▨
Feb-98	42	▨	▨		▨	▨	▨	▨		▨
Jun-98	42	▨	▨	▨	▨	▨	▨	▨	▨	▨
Sep-98	42	▨	▨	▨	▨	▨	▨	▨	▨	▨
Dec-98	42	▨	▨	▨	▨	▨	▨	▨	▨	▨
Mar-99	42	▨	▨	▨	▨	▨	▨	▨	▨	▨
Jun-99	42	▨	▨	▨	▨	▨	▨	▨	▨	▨
Sep-99	42	▨	▨	▨	▨	▨	▨	▨	▨	▨
Nov-99	42	▨	▨	▨	▨	▨	▨	▨	▨	▨

Table 2. Site FTA-02 sampling events

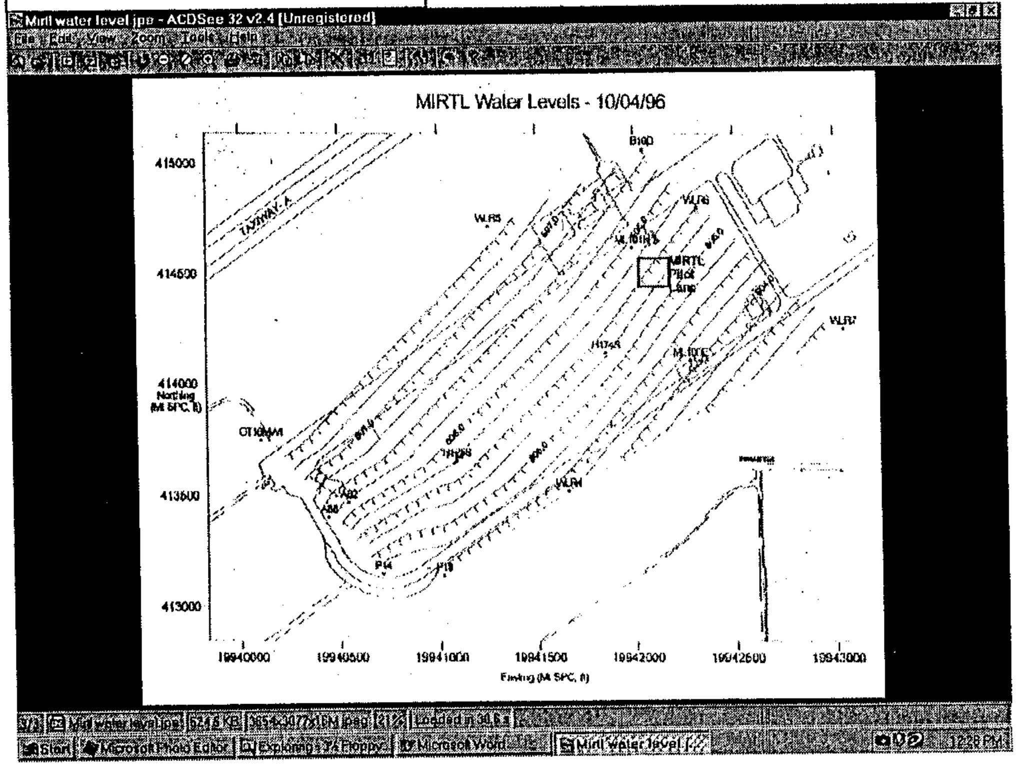
		PARAMETER SAMPLES							
DATE	# OF WELLS	VOC	IC	ISOTOPE	METHANE	METABOLITES	CATIONS	MICROTOX	PURGE
Dec-93	2	▨							
Feb-94	10	▨							
Mar-94	2	▨							
Jun-94	21	▨							▨
Sep-94	21	▨							▨
Jan-95	37	▨					▨		▨
Mar-95	37	▨					▨		▨
Jun-95	37	▨							▨
Oct-95	38	▨	▨						▨
Jan-96	38	▨	▨						▨
Apr-96	38	▨	▨						▨
Jul-96	38	▨	▨						▨
Oct-96	38	▨	▨						▨
Jan-97	38	▨	▨						▨
Apr-97	38	▨	▨						▨
Jul-97	38	▨	▨						▨
Oct-97	38	▨	▨						▨
Feb-98	38	▨	▨				▨		▨
Jul-98	38	▨	▨						▨
Aug-98	38	▨	▨						▨
Dec-98	38	▨	▨						▨
Mar-99	38	▨	▨						▨
Jun-99	38	▨	▨						▨
Aug-99	38	▨	▨						▨
Dec-99	38	▨	▨						▨

Figure 1: Detail of WAFB Study Sites

1a) Detail of Fire-Training Area site with historical plume outline and general ground-water flow vectors.



1b) Detail of MIRTL Test Lane Layout with Estimated Time of Arrival of Br^- (unretarded tracer) dispersion front with ground-water flow vectors from 8-10/96.



1c) KC-135 Site Map showing general plume outline, ground-water flow direction and monitoring points.

The KC-135 Site

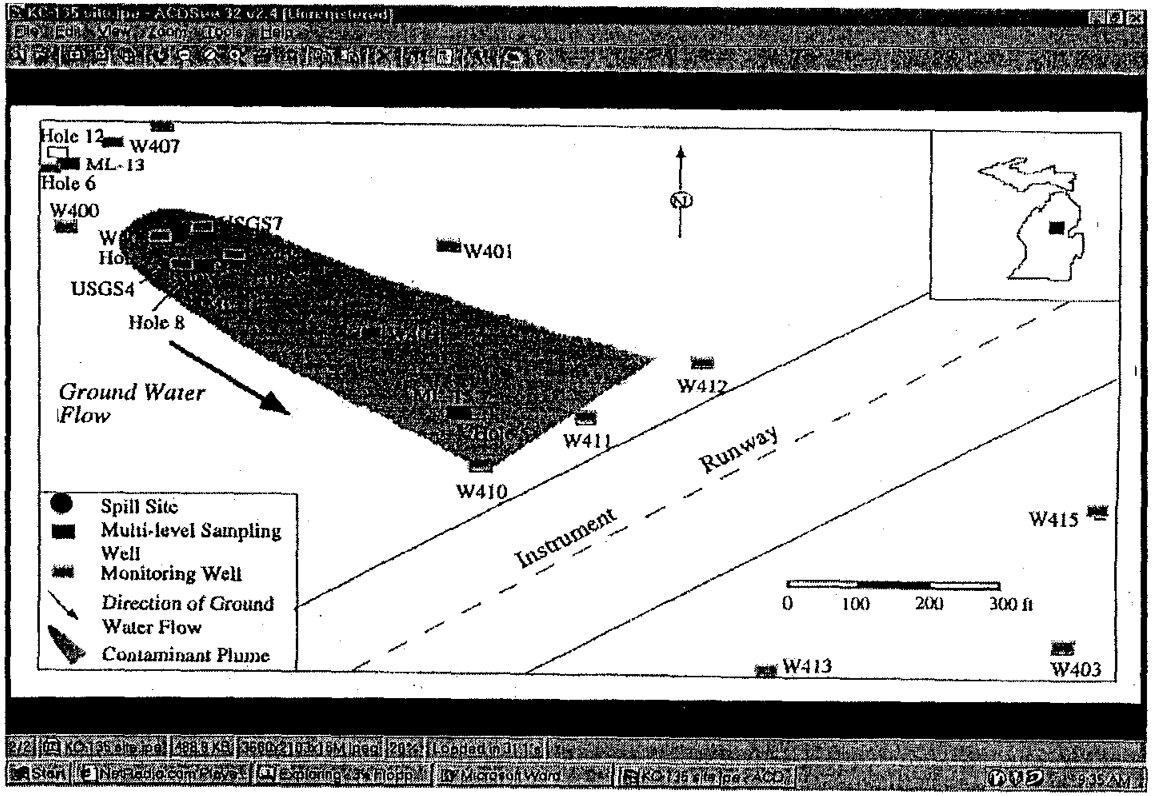
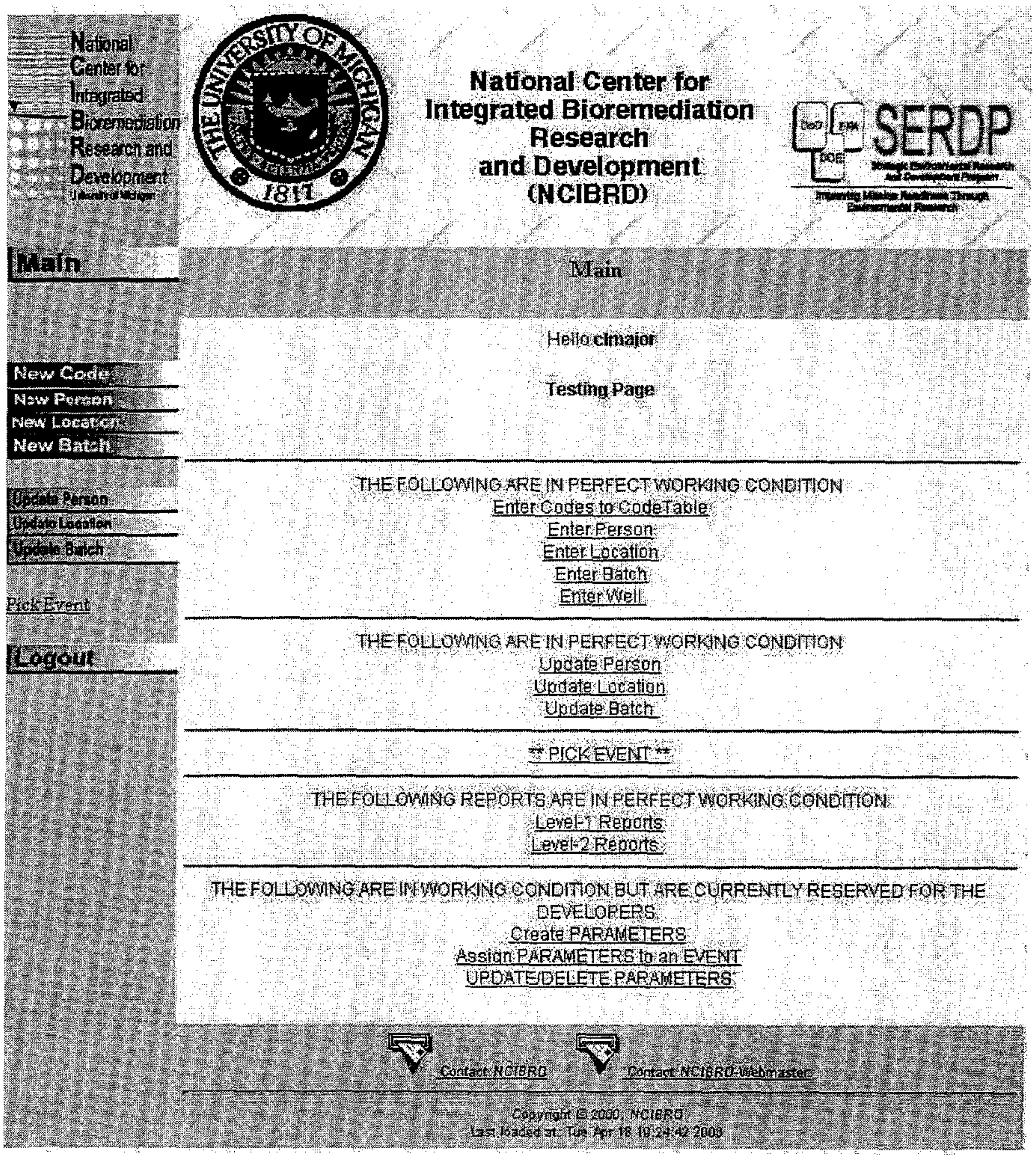


Figure 2, RDBMS Entry Screen



National Center for Integrated Bioremediation Research and Development (NCIBRD)

Hello **clmajor**

Testing Page

THE FOLLOWING ARE IN PERFECT WORKING CONDITION
Enter Codes to CodeTable
Enter Person
Enter Location
Enter Batch
Enter Well

THE FOLLOWING ARE IN PERFECT WORKING CONDITION
Update Person
Update Location
Update Batch

** PICK EVENT **

THE FOLLOWING REPORTS ARE IN PERFECT WORKING CONDITION
Level-1 Reports
Level-2 Reports

THE FOLLOWING ARE IN WORKING CONDITION BUT ARE CURRENTLY RESERVED FOR THE DEVELOPERS
Create PARAMETERS
Assign PARAMETERS to an EVENT
UPDATE/DELETE PARAMETERS

Contact NCIBRD
Contact NCIBRD-Webmaster

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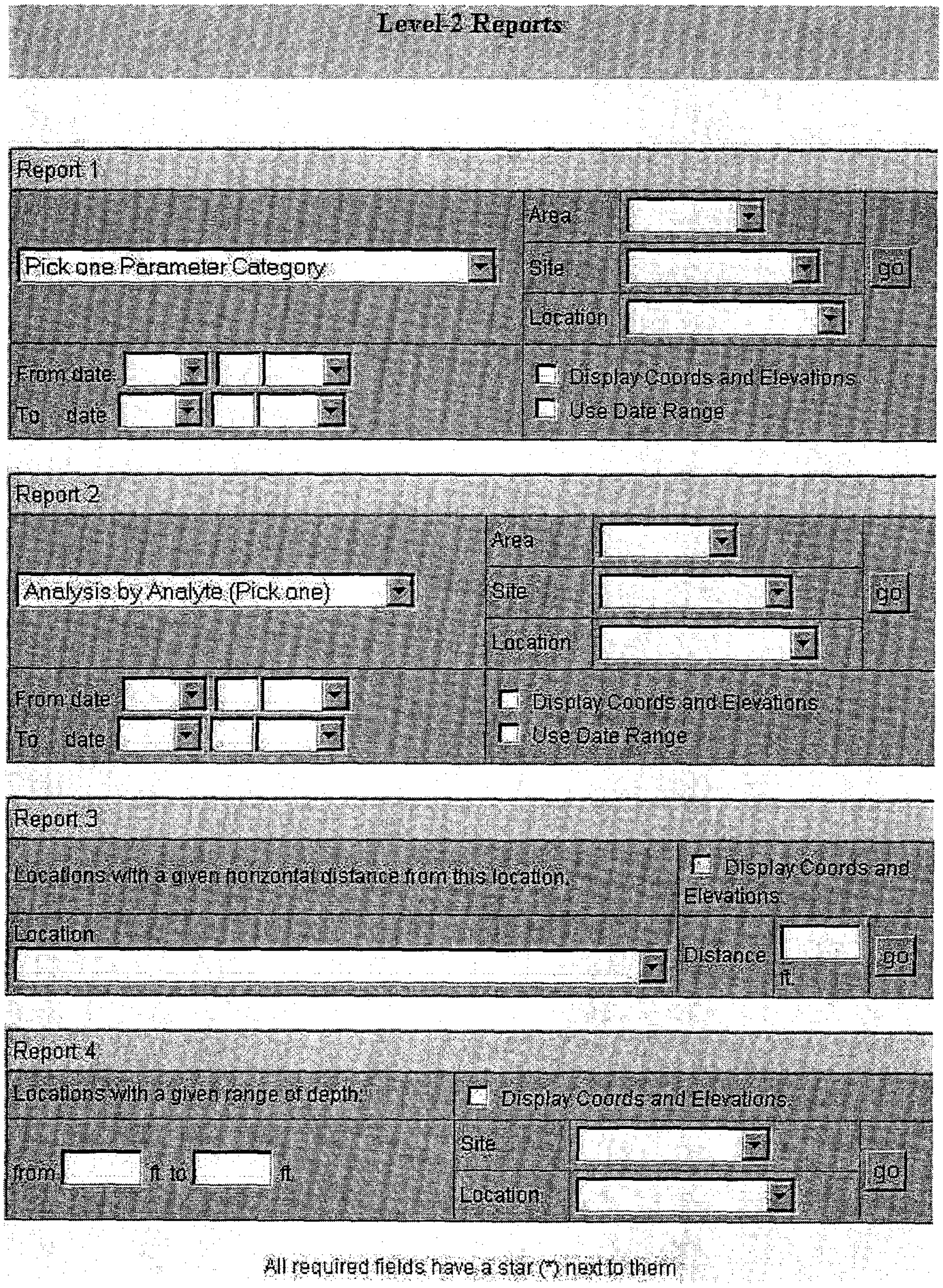
Last loaded at: Tue Apr 18 10:24:42 2000

3, RDBMS Query Structure/Screen

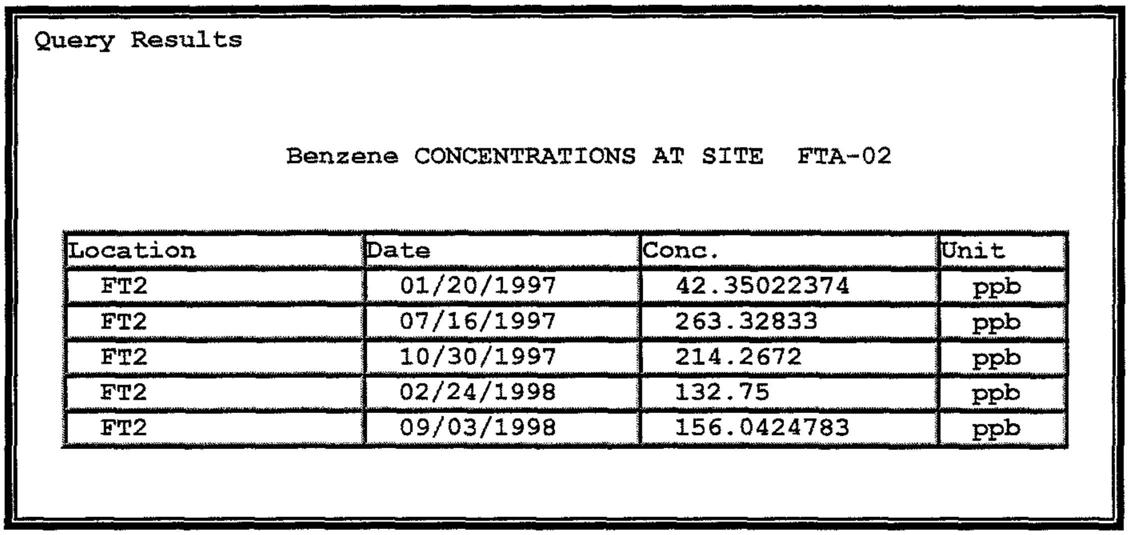


Locations with a given horizontal distance from this location.

Locations with a given range of depth:

All required fields have a star (*) next to them

4, **Results report for single contaminant at all wells**

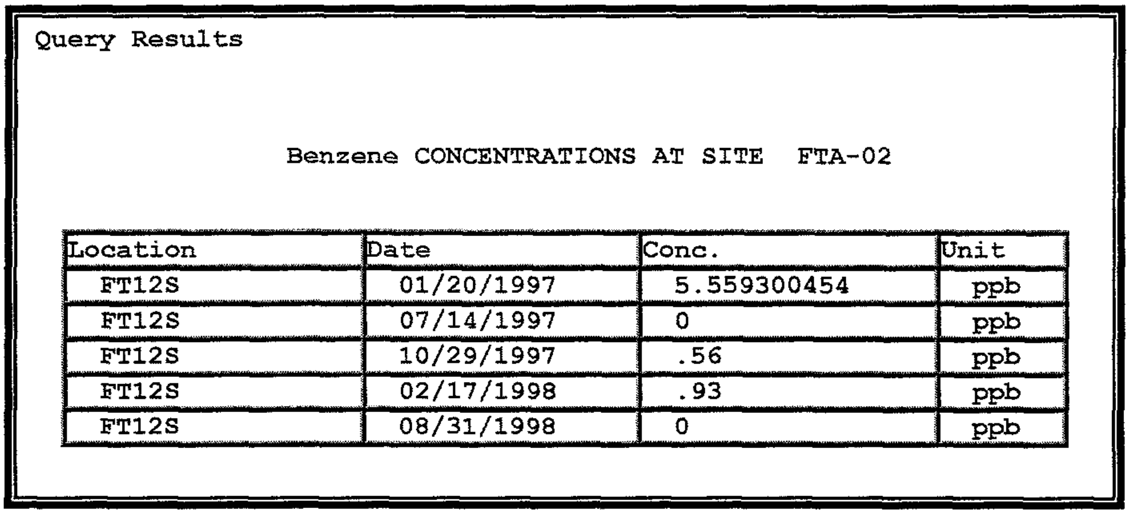


Query Results

Benzene CONCENTRATIONS AT SITE FTA-02

Location	Date	Conc.	Unit
FT2	01/20/1997	42.35022374	ppb
FT2	07/16/1997	263.32833	ppb
FT2	10/30/1997	214.2672	ppb
FT2	02/24/1998	132.75	ppb
FT2	09/03/1998	156.0424783	ppb

5, Results report for single contaminant at one well over time.



Query Results

Benzene CONCENTRATIONS AT SITE FTA-02

Location	Date	Conc.	Unit
FT12S	01/20/1997	5.559300454	ppb
FT12S	07/14/1997	0	ppb
FT12S	10/29/1997	.56	ppb
FT12S	02/17/1998	.93	ppb
FT12S	08/31/1998	0	ppb

Accuracy, Precision and Contaminant Variability

During the course of the project, field spikes, blanks, field duplicates and laboratory standards were introduced into the analytical process to evaluate contributing sources of error. Once the sources of error were determined their contributions could be subtracted from the total variability at selected wells over time. The remainder would constitute natural variability which predictive models of fate, transport and potential exposure predictions at known points should capture.

In this work, laboratory standards, blanks and duplicates over time were evaluated for the major dissolved contaminants at selected wells. The normalized variance of these samples was identified as laboratory error or variability. Spiked samples from the field, "matrix spikes", were evaluated similarly to identify field and laboratory error. This quantity was subtracted from the total observed variability to identify natural variability. Each contribution was tabulated with respect to contemporaneous sampling/lab events. The overall mean values are reported.

The results of this analysis for major contaminants are shown in Table 3 and 4 for the two sites of interest.

Table 3 : Sources of Variability in Groundwater Sample Results: KC135 site
(Variances expressed in percentage of mean)

			Variability		
	Mean(µg/l)	**Lab**	**Field**	**Natural**	**Total**
Source Wells					
ML14 17.20					
Toluene	343.7	0.01	1.03	98.96	100
Ethyl Benzene	375.9	0.03	20.47	79.50	100
Xylenes (m,p)	1455	0.00	2.15	97.85	100
Xylene (o)	412.6	0.02	7.01	92.97	100
ML14 15.73					
Toluene	1509	0.00	0.07	99.93	100
Ethyl Benzene	576.5	0.01	7.47	92.52	100
Xylenes (m,p)	2113	0.00	1.92	98.08	100
Xylene (o)	790.9	0.01	4.89	95.10	100
ML14 13.60					
Toluene	267.8	0.01	1.52	98.47	100
Ethyl Benzene	97.5	0.13	85.18	14.69	100 **
Xylenes (m,p)	596.8	0.06	1.10	98.84	100
Xylene (o)	212.6	2.53	3.04	94.43	100
Downgradient Well					
W409S					
Toluene	15.8	1.68	NA	98.32	100
Ethyl Benzene	157.1	0.11	0.60	99.29	100
Xylenes (m,p)	245.5	0.06	15.35	84.59	100
Xylene (o)	20.5	0.76	5.45	93.79	100

**	Small sample size
NA	The estimated variance was negative

Table 4 : Sources of Variability in Groundwater Sample Results: FT2 site
(Variances expressed in percentage of mean)

		Variability			
	Mean(µg/l)	**Lab**	**Field**	**Natural**	**Total**
Source Wells					
FT2					
Benzene	120.8	0.03	0.06	99.91	100
Toluene	31.7	0.03	1.03	98.93	100
Ethyl Benzene	205.0	0.01	0.12	99.87	100
Xylenes (m,p)	403.1	0.06	1.10	98.84	100
Xylene (o)	14.1	2.53	3.04	94.43	100
Chlorobenzene	11.6	16.48	NA	83.52	100
cis 1,2-Dichloroethene	359.0	0.00	0.05	99.95	100
1,4-Dichlorobenzene	8.2	14.17	NA	85.83	100
1,2-Dichlorobenzene	8.2	17.59	NA	82.41	100
FT4S					
Benzene	119.8	0.01	0.02	99.98	100
Toluene	63.8	0.00	0.09	99.91	100
Ethyl Benzene	165.3	0.01	0.11	99.88	100
Xylenes (m,p)	251.3	0.02	0.31	99.68	100
Xylene (o)	28.7	0.17	0.20	99.63	100
cis 1,2-Dichloroethene	370.4	0.00	0.02	99.98	100
Vinyl Chloride	108.8	0.02	0.01	99.97	100
Plume Wells					
FT8S					
Benzene	74.9	0.05	0.12	99.84	100
Ethyl Benzene	151.8	0.01	0.07	99.93	100
Xylenes (m,p)	122.1	0.10	1.78	98.13	100
Xylene (o)	3.9	24.01	28.89	47.09	100 *
Chlorobenzene	15.8	4.40	NA	95.60	100
1,4-Dichlorobenzene	3.3	66.63	NA	33.37	100 *
Vinyl Chloride	17.4	2.15	NA	97.85	100
FT8W					
Benzene	90.1	0.05	0.12	99.83	100
Ethyl Benzene	224.0	0.15	1.32	98.53	100
Xylenes (m,p)	469.2	0.06	1.07	98.87	100
Xylene (o)	11.7	2.85	3.43	93.71	100
Chlorobenzene	49.4	1.17	NA	98.83	100
1,4-Dichlorobenzene	6.7	43.39	NA	56.61	100 *
Vinyl Chloride	12.5	5.48	NA	94.52	100
Downgradient Well					
FT13S					
Benzene	63.4	0.04	0.09	99.87	100
Ethyl Benzene	122.9	0.05	0.5	99.44	100
Xylenes (m,p)	314.8	0.15	2.69	97.16	100
Xylene (o)	6.8	25.55	30.74	43.71	100 *
Vinyl Chloride	26.7	0.84	0.01	99.15	100
1,4-Dichlorobenzene	3.8	51.16	NA	48.84	100 *
Chlorobenzene	19.5	6.13	NA	93.87	100

*	Concentrations < 10 µg/l
NA	The estimated variance was negative

It is evident from these data that analytical and sampling errors were effectively controlled during the course of the project and high levels of natural variability are indeed real. This assures the integrity of the contents of the RDBMS which stands as a principal deliverable of the project. It further documents the minimum level of variability which model predictions could show.

Temporal and Spatial Variability of the Plumes.

With the effects of field and laboratory error removed from the contaminant dataset, it was possible to evaluate the trends in their concentrations over time and space. It should be noted that field and laboratory errors were generally < 20% representing a constant small contribution to total concentration variability. Due to the use of simple consistent field methods and maintenance of analytical method control throughout the project.

KC-135.

Observed trends in contaminant concentrations have been depicted for selected contaminants at wells in both source and plume areas.

Trends in BTEX Constituents and Redox Indicators at KC-135.

The KC-135 site (designated 55-51) resulted from the tragic crash of a KC-135 tanker aircraft in October 1988. Monitoring of a sporadic nature occurred shortly after the crash through 1994 as a part of the former Wurtsmith, AFB Installation Restoration Program (IRP).

In the decade that followed the incident, water levels at the site rose from 1992 through 1995 and since then have declined, as have regional water levels in the Great Lakes states. Wells USGS4 and 409s were in place before 1994 in the source area and ~ 275 feet downgradient in the plume, respectively. (Figures 6 and 7). Over the past five years, these wells show the typical two-to five-fold variability in total BTEX constituents between sampling events. At ~ 0.5 ft/day bulk ground-water flow rates, the travel time between the wells would be expected to be ~ 550 days. The results of advective dispersion, volatilization, biodegradation, and sorptive loss mechanisms caused an approximate two to five fold decrease in overall BTEX concentrations in this shallow contaminant plume. It is of note that benzene, considered the most easily degradable BTEX constituent, had nearly disappeared as a major contaminant during the same time period. Given this known human carcinogen is a principal risk driver the documentation of benzene disappearance is a major output of the project.

Table 5 contains the estimates of KC-135 plume area in meters squared from 1995 through 1999. The areas were estimated from the indicated contours developed for each sampling event by manual planimetry. The largest plume "footprint" was identified from < 0.5 mg/l oxygen concentrations within the consistently > 6 mg/l background condition. This footprint and the corresponding suboxic to reducing portions (i.e. < 1 mg/l and < 0.5 mg/l) varied by ± 50% or more on an event basis over the time period. Owing to the relative stability of the single limited source conditions at the KC-135, the BTEX (> 50 μg/l) footprint varied by less that ± 20% over the same time period. The plume's overall indication is stable in overall dimension super imposed over significant geochemical variability on a quarterly basis.

Temporal trends in BTEX constituents at wells USGS4 (Figure 6) and 409S (Figure 7).

Figure 6

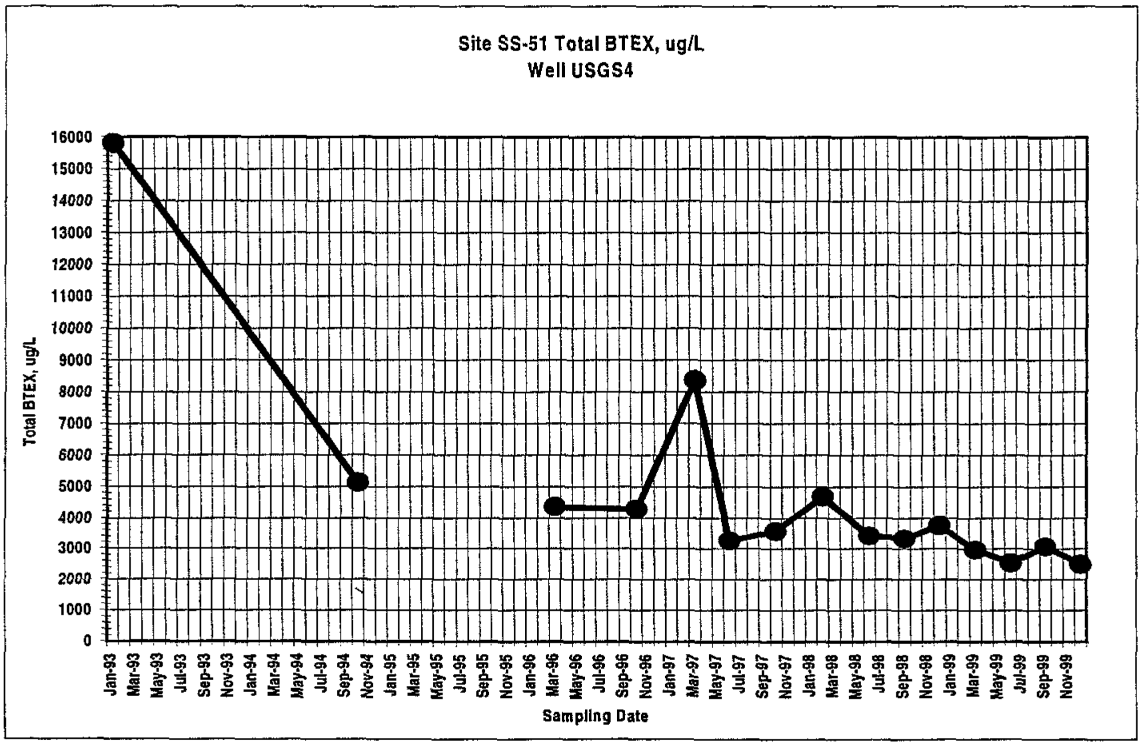


Figure 7

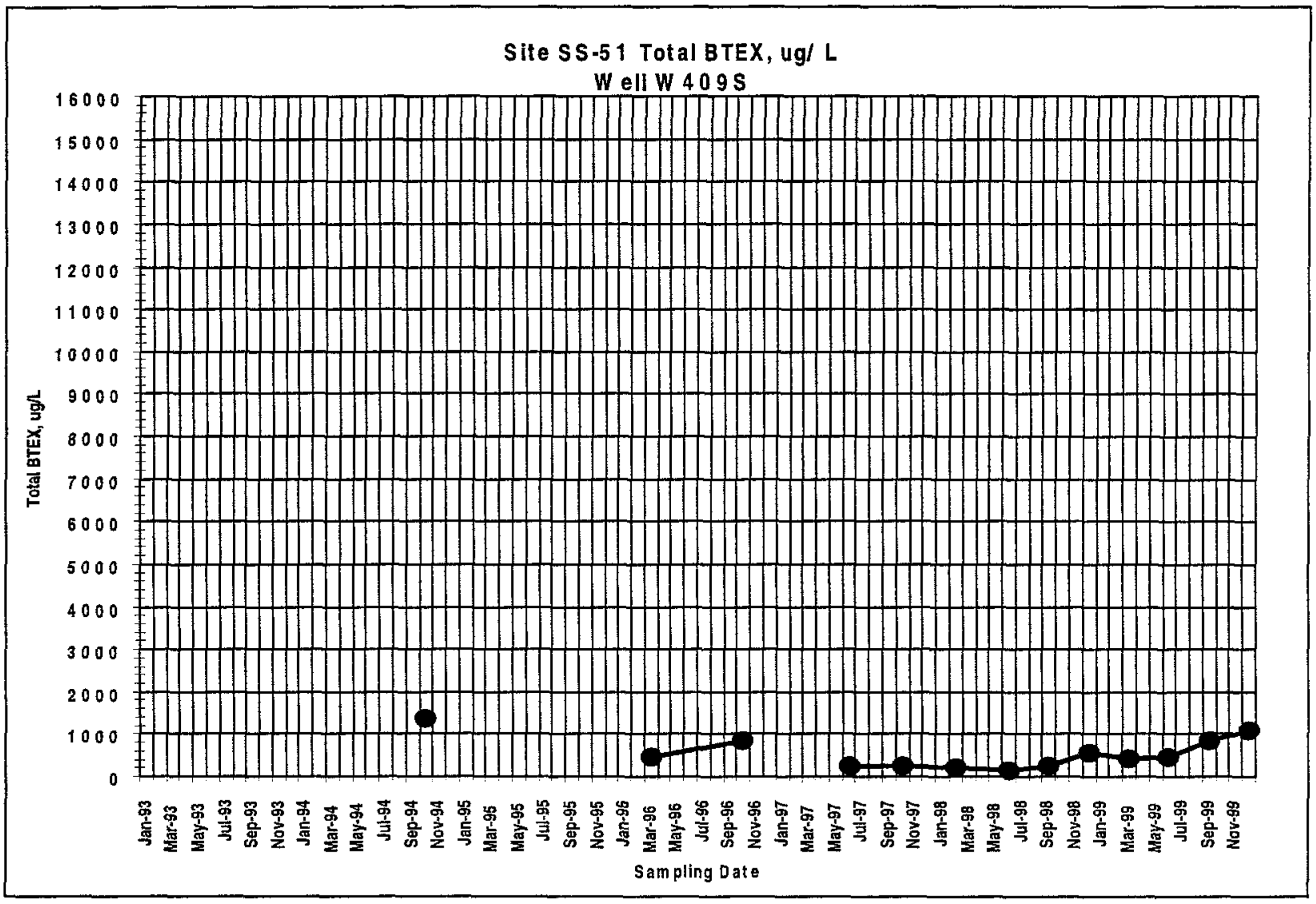


Table 5 KC-135 plume area(meters squared X10-3) over time

DATE	DO<5mg/l	DO<1mg/l	DO<0.5mg/l	BTEX>50ug/l
Jul-95	4.32	0.01		1.92
Mar-96	4.45	0.46	0.11	1.48
Jun-96	4.34	0.44	0.05	
Nov-96	3.94	0.34	0.11	1.63
Mar-97	4.8	1.01	0.23	
Jun-97	1.68	0.21	0.07	1.71
Oct-97	2.07	0.4	0.1	1.71
Feb-98	2.77	0.16	0.03	1.41
Jun-98	3.28	0.62	0.29	1.3
Sep-98	1.39	0.28	0.1	1.34
Dec-98	3.3	0.69	0.18	1.94
Mar-99	2.83	0.41	0.11	1.69
Jun-99	2.61	0.73	0.26	1.68
Sep-99	2.62	0.41	0.11	1.78
Dec-99	2.36	0.44	0.11	1.89
AVERAGE	2.36	0.440666667	0.132857143	1.652307692
STDEV	1.0594235	0.247774859	0.08068616	0.213430467

FT-2

The Fire-Training Area Site FT-2 (IRP designation FTA-02) resulted from more than 40 years of fire-training activity at the former Wurtsmith AFB. These activities were conducted at a large number of locations in the overall area. Quantities of waste solvents, fuels, lubricants and other liquid wastes were used in the course of these exercises. The current monitoring network was set up in the late '80's and early '90's by the USGS and accordingly focuses mainly on a central source area near the existing training pad, shown in Figure 1. The ground water flow gradient in this portion of the base is more pronounced than at the KC-135 site, giving rise to flow conditions quite similar to those at MIRTL 2 to the E-NE. (see following section)

Consistently high (i.e. > 500 µg/l) BTEX concentration have been documented at or near the training pad as depicted in Figure 8 for well FT-2. Average BTEX concentration at this well have been > 600 µg/l ± 50% from 1994 through 1999. At well 8S (Figure 9) approximately 800 feet downgradient, BTEX concentration have lower, averaging ~ 200 µg/l ± 50%. Since a well-defined source term has not been identified at the FT-2 site, speculations on travel time and loss mechanisms are more difficult to unravel.

Nonetheless, the distal end of the plume has been consistently found between the transects at wells 12, 13, 14 and that of 15, 16, 17 ~ 1,000 feet downgradient over the past five years. Clearly, loss mechanisms have been at work at the site controlling downgradient movement of the plume constituents.

At the FT-2 site the effects of oxygen utilization as an electron acceptor resulted in a consistently larger plume "footprint" than other indicators (Table 6) as was the case at the KC-135 site. Spatially, the plume at FT-2 has been more variable than that at KC-135 due to the presence of multiple "hot-spots," presumably coincident with localized past releases. Accordingly, the > 50 µg/l BTEX footprint was also highly variable over the past five years averaging ~ 45 x 10^3 m^2 ± 30%.

Overall, the dissolved oxygen and elevated conductance plume areas clearly delimited the spatial extent of the plume and it" response to transient electron acceptor (i.e. O_2) influx and the progress of degradation process.

Figure 8

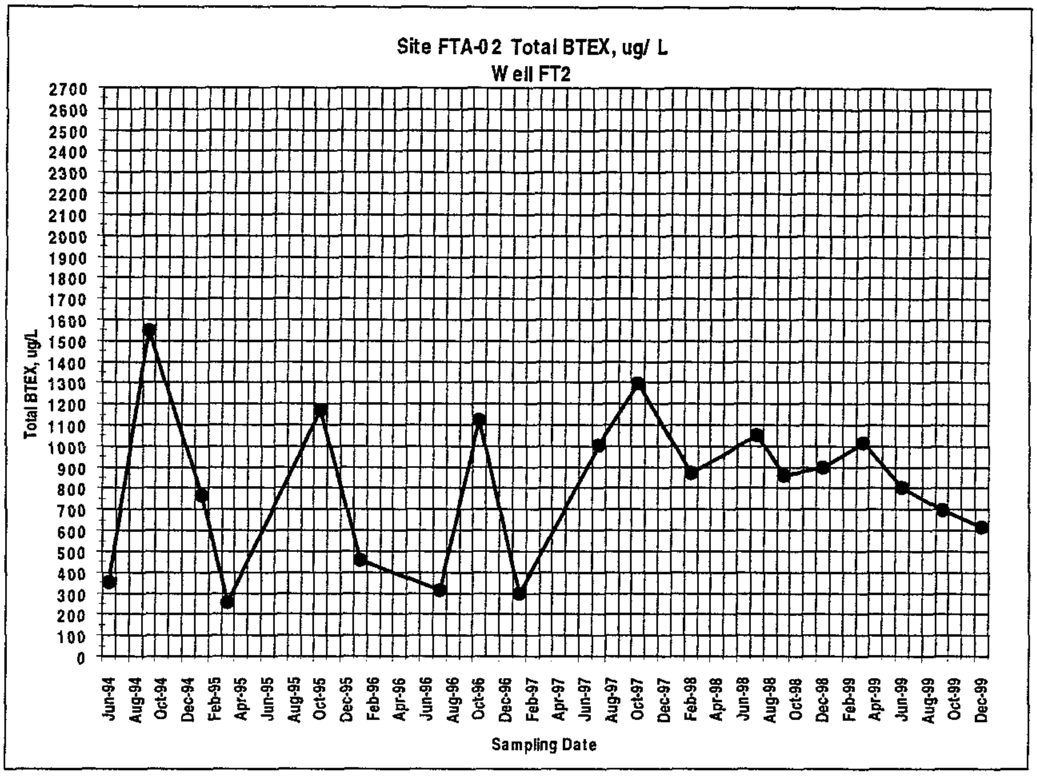


Figure 9

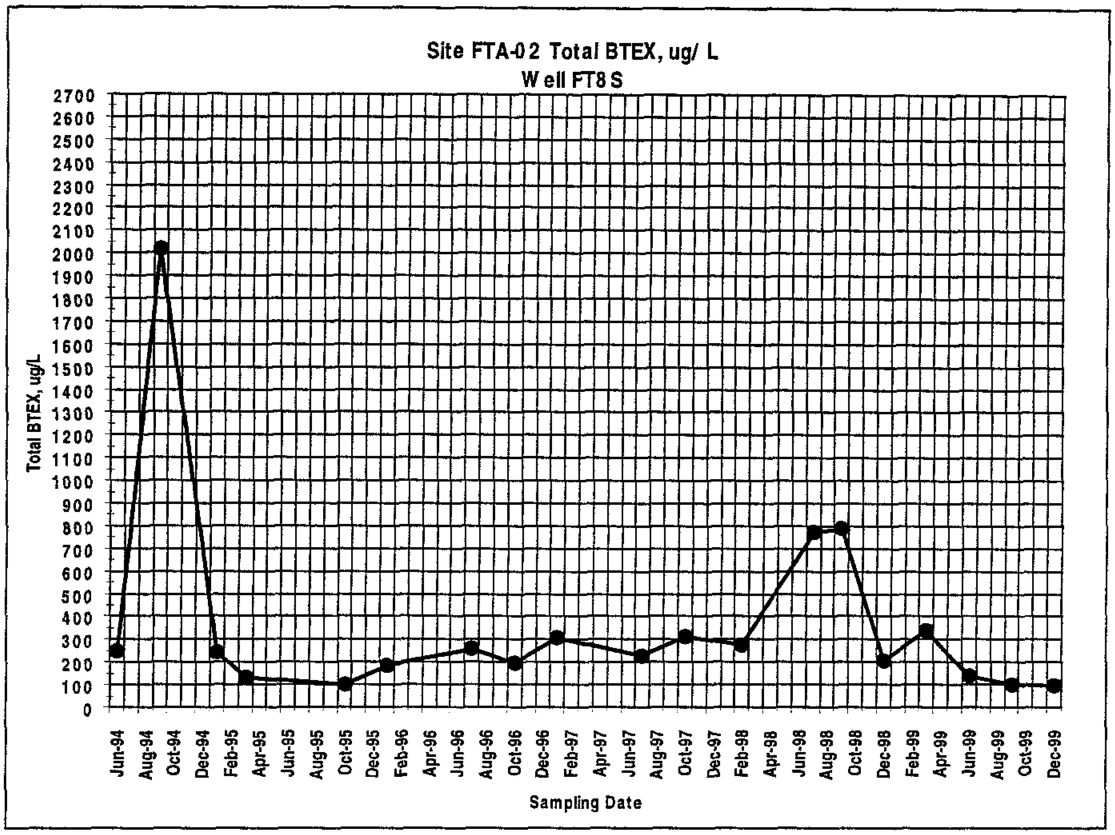


Table 6

FT2 Plume area with time in meters squared X10-3

Date	Diss.O2(<5mg/l)	Diss. O2(<1.0mg/l)	Diss. O2(<0.5mg/l)	Conductance (>300uS/cm)	Benzene(>50ug/l)	BTEX(>50ug/l)
Dec-99	125	59	14.2	11.1	3.6	48.6
Sep-99	119	22	5.3	61.1	4.1	42.4
Jun-99	107	60	3.5	42.5	3.3	50.2
Mar-99	116	16.8	1.8	44.3	2.8	49.3
Dec-98	80.6	5.3	1.6	80.6	3.9	59.8
Sep-98	27.9	9.3	6.2	40.3	24.8	34.1
Jul-98	55.8	21.7	9.3	43.4	20.5	34.1
Jul-97	52.7	15.5	6.2	31	9.9	40.3
Jul-96	71.3	21.7	6.2	43.4	12.4	24.8
Sep-94	124	43.4	3.1	43.4	15.5	40.3
Jun-94	102	6.2	0.62	52.7	6.2	46.5
Aug-90				77.5		
Jun-88				68.2		74.4
average	89.20909091	25.53636364	5.274545455	49.19230769	9.727272727	45.4
std.dev.	33.4357729	19.72988965	3.918612927	19.00348484	7.672299643	12.92924803

MIRTL 2 Experiment

Experiments at MIRTL take place within the primary unconfined aquifer underlying the former Wurtsmith Air Force base in Oscoda, MI. At the test location, the aquifer consists of uncontaminated, unconsolidated medium to fine-grained sand and gravel approximately 60 ft. thick. This formation is underlain by lacustrine silts and clays estimated to be several hundred feet thick. The ground water table is approximately 10-20 feet below ground surface, varying moderately with location and season. The test area is monitored by a network of recorders that sample water levels and ground water temperatures every 6 hours when possible (Figures 10, 11, and 12). Detailed data collection at the site commenced in June 1995 and has indicated that both the hydraulic gradient and the direction of ground water flow at the site are extremely stable (Figures 13 and 14). The site has already been characterized extensively including: slug testing, grain size analyses of aquifer core samples, mineralogical analysis, organic and inorganic carbon assays, and other testing associated with both previous research and an Environmental Impact Statement created by the U.S.A.F. during decommissioning of the base (USAF, 1993).

During 1996-1997, a pilot study similar to the MIRTL2 study being described was run to evaluate the feasibility of conducting side-by-side experiments without the use of expensive interlane barriers or artificial hydraulic controls. Approximately 400 L of a tracer solution containing potassium bromide (200 mg/L as bromide) and Intracid Rhodamine-WT (200 mg/L) was injected at 1 L/min and allowed to migrate under natural gradient conditions. Transport of the tracers was observed and analyzed at distances up to 290 ft from the point of injection, using both 3 dimensional sampling and a flux analysis approach. The final stage of the experiment encompassed two months of intensive sampling at the downgradient end of the pilot lane, during which the migration of bromide out of the test area was monitored and used to calculate long range averages and upper bounds for hydraulic conductivity, porosity, and longitudinal and transverse dispersivities. These results were then compared against previous estimates of the parameters obtained via analysis of aquifer cores and slug testing of wells near the test area. Average porosity was estimated to be 0.28, which compares favorably with prior work that has cited an average value of 0.30. Hydraulic conductivity was estimated to be 120 ft/day, which was within the 95-140 ft/day range of conductivities that had been estimated by permeametry and grain size analyses. Dispersivities estimated from the experiment (α_L=0.545 ft, α_{TH}=0.0075 ft) after 290 ft of migration are well in line with the trend of dispersivity vs. distance in sandy aquifers that has been summarized in reviews of prior work by Gelhar et al. (Gelhar et al., 1992)

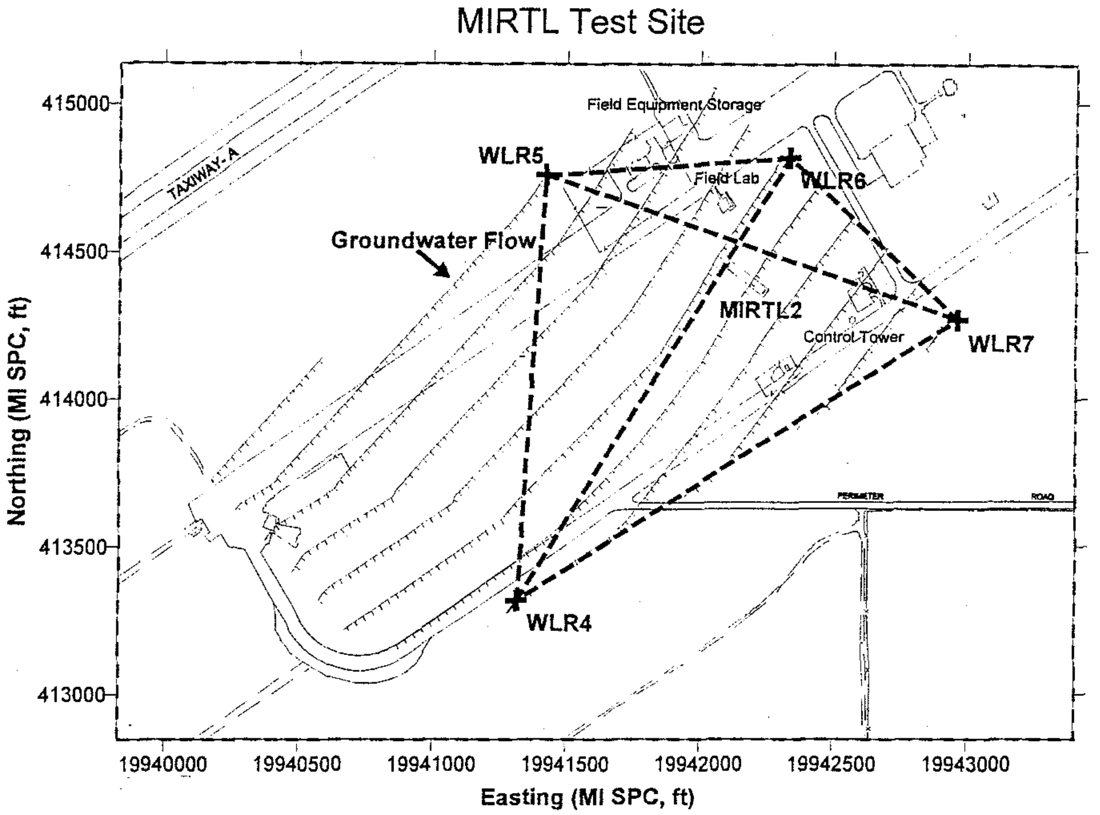


Figure 10: A map of the test location and the water level recorders. The dashed outlines delineate the four triangular regions desribed in the calculations leading to Figures 4 and 5. Region 1 (WLRs 4,5, and 7), Region 2 (WLRs 4,5, and 6), Region 3 (WLRs 4,6, and 7), and Region 4 (WLRs 5,6, and 7).

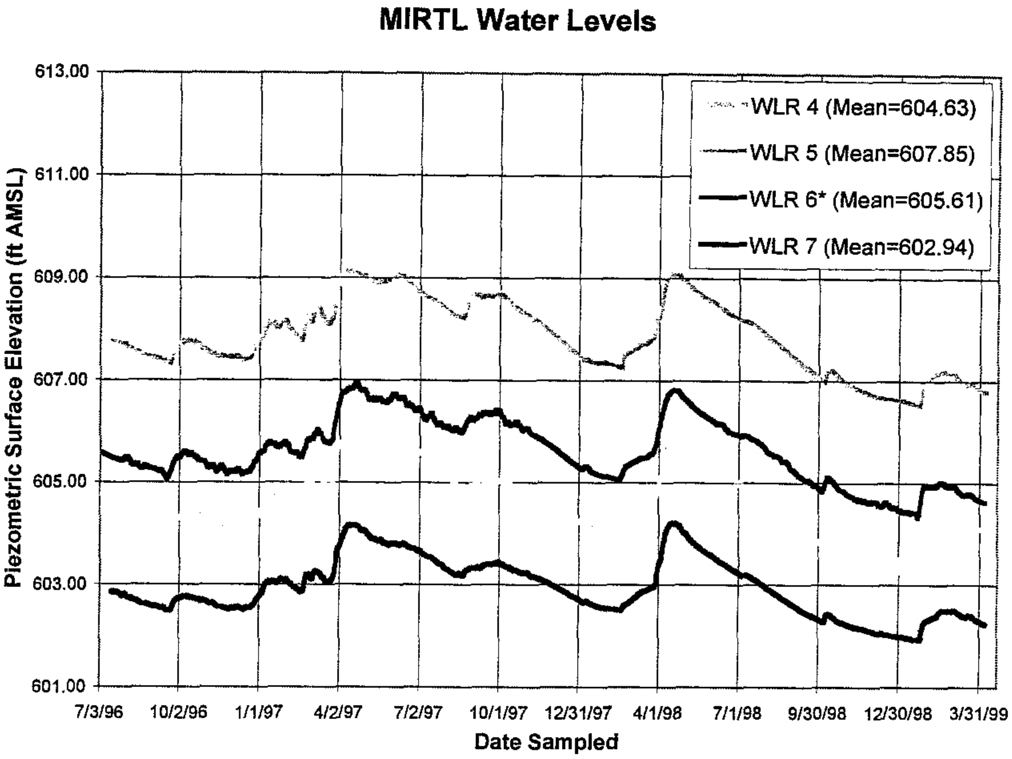


Figure 11: Water level record at locations surrounding the test lane. Average surface elevation is 620 ft AMSL.

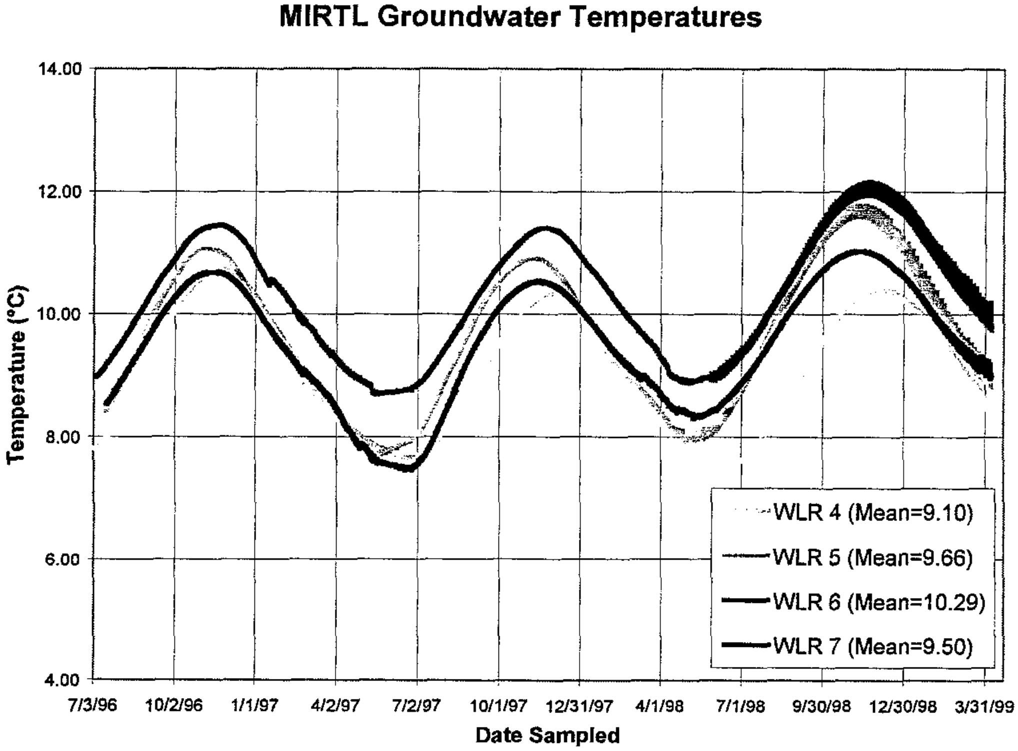


Figure 12: Groundwater temperature record at locations surrounding the test lane.

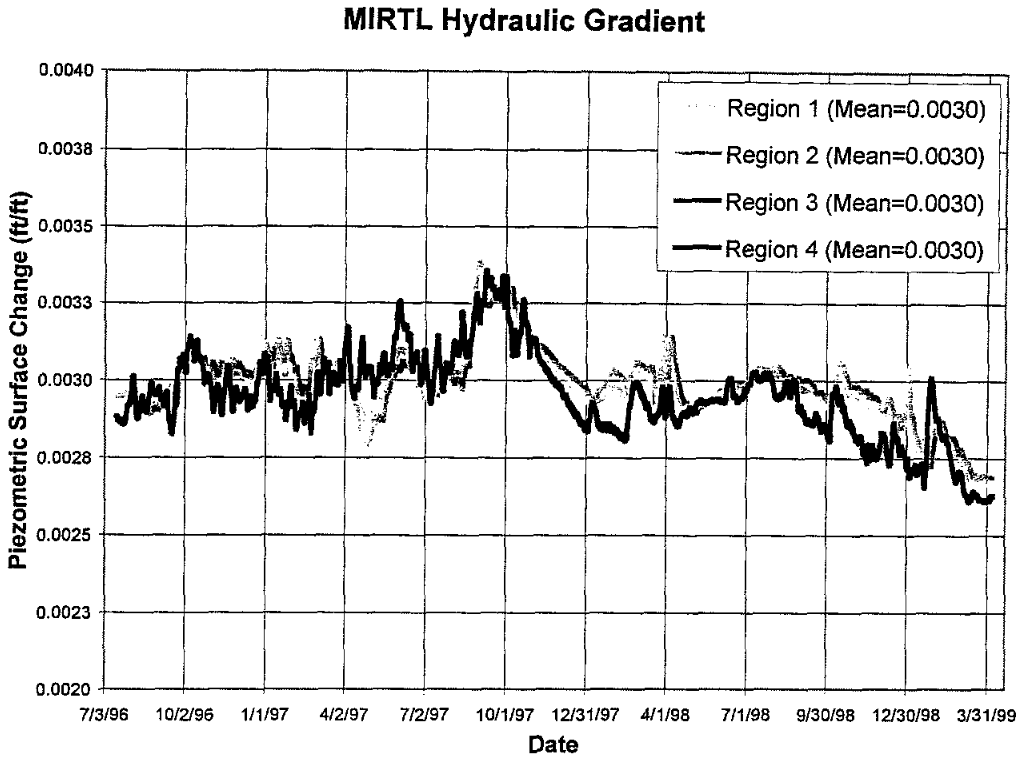


Figure 13: Hydraulic gradient record for regions enclosing the test lane. A planar piezometric surface was assumed to connect the water level recorders describing each region.

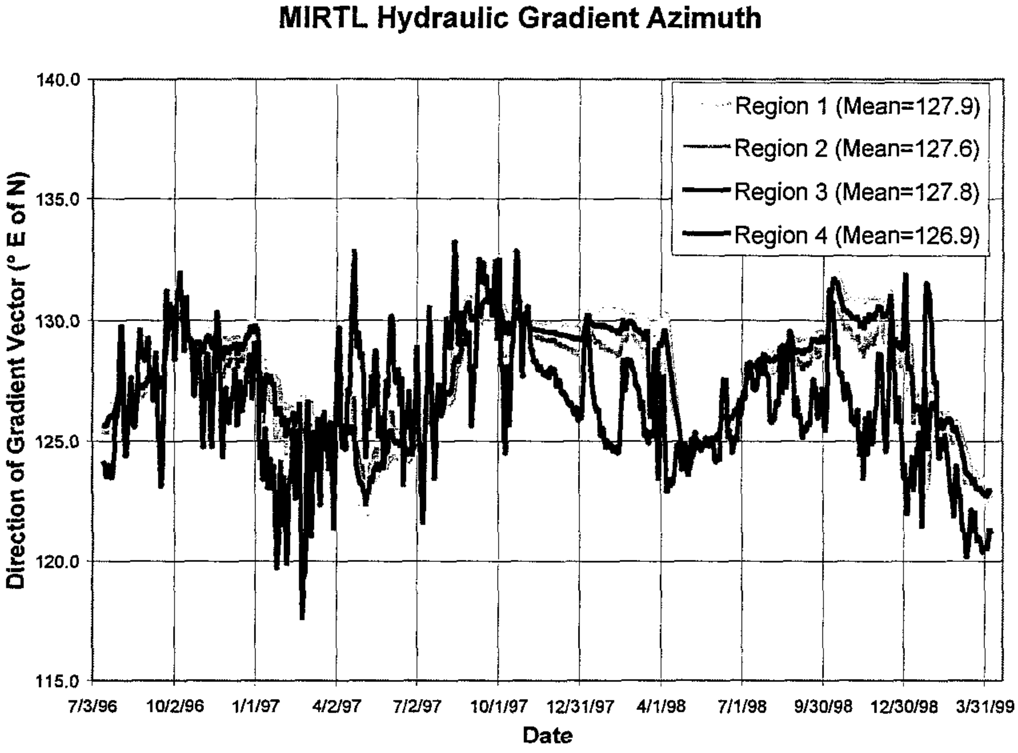


Figure 14: Groundwater flow direction record for regions enclosing the test lane. The azimuth of the hydraulic gradient vector is used, since evidence of significant anisotropy in the aquifer's properties has not been found.

The results of this pilot experiment, along with the detailed hydrologic data gathered to support its execution, led us to conclude that aqueous tracer releases could be reliably tracked as they migrated through experimentally significant distances at the site. Furthermore, given the limited variability in hydrologic conditions at the site, experiments could be run in adjacent test lanes over distances of 100-300 ft with interlane separations of 30-50 ft providing adequate isolation, negating the need for artificial hydraulic controls (*i.e.* sheetpile or slurry walls).

Design of the MIRTL2 Study

The purpose of the MIRTL2 experiment was to examine the fate and transport of both MTBE (methyl-t-butyl-ether) and the more commonly studied BTEX constituents after an oxygenated fuel spill. In order to generate a sufficiently large plume while minimizing the long term environmental impact of the study, a simulated release using dissolved phase constituents and a redox adjustment barrier was planned. The test lane was installed near the center of a ~40 acre field within the airport boundaries, providing a controlled access environment that was isolated from day-to-day vehicular traffic. Testing confirmed that conditions within the selected portion of the aquifer were essentially pristine – groundwater at the site was oxic, averaging 7.7 mg/L D.O., while specific conductivities, pH levels, chloride concentrations, and levels of dissolved organic carbon were similar to those observed at other background locations at the base. VOC samples taken from the site yielded scattered indications of TCE at < 2 ppb, but no other chlorinated or aromatic organics were detected.

The first phase of the experiment was the installation of an upgradient redox adjustment barrier, which was used to simulate the impact of oxygenated fuel constituents that were not being introduced in the tracer solution, namely the alkanes, alkenes, and less mobile aromatic constituents of these fuels that result in the creation of an anoxic to highly reducing source zone. An in-situ permeable barrier (see Figures 15 and 16) was created 10 ft upgradient from the injection well by introducing an aqueous suspension of sweet dry dairy whey into an array of temporary boreholes using a high pressure chemical grouter. The amended saturated volume was approximately 16 ft wide by 15 ft deep by 3 ft 'thick' (along the direction of groundwater flow), with the injection beginning just above the mid-summer elevation of the water table.

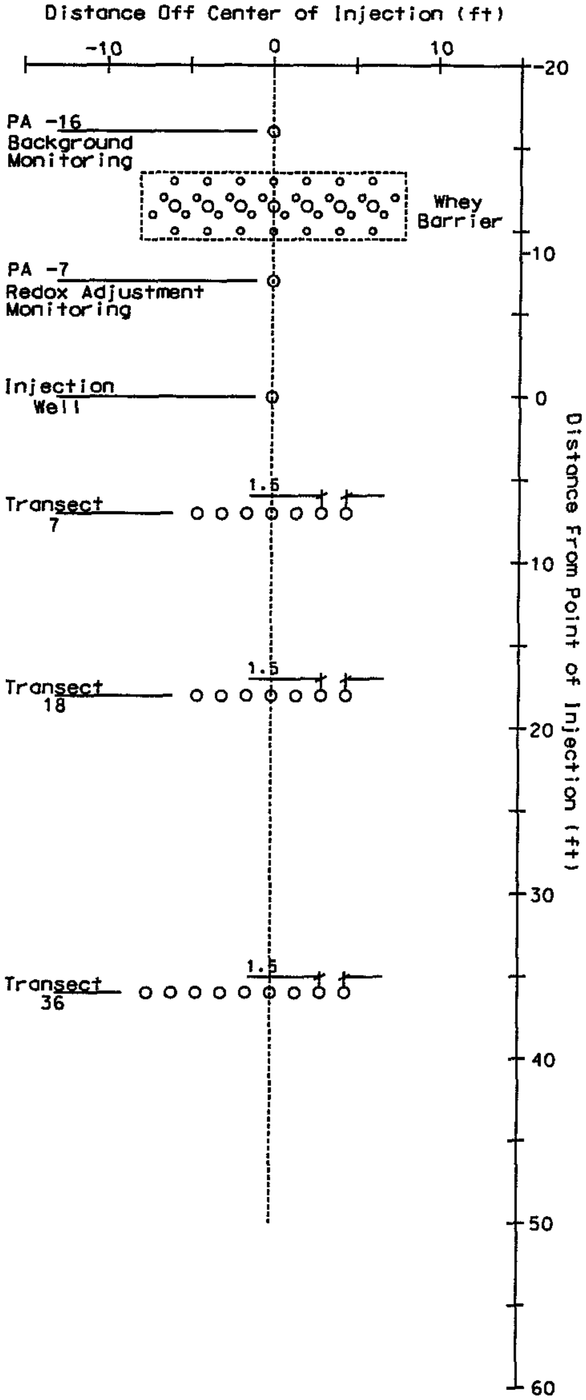


Figure 15: Plan view of the test lane near the injection point, including sampling array spacings. Each sampling array consists of 9 vertically spaced sampling points. Groundwater flow is from top to bottom.

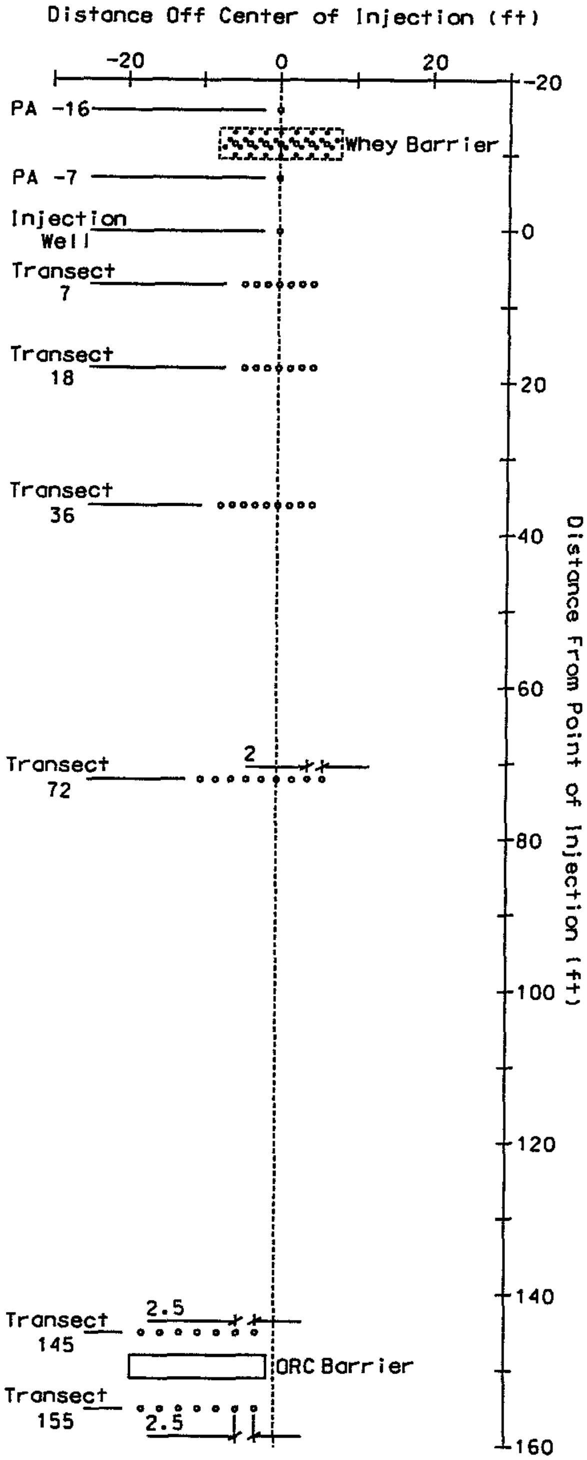


Figure 16: Plan view of the entire test lane, including sampling array spacings. The final transects and ORC barrier is offset due to a slight shift in groundwater flow direction caused by lower than normal water levels at the site.

The effect of the barrier upon redox conditions and groundwater chemistry was monitored at piezometer arrays located immediately upgradient (PA –16) and downgradient (PA –7) from the barrier via the use of multiparameter flow cells, dissolved organic carbon measurements, ion chromatography, and colorimetric wet chemical methods. Monitoring of dissolved oxygen concentrations in pre-injection water samples taken from the injection well revealed a change to suboxic (<2.0 mg/L) conditions immediately downgradient from the whey barrier. Monitoring of dissolved oxygen concentrations at Transects 145 and 155 confirmed that a substantial plume of anoxic groundwater was being generated within the test lane.

The second phase of the experiment encompassed the injection of the aqueous tracer solution and monitoring of tracer migration through the first 100 ft of the test lane. The injection well consisted of a 3 ft stainless steel wire wrapped screen placed roughly 4 ft below the water table surface, which was connected to a 3 ft stainless steel riser and a 2” PVC well casing. The tracer solution was prepared as two solutions, a nonvolatile bulk solution and a saturated aqueous phase volatile solution, which were mixed during introduction to the injection well. The bulk solution consisted of groundwater collected from the injection well and mixed with potassium bromide under a nitrogen gas blanket. The volatile solution consisted of 40 L of distilled water that had been saturated with sulfur hexafluoride and equilibrated with a NAPL containing the other components introduced in the study. On October 15, 1998, 660 L of combined tracer solution was pumped into the screened interval of the injection well at 2 L/min to minimize mounding in and around the well screen. The final composition of the injection solution, averaged from subsamples collected every half-hour, is shown in Table 7.

Table 7. Composition of the Tracer Injection Solution

Compound	Average Injected Concentration	Injected Mass
Potassium bromide	200 mg/L	132 g
Sulfur hexafluoride	20 mg/L (nominal)	13 g
MTBE	4500 µg/L	2.97 g
Benzene	1700 µg/L	1.12 g
Hexafluorobenzene	1000 µg/L	0.66 g
Toluene	1000 µg/L	0.66 g
Octafluorotoluene	500 µg/L	0.33 g
Ethylbenzene	1000 µg/L	0.66 g
O-Xylene	1000 µg/L	0.66 g

On October 18, 1998, sampling at Transect 7 commenced. Each transect in the test lane consisted of 7-9 multilevel arrays, each containing 9 sampling points distributed at various depths. The sampling points were constructed of 3" long 1/4" I.D. stainless steel screens attached to 1/8" stainless steel risers, and had dead volumes of approximately 10 ml. Transects were placed so that their longitudinal separation increased by a factor of ~2 at each interval, to allow for multiple estimates of tracer mass and to allow for an examination of plume behavior at increasingly large scales of interest. Sampling points within the transects were placed with horizontal and vertical separations of 1.5 ft – the spacings increasing by 0.5 ft downgradient from Transect 36 and by an additional 0.5 ft downgradient from Transect 72. At regular time intervals, samples were collected from each screened point within a transect using peristaltic pumps and 60 mL syringes. Field personnel purged each sampling point by discarding 50 mL of groundwater before collecting samples for analysis. Bromide samples were collected in 40 mL EPA VOA vials and analyzed on a Dionex ion chromatograph. Volatile organic samples were collected in 40 mL EPA VOA vials and preserved with 1 mL of a 40% saturated solution of $NaHSO_4$ before analysis on a purge and trap GC/MS or a headspace PID/ECD in halogen sensitive mode. Additional samples were periodically collected to seek evidence of BTEX and MTBE degradation through the appearance of aromatic acid metabolites of BTEX and/or alcohol/aliphatic acid metabolites of MTBE (Fang and Barcelona, 1998a,b).

The final phase of the experiment was the installation and monitoring of a downgradient oxidizing barrier utilizing ORC (Oxygen Releasing Compound, Regenesis Bioremediation Products, Inc.). Two transects, Transect 145 and Transect 155, were installed upgradient and downgradient from the barrier to allow for an evaluation of this technology's effectiveness with respect to MTBE. A combination of high pressure grouting and in-situ mixing with a 6" hollow stem auger was used to emplace 800 lbs. of ORC in a permeable wall that was approximately 18 ft wide by 15 ft deep by 3 ft 'thick' (along the direction of groundwater flow). In addition to collection the samples described previously, two sampling events were conducted to examine levels of peroxide and dissolved oxygen on either side of the in-situ barrier.

Data Analysis Method

Each transect sampling event yielded a two dimensional array of results corresponding to the locations of the individual sampling points, as in the example presented in Figure 17. These results were linearly interpolated onto a higher resolution rectangular grid before further processing. If the groundwater velocity through the array of sampling points is known, multiplying the values of the individual grid cells by the velocity and the porosity of the aquifer material will result in a dataset containing the 'instantaneous' flux of an analyte through the transect (not shown).

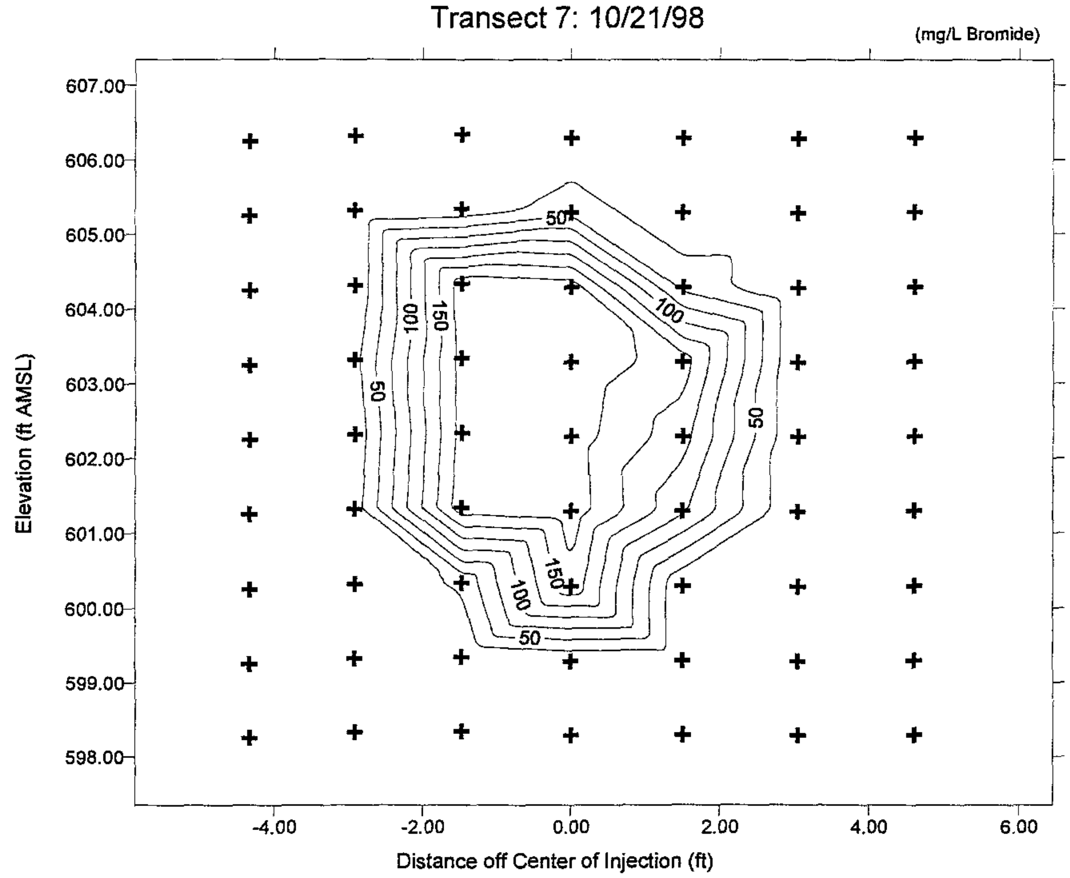


Figure 17: A contoured display of bromide migrating through Transect 7, 6 days after injection of the tracer solution. + symbols depict the location of sampling points.

If groundwater velocities through the transect are assumed to be constant during transit of an analyte, a spatiotemporal transformation can be used to provide estimates of mass passing through the transect and dispersivities via a slightly modified three-dimensional method of moments. The 'standard' three dimensional method of moments integrates concentration along the three spatial dimensions to yield estimates of the 0th statistical moment (mass), 1st statistical moment (velocity vector), and 2nd statistical moment (variance, which leads directly to dispersivity estimates). By aligning a spatial axis with the mean groundwater flow path and transforming it into a time axis using the mean groundwater velocity, successive samplings of a single two dimensional array of wells, or in this experiment a transect, can be used to produce the same statistical summary of an analyte's behavior in transport.

Utilizing this transformation provides several distinct advantages. If only a few estimates of mass are needed, or if an estimate of mass is needed repeatedly in a specific location, the number of wells and sampling points that must be installed to provide a given level of detail is greatly reduced – instead of 'going to the plume', the plume 'comes to you'. Furthermore, sample collection efforts and analytical load can be spread out over much longer periods of time. Finally, since this method quantitates mass by examining the flux of an analyte through a two dimensional grid of sampling points rather than 'static' concentration data over a three dimensional field, estimates of the mass of a reversibly sorbing analyte upon the aquifer solids, which is 'hidden' from a three dimensional method until a sorption isotherm is applied, are no longer required. This limitation is instead replaced with, at least in the instance used in this study, an assumption that the groundwater velocity across the two dimensional grid is uniform.

If multiple transects are used in the study, the average groundwater flow velocity does not have to be known to use this method. A simple estimate of velocity can be used in a preliminary round of calculations, which will yield the arrival time of the center of mass (*i.e.* the 1st statistical moment with respect to the time axis) at each location, which is insensitive to this parameter. The correct velocity can be estimated from the two arrival times and used in a final round of calculations to yield correct values of each of the statistical moments.

Development of the Plume and Initial Transport

Injection of the aqueous tracer solution took place on 10/15/98. Geochemical conditions within the test lane were suboxic, with $O_2 \leq 2$ mg/L, Fe^{2+} occasionally detectable at 0.1-5 mg/L, and dissolved organic carbon concentrations at 5 to 50 times background levels (~0.5 mg/L) due to the slow release of soluble material from the upgradient redox adjustment barrier. In excess of 11,000 analytical determinations were made upon more than 3,500 sampled locations/times during the eight months following injection of the tracer solution. Condensed profiles of bromide passing through successive transects (see Figures 17, 18, and 19) demonstrate the existence of reasonably well behaved transport conditions during the experiment. The tracer plume developed as expected, with bromide, SF_6, and MTBE eventually separating from the sorptive BTEX and perfluorinated constituents (Figures 20 and 21). The retardation coefficients of SF_6 and MTBE, relative to bromide and averaged through all six transects, were 1.02 and 1.03, respectively – considering the bounds of experimental error resulting from the sampling frequencies that proved practical during this study, these constituents can be considered to be non-sorptive within the environment of the test lane.

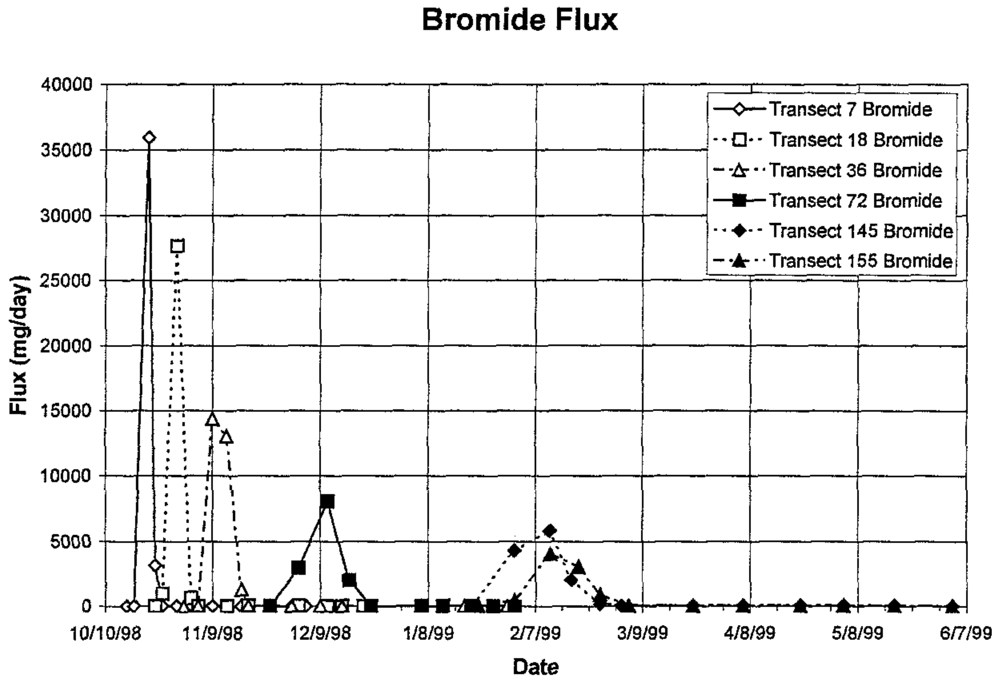


Figure 18: Bromide flux (mg/day) through the sampling transects. Sampling events are marked by their respective symbols. Piecewise linear integration can be used to calculate the mass passing each transect.

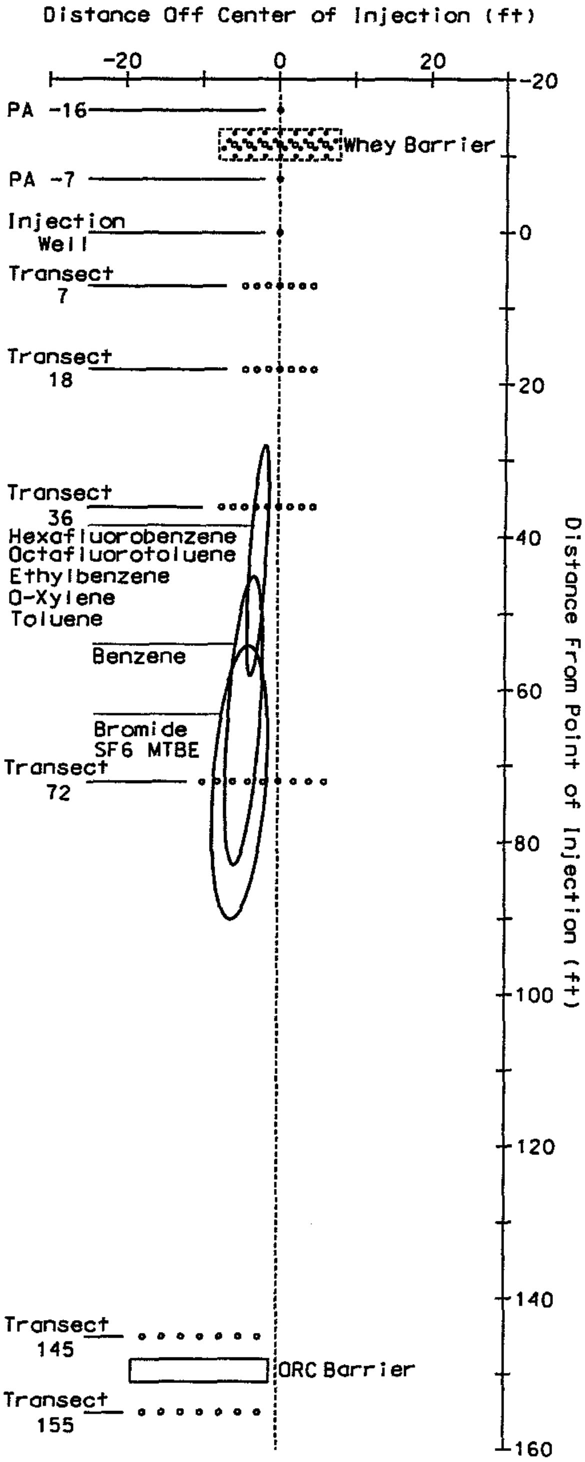


Figure 19: Outlines of the extents of various components of the tracer solution after 62 days of transport. Since samples were only collected at the transects, these outlines were estimated by using the known lateral extents of the plumes along with arrival and departure dates.

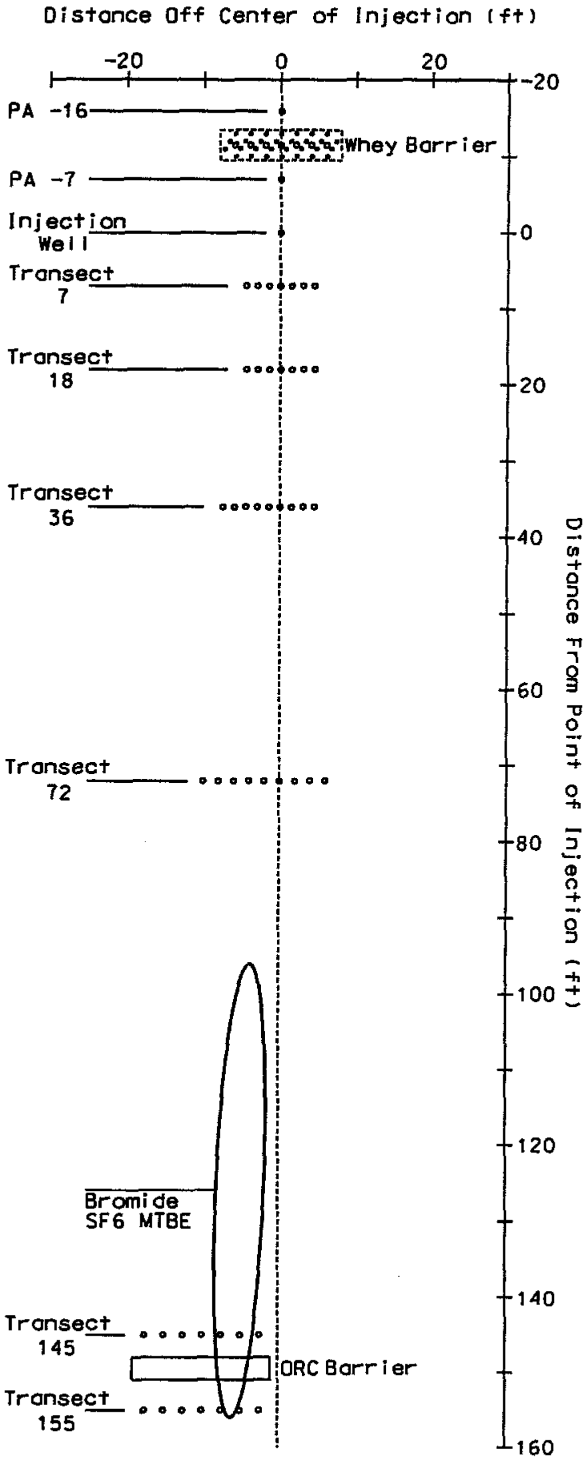


Figure 20: Outlines of the extents of the nonsorbing components of the tracer solution after 123 days of transport. Detectable concentrations of benzene did not reach Transects 145 and 155. Concentrations of other constituents were near or below quantitation limits upon reaching Transect 72.

The only unexpected outcome of the second phase of the study was the appearance of TBA (tertiary-butyl alcohol), an MTBE degradation intermediate, at concentrations of 1-10 µg/L within a week of injection of the tracer solution at Transect 7. TBA at more significant concentrations, up to 70 µg/L, appeared sporadically at Transects 18 and 36 from 3-8 weeks after injection of the tracer solution. Eleven subsamples of the tracer solution injected on October 15th were analyzed by GC/MS to determine both the concentrations of the volatile tracer constituents and detect contamination of the tracer solution – TBA was not detected in any of the samples. Samples collected before the introduction or arrival of the plume constituents at transects in the test lane were similarly devoid of TBA.

Effects of Contributing Loss Mechanisms (Dispersion, Volatilization, and Sorption)

The dataset obtained from this experiment is currently being modeled to refine the quality of the mass estimates obtained by the flux analysis approach. Limitations to the sampling frequency achievable in the field, given the number and varying transport characteristics of the compounds used, have resulted in some truncation errors, causing raw inter-constituent behavioral comparisons to be excessively 'noisy'. Simulations using Visual MODFLOW and MT3D/RT3D will be performed to enable improved estimates of the contributions of volatilization and dispersion to transport behavior and apparent fate.

Rough analysis utilizing peak observed concentrations were less susceptible to truncation error, and comparisons between bromide, MTBE, and SF_6 could be made. 'Apparent' mass loss was greatest for SF_6, followed by MTBE and the bromide. Relative to bromide, an estimated 15% of the injected SF_6 may have been lost due to volatilization. This serves as an extreme upper bound for volatilization losses, since SF_6 is an inert, non-polar gas whereas attempts to remediate MTBE via air stripping have demonstrated that, when dissolved in water, it is an extremely difficult contaminant to remove through volatilization. Relative to bromide, an estimated 10% of the injected MTBE may have been lost to a combination of mechanisms. Depending upon the rate of TBA turnover, the mass of TBA observed within the lane *may* have been sufficient to account for the majority of the discrepancy in MTBE (see Table 8).

Table 8. Uncorrected Tertiary-Butyl Alcohol Observations

Location	Peak Concentration of TBA (ug/L)	Mass of TBA (ug)
Injection	0	0
Transect 7	10	2606
Transect 18	46	33467
Transect 36	72	118571
Transect 72	7	6783
Transect 145	64	78277
Transect 155	101	61704

With respect to the ORC barrier study, both peak observed concentrations and mass estimates are insufficiently dissimilar in comparison to the bounds of experimental error to allow for conclusions to be drawn in this report. However, the presence of ~ 4 µmole/L of TBA immediately behind the barrier, the highest concentration observed during this study by a significant margin, suggests that transformation rates of MTBE, presumably the precursor compound, were increased relative to conditions in the anoxic aquifer upgradient from the barrier. It is not clear whether this transformation may have occurred via biotic or abiotic means.

Source Stability at Petroleum Hydrocarbon Spill Sites.

The evaluation of fuel and mixed fuel and solvent sites requires in depth and spatially intensive sampling and analysis activities. These are time consuming and expensive efforts which are rare in the practice of site investigation and remediation programs.

This study was undertaken to evaluate source conditions at sites with existing historical monitoring records of contaminant plumes. It was originally planned to be a three-year effort so as to capture changes in plume conditions coincident with serial evaluations of source dimensions.

Due to the termination of the project in the second year, the project's major output consisted of an evaluation of a rapid field measurement for sediment associated total petroleum hydrocarbon (TPH) determinations relative to standard methods, (Xie et al. 1999). The rapid field method, Petroflag ®, developed by Dexsil, Corp., proved to be better than the standard EPA method 418.1 as compared to the compound specific gas chromatography – mass spectrometry method. The latter two methods are more time consuming and expensive than the Petroflag ® which can guide on-site evaluations of sources while field crews are in place. In addition to the ability to screen large numbers of samples inexpensively, avoidance of mobilization and laboratory costs will facilitate site characterization efforts for the DoD. Detailed results of this part of the project are contained in Appendix A and a paper in review detailing applications in the field. (Xie and Barcelona, 2000).

Biodegradation Rate Constants at KC-135

In a previous study, and those of collaborators, there have been a number of publications developed on the verification of ongoing biodegradation processes at the KC-135 Site. (References: Stephen et al., 1999, Fang et al., 2000, Fang and Barcelona, 1999 and Fang et al. 1997.) The references show that major increases in microbial biomass, activity and the presence of intermediate degradation products have occurred over the past decade at this site.

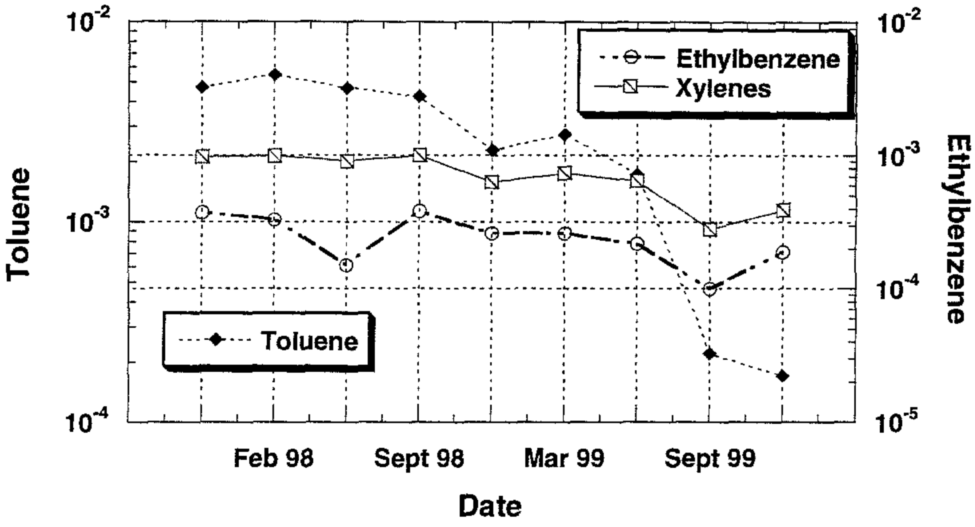
In the preceding sections of this report, it was established that plume contaminant and redox indicators at the site have exhibited considerable temporal and spatial variability. Also evident, were the effects of multiple loss mechanisms in the initial two years of transport from the known source area (Figure 6 and 7). Analyses of these data were conducted by the method of Buscheck and Alcantar (1995), a one-dimensional advective/dispersive transport model with retardation effects included. Estimates of apparent biodegradation rates (and perhaps some volatilization effects) made for total BTEX constituents and each constituent compound in both source and plume areas they have been included in Table 9 and 10 for selected sampling events.

Table 9 Overall apparent biodegradation rate constants at KC-135

Date	**BTEX**	
	Source	Downgradient
Mar 96	0.00737	0.01171
Jun 96	**0.01419**	**0.02281**
Sept 96	0.02414	0.02790
Sept 97	0.01560	0.02094
Jun 98	0.01148	0.02038
Sept 98	0.02007	0.05533
Mar 99	0.00526	0.02513
Sept 99	**-0.00193**	**0.03153**
Dec 99	0.01543	0.03388
Average	0.012401	0.027734

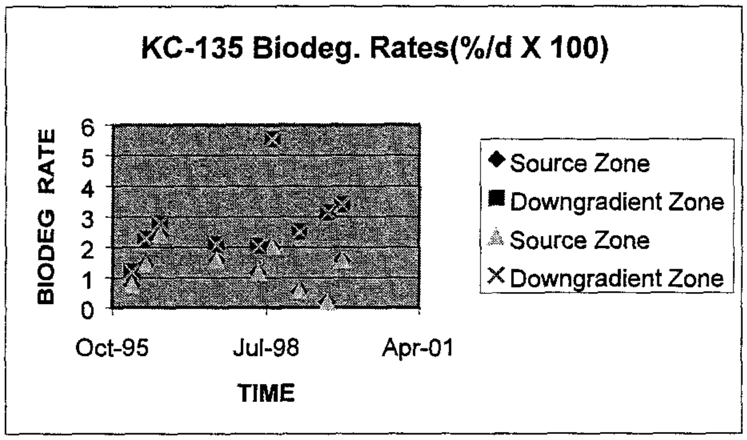
Table 10 Apparent biodegradation rate constants at KC-135

Date	Toluene	Ethylbenzene	Xylenes
Sept 97	0.00467	0.00037	0.00097
Feb 98	0.00544	0.00033	0.00099
Jun 98	0.00464	0.00015	0.00090
Sept 98	0.00421	0.00038	0.00100
Dec 98	0.00228	0.00026	0.00063
Mar 99	0.00273	0.00026	0.00073
Jun 99	0.00173	0.00022	0.00064
Sept 99	**0.00022**	**0.00010**	**0.00028**
Dec 99	0.00017	0.00019	0.00039
Average	0.00290	0.000251	0.000726



The results for total BTEX degradation rates are shown in Figure 21 from 10/95 through 12/95. Downgradient zone rate contents were consistently greater than those in the reducing (i.e. < 1 mg/l O_2) source zone, reflecting more favorable degradation conditions as the plume was reoxyzenated. This is consistent with the range of biodegradation rates reported recently by Suarez and Rifai (1999) for reducing (i.e. source) and aerobic (i.e. plume) areas.

Figure 21



CONCLUSIONS

- Analytical and sampling error can be controlled effectively by careful QA/QC procedures coupled with the use of dedicated sampling pumps and sampling protocols.

- The relation database management systems facilitates the review, recovery and interpretation of field data which can now be made available to collaborative researchers.

- Natural variability of major volatile constituents at the KC-135 and FT-2 sites was two-to-five fold from overall mean levels. Plume "footprints" vary significantly from quarter to quarter due to combined flow field and recharge effects.

- The viability of an unrestricted natural gradient experiment has been confirmed.

- The appearance of TBA in the absence of introduced or background sources strongly implies that MTBE has been observed to degrade under suboxic conditions in previously uncontaminated aquifer materials. Degradation is likely to account for a larger fraction of this loss than volatilization.

- Evidence exists for the degradation of MTBE through TBA in a highly oxidizing environment.

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APPENDICES

1. Xie, G., M.J., Barcelona, and J. Fang. Analytical Chemistry, 71, 9, 1899-1904. 1999. Quantification and Interpretation of TPH in Sediment Samples by a GC-MS Method and Comparison with EPA 418.1 and a Rapid Field Method.

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Quantification and Interpretation of TPH in Sediment Samples by a GC/MS Method and Comparison with EPA 418.1 and PetroFLAG®

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ABSTRACT

Total petroleum hydrocarbons (TPH) as a lumped parameter can be easily and rapidly measured or monitored. Despite interpretational problems, it has become an accepted regulatory benchmark used widely to evaluate the extent of petroleum product contamination. Three currently-used methods (GC/MS, conventional EPA 418.1 and a rapid field method PetroFLAG®) were performed to quantify the TPH content in samples collected from a site contaminated by transformer oil. To standardize the method and improve the comparability of TPH data, crucial GC-based quantification issues were examined, e.g., quantification based on internal standards (ISTD) vs. external standards (ESTD), single vs. multiple ISTD, and various area integration approaches. The interpretation of hydrocarbon chromatographic results was examined in the context of field samples. The performance of the GC/MS method was compared with those of EPA 418.1 and PetroFLAG®. As a result, it was observed that the ISTD quantification method was preferred to the ESTD method; multiple ISTD might be better than single ISTD; and three different area integration approaches did not have a significant effect on TPH results. Evaluation of the chromatograms between a reference sample and three unknown samples showed that the extent of contamination varied appreciably with sample depth. It was also found that there existed a good positive correlation between GC/MS and both EPA 418.1 and PetroFLAG®, and that EPA 418.1 produced the higher overall estimate while GC/MS and PetroFLAG® resulted in lower, more statistically comparable TPH values.

Keywords: total petroleum hydrocarbons (TPH), contamination, GC/MS, EPA 418.1, PetroFLAG®

INTRODUCTION

Crude and refined petroleum products constitute a major class of contaminants that environmental professionals are likely to encounter in conventional or environmental forensic site investigations and remediations. Compared to time-consuming, complex separation methods identifying individual compounds in weathered petroleum products, total petroleum hydrocarbons (TPH) as a collective parameter can be relatively easily and rapidly measured and monitored. TPH is, thus, an accepted regulatory benchmark widely used to evaluate petroleum contamination by environmental professionals. The Association for the Environmental Health of Soils (AEHS)'s eighth annual survey of states' cleanup standards for hydrocarbon contaminated soil and groundwater has been published recently[1]. By 1998, all 50 states had set site cleanup standards or guidelines based on TPH measurements by various methods. These methods may include specific determination of known toxic fractions (eg. benzene, toluene, ethylbenzene, xylene (BTEX), methyl *tert*-butyl ether (MTBE), and/or polyaromatic hydrocarbons (PAHs)).

Methods of measuring TPH and its components have been explored extensively. Currently a variety of analytical methods are used to measure TPH due to the complicated composition of petroleum mixtures. No single method, however, can be used as a representative, non-specific procedure for TPH measurement. TPH measurements generally include several crucial steps: retention of volatile $<C_8$ compounds and selection of an appropriate solvent or mixture of solvents to extract the petroleum hydrocarbons from environmental samples; preparation of calibration standards by mixing petroleum products or specific hydrocarbons in a proper ratio; and instrumental analysis of the

calibration standards and sample extractions. All of these steps may result in selective capture of individual components of hydrocarbon mixtures. Major problems can arise in risk driven site cleanup decisions. This is because environmental or human health risk may arise from various subfractions or specific components of petroleum hydrocarbon mixtures, which are not selectively determined by some TPH methods[2].

Various approaches to instrumental analysis allow us to classify the TPH methods into (a) gravimetric: EPA 413.1[3], Method 9070[4]; (b) spectroscopic: EPA 418.1[5], PetroFLAG®[6]; (c) gas chromatography: Methods 8015B[7], NWTPH[8]; (d) others: ^{1}H- and ^{14}C-Nuclear Magnetic Resonance (NMR)[9], Thin-Layer Chromatography (TLC)[10].

Gravimetric and spectroscopic methods were developed to rapidly identify the hydrocarbon contamination as TPH. Consequently, they tell us little about the individual components and fragments of petroleum products. In general, these methods exhibit low specificity, high detection limits ($\geq$10 ppm), and sensitivity to matrix effects, which require elective drying and separation steps. Briefly, EPA 418.1 may overestimate TPH as a result of (1) differences in infrared molar absorptivity for calibration standards and petroleum products, (2) detection of naturally occurring hydrocarbons, and (3) infrared dispersion by mineral particles. Negative bias may also be introduced by EPA 418.1 via (1) poor extraction efficiency of Freon-113 for high molecular weight hydrocarbons, (2) differences in molar absorptivity, and (3) removal of 5-to 6-ring alkylated aromatics during the silica gel cleanup procedure[10,11]. TPH measurements have been greatly improved by GC methods. The advantages of GC analysis and the analytical bias associated with EPA 418.1 have been examined previously.

Purge and trap or solvent-extraction capillary GC methods may overcome many such biases with the use of high-resolution columns. Moreover, TPH, by solvent-extraction GC methods (usually with the flame ionization detector), can be used as a "fingerprint" to identify the source of semivolatile hydrocarbon contamination, the content of some potentially high-risk compounds, and the rough "age" of petroleum mixtures when combined with other information (e.g., $^{13}C/^{12}C$ ratios, oxygenate or Pb content, etc.). These methods have become the most popular tool for identification and quantification of petroleum products in both forensic and environmental work. As a result, high-resolution capillary GC-flame ionization detection (GC/FID) or high-resolution capillary GC with mass spectrometry detection (GC/MS) are the most widely used techniques for petroleum hydrocarbon analyses. Recently, researchers have documented the potential advantages of GC/MS over GC/FID because valuable additional compound-specific information (e.g., PAHs) and unique TPH distribution patterns required for risk-based assessment may be derived from the mass spectra[12].

TPH represents a lumped parameter rather than an ensemble of individual compounds. Applying GC methods (both GC/MS and GC/FID) to TPH characterization relies on the total area (detector response) of the resolved and unresolved components of petroleum mixtures. Therefore, quantification methods differ from those of the conventional GC procedures for a single compound. A number of relevant issues need to be addressed in more detail in order to standardize the method and improve the comparability of TPH data.

Utilizing subsurface sediment samples from a contaminated site, our study examined crucial GC-based quantification issues including internal standard (ISTD) and external standard (ESTD) methods, single and multiple ISTD, manual and other area integration approaches employed to obtain the total chromatographic area. The performance of this solvent extraction GC/MS method was further compared with those of other lab and field methods (e.g., EPA 418.1 and PetroFLAG®).

MATERIALS AND METHODS

1. Sample Collection

Sampling was conducted at a power station in the Pacific NW where mineral oil had been in historical use as a dielectric cooling fluid. Cores were collected via a hollow-stem auger drilling technique in solvent-washed core liners. These sediment cores were sealed with Teflon tape and end caps, placed in double Ziplock bags, photographed, and stored in a cooler with ice - sufficient to maintain at 4 °C, and then sent to our lab by overnight courier. Each core sample was homogenized prior to subsampling for individual analyses. Sub-samples were transferred into dark brown glass containers with Teflon caps, and stored in dark, cold room at 4 °C.

2. Methods

(1) GC/MS

Theoretical Considerations: Generally speaking, ISTD methods are broadly applied for GC to quantify the concentrations of specific compounds in environmental samples due to matrix interferences that affect individual sample recovery and detection uniquely. Given that TPH is a collective parameter concerning various compounds with a broad range of carbon number, solubility, volatility and persistence, the performance of single-ISTD quantification methods versus multiple-ISTD methods is worthy of examination. On the other hand, ESTD methods have been used by most of the previous TPH studies. The actual performance of ESTD methods versus various ISTD methods should be re-evaluated.

Petroleum mixtures such as tank bottoms, coal tars, and creosote may contain up to 90% PAHs which are known carcinogens and concerned in risk based correction action (RBCA)[10]. PAHs consist of the fractions of petroleum products with high boiling points and low aqueous mobility[13]. These compounds may represent the bulk of the risk associated with coal tar/creosote-like petroleum contamination or significantly weathered heavy oil. To estimate semivolatile TPH toxicity reliably, it is necessary to carefully select calibration standards, ISTD and surrogate standards (e.g., at least including aromatics).

Procedures: Samples were freeze-dried on LABCONCO Freeze Dry System (LABCONCO Corp., Kansas City, MO). Ten grams of each of duplicate dried samples were further Soxhlet extracted with methylene chloride (Fisher, GC Resolv) for 12 hours, concentrated to a graduated volume using a TurboVap® II Concentration Workstation (Zymark Corp., Hopkinton, MA) with N_2 as the auxiliary gas. Extracts were analyzed by GC/MS on a Hewlett-Packard 5890 series II Gas Chromatograph equipped with a HP 5972 Mass Selective Detector and a HP Automatic Liquid Sampler. HP MS-ChemStation (DOS series) was used to program the data acquisition and analysis. External standards were prepared from Shell Diala oil (i.e., a transformer oil standard for the product used at the Pacific NW site). The two internal standards were: naphthalene-d_8 (99.2 atom % D, Protocol Analytical, Inc., Middlesex, NJ) and n-hexadecane-d_{34} (99 atom % D, Protocol). The two surrogate standards were: anthracene-d_{10} (99.5% atom % D, Protocol) and n-tetracosane-d_{50} (98.2% atom % D, Protocol). A HP-1 (60-m × .25-mm × .25-µm film thickness) cross-linked methyl silicone gum column was used. The injector and detector temperatures were set at 280°C and 300 °C, respectively. The initial temperature was kept at 50 °C for 1 min, ramped to 110 °C at 10 °C /min, to 270 °C at 3 °C /min, finally to 300 °C at 15 °C /min and held at that temperature for 10 min. A 2-µl aliquot was injected in the splitless mode with a 1-min purge-off. Helium was the carrier gas at 0.9 ml/min. The MS was scanned from 50 to 550 amu at 0.9 scan/sec by selecting full scan mode. The quantification of TPH in a sample from the same GC run was conducted via total chromatographic area counts based on both ISTD and ESTD, separately. Three integration approaches were used to obtain the total area of a total ion chromatogram: (a) manual integration along the lowest-point baseline; (b) sum of resolved individual compounds after integrated with the lowest-point baseline held on; (c) sum of resolved individual compounds after integrated with the baseline established by MS ChemStation integration.

(2) EPA418.1 Modified and PetroFLAG® methods.

Method details of EPA 418.1 as modified are provided in a reference[5]. Briefly, 20 gram samples were extracted with Freon-113 (Aldrich, 99+% spectrophotometric grade) by sonication for 15 min and then measured by infrared spectroscopy (BUCH Scientific, Model HC-404). Method details of PetroFLAG® are documented in the reference[6], which is basically a rapid field method. Samples were extracted by a mixture of methanol and other solvents of which detailed information was not provided by the company, and then measured by UV-VIS spectroscopy (Dexsil, Hydrocarbon Analyzer).

RESULT AND DISCUSSION

In this section we discuss: the advantages of the GC-based TPH measurement (e.g., deriving valuable information on oil degradation from chromatograms), GC quantification issues such as the ISTD and ESTD quantification methods in the context of TPH analysis, and we compare the GC/MS method with EPA 418.1 and PetroFLAG® based on measurement precision and statistical analysis.

Evaluation of the Chromatograms. Typically, chromatograms may demonstrate the effect of physicochemical and biochemical weathering on the chemical composition of hydrocarbons by comparing the retention time and elution profiles of unknown samples with reference samples[14,15]. For example, as petroleum products weather, more labile compounds are generally transferred or transformed. As a result, the gross chromatogram of a product becomes increasingly dominated by an unresolved complex mixture (UCM) of hydrocarbons and by hydrocarbons with high carbon numbers such as PAHs. UCM is represented by a large hump in the chromatogram. Such chromatographic features typically reflect that the product has been degraded or weathered significantly[7,16]. Heavier refined products, like lubricating and heat transfer fluids, may also show the presence of UCM without weathering. Various ratios may also be calculated from chromatograms/spectra and used to identify the hydrocarbon source, characterize the degree of weathering, and evaluate the effect of a variety of environmental conditions[9,17,18]. We did not explore these ratios in this study.

A simplified comparison of the GC profiles of the unknown samples with the reference sample Shell Diala oil (i.e., the primary petroleum compounds) in Figure 1 shows that the retention time windows of concern (e.g., 13-60 min covering the entire range of elution for TPH) and the GC trace patterns were very similar among the reference and unknown samples. It was also established that all the chromatograms showed the notable presence of unresolved mixtures (i.e., UCM) with similar shapes. It may also be noted in Figure 1 that the concentration or extent of contamination, on the other hand, changed with sample depth. The contaminant distribution patterns in this case may have been determined by hydrogeologic factors or biotransformation processes.

ISTD vs. ESTD methods: Table 1 presents the TPH results and recoveries of surrogate standards corresponding to the samples measured by the GC/MS method. The results were grouped in columns corresponding to: the ESTD method, ISTD methods with single (n-hexadecane-d_{34}) or multiple internal standards (napthalene-d_8 and n-hexadecane-d_{34}), and three total-area integration approaches (Table 1 a, b, c). The recovery is understood as a relative rather than an absolute parameter. The reason is that the relative response factors (based on molar concentrations) required to calculate the recoveries were basically lumped parameters corresponding to a mixture (i.e., Shell Diala oil) rather than the aforementioned individual internal standards[12]. This procedure was reversed by Wang and co-workers to calculate the relative response factor[9]. An average relative response factor for the TPH mixture was obtained by arithmetically averaging the relative response factors of all individual compounds that were mixed to make the calibration reference. Actually, the response factors of the calibration standard and the internal standards may not be necessarily the same. Careful selection of multiple ISTD mixtures may narrow this difference.

Examination of the recoveries of the two surrogate standards (anthracene-d_{10} and n-tetracosane-d_{50}) in Table 1 allows us to rank the ESTD and various ISTD methods in decreasing order of recovery. The multiple-ISTD method (ISTD: naphthalene-d_8 + n-hexadecane-d_{34}) had the highest recoveries. The single-ISTD method (ISTD: n-hexadecane-d_{34}) was lower, and the ESTD method was the lowest. In other words, depending on the composition of petroleum products, multiple-ISTD methods are the best choice for TPH measurements, especially when we do not know the composition of petroleum products. Single-ISTD methods can also be used if single representative (similar C_x range and response, etc.) ISTD are available. ESTD methods are less desirable alternatives to ISTD methods for TPH measurement in this range although they have been applied by previous studies[8,16,17].

Another issue closely associated with GC based methods is the algorithm used to integrate chromatograms as a group. MS ChemStation supports several integration approaches. There exist various regulatory recommendations for integration from a baseline established through the lowest point in a chromatogram[17]. Other documents pose a general requirement such as "integration as a group"[8]. Three approaches available in the MS ChemStation software were used to examine this issue. Clarification of this question is central to achieve more comparable TPH data. In our study, comparison of the three integration approaches (Table 1 a, b, c) indicated that there were no significant differences in the outcome. The results matched each other very well.

Comparison with other two TPH methods: Table 2 presents the comparison of the TPH results measured by the three TPH methods (GC/MS, conventional EPA 418.1 and a rapid field method PetroFLAG®). The comparison illustrated that reasonable positive correlations existed between GC/MS and both EPA 418.1 and PetroFLAG® in this mass range. In other words, the three methods yielded similar trends in TPH concentration changes with depth. In addition, EPA 418.1 produced a higher overall estimate of TPH while the other two methods resulted in lower, more comparable values. It is worth emphasizing that, even though it is basically a field method, PetroFLAG® produced quite comparable results with GC/MS method.

Previous research has argued that a modified EPA Method 9071 (similar to EPA 418.1) detected compounds other than petroleum hydrocarbons and, therefore, gave erroneously high TPH values while GC/FID yielded more reliable results[20,22]. Douglas and co-workers further summarized the reasons why EPA 418.1 might result in either negative or positive method bias[11].

The PetroFLAG® User's Manual suggests that TPH values measured by PetroFLAG® are very likely to be overestimated, even higher than those by EPA 418.1, because the PetroFLAG® system responds to the full range of hydrocarbons, and therefore, it also detects some naturally occurring hydrocarbon-like compounds[6]. The reason why the PetroFLAG® method gave significantly lower TPH values than EPA 418.1 in our experiment was not obvious. Part of the reason may be due to the proprietary absorptometry instrument's response setting. It is possible that it was not matched to the actual response factor for the samples. Another contributing factor may be that the generally higher molecular weight compounds in the samples absorb less UV-VIS intensity than the lower molecular weight, particularly aromatic, compounds in diesel oil or fuel oil.

The precision values for these three methods are presented in Table 2 in terms of mean relative percentage difference (RPD) on duplicate sediment samples. The GC/MS method yielded good method precision (RPD 4.5%) while EPA 418.1 was less precise

(RPD 12.3%). The performance of PetroFLAG® (RPD 7.5%) fell into the range between those of GC/MS and EPA 418.1. From our experience, PetroFLAG® performance is empirical (i.e., dependent on both sample attributes and instrument settings). Duplicate results can be obtained only by strict adherence to the same procedure for similar samples. To use the PetroFLAG® method, the optimum TPH concentration in a sediment sample is above 100 mg/kg dry weight. Nonetheless, it is still an inexpensive and rapid field test method.

Statistical analysis (SPSS 8.0 for Windows, SPSS Inc., Chicago, IL) was executed to estimate the significance of observed differences between the methods (Table 2). The ANOVA resulted in a critical F value of 0.048 (P-value for F-test). It was quite close to the significance level of the test (i.e., $\alpha = 0.05$). This means that the null hypothesis may be rejected, but the difference was not remarkable. Further paired T-tests were applied to specifically identify the level of significance. The P-values were 0.005, 0.003, and 0.199 for the GC/MS-EPA 418.1, EPA 418.1-PetroFLAG®, and GC/MS-PetroFLAG® paired T-tests, respectively. Compared at the same significance level of test ($\alpha = 0.05$), it can be seen that there was a significant difference between the GC/MS method and EPA 418.1, and between EPA 418.1 and PetroFLAG®. No significant differences were observed between the GC/MS and PetroFLAG® methods. Moreover, based on the P-values of the paired T-tests, we conclude that there was a slightly greater difference between EPA 418.1 and PetroFLAG® than between EPA 418.1 and GC/MS methods. In summary, even though the three currently used TPH methods presented good positive correlations between them, the EPA 418.1 gave higher TPH values and showed significant differences from both the GC/MS and PetroFLAG® methods. PetroFLAG® gave the lowest TPH values and showed no significant differences from the GC/MS method.

We conclude that multiple internal standard GC/MS methods have the most promise for quantitative, reproducible evaluations of petroleum product contamination of sediments. Preliminary sampling of sediments and GC/MS analyses will permit the selection of appropriate PetroFLAG® calibration and the instrument settings. Then mass sampling, followed by rapid, inexpensive PetroFLAG® measurements with a subset of GC/MS confirmations, should result in more efficient site characterization or treatment monitoring programs.

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FIGURE CAPTIONS

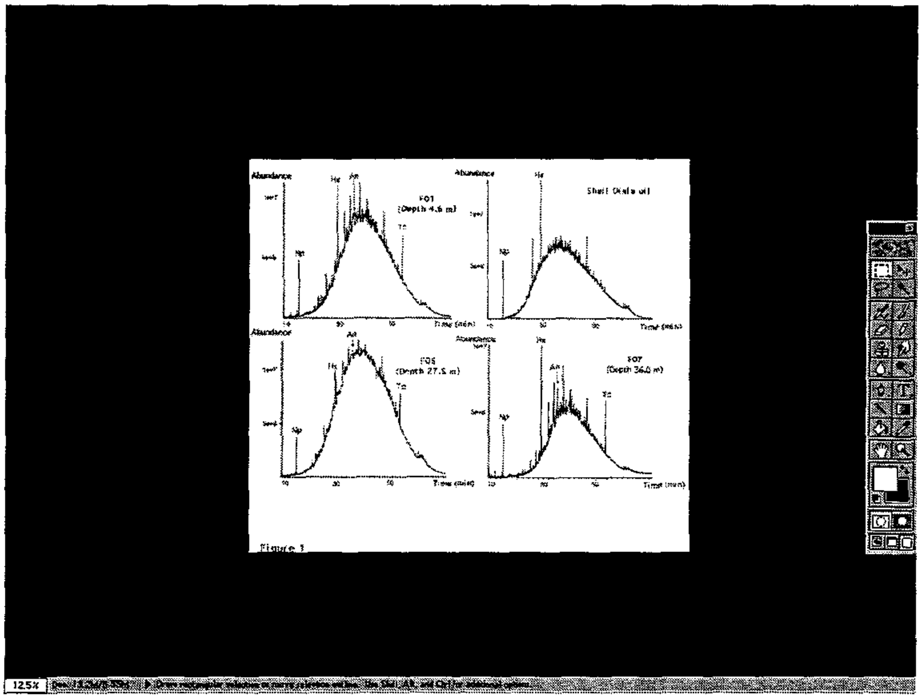

Figure 1. Comparison of the total ion chromatograms of one reference standard (Shell Diala oil) and three unknown samples over depth (F01, F05, F07): Np = napthalene-d_8; Hx = n-hexadecane-d_{34}; An = anthracene-d_{10}; Tc = tetracosane-d_{50}.

Table 1. Total Petroleum Hydrocarbons (TPH) Results Measured by the GC/MS Method for Power Substation Samples

		ESTD Method			ISTD Method					
					Single ISTD: Hx[a]			Multiple ISTD: Np + Hx[b]		
		TPH	Recovery (%)[c]		TPH	Recovery (%)[d]		TPH	Recovery (%)[e]	
Sample ID	Depth (m)	(10^3 mg/kg)	An[f]	Tc[f]	(10^3 mg/kg)	An[f]	Tc[f]	(10^3 mg/kg)	An[f]	Tc[f]
a. Integration Approach 1: Manual Integration along the Lowest-Point Baseline										
F01	4.6	13.40	N/A[g]	65.8	10.13	N/A	67.1	16.06	N/A	79.0
F02	5.7	15.89	N/A	58.2	13.64	N/A	66.9	21.04	N/A	77.0
F03	6.1	15.27	N/A	60.9	12.30	N/A	66.1	19.57	N/A	78.0
F04	7.7	7.59	51.0	73.2	5.72	52.8	75.7	10.01	67.3	96.5
F05	8.4	19.84	N/A	48.0	19.59	N/A	61.2	25.37	N/A	61.4
F06	8.9	14.76	N/A	62.4	11.19	N/A	64.8	19.33	N/A	81.8
F07	11.0	7.15	59.0	73.4	5.36	60.4	75.3	9.24	76.2	94.9
F08	11.7	7.53	54.9	71.9	5.78	58.2	76.4	10.62	77.3	101.4
F09	12.9	15.70	N/A	55.8	13.38	N/A	65.0	22.88	N/A	81.3
F10	13.9	10.59	N/A	68.0	8.33	N/A	73.1	14.32	N/A	91.9
F11	14.5	0.13	58.1	65.0	0.13	73.9	82.7	0.24	98.1	109.7
F12	14.6	0.13	46.4	79.6	0.10	48.5	83.3	0.18	63.4	109.0
F13	15.3	0.06	49.6	80.5	0.04	51.7	84.0	0.08	67.9	110.1
Mean			**53.2**	**66.4**		**57.6**	**72.4**		**75.0**	**90.2**
b. Integration Approach 2: Sum of Resolved Individual Compounds after Integrated with the Lowest-Point Baseline Held On										
F01	4.6	13.17	N/A	68.0	9.88	N/A	68.9	15.81	N/A	81.7
F02	5.7	15.78	N/A	60.1	13.42	N/A	68.6	20.88	N/A	79.6
F03	6.1	15.08	N/A	62.9	12.04	N/A	67.8	19.32	N/A	80.6
F04	7.7	7.15	52.7	75.6	5.34	54.1	77.6	9.43	69.6	99.7
F05	8.4	19.77	N/A	49.6	19.33	N/A	62.8	25.28	N/A	63.4
F06	8.9	14.83	N/A	64.5	11.15	N/A	66.4	19.44	N/A	84.5
F07	11.0	7.02	60.9	75.9	5.22	62.0	77.2	9.08	78.7	98.1
F08	11.7	7.22	56.7	74.3	5.50	59.7	78.3	10.19	79.9	104.8
F09	12.9	15.74	N/A	57.7	13.29	N/A	66.7	22.93	N/A	84.1
F10	13.9	10.52	N/A	70.2	8.20	N/A	74.9	14.23	N/A	95.0
F11	14.5	0.09	60.0	67.1	0.10	75.8	84.8	0.18	101.4	113.4
F12	14.6	0.03	47.9	82.3	0.02	49.7	85.4	0.04	65.5	112.6
F13	15.3	0.02	51.3	83.2	0.01	53.1	86.1	0.02	70.1	113.8
Mean			**54.9**	**68.6**		**59.1**	**74.3**		**77.5**	**93.2**
c. Integration Approach 3: Sum of Resolved Individual Compounds after Integrated with the Baseline Established by MS ChemStation										
F01	4.6	13.72	N/A	77.6	10.39	N/A	79.2	16.47	N/A	93.2
F02	5.7	16.53	N/A	68.6	14.19	N/A	78.9	21.89	N/A	90.8
F03	6.1	15.55	N/A	71.8	12.53	N/A	78.0	19.93	N/A	92.0
F04	7.7	7.08	60.2	86.3	5.34	62.3	89.3	9.34	79.4	113.9
F05	8.4	19.90	N/A	56.6	19.63	N/A	72.2	25.45	N/A	72.4
F06	8.9	15.96	N/A	73.7	12.10	N/A	76.4	20.91	N/A	96.5
F07	11.0	7.41	69.6	86.6	5.55	71.3	88.8	9.57	89.9	112.0
F08	11.7	7.71	64.7	84.9	5.92	68.7	90.1	10.88	91.3	119.7
F09	12.9	17.16	N/A	65.9	14.62	N/A	76.7	25	N/A	96.0
F10	13.9	10.66	N/A	80.2	8.38	N/A	86.2	14.41	N/A	108.5
F11	14.5	0.01	68.5	76.6	0.01	87.3	97.6	0.03	115.8	129.5
F12	14.6	0.03	54.7	94.0	0.02	57.2	98.3	0.04	74.8	128.6
F13	15.3	0.02	58.5	95.0	0.02	61.0	99.1	0.03	80.1	129.9
Mean			**62.7**	**78.3**		**68.0**	**85.4**		**88.6**	**106.4**

[a] Single internal standards (ISTD) method: Hx = n-Hexadecane-d_{34}. [b] Multiple ISTD method (Np = Napthalene-d_8): Np and Hx were mixed at 1:1. [c] Recoveries were based on the external standard (ESTD) (Shell Diala oil). [d,e] Recoveries were based on the relative response factors of the external standard to single ISTD (Hx) and multiple ISTD (Np + Hx), respectively. [f] Surrogate standards An = Anthracene-d_{10}; Tc = n-Tetracosane-d_{50}. [g] N/A = not available

Table 2. Comparison between GC/MS and EPA 418.1 and PetroFLAG®

Sample ID	Depth (m)	TPH (10^3 mg/kg)		
		GC/MS	EPA 418.1	PetroFLAG®
F01	4.6	16.47	30.82	11.64
F02	5.7	21.89	30.58	14.45
F03	6.1	19.93	27.78	14.69
F04	7.7	9.34	13.34	6.24
F05	8.4	25.45	60.04	22.05
F06	8.9	20.91	29.98	18.29
F07	11.0	9.57	20.19	14.02
F08	11.7	10.88	20.93	16.48
F09	12.9	25.00	59.92	27.13
F10	13.9	14.41	22.12	9.66
F11	14.5	0.03	0.04	0.02
F12	14.6	0.04	0.11	0.07
F13	15.3	0.03	0.04	0.02
Mean RPD[a] (standard deviation, sample size)		4.5% (2.8%,5)	12.3% (5.5%, 5)	7.5% (9.4%, 9)

Statistic Analysis at Significance Level 0.05	DF[c]	F or T[d]	P value
ANOVA[b]	36	3.30	0.048
Paired T-test (two-tailed)			
GC/MS – EPA 418.1	12	3.430	0.005
EPA 418.1 - PetroFLAG®	12	3.732	0.003
GC/MS - PetroFLAG®	12	1.360	0.199

[a] Relative percent difference (RPD) between two duplicate samples. [b] Analysis of variance. [c] Degree of freedom. [d] F or T values for ANOVA and T-test, respectively.

Efficient Quantification of Total Petroleum Hydrocarbons and Applications at Two Contaminated Sites

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Abstract

Characterization and remediation of petroleum contamination are complicated issues due to variable product compositions and site conditions. Generic group analytical methods such as for total petroleum hydrocarbons (TPH) have played important field screening and regulatory functions for site characterization and cleanup. Our research evaluated three TPH methods (a GC/MS method, EPA 418.1, and a rapid field method PetroFLAG). The results show that efficient quantification of TPH can be attained by a combination of rapid field methods (i.e., PetroFLAG) and more sophisticated fraction-specific and target-compound methods. TPH distributions suggested different source release information for two sites with different contaminant mixtures and climate conditions. TPH was also found to correlate with reductive redox capacity (RDC), an important parameter for the design of oxidative remediation schemes. The results indicated that good site specific correlations could be established to better estimate costs of the injection of chemical oxidants if necessary. RDC values varied broadly for both background (83 ~ 569 meq/kg) and contaminated source (520 ~ 6044 meq/kg) samples from actual sites.

Keywords: total petroleum hydrocarbons (TPH), contamination, remediation, reductive redox capacity (RDC)

1. Introduction

Petroleum and refined petroleum product contamination is typically characterized by a mixture of hundreds, even thousands, of individual hydrocarbon contaminants with a broad range of physical and chemical properties. To further complicate the issue, these compounds behave extremely differently after release to the environment. This situation leads to complicated interpretational problems with various analytical methods for detection of petroleum contamination in support of site investigation and remediation efforts. The current methods for total petroleum hydrocarbon (TPH) measurement fit into two categories: generic methods and target-compound methods. Generic methods, including TPH and petroleum hydrocarbon fraction methods, determine and report the sum total of contaminants without differentiating individual compounds in petroleum mixtures. Target-compound methods, on the other hand, have been developed to quantify the content of individual compounds.

Target-compound methods for identification and quantification of specific compounds in petroleum contaminated soil and water were systematically reviewed (Douglas et al.., 1992, Potter, T. L., 1993, Weisman, 1998, pp. 38-48). A common feature of these methods is that nearly all utilize gas chromatography (GC) with packed or capillary columns and various detectors (e.g., flame ionization detectors and mass spectrometers). Target-compound methods alone may not efficiently evaluate petroleum-related contamination for several reasons. They involve time and laboratory analysis for results which can slow source identification or removal efforts. They will increase the cost of the project when drill rigs or excavation equipment must be remobilized to complete the job. It is a formidable challenge to differentiate all individual constituents in petroleum-related mixtures. To date, approximately 250 of the thousands of compounds in petroleum have been successfully separated and identified (Edwards et al., 1997, pp. 7-8). Toxicity data on petroleum hydrocarbons are so limited that only approximately 40 of the 250 identified have enough data to develop such criteria as reference doses (RfDs) and reference concentrations (RfCs). It is expected that completing all individual component toxicity studies, if not impossible, would be extremely costly. Such an expensive undertaking probably would not be worth the benefit. Finally, the toxic potency of any compound in a mixture can be enhanced or diminished in the presence of other components. Specific compound toxicity may not accurately evaluate the toxicity of the whole mixture.

Conventional TPH methods include: gravimetry, spectroscopy, gas chromatography, and immunoassay (Weisman, 1998). In addition, ^{1}H- and ^{14}C-nuclear magnetic resonance (NMR)

(Wang et al., 1994), and thin-layer chromatography (TLC) (Michelsen and Boyce, 1993) methods exist as well. GC-based methods have been commonly considered to produce more accurate and precise results for hydrocarbons with carbon numbers ranging from C_6 to C_{35+} (Novak et al, 1993, Weisman, 1998). Some concerns exist such as: (a) different analytical methods selectively detect different fractions of petroleum hydrocarbons depending on the separation method applied and detector response of the mixture. This can lead to poor comparability of results when contamination is only reported as a single TPH value. (b) Some methods are susceptible to interferences from naturally occurring materials such as waxes, animal and vegetable oils. (c) TPH data cannot be used to quantitatively estimate human health risk.

To address these crucial methodological questions, a national group, called the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG), was formed in 1993 with 400 diverse representatives from industries, governments and academia. This group classified hydrocarbons in petroleum mixtures into 13 fractions according to equivalent carbon numbers with similar fate and transport environmental behaviors (and hence similar chemical/physical properties and toxicity) within each fraction. A fraction-specific method using a simulated distillation GC column was developed and toxicity criteria were assigned to each of the 13 fractions (Weisman, 1998, Gustafson et al., 1997, Edwards et al., 1997). Following the work of this group, the main deficiencies of generic versus specific compound methods may be minimized. For example, once the specific fractions of petroleum contaminants have been delineated by the GC method, a generic method could be used for field screening and a single site-specific human health based TPH cleanup standard may be set following the risk-based corrective action (RBCA) procedures (Gustafson et al., 1997, pp. 2-3).

What remains to be done is to evaluate the comparability of generic TPH methods results with those of specific fraction or compound methods. The expectation is that conventional rapid inexpensive TPH methods may be calibrated with GC-based methods and a correlation may be established between them. Therefore, our study was designed to compare a GC/MS method with two rapid methods, PetroFLAG and EPA 418.1. These methods were applied to two sites widely contaminated with hydrocarbons. TPH distribution profiles were explored to support potential source release scenarios for the two sites. TPH values were then evaluated as reasonable measures of reductive redox capacity (RDC) to assist in the design of chemical oxidant based remediation schemes at such sites.

2. Materials and methods

2.1. Sample collection. Sampling was conducted at an electrical distribution facility in the Pacific Northwest, where mineral oil had been in historical use as a dielectric cooling fluid, and at the FT-02 fire training site (the former Wurtsmith AFB, Oscoda, Michigan), where jet fuels and chlorinated solvents were the primary contaminants. Detailed sampling procedures were addressed by Xie et al. (1990).

2.2. Methods. Three methods (a GC/MS method, EPA 418.1 and PetroFLAG) were employed to quantify total petroleum hydrocarbons (TPH) for our research. The experimental details were provided by Xie et al. (1999). Briefly, to use the GC/MS method, 10-g duplicate samples were Soxhlet extracted with methylene chloride for 12 hr; the concentrated extracts were then analyzed on GC/MS. To use EPA 418.1, 20-g samples were extracted with Freon-113 for 15 min and then measured by infrared spectroscopy. PetroFLAG is a rapid field method in which sediment samples are extracted by an alcohol mixture and then measured by UV-VIS spectroscopy.

Reductive redox capacity (RDC) was measured by a modified conventional chemical oxygen demand (COD) method (Greenberg et al., 1992). Approximately 0.5 gram aliquots of homogenized wet samples were digested in a Teflon sealed test tube for 3 hr at 150 °C after adding 2.5 ml deionized water, 5 ml $K_2Cr_2O_7$/conc. H_2SO_4/$HgSO_4$ solution, and 3.5 ml H_2SO_4/Ag_2SO_4

reagent. After being cooled, the tubes were centrifuged at about 500-g relative centrifugal force for 1 h to clear the supernatant solution for spectrophotometric measurement of the Cr (III) reaction product. A DMS 200 UV-VIS Spectrophotometer (Varian Instrument Group, CA) was employed to choose the maximum absorbance wavelength (587.5 nm) and determine the absorbance of standards and samples by setting smooth constant 0.2 and spectral bandwith 2.0 nm. Potassium hydrogen phthalate (KHP) standards were run simultaneously. Measured RDC were corrected for moisture content to dry weight basis.

Individual volatile hydrocarbons (e.g., BTEX) were measured by EPA Method 8260 (EPA, 1996).

3. Results and discussion

3.1. Efficient quantification of TPH. It was assumed that a good correlation of conventional rapid inexpensive TPH measurement results with those of more expensive time-consuming GC-based measurements (by GC/MS or fraction-specific GC methods) would produce an efficient combined TPH quantification strategy for mass sampling, contamination hot spot and boundary location, and contaminant degradation monitoring. Fig.1 shows the comparison of the TPH values of the electrical utility samples analyzed by the GC/MS method, EPA 418.1 and the rapid field method PetroFLAG. The comparison illustrated that statistically significant positive correlations existed between them in the tested transformer oil mass range (~ C_{12}-C_{36}). EPA 418.1 produced the highest overall TPH estimate and showed a linear coefficient of determination $r^2 = 0.86$ (n= 13) with the GC/MS results while PetroFLAG produced more comparable values to GC/MS with a linear coefficient of determination $r^2 = 0.83$ (n= 13).

Given the good observed correlations, one could confidently use the inexpensive field PetroFLAG method to evaluate spatial distributions of hydrocarbons, supplemented by GC/MS measurement on 5 to 10% of the samples for calibration and potential risk assessments. This could reduce the costs of site/source characterization by 50% or more over conventional approaches.

Caution should be used when volatile hydrocarbon fractions are measured as TPH because partial, sometimes total, loss of volatiles may occur through using rapid field methods. Also, the volatile fraction often exists appreciable toxicity as well as carcinogenicity. At the FT-02 site, the PetroFLAG results were compared with the GC/MS results for the volatile aromatic fraction of TPH. The results shown in Table 1 indicate that (a) the volatile fraction (i.e., BTEX) only accounted for a small part of total TPH for highly contaminated areas. For example, the ratios of BTEX/TPH ranged from 0.1% to 7.0% with an average 1.2% for samples with TPH values >100 mg/kg. (b) BTEX was poorly correlated with TPH even for samples with TPH values >100 mg/kg. (c) Comparison of the ratios of BTEX/TPH in 1998 and 1999 data illustrated that BTEX apparently was released or degraded faster than other fractions in TPH for most locations. In this type of case, the use of generic TPH methods must be done with care because the potential risk posed by BTEX compounds may not be adequately addressed. Clearly, a larger subset of GC based analyses must be done to capture this detail.

3.2. Distribution of TPH and source release patterns. TPH distributions may provide clues as to source release patterns under site conditions. For example, as shown in Fig.1 for the electrical utility site (with an arid climate, precipitation 17.5 cm/yr), TPH profiles in the vadose zone presented three peaks suggesting three possible major periods of release. If we assume the first peak (at ~ 12.8 m) was resulted from a release 40 years ago (the earliest estimated operating age of the electrical facility), the other two peaks (at ~ 6.1 m and 8.2 m) may have occurred approximately 26 and 19 years ago, respectively. However, in temperate humid climate areas, TPH distributions present be clustered at or near the water table, exhibiting patterns such as shown in Fig. 2 for FT-02 site (precipitation 76.2 cm/yr). This does not mean there was only one release.

This is because gravity-driven flow, rather than capillary flow, is expected to be dominant in these areas (Kramer and Keller, 1995). Therefore, contaminants, even though from multiple releases, easily move through the vadose zone by gravity and concentrate in the capillary fringe and water table zone.

3.3. Correlation between TPH and reductive redox capacity (RDC). TPH measurements may also be useful in remedial design. Enhancement (i.e., stimulation or augmentation) of intrinsic bioremedation or engineered controls for in situ remediation technologies frequently require maintenance of an appropriate redox status in the subsurface (Barcelona and Holm, 1991, Korom et al.., 1996). High redox potentials in aerobic oxidizing systems favor hydrocarbon degradation. Oxygen may be depleted in the immediate source zone and oxidant addition may be necessary.

Redox status of a system may be characterized by an intensity factor (i.e., redox potential, Eh) and an extensive factor (i.e., redox capacity or redox poise) (Scott and Morgan, 1990, Barcelona and Holm, 1991, Grundl, 1994). Redox capacity represents the resistance to change in redox potential. Theoretically, oxidative redox capacity (OXC) can be defined as the net sum of the equivalents of electrons that a system can demand compared to an electron reference level (ERL, i.e., a redox potential value). Similarly, reductive redox capacity (RDC) can be defined as the net sum of the equivalents of electrons that a system can supply compared to an ERL. Measurable total RDC is typically determined by titrating with a strong oxidant in favorable conditions (e.g., temperature and pH) for complete redox reactions. RDC is a valuable parameter to be used to estimate the necessary quantity of oxidants and approximate time frame for using oxidant assisted remediation strategies. Total petroleum hydrocarbons (TPH), which directly measures the content of hydrocarbon contaminants in samples, represent a major contribution to RDC.

A good correlation between measured TPH and calculated RDC was obtained by recalculating RDC from the chemical oxidant demand (COD) data given by Armstrong et al. (1988) and Powell et al. (1988) for a fuel contaminated aquifer (Fig.3). This yielded the relation: RDC (meq/kg) = 0.044 TPH (mg/kg) + 83 with $r^2 = 0.93$, n=14. Based on this correlation, the background RDC (e.g., TPH =0 mg/kg) was further estimated to be ~ 83 meq/kg for this fuel contaminated site. The most contaminated source area RDC was 523 meq/kg at the same site (e.g., TPH = 10000 mg/kg).

For the electrical utility site in this study, there was also a good correlation between TPH and RDC (Fig. 3). The correlation was RDC (meq/kg)= 0.219 TPH (mg/kg)+ 569 with $r^2 = 0.91$, n= 13. Using this relationship, the background area RDC at this electrical utility site was estimated to be ~ 569 meq/kg while the most contaminated source area RDC was 6044 meq/kg (e.g., TPH = 25000 mg/kg).

Thus, as expected, both background (from 83 to 569 meq/kg) and contaminated source (from 520 to 6044 meq/kg) RDC values vary widely, dependent on background site conditions, and petroleum contaminant quantity and type. In either case, the levels of TPH (and RDC) in the source zones would require application of a considerable oxidant dose to approach background values. Using the cost per oxidizing equivalent values in Barcelona and Holm (1991), and assuming 1500 kg/m^3 of subsurface contaminated material and 100% efficiency of oxidation by candidate oxidants, the reagent costs was estimated to range from \$55/ m^3 to \$6981/ m^3 necessary to titrate the measured source reductive redox capacity (Table 2).

4. Conclusions

The rapid generic TPH method results correlated well with those of the GC/MS method. The results indicate that efficient evaluation of TPH distributions in the subsurface can be obtained by field screening a large number of samples with the PetroFLAG field method coupled with analysis of a subset (i.e., 5 to 10%) of samples by fraction-specific and target-compound GC determinations. This approach could save significant time and cost in site characterization and remediation methods. Caution should be exercised in using TPH methods for volatile contaminants due to potential method bias. To some extent site specific TPH distributions may suggest source release patterns if assumptions can be made on historical site conditions. TPH values may also correlate with reductive redox capacity (RDC) for facilitating the design of oxidative remediation approaches to petroleum contamination. Further research will focus on the evaluation of methods to identify specific reactive fractions in RDC (i.e., the fraction of RDC accessible to oxidants) with an emphasis on reducing toxicity.

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Figure captions

Fig. 1. Comparison of the total petroleum hydrocarbon (TPH) values of the electrical utility samples analyzed by the GC/MS method, EPA 418.1, and the rapid PetroFLAG field method. The electrical utility site was contaminated with transformer oil.

Fig. 2. Total petroleum hydrocarbon (TPH) distribution over depth at FT-02 site. TPH was measured by a rapid PetroFLAG field method.

Fig. 3. Correlation between total petroleum hydrocarbon (TPH) and reductive redox capacity (RDC). Armstrong data was obtained from the recalculation of the chemical oxygen demand

(COD) data given by Armstrong et al. (1988) and Powell et al. (1988) for a fuel contaminated aquifer. The electrical utility data were obtained by our study via measuring samples of a transformer oil contaminated vadose zone.

Table 1

Concentration of BTEX and TPH for the FT-02 site

	Feb. 1998			Jan. 1999		
Depth (m)	BTEX[a] (mg/kg)	TPH[b] (mg/kg)	BTEX/TPH[c] (%)	BTEX (mg/kg)	TPH (mg/kg)	BTEX/TPH (%)
			Location ML311			
4.1	0.062	22	0.3	-[d]	-	-
4.7	8.470	3272	0.3	0.766	850	0.1
5.3	204.970	13180	1.6	102.605	10860	0.9
5.9	73.530	4420	1.7	45.085	646	7.0
6.6	0.477	8	6.0	1.141	-	-
7.2	0.099	68	0.1	-	-	-
7.8	0.146	80	0.2	-	-	-
			Location ML312			
4.1	0.269	16	1.7	-	-	-
4.7	7.636	1405	0.5	8.282	1508	0.5
5.3	115.970	8060	1.4	137.968	26980	0.5
5.9	72.330	54	133.9	2.062	163	1.3
6.6	1.019	-	-	2.846	30	9.5
7.2	0.278	-	-	-	-	-
7.8	0.292	-	-	-	-	-
			Location ML314			
4.1	0.205	24	0.9	-	-	-
4.7	6.622	4370	0.2	61.020	3600	1.7
5.3	122.530	15160	0.8	99.281	6010	1.7
5.9	63.890	42	152.1	228.651	19720	1.2
6.6	0.541	20	2.7	3.077	167	1.8
7.2	0.338	38	0.9	-	-	-
7.8	0.031	6	0.5	-	-	-
			Location ML315			
4.1	0.519	4	13.0	-	-	-
4.7	7.280	7340	0.1	7.558	1432	0.5
5.3	153.550	12600	1.2	150.818	23920	0.6
5.9	36.007	56	64.3	4.317	274	1.6
6.6	0.446	-	-	0.797	-	-
7.2	0.130	6	2.2	-	-	-
7.8	0.156	66	0.2	-	-	-

[a] Benzene, toluene, ethylbenzene, and xylene (BTEX) were measured by a GC/MS method.

[b] Total petroleum hydrocarbons (TPH) were measured by the PetroFLAG method.

[c] Percent fraction of BTEX in total petroleum hydrocarbons.

[d] - not detectable.

Table 2

Reagent costs for oxidative remediation schemes

			Armstrong site[a]		Electrical utility site	
			Background zone	Source zone	Background zone	Source zone
TPH[b] (mg/kg sediment)			0	10000	0	25000
RDC[c] (meq/kg sediment)			83	523	569	6044
RDC (eq/m^3 sediment[d])			124	784	854	9066
Oxidant	Electrons (eq/mol)	Cost[e] ($/eq)	Reagent cost ($/$m^3$ sediment[d])			
H_2O_2	2	0.13	16	102	111	1179
MgO_2	2	0.70	87	549	598	6346
$KMnO_4$	3	0.07	9	55	60	635
$K_2S_2O_8$	2	0.77	95	604	658	6981

[a] A fuel contaminated site which was depicted by Armstrong et al. (1988) and Powell et al. (1988).

[b] Total petroleum hydrocarbons.

[c] Reductive redox capacity.

[d] Assuming the bulk density of the sediment is 1500 kg/m^3.

[e] Values excerpted from Barcelona and Holm (1991) except for MgO_2.

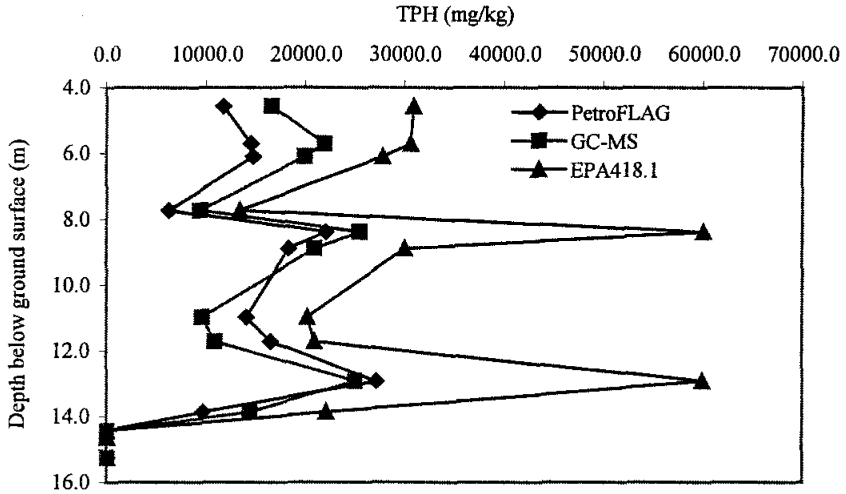

Fig. 1.

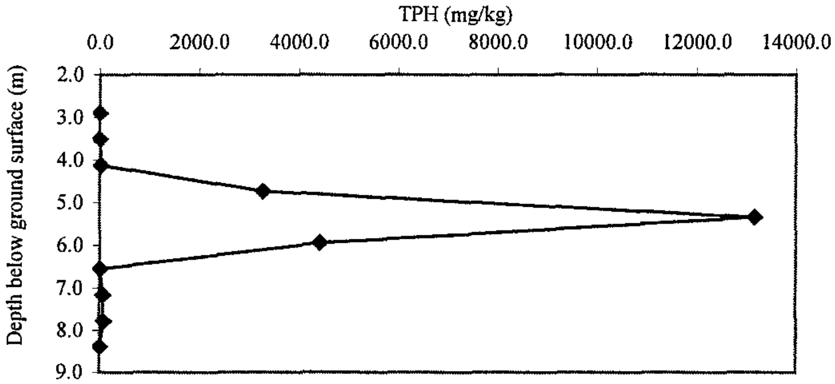

Fig. 2.

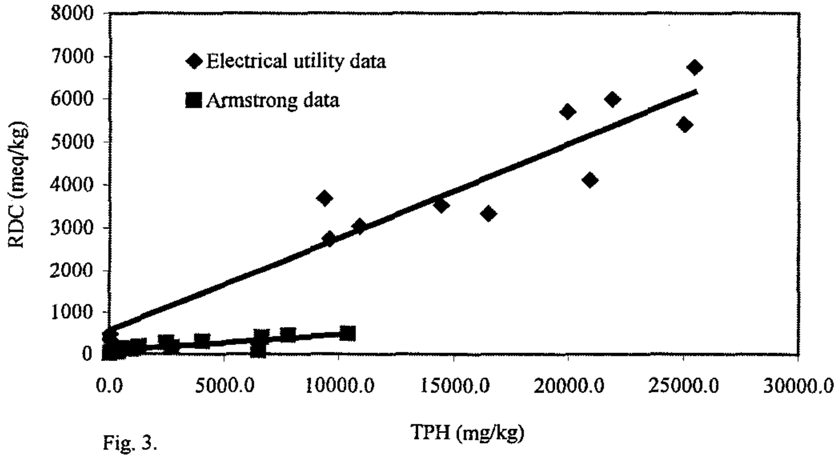

Fig. 3.