Shell Oil Products US

June 30, 2004

Mr. Scott Seery
Alameda County Health Care Services Agency
1131 Harbor Bay Parkway, Suite 250
Alameda, California 94502-6577

Subject: **Shell-branded Service Station**
3790 Hopyard Road
Pleasanton, California

Dear Mr. Seery:

Attached for your review and comment is a copy of the *Agency Response, Revised SCM, & Modified Work Plan* for the above referenced site. Upon information and belief, I declare, under penalty of perjury, that the information contained in the attached document is true and correct.

As always, please feel free to contact me directly at (559) 645-9306 with any questions or concerns.

Sincerely,

Shell Oil Products US

Karen Petryna

Karen Petryna
Sr. Environmental Engineer

20945 S. Wilmington Ave., Carson, CA 90810 Phone (559) 645-9306 Facsimile (559) 645-5643

CAMBRIA

June 30, 2004

Mr. Scott Seery
Alameda County Health Care Services Agency
1131 Harbor Bay Parkway, Suite 250
Alameda, California 94502-6577

Re: **Agency Response, Revised SCM, & Modified Work Plan**
Shell-branded Service Station
3790 Hopyard Road
Pleasanton, California
SAP Code 135784
Incident #98995842
ACHCSA # RO0000363

Dear Mr. Seery:

Cambria Environmental Technology, Inc. prepared this document on behalf of Equilon Enterprises LLC dba Shell Oil Products US (Shell) to respond to the Alameda County Health Care Services Agency (ACHCSA) letter dated May 5, 2004. The ACHCSA technical comments included, a request for an updated SCM, a request for a modified work plan, requests relating to routine quarterly sampling reports, and corrections to a previously submitted data table with errors.

SITE CONCEPTUAL MODEL (SCM)

MTBE Detections in S-11 & S-12: The ACHCSA stated that MTBE began appearing in offsite wells S-11 and S-12 in May 2003. It should be noted that the laboratory method detection limit was decreased from 5.0 to 0.5 parts per billion (ppb), beginning in May 2003. If the method detection limit had remained at 5.0 ppb, then the detections in these wells would continue to be non-detect. Therefore, the MTBE concentrations at S-11 and S-12 have been and continue to be stable, at concentrations below 5 ppb.

Discussion of TBA Occurrence/Trend: The ACHCSA requested a discussion of the genesis of elevated TBA in both onsite and offsite wells and appropriate additions/revisions to the SCM regarding TBA. In response to similar requests by other agencies, Shell Global Solutions (US), Inc., a research division of Shell, conducted a study of TBA at selected UST sites in Orange County California. Their final report dated November 14, 2003, and slides from a corresponding presentation are included herein as **Attachment A**, for reference.

Cambria Environmental Technology, Inc.

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Shell Global Solutions' study was intended to identify the source of TBA in groundwater at numerous gasoline stations. A summary of the study's conclusions regarding the origin of TBA is:

- The **occurrence of TBA is predominantly an intermediate biological degradation product from the biodegradation of MTBE**
- The biodegradation process is more significant under reduced conditions (anaerobic/methanogenic) than aerobic conditions;
- Some TBA may be due to dissolution from gasoline product, but not where MTBE and BTEX concentrations are low or non-detect;
- Abiotic generation of TBA was not observed and is unlikely;
- TBA generation as an analytical artifact is insignificant.

In order to address the ACHCSA's request for this site, Cambria evaluated the occurrence of TBA at the subject site. To assist with the evaluation, Cambria generated concentration versus time graphs for MTBE and TBA in near-source-area site wells (S-2 and S-4) and in downgradient wells with significant TBA (S-5 and S-6). These graphs are included in **Attachment B**. Since these wells do not have elevated concentrations of other fuel constituents, the TBA is not coming directly from the fuel product. The concentration versus time graphs for MTBE and TBA suggest that the occurrence and concentration trends of TBA at this site are directly related to the decreased concentrations of MTBE (partly due to active extraction activities and also from biological activity). Thus, it appears that TBA is a result of biological degradation of MTBE. Further, the biological degradation of TBA appears to be relatively rapid after its peak concentration (refer to graph 4 of well S-6).

Since TBA appears to be a breakdown byproduct of MTBE, and based on the graphs for wells S-2 and S-6 it also appears to degrade quickly, its migration pattern is not expected to differ significantly from MTBE at this site. This point is demonstrated by comparing the isoconcentration contour maps for MTBE and TBA generated for the second quarter 2004 monitoring event, and included in **Attachment C**. These figures show that the lateral extent of TBA is similar to, or smaller than, the MTBE plume, even though TBA concentrations onsite currently exceed MTBE concentrations by an order of magnitude.

The ACHCSA questioned the occurrence of MTBE and TBA in well S-6 since S-6 is located outside of the "Downgradient Flow Zone" as presented in a previous document. Historical groundwater contour maps for this site depict some radial flow outward from the site, although the primary direction of groundwater is to the southeast. The referenced "Downgradient Flow Zone" lines were drawn from an origin centered in the UST complex, instead of including the

entire UST complex or dispenser island to the west as points of origin for plume migration. If the northern boundary had been drawn from the northern edge of the UST complex, well S-6 would lie much closer to the "Zone"(see Figure 2). Additionally, Cambria reviewed the boring logs for the site wells to assess the presence of preferential pathways. Although the lithologic descriptions are limited by the sampling interval, it appears that the clayey sand lens encountered in most site wells at approximately 30 feet below grade contained less fines and more coarse sand at the location of well S-6, which may allow for preferential migration of contaminants in that direction. Based on the depth to the water-bearing unit (over 25 fbg), the utilities in this area do not appear to be directly causing preferential migration of constituents in groundwater.

The SCM included in **Attachment D** has been updated to include a discussion of TBA as a chemical of concern at this site, and to reflect more current remediation and monitoring data.

Correction to SCM Item 4.6 Regarding the Arroyo Mocho Canal: As cited in the April 30, 2003 Cambria document, the Arroyo Mocho Canal was found to be a losing stream, based on the elevation of the bottom of the canal and groundwater elevation data from the nearby monitoring well (S-12). The SCM in ATTACHMENT B of that document contained erroneous text, referring to the Arroyo Mocho as a gaining stream. This error has been corrected in the updated SCM in **Attachment D**. Since the Arroyo Mocho is a losing stream, impact from groundwater to the surface water body is very unlikely.

MODIFIED WORK PLAN

In order to assess the vertical extent of groundwater impact at the site and downgradient of the site, the ACHCSA has requested a significant increase in the scope of work previously proposed by Cambria in the April 30, 2003 *Subsurface Investigation Work Plan*. The previously proposed CPT pairs were increased in number from 9 to 13. And the proposed total depths of 40 fbg at seven locations and 75 fbg at two locations were also increased to 120 fbg at all locations. Cambria asserts that; given what is already known about the site conditions, the decreased concentrations of chemicals of concern on site, the limited lateral extent of impact in the shallow zone, the significant separation from the site to potential receptors and the documented absence of groundwater impact with depth at CPT-2 positioned between the Shell site and the downgradient municipal well, this level of increased effort does not appear to be warranted.

Rather, Cambria proposes modifying the locations of several of the original proposed CPT locations to better address the area of coverage requested by the ACHCSA, and extending each CPT pair (except CPT-3 in the source area) to a total depth of 80 fbg. Extending beyond 80 fbg

prior to understanding whether vertical migration to this depth is known would be unadvisable. If the data suggests that additional data points or deeper samples are needed to complete the vertical assessment, then additional work will be proposed.

Proposed Scope: Cambria proposes installing nine CPT pairs for this phase of work. The proposed locations for CPT-3 through CPT-11 are shown on Figure 2. At each location (except CPT-3) an initial CPT boring will be extended to a total depth of 80 fbg for complete lithologic logging information. CPT-3 is proposed to be extended no deeper than 45 fbg, to avoid possible dragging down of source area contaminants to the deeper water-bearing zone known to occur between 45 and 75 fbg. A second CPT boring will be extended for the purpose of obtaining depth discrete groundwater samples targeted at approximately 35, 55 and 75 fbg, depending on the lithology encountered. In CPT-3, groundwater sample collection will be targeted for 35 and 45 fbg, depending on lithology. These depths may be adjusted to target a specific zone if one is identified during the logging of that location; however, if a water-bearing unit is not observed near one of the target intervals, an attempt to collect a water sample will be performed anyway. Not only would the chemical data be valuable if a water sample is retained, but, the lack of available water at certain intervals would also be valuable information for this assessment.

From the CPT borings, soil samples are only proposed to be collected from the two onsite CPT pairs (CPT-3 and CPT-5 at 5, 10, 15 and 20 fbg) for chemical analysis, and from CPT-10, for confirmation of soil type from intervals which could be screened if a deeper well is proposed.

While Shell feels that the remediation program in place at this site is sufficiently remediating the source area and is providing adequate protection of nearby receptors, the following scope of work is presented in direct response to the ACHCSA's request to assess the nature and extent of soil impact associated with the current and historical fueling operations at this site. Cambria proposes installing 16 soil borings depicted as SB-1 through SB-16 on Figure 3. The borings will be advanced to approximately 20 fbg using direct push technology. Because many of these borings are located near operating USTs and piping, the top five to ten feet of each boring will be advanced using an air-knife, for safety. Soil sampling of the portion of the borings that are air-knifed will be sampled using a hand auger at 2.5 foot intervals. The remainder of the borings will be continuously logged by retrieval of the direct push sample tubes. Soil samples will be retained from approximately 5-, 10-, 15- and 20-fbg, for chemical analyses. Cambria is not proposing extending these borings past 20 fbg, unless field observations indicate significant soil impact at 20 fbg. Previous soil sampling activities at this site indicate that impact to soils does not extend significantly beneath saturated soils (refer to the data table included as **Attachment E** that demonstrates significant attenuation of constituent concentrations between 14 and 20 fbg).

Chemical Analyses: All groundwater samples, select soil samples from CPT-3 and CPT-5, and all soil samples from borings SB-1 through SB-16 will be submitted to a California certified analytical laboratory for analyses of TPHg, BTEX, MTBE and TBA by EPA Method 8260B.

Scheduling: Cambria will initiate implementation of this work upon receipt of approval from the ACHCSA, or within 60-days of submittal of this work plan, whichever is sooner.

Reporting: Upon completion of the field activities and receipt of the analytical results, Cambria will prepare a report of findings which will include a summary of the site background and history, descriptions of the field activities, CPT logs and soil boring logs, tabulated analytical results, a figure presenting the site boring and well locations, an updated cross section, an updated SCM, analytical reports and chain-of-custody forms, a discussion of hydrocarbon distribution in soil and groundwater, conclusions and recommendations. The report will be submitted approximately 60 days following receipt of all analytical data.

QUARTERLY MONITORING PROGRAM

The ACHCSA requested analyses of the full oxygenates suite (MTBE, TBA, DIPE, TAME, and ETBE), plus ethanol to be performed during the second quarter 2004 monitoring event. However, the revised analytical suite could not be applied to the second quarter sample event, as the event had already been performed and samples were past the EPA recommended hold time for these analyses by the time we received the agency letter. Internal Shell protocol requires periodic sampling for these constituents. In the third quarter of 2001, based on Shell's internal oxygenates monitoring requirements, wells S-2 and S-6 were analyzed for the full oxygenates suite and ethanol, and neither well contained constituents other than MTBE and TBA above the detection limits. In December of 2002, wells S-2 through S-7 and S-9 through S-12 were analyzed for the full suite of oxygenates, and again, only MTBE and TBA were present. Coincidentally, the next annual event for oxygenates was slated for the third quarter of 2004. Thus, to address both Shell's monitoring requirements and the ACHCSA's request, the third quarter monitoring event will include analyses of TPHg, BTEX, the five fuel oxygenates and ethanol in all 13 wells. Based on the results of the additional analyses, Cambria will propose an appropriate sampling plan for future events.

The second quarter monitoring report was recently submitted under separate cover. As requested, that document included an historical groundwater data table in the appendix, which had been revised to include data obtained prior to March 1991. Also, isoconcentration contour maps for TPHg, benzene, and all detected oxygenates (MTBE and TBA) were included.

CORRECTION OF DATA TABLE

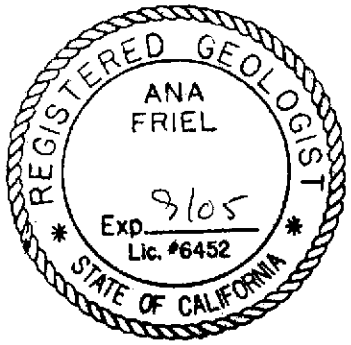
As requested by the ACHCSA, Cambria reviewed the data that was presented on Table 1 of Cambria's April 30, 2003 *Subsurface Investigation Work Plan*. Through this review it was noted that every sample date on the data table was off by four years and one day. This was a function of the software package. The correct sample dates are now shown on the data table, included herein as **Attachment E**. Also, through this review, we discovered additional analytical data that was not previously tabulated. The samples labeled S-B through S-E were found to have analytical data for benzene, toluene and xylenes; which have been added to the table.

CLOSING

If you have any questions regarding the contents of this document, please call Ana Friel at (707) 442-2700.

Sincerely,
Cambria Environmental Technology, Inc

Ana Friel, RG
Senior Project Geologist
RG 6452

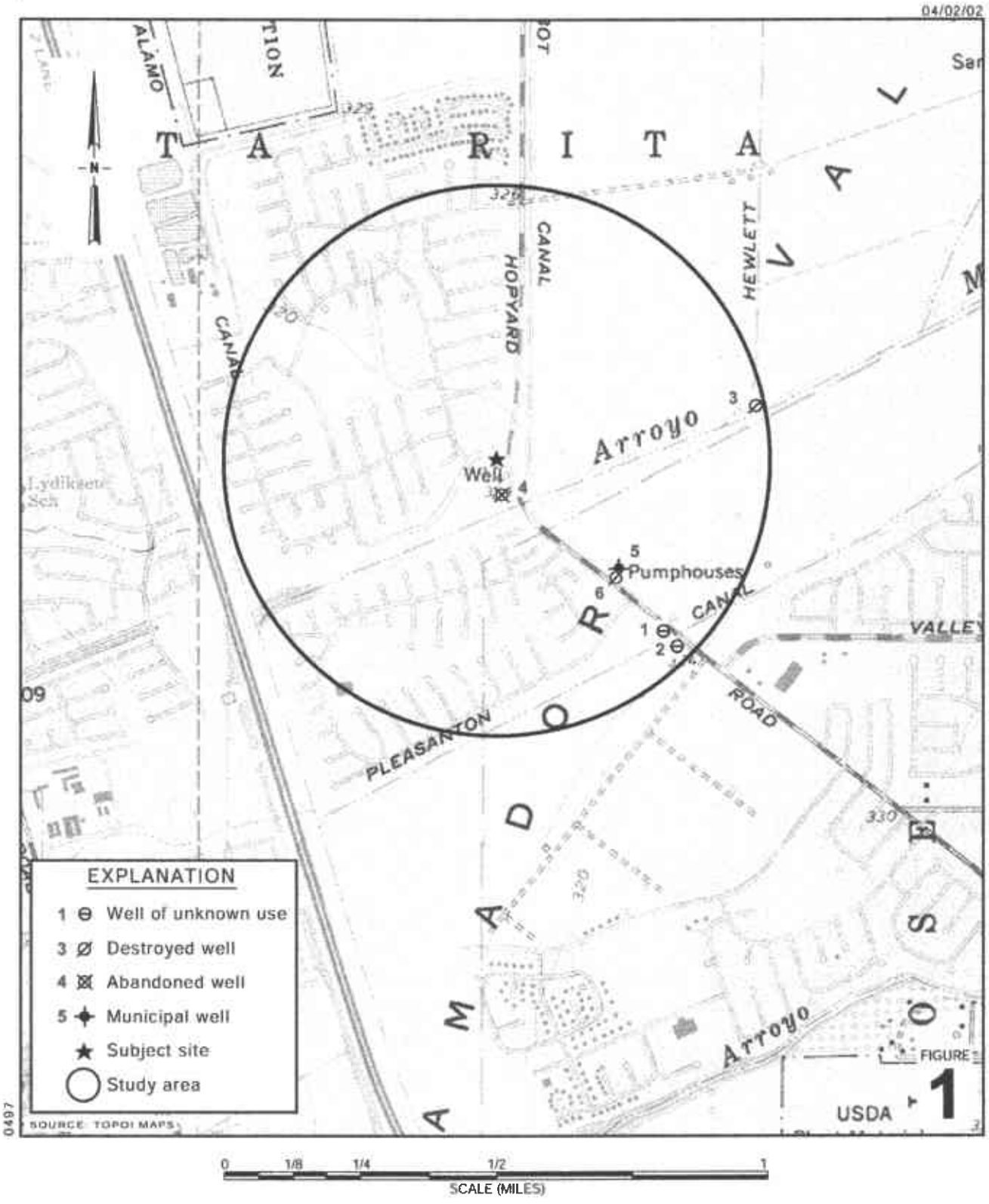


ENCLOSURES

Figure 1. Vicinity/Area Well Survey Map
Figure 2. Proposed CPT Boring Locations
Figure 3. Proposed On-Site Boring Locations

Attachment A. Study of TBA at Selected UST Remediation Project Sites in Orange County, CA – Shell Global Solutions, November 14, 2003
Attachment B. MTBE and TBA Concentration versus Time Graphs
Attachment C. MTBE and TBA Isoconcentration Contour Maps – Second Quarter 2004
Attachment D. Updated Site Conceptual Model
Attachment E. Historical Soil Analytical Data Table (revised)

cc: Karen Petryna, Shell Oil Products US
Chuck Headlee, RWQCB
Danielle Stefani, Livermore-Pleasanton Fire Department
Matthew W. Katen, Zone 7 Water Agency
Tri-Valley Management



Shell-branded Service Station
3790 Hopyard Road
Pleasanton, California

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Vicinity/Area Well Survey Map

1/2 Mile Radius

28-Jun-04

Proposed CPT Boring Locations

EXPLANATION

- Proposed CPT boring
- CPT boring
- Shell groundwater monitoring well
- Groundwater recovery well
- Tank backfill well

Note: Map features not a product of survey

Scale (ft)
0 30 60 120

Municipal Well
Located 1,500 ft. SE
of Shell site

Las Positas
Office Plaza

LAS POSITAS BOULEVARD

planter
walkway
planter

CPT-9
S-10
CPT-11
S-11
CPT-2
S-12
S-6
CPT-4
CPT-8
S-7
T-2
S-4
former USTs
T-1
T-4
SR-2
T-3
CPT-3
dispensers
CPT-5
S-5
SR-3
SR-1
S-2
former dispensers
7-Eleven
3760 Hopyard
CPT-7
CPT-10
S-9
S-3
CPT-1
W/O UST
former W/O UST
Exploratory excavation ~6' deep
Exploratory excavation ~6.5' deep
CPT-6
S-8
DMV
6280 Las Positas
Business Center
3730 Hopyard

Downgradient Flow Zione

HOPYARD ROAD

ARROYO MOCHO CANAL

fence
bike path
creek bridge
Storm Drain culvert flows to creek
invert elevation = 315'
10.2 fbg
11.3 fbg
FL 317.65
SS 6"ϕ
SS 8"ϕ
G 6"ϕ (high pressure)
W 14"ϕ 9 fbg
W 20"ϕ 9 fbg
W 16"ϕ ~6.5 fbg
SD 12"ϕ ~4 fbg
T, 6 - 4"ϕ ducts
fire hydrant
PG&E vault

0497

FIGURE
2

Shell-branded Service Station
3790 Hopyard Road
Pleasanton, California

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29-Jun-04

Proposed Onsite Boring Locations

HOPYARD ROAD

LAS POSITAS BOULEVARD

SD 12"ϕ, ~4 fbg

planter

W 14"ϕ 9 fbg

E

G, ~5 fbg

G 6"ϕ (high pressure)

SS 6"ϕ

Scale (ft)

0 10 20 40

SB-8 T-2 S-4 SR-2 SB-13 SB-12 SB-9 SB-14 SB-11 SB-7 T-1 T-4 T-3 SB-10 SB-6 SB-15 SB-1 SR-3 SB-16 SR-1 S-5 SB-5 S-2 SB-2 SB-4 SB-3 S-3

former USTs

USTs

former dispensers

dispensers

fire hydrant

PG&E vault

7-Eleven
3760 Hopyard

Shell-branded
Service Station
3790 Hopyard

W/O UST

former W/O UST

Exploratory excavation ~6' deep

Exploratory excavation ~6.5' deep

EXPLANATION

- Groundwater monitoring well
- Groundwater recovery well
- Tank backfill well
- Proposed boring location
- Storm drain line (SD)
- Sanitary sewer line (SS)
- Water main (W)
- Electrical line (E)
- Telephone (T)
- Gas line (G)

FIGURE
3

Shell-branded Service Station
3790 Hopyard Road
Pleasanton, California

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PATH

ATTACHMENT A

Study of TBA at Selected Remediation Project Sites in Orange County, California

Shell Global Solutions

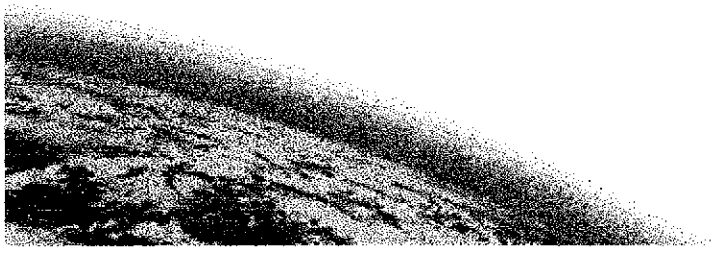
Study of Tert-Butyl Alcohol (TBA) at Selected Underground Storage Tank Remediation Project Sites in Orange County, California

Final Report

prepared for:
Seth J. Daugherty
Orange County Health Care Agency
Santa Ana, California

prepared by:
Shell Global Solutions (US), Inc.
Houston, Texas

November 14, 2003



Study of Tert-Butyl Alcohol (TBA) at Selected Underground Storage Tank Remediation Project Sites in Orange County, California - Final Report

by:

George E. DeVaull, Ph. D.
Paul T. Sun, Ph. D.
Ileana A. L. Rhodes, Ph. D.
Daniel F. Walsh, CPG

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reviewer:

Gerard E. Spinnler, Ph. D.

for:

Seth J. Daugherty
Supervising Hazardous Waste Specialist
Hazardous Materials Mitigation
Orange County Health Care Agency

November 14, 2003

Shell Global Solutions

Shell Global Solutions (US) Inc.
P. O. Box 1380
Houston, Texas 77251-1380

14 November 2003

Seth J. Daugherty
Supervising Hazardous Waste Specialist
Hazardous Materials Mitigation
Orange County Health Care Agency
2009 East Edinger Avenue
Santa Ana, CA 92705-4720

Subject: Study of Tert-Butyl Alcohol (TBA) at Selected Underground Storage Tank Remediation Project Sites in Orange County, California - Final Report

Seth,

The attached report summarizes work completed as part of a study design and work plan initially approved by Orange County Local Oversight Program (OCLOP) on August 9, 2002. This effort was initiated in response to a series of Directives issued by the OCLOP dated from June 4, 2002.

If you have questions or comments on the work, please contact George DeVaull, ph. 281-544-7430, e-mail: george.devaull@shell.com or Dan Walsh, ph. 281-544-8682, e-mail: dan.walsh@shell.com.

Sincerely,

original signed by

George DeVaull

Attachments

copy:
Marvin Katz, Shell Oil Products US
Dan Walsh, Shell Global Soutions (US)

Study of Tert-Butyl Alcohol (TBA) at Selected Underground Storage Tank Remediation Project Sites in Orange County, California - Final Report

Shell Global Solutions (US), Inc.
George DeVaull, Ph. D.
Paul T. Sun, Ph. D.
Ileana A. L. Rhodes, Ph. D.
Daniel F. Walsh, CPG

November 14, 2003

1. Summary of Results

This report summarizes a study concerning the possible origin of TBA in groundwater at selected LUST sites in Orange County, California. The most plausible explanation for the anomalous concentrations of TBA in groundwater is that TBA is predominately an intermediate biological degradation product, produced from MTBE (methyl tert-butyl ether) primarily in either low-oxygen or methanogenic environmental conditions.

Measured soluble concentrations of TBA in groundwater at the investigated sites are also consistent with estimates of TBA in water in contact with unweathered gasoline. Dissolution from gasoline as a sole source of TBA in groundwater cannot, however, explain observed instances of high measured levels of TBA with low (or non-detect) co-located measurement of either MTBE or BTEX constituents. Dilution, partitioning, and transport alone cannot explain the observed relative concentration levels of these chemicals. Transformation - in this case laboratory confirmation of biological degradation and transformation - helps explain the measured site data.

Other possible sources of measured TBA in groundwater, including abiotic transformation in the environment, or presence of TBA as an artifact of chemical analysis methods, for the conditions investigated, are not likely possible explanations for the elevated levels of TBA observed at the investigated sites.

In further results, microcosm analyses conducted on soils (collected below the water table) as part of this work showed degradation of MTBE and TBA in both aerobic and anaerobic conditions. Investigation of co-metabolism of TBA or MTBE in the presence of propane was inconclusive, since degradation had been observed without the presence of the selected (propane) co-metabolic substrate.

2. Introduction

A series of directives issued by Orange County Local Oversight Program (OCLOP) have been received by Shell, dated from 4 June 2002, indicating a request for study of the origin of tert-butyl alcohol (TBA) at leaking underground storage tank sites. Notification of approval of the Shell's Proposed TBA Work Plan dated July 19, 2002 was received

from the Orange County Health Care Agency (OCHCA) on August 14, 2002 [letter from Seth J. Daugherty to Marvin Katz, 9 August 2002]. The task items in the work plan are as follows:

Task 1. Site screening
Task 2. Evaluate likelihood of TBA being derived from gasoline product sold at service stations
Task 3. Evaluate biological transformation of MTBE to TBA in the groundwater environment
Task 4. Evaluate possible abiotic transformation of TBA from MTBE
Task 5. Evaluate possibility of TBA detections being an artifact of sample collection and/or laboratory analytical methods

Updates on the progress of this work were provided beginning in September 2002. Task 3 included laboratory microcosms of up to 150 days duration; with the last batch concluding at the end of September 2003. Discussion of the results and conclusions from executing these tasks is included in this report.

3. Site Screening

A total of 6 sites in Orange County with reported TBA levels in groundwater greater than 50 mg/L (ppm) have been identified by OCHCA, and the available site-specific environmental reports and data have been collected, consolidated, and reviewed. Table 3.1 provides a brief summary of site conditions at the initiation of the TBA Study. At five of the six sites, measured TBA in groundwater was significantly greater than measured MTBE concentrations, and BTEX concentrations in groundwater at five of the six sites were comparably insignificant.

Based on the summary results, a review of the hydrogeologic settings, as well as site logistics and history, three sites were selected for detailed follow-up study. These sites include 30011 Crown Valley Parkway, 16969 Brookhurst, and 27101 Ortega Highway.

Table 3.1. Summary Information - Orange County sites identified by OCHCA.

	Street, City	Operating Facility?	Nominal Maximum MTBE (ppb)	Nominal Maximum TBA (ppb)	Nominal Maximum BTEX (ppb)	Recent Site Activities
1.	30011 Crown Valley Pkwy, Laguna Niguel	yes	65,000	340,000	950	Screening modeling completed, attenuation shown.
2.	6011 Manchester, Buena Park	yes	220	240,000	non-detect	Recent VacOps. Prior excavation for diesel impacts.
3.	32342 Pacific Coast Highway, Laguna Beach	no	28,000	2,600	36,100	3 triple-nested SVE wells, ongoing vapor extraction.
4.	27101 Ortega Highway, San Juan Capistrano	no	9,300	390,000	non-detect	Tank removal and excavation.
5.	16969 Brookhurst, Fountain Valley	yes	2,500	45,000	46	Finalizing site assessment and site conceptual model.
6.	1000 Irvine, Newport Beach	yes	250,000	120,000	non-detect	Finalizing site assessment and RAP in near future.

Plan view maps for each of these three sites are included in Appendix 1. These maps show relevant site features and a set of time-series plots of historical groundwater concentration data for each monitor well.

At each of the three sites, soil cores were collected below the water table at three locations, nominally two within the plume and one background sample. Soil sampling locations are indicated on the individual site maps included in Appendix 1. The soil samples were subjected to laboratory microcosm analysis under a variety of environmental conditions. These tests were intended to help confirm the presence and activity of microbes capable of degrading MTBE and TBA, as well as to provide an indication of a possible pathway of TBA formation from MtBE. Additional discussion of these tests and test results are included in Section 5 of this report.

3.1. Statistical analysis of groundwater monitoring data

Statistical analysis of the time-dependent groundwater TBA and MTBE concentration data has been completed. This analysis provides interpretation of increasing, steady, or decreasing trends in concentration, as well as confidence intervals of the trend. A summary of the statistical tests used in the data evaluation follows. Time (t) versus concentration (c) data for a single chemical (either TBA or MTBE) and single well, is examined in each analysis.

- Only detected data, and data without qualified data codes are included in the trend evaluation. Non-detected data and data with qualified data codes are neglected in that they have higher levels of associated error than the detected, unqualified data.
- Simple substitution was not used (that is substituting a non-detect level or a fraction of non-detect level, as commonly done in risk assessment analysis) as the detection levels in this data set are generally variable and can be higher than other detected data in the same data set. This approach for non-detects is reasonable for a trend analysis.
- A minimum of four detected data samples per well per chemical has been set as a criterion before inferring trends based on the statistical calculations. More samples will yield narrower confidence limits.

The analysis is confined to a set of non-parametric statistical tests. As a general point, non-parametric tests can be more indicative of a central tendency in the data; regression tests (which we have not applied) can be more significantly influenced by infrequent extreme values. In analysis for each well:

- The data is transformed as $x = t$, $y = \ln(c)$. Non-parametric tests do not depend on the data distribution (by definition). This transformation yields a first-order estimate (in concentration) of a rate parameter.
- A Mann-Kendall statistic, S (Kendall, 1970; Gibbons and Coleman, 2001), is calculated, and an associated probability is estimated.
  - The Mann-Kendall statistic as applied to trend, evaluates a total count in change of concentration (increasing, +1; equal, 0; decreasing, -1) between all sequential permutations of data pairs $(y_j - y_i)$ with $x_j > x_i$, in the N data points (x, y).

- Probability is estimated from available tables for the test of S = 0 (no trend), based on the calculated statistic and the number of data points.
- A "no-trend" interpretation is given for data within a 95% confidence interval of the S = 0 hypothesis.
- If a trend is evident, negative values of S indicate a decreasing trend, while positive values of S indicate an increasing trend.

- Sen's test is applied (Sen, 1968; Gibbons and Coleman, 2001).
  - This test is applied to a set of slope estimates $(y_j - y_i)/(x_j - x_i)$ with $x_j > x_i$ and i and j are drawn from the N data points (x, y).
  - The median value of the distribution of slopes is taken as the best estimate of slope. A two-sided confidence interval on slope is estimated from a calculated variance, as is a one-sided confidence interval for zero or decreasing slope.
  - A best-estimate slope within a 95% confidence interval of zero slope is interpreted as "no trend"
  - If a trend is evident, a negative slope is a decreasing trend, and a positive slope is an increasing trend.
  - Consistencies of results from the two non-parametric tests are used in interpreting the data trend.

Data for the time period from January 2000 to the latest available (either 2nd or 3rd Quarterly monitoring data for 2003) is included in the trend analysis. Results of the statistical analysis for the three sites are included in Table 3.2. Plots of time versus concentration for the monitoring well data are included in Appendix 1.

30011 Crown Valley Parkway site: The site stratigraphy consists of silt to a depth of 25 ft, and fine- to medium-grained silty sand from 25 to 35 ft below ground surface. Siltstone is also present at 25 ft below ground surface. MW-1 through MW-6 are screened at a depth of approximately 15 to 18 ft in perched water. Unconfined groundwater is present at approximately 24 ft depth in MW-7, MW-8, MW-10 through MW-13, which are screened from 10 to 30 ft in native sediments. Groundwater flow varies from east to northeast with a gradient of 0.01 to 0.02 ft/ft. Hydraulic conductivity was measured at 5.1×10^{-5} ft/sec (4.4 ft/day) based on slug tests, consistent with literature and site lithology.

Over the time period from March 2000 to September 2003, MTBE is evidently either stable or decreasing at this site in every monitoring well that met the statistical evaluation criteria (at least four sampling events with detected concentrations). TBA is apparently decreasing or stable, except for wells MW-05, MW-07, MW-08, and MW-11. MW-05 is screened within a shallow perched zone adjacent to the tank pit, where the highest on-site concentrations have been detected. The other identified increasing wells are screened in shallow groundwater either adjacent to the tank pit (MW-08; weak confidence in increasing trend) or within approximately 30 feet of the tank pit (MW-07, MW-11).

16969 Brookhurst site: Depth from surface to first encountered groundwater on the site is 7 to 12 ft. The water table gradient is from west to east at approximately 0.023 ft/ft.

Over the time period from April 2000 to September 2003, MTBE is evidently either stable or decreasing at this site for all of the monitoring wells that met the statistical evaluation criteria. TBA is apparently decreasing or stable except for wells MW-02, MW-07, MW-14, and MW-15. The highest TBA on-site is at MW-08, which shows either a decreasing trend or no trend, and non-detect MTBE concentrations. MW-07 is downgradient of the tanks and dispenser island. MW-14 and MW-15 are also downgradient monitor wells.

Wells MW-16 through MW-20 were recently installed at the site. These wells have not yet met minimum sampling criterion of detected data, and a trend cannot yet be established.

27101 Ortega Highway site: The regional setting for the site is in a valley. On-site depth to groundwater varies from approximately 30 to 40 feet below ground surface. The groundwater gradient at the eastern edge of the site is approximately 0.2 ft/ft to the west. The groundwater gradient on the central and western part of the site, including the former tank pit and dispenser islands, is approximately 0.01 ft/ft to the south.

Over the time period from March 2000 to September 2003, MTBE is evidently either stable or decreasing for all of the monitored wells at this site except for MW-2. TBA is apparently decreasing or stable except for wells MW-2, MW-8, MW-9, MW-12, and W-2.

Table 3.2a 30011 Crown Valley Parkway, Laguna Niguel - Single Well Statistics - Trend Analysis

MTBE

			data ranges (for data without qualifiers)						sample statistics (detected data)				minimum number of samples (4) in data set?	Mann-Kendall test for trend			Sen's test x = time (years), y = ln(c), and c = concentration (ug/L)					
			non-detect (<)			meas. (detected) samples																
Well No.	first date	last date	count	min. (ug/L)	max. (ug/L)	count	min. (ug/L)	max. (ug/L)	arithmetic average (ug/L)	std dev (ug/L)	geometric mean (ug/L)	geometric std dev (--)		Mann-Kendall statistic	decreas. trend evident (CI)	decreas. trend?	log slope d ln(c)/dt (1/year)	err in slope (at 95% CI) (1/year)		zero slope?	decreas. trend evident (CI)	decreas. trend?	combined interpretation of trend
MW-01	3/3/00	5/8/03	1	1	1	4	26	1800	616	801	263	1.75	yes	-6	0.958	decreas.	-3.2	-1.06	--	no	1	decreas.	decreas.
MW-02	3/3/00	5/8/03	0			0	--	--	--	--	--	--	no										
MW-03	3/3/00	5/8/03	0			6	180	46000	9680	17900	2650	1.83	yes	-9	0.932	decreas.	-3.17	0.487	-8.29	yes	0.823	no trend	decreas. / no trend
MW-04	3/3/00	5/8/03	0			2	38000	42000	39000	4240	38900	0.109	no										
MW-05	3/3/00	5/8/03	0			7	4000	330000	102000	117000	48000	1.53	yes	-7	0.809	decreas.	-1.75	2.29	-3.22	yes	0.732	no trend	decreas. / no trend
MW-06	3/3/00	5/8/03	0			1	71	71	71	--	71	--	no										
MW-07	3/3/00	9/16/03	6	50	200	6	22	910	212	344	93.1	1.31	yes	-13	0.992	decreas.	-2.1	-1.47	-2.8	no	0.907	decreas.	decreas.
MW-08	3/3/00	9/16/03	0			12	170	18000	3370	4760	1590	1.3	yes	-62	1	decreas.	-1.14	-0.912	-1.46	no	0.984	decreas.	decreas.
MW-09	3/3/00	9/16/03	0			0		--	--	--	--	--	no										
MW-10	3/3/00	9/16/03	0			15	450	530000	40700	136000	2920	1.99	yes	-79	1	decreas.	-1.37	-0.812	-1.85	no	0.976	decreas.	decreas.
MW-11	3/3/00	9/16/03	0			13	240	20000	3210	5570	1140	1.42	yes	-45	0.996	decreas.	-1.26	-0.649	-1.8	no	0.92	decreas.	decreas.
MW-12	3/3/00	9/16/03	3	1	1	9	1	9.2	2.51	2.54	1.97	0.631	yes	-16	0.94	decreas.	-0.218	0.009	-1.3	yes	0.799	no trend	decreas. / no trend
MW-13	3/3/00	9/16/03	0			12	110	830	272	210	225	0.603	yes	-53	1	decreas.	-0.514	-0.288	-0.833	no	0.968	decreas.	decreas.

TBA

			non-detect (<)			meas. (detected) samples																
Well No.	first date	last date	count	min. (ug/L)	max. (ug/L)	count	min. (ug/L)	max. (ug/L)	arithmetic average (ug/L)	std dev (ug/L)	geometric mean (ug/L)	geometric std dev (--)	minimum samples?	Mann-Kendall statistic	decreas. trend evident (CI)	decreas. trend?	log slope d ln(c)/dt (1/year)	err in slope (at 95% CI) (1/year)		zero slope?	decreas. trend evident (CI)	decreas. trend?	combined interpretation of trend
MW-01	3/3/00	5/8/03	0			5	4100	30000	13200	10300	10300	0.784	yes	-4	0.758	decreas.	-0.71	4.04	--	no	0.707	decreas.	decreas.
MW-02	3/3/00	5/8/03	0			0		--	--	--	--	--	no										
MW-03	3/3/00	5/8/03	0			5	16000	110000	63800	37200	52400	0.774	yes	-6	0.883	decreas.	-0.727	1.61	--	no	0.774	decreas.	decreas.
MW-04	3/3/00	5/8/03	0			2	170000	260000	215000	63600	210000	0.3	no										
MW-05	3/3/00	5/8/03	0			7	140000	1100000	550000	324000	460000	0.691	yes	17	0.0054	increas.	1.02	2.21	0.164	no	0.129	increas.	[illegible]
MW-06	3/3/00	5/8/03	0			1	5400	5400	5400	--	5400	--	no										
MW-07	3/3/00	9/16/03	0			13	440	51000	20500	19700	8980	1.59	yes	57	0.000317	increas.	1.34	1.82	0.83	no	0.0374	increas.	[illegible]
MW-08	3/3/00	9/16/03	1	10000	10000	11	1200	24000	9850	5940	8050	0.757	yes	3	0.438	increas.	0.15	0.652	-0.309	yes	0.468	no trend	[illegible]
MW-09	3/3/00	9/16/03	0			0		--	--	--	--	--	no										
MW-10	3/3/00	9/16/03	0			13	30000	1600000	267000	421000	99600	0.992	yes	-38	0.988	decreas.	-0.446	-0.133	-0.841	no	0.886	decreas.	decreas.
MW-11	3/3/00	9/16/03	0			13	110	50000	29400	12400	19800	1.59	yes	51	0.00114	increas.	0.358	0.577	0.162	no	0.0636	increas.	[illegible]
MW-12	3/3/00	9/16/03	11	10	50	1	780	780	780	--	780	--	no										
MW-13	3/3/00	9/16/03	3	100	250	9	210	390	314	61.7	309	0.208	yes	-7	0.728	decreas.	-0.144	0.219	-0.377	yes	0.662	no trend	decreas. / no trend

Notes:
The range of first date to last date of data included in the trend analysis is as indicated. Data counts and ranges for detect and non-detect data are shown. Analytical flagged data (J-code) are not included. A minimum of 4 samples is set as a criterion for the trend analysis. For the Mann-Kendall statistic, a single-sided confidence interval (CI) for a decreasing trend is indicated [CI = 1 is certainty in a decrease and CI = 0 is certainty in an increase]. For Sen's test, a logarithmic slope is shown, along with a 95% confidence interval range in the slope. A no-trend judgment is made if the 95% confidence interval intersects the zero-slope trend, otherwise a positive slope is increasing and a negative slope is decreasing. The Sen's test confidence interval (CI) for decreasing trend is also shown [CI = 1 is certainty in a decrease and CI = 0 is certainty in an increase].

Table 3.2b 16969 Brookhurst Street, Fountain Valley - Single Well Statistics - Trend Analysis

MTBE

			data ranges (for data without qualifiers)						sample statistics (detected data)				minimum number of samples (4)	Mann-Kendall test for trend			Sen's test x = time (years), y = ln(c), and c = concentration (ug/L)					
			non-detect (<)			meas. (detected) samples																
Well No.	first date	last date	count	min. (ug/L)	max. (ug/L)	count	min. (ug/L)	max. (ug/L)	arithmetic average (ug/L)	std dev (ug/L)	geometric mean (ug/L)	geometric std dev (--)	in data set?	Mann-Kendall statistic	decreas. trend evident (CI)	decreas. trend?	log slope d ln(c)/dt (1/year)	err in slope (at 95% CI) (1/year)		zero slope?	decreas. trend evident (CI)	decreas. trend?	combined interpretation of trend
MW-01	4/3/00	9/2/03	1	1	1	8	1	230	45.2	78.1	11.3	1.95	yes	-26	1	decreas.	-2.89	-2.66	-3.36	no	0.955	decreas.	decreas.
MW-02	4/3/00	9/2/03	0			4	9.6	150	47.1	68.8	22.7	1.3	yes	-2	0.625	decreas.	-0.96	8.24	--	no	0.744	decreas.	decreas.
MW-03	4/3/00	9/2/03	0			6	1.5	2500	496	989	59.8	2.62	yes	-5	0.765	decreas.	-1.95	2.9	-8.39	yes	0.712	no trend	decreas. / no trend
MW-04	4/3/00	9/2/03	0			5	1.2	290	86	120	27.2	2.07	yes	0	0.592	decreas.	-0.0842	4.17	--	no	0.554	decreas.	decreas.
MW-05	4/3/00	9/2/03	0			7	14	530	124	183	60.9	1.23	yes	-9	0.881	decreas.	-1.12	0.184	-2.76	yes	0.773	no trend	decreas. / no trend
MW-06	4/3/00	9/2/03	0			11	8.3	81000	16700	32400	401	3.3	yes	-42	0.999	decreas.	-2.66	-1.34	-4.32	no	0.953	decreas.	decreas.
MW-07	8/14/01	9/2/03	6	50	200	5	1.3	20	7.34	7.3	5.08	0.977	yes	-2	0.592	decreas.	-0.486	3.16	--	no	0.681	decreas.	decreas.
MW-08	8/14/01	9/2/03	0			1	44	44	44	--	44	--	no										
MW-09	8/14/01	9/2/03	0			0		--	--	--	--	--	no										
MW-10	8/14/01	9/2/03	0			0		--	--	--	--	--	no										
MW-11	8/14/01	9/2/03	0			0		--	--	--	--	--	no										
MW-12	3/19/02	9/2/03	3	1	1	0		--	--	--	--	--	no										
MW-13	3/19/02	9/2/03	0			3	38	96	59.7	31.7	54.8	0.494	no										
MW-14	3/19/02	9/2/03	0			6	5.7	680	136	269	26.4	1.94	yes	-15	0.999	decreas.	-4.01	-0.728	-7.1	no	1	decreas.	decreas.
MW-15	3/19/02	9/2/03	0			6	10	79	32.5	26.1	24.8	0.815	yes	-15	0.999	decreas.	-1.76	-1.29	-2.59	no	1	decreas.	decreas.
MW-16	5/28/03	9/2/03	0			1	52	52	52	--	52	--	no										
MW-17	5/28/03	9/2/03	0			0		--	--	--	--	--	no										
MW-18	5/28/03	9/2/03	0			1	2.5	2.5	2.5	--	2.5	--	no										
MW-19	5/28/03	9/2/03	0			0		--	--	--	--	--	no										
MW-20	5/28/03	9/2/03	0			1	2.7	2.7	2.7	--	2.7	--	no										

TBA

			non-detect (<)			meas. (detected) samples																
Well No.	first date	last date	count	min (ug/L)	max (ug/L)	count	min. (ug/L)	max. (ug/L)	arithmetic average (ug/L)	std dev (ug/L)	geometric mean (ug/L)	geometric std dev (--)	minimum samples?	Mann-Kendall statistic	decreas. trend evident (CI)	decreas. trend?	log slope d ln(c)/dt (1/year)	err in slope (at 95% CI) (1/year)		zero slope?	decreas. trend evident (CI)	decreas. trend?	combined interpretation of trend
MW-01	4/3/00	9/2/03	0			11	80	1600	596	539	367	1.1	yes	-35	0.996	decreas.	-1.25	-0.543	-1.72	no	0.918	decreas.	decreas.
MW-02	4/3/00	9/2/03	0			10	1200	11000	4000	3080	3160	0.711	yes	17	0.078	increas.	0.533	0.83	-0.273	yes	0.232	no trend	increas. / no trend
MW-03	4/3/00	9/2/03	0			6	14	1500	552	673	181	1.91	yes	-11	0.972	decreas.	-1.97	-0.522	-5.32	no	0.868	decreas.	decreas.
MW-04	4/3/00	9/2/03	0			2	71	140	106	48.8	99.7	0.48	no										
MW-05	4/3/00	9/2/03	0			10	750	14000	6440	4500	4540	1.01	yes	-7	0.7	decreas.	-0.328	0.551	-1.48	yes	0.646	no trend	decreas. / no trend
MW-06	4/3/00	9/2/03	0			11	1200	81000	20200	16700	13100	1.16	yes	-7	0.68	decreas.	-0.397	0.222	-1.97	yes	0.633	no trend	decreas. / no trend
MW-07	8/14/01	9/2/03	0			8	410	6400	2510	1970	1840	0.908	yes	2	0.452	increas.	0.259	1.57	-1.86	yes	0.481	no trend	increas. / no trend
MW-08	8/14/01	9/2/03	1	10000	10000	9	37000	64000	50900	9010	50200	0.18	yes	-18	0.962	decreas.	-0.189	0.0039 3	-0.377	yes	0.834	no trend	decreas. / no trend
MW-09	8/14/01	9/2/03	0			0		--	--	--	--	--	no										
MW-10	8/14/01	9/2/03	0			0		--	--	--	--	--	no										
MW-11	8/14/01	9/2/03	0			8	370	2500	1390	696	1210	0.615	yes	-8	0.801	decreas.	-0.448	0.763	-0.927	yes	0.71	no trend	decreas. / no trend
MW-12	3/19/02	9/2/03	11	10	50	7	20000	37000	26100	5790	25600	0.211	yes	-11	0.932	decreas.	-0.245	0.0769	-0.811	yes	0.814	no trend	decreas. / no trend
MW-13	3/19/02	9/2/03	3	100	250	7	5300	20000	12400	6360	11000	0.539	yes	-4	0.666	decreas.	-0.223	0.934	-2.04	yes	0.646	no trend	decreas. / no trend
MW-14	3/19/02	9/2/03	0			5	75	750	505	277	393	0.958	yes	2	0.408	increas.	0.206	4.86	--	no	0.47	increas.	increas.
MW-15	3/19/02	9/2/03	0			7	280	3500	1810	1160	1380	0.898	yes	17	0.0054	increas.	1.42	2.4	0.506	no	0.116	increas.	increas.
MW-16	5/28/03	9/2/03	0			2	130	150	140	14.1	140	0.101	no										
MW-17	5/28/03	9/2/03	0			0		--	--	--	--	--	no										
MW-18	5/28/03	9/2/03	0			2	480	730	605	177	592	0.296	no										
MW-19	5/28/03	9/2/03	0			0		--	--	--	--	--	no										
MW-20	5/28/03	9/2/03	0			0		--	--	--	--	--	no										

Table 3.2c 27101 Ortega Highway - Single Well Statistics - Trend Analysis

MTBE

Well No.	first date	last date	data ranges (for data without qualifiers) non-detect (<) count	non-detect (<) min. (ug/L)	non-detect (<) max. (ug/L)	meas. (detected) samples count	meas. (detected) samples min. (ug/L)	meas. (detected) samples max. (ug/L)	sample statistics (detected data) arithmetic average (ug/L)	std dev (ug/L)	geometric mean (ug/L)	geometric std dev (--)	minimum number of samples 4 in data set?	Mann-Kendall test for trend Mann-Kendall statistic	decreas. trend evident (CI)	decreas. trend?	Sen's test x = time (years), y = ln(c), and c = concentration (ug/L) log slope d ln(c)/dt (1/year)	err in slope (at 95% CI) (1/year)		zero slope?	decreas. trend evident (CI)	decreas. trend?	combined interpretation of trend
MW-1	3/14/00	9/28/00	0			2	36000	43000	39500	4950	39300	0.126	no										
MW-2	3/14/00	8/1/03	2	100	200	8	35	250	135	83.1	110	0.729	yes	12	0.089	increas.	0.61	1.18	-0.857	yes	0.266	no trend	increas. / no trend
MW-4	3/14/00	8/1/03	0			11	200	100000	13700	30200	2070	1.99	yes	-49	1	decreas.	-2.08	-1.69	-2.29	no	0.973	decreas.	decreas.
MW-5	3/14/00	8/1/03	6	2	10	5	11	310	103	121	58.4	1.25	yes	-8	0.958	decreas.	-3.08	-1.98	--	no	0.867	decreas.	decreas.
MW-6	3/14/00	8/1/03	6	2	1000	5	14	4100	951	1780	218	2.03	yes	-9	0.958	decreas.	-4.32	-0.821	--	no	0.851	decreas.	decreas.
MW-8	3/14/00	8/1/03	4	10	25	6	52	340	130	110	103	0.714	yes	-5	0.765	decreas.	-0.711	1.43	-4.59	yes	0.727	no trend	decreas. / no trend
MW-9	3/14/00	8/1/03	0			11	230	35000	15600	13100	6970	1.76	yes	-44	1	decreas.	-1.77	-1.09	-2.53	no	0.96	decreas.	decreas.
MW-10	3/14/00	8/1/03	2	100	250	3	2200	7600	5030	2710	4480	0.638	no										
MW-11	8/3/01	8/1/03	1	100	100	8	100	4800	1410	1890	646	1.32	yes	-24	0.999	decreas.	-1.85	-1.07	-2.66	no	0.944	decreas.	decreas.
MW-12	8/3/01	8/1/03	0			9	620	19000	4220	5740	2550	0.967	yes	-30	1	decreas.	-1.06	-0.78	-1.86	no	0.943	decreas.	decreas.
MW-13	8/3/01	8/1/03	0			9	14	590	220	203	146	1.08	yes	-28	0.999	decreas.	-1.1	-0.347	-2.02	no	0.929	decreas.	decreas.
MW-14	10/24/02	8/1/03	0			4	53	79	70.5	11.9	69.7	0.185	yes										
MW-15	10/24/02	8/1/03	0			4	23	270	163	104	119	1.12	yes										
MW-16	10/24/02	8/1/03	0			4	140	360	230	94.2	217	0.396	yes										
W-1	3/14/00	9/28/00	0			0			--	--	--	--	no										
W-2	3/14/00	8/1/03	0			11	23	40000	5230	12100	493	2.35	yes	-33	0.994	decreas.	-2.46	-0.834	-4.84	no	0.902	decreas.	decreas.

TBA

Well No.	first date	last date	non-detect (<) count	non-detect (<) min. (ug/L)	non-detect (<) max. (ug/L)	meas. (detected) samples count	meas. (detected) samples min. (ug/L)	meas. (detected) samples max. (ug/L)	arithmetic average (ug/L)	std dev (ug/L)	geometric mean (ug/L)	geometric std dev (--)	minimum samples?	Mann-Kendall statistic	decreas. trend evident (CI)	decreas. trend?	log slope d ln(c)/dt (1/year)	err in slope (at 95% CI) (1/year)		zero slope?	decreas. trend evident (CI)	decreas. trend?	combined interpretation of trend
MW-1	3/14/00	9/28/00	0			0			--	--	--	--	no										
MW-2	3/14/00	8/1/03	0			10	8400	110000	59500	35700	43000	1.03	yes	11	0.19	increas.	0.59	1.45	-0.407	yes	0.318	no trend	increas. / no trend
MW-4	3/14/00	8/1/03	0			9	48000	88000	68700	16800	66800	0.256	yes	-4	0.619	decreas.	-0.0562	0.359	-0.529	yes	0.583	no trend	decreas. / no trend
MW-5	3/14/00	8/1/03	0			10	1300	23000	7280	7630	4490	1.04	yes	1	0.5	no trend	0.0669	1.17	-1.84	yes	0.495	no trend	no trend
MW-6	3/14/00	8/1/03	0			10	740	390000	44100	122000	6030	1.73	yes	-3	0.589	decreas.	-0.154	1.56	-1.87	yes	0.567	no trend	decreas. / no trend
MW-8	3/14/00	8/1/03	0			10	3100	100000	27600	37300	13700	1.19	yes	7	0.3	increas.	0.348	1.17	-1.83	yes	0.403	no trend	increas. / no trend
MW-9	3/14/00	8/1/03	2	10000	13000	7	8900	43000	23300	11800	20700	0.53	yes	16	0.0102	increas.	0.716	1.31	0.168	no	0.13	increas.	increas.
MW-10	3/14/00	8/1/03	0			5	86000	170000	132000	40100	127000	0.322	yes	-7	0.92	decreas.	-0.645	0.00	--	no	0.836	decreas.	decreas.
MW-11	8/3/01	8/1/03	0			9	35000	95000	64100	17500	61900	0.288	yes	-19	0.97	decreas.	-0.352	-0.0247	-0.555	no	0.851	decreas.	decreas.
MW-12	8/3/01	8/1/03	1	2500	2500	8	3500	6500	5200	977	5110	0.201	yes	16	0.031	increas.	0.219	0.589	-0.0133	yes	0.172	no trend	increas. / no trend
MW-13	8/3/01	8/1/03	0			9	390	2400	1190	622	1050	0.551	yes	-16	0.94	decreas.	-0.625	0.121	-1.25	yes	0.807	no trend	decreas. / no trend
MW-14	10/24/02	8/1/03	1	10	10	3	11	21	15.3	5.13	14.8	0.327	no										
MW-15	10/24/02	8/1/03	1	10	10	3	36	84	64.7	25.3	60.7	0.457	no										
MW-16	10/24/02	8/1/03	0			4	61000	64000	62800	1500	62700	0.024	yes	1	0.5	no trend	0.0106	0.217	--	no	0.5	increas.	note [1]
W-1	3/14/00	9/28/00	0			0			--	--	--	--	no										
W-2	3/14/00	8/1/03	0			10	750	27000	8740	8350	4960	1.26	yes	13	0.146	increas.	0.63	2.24	-0.868	yes	0.302	no trend	increas. / no trend

note [1] (in table) - Confidence interval on decreasing trend is P=0.5, or just as likely to be decreasing as increasing.

4. Likelihood of TBA being derived from gasoline product sold at service stations

Task 2 of the work plan included quantifying gasoline as a potential source of TBA detected in groundwater.

There are no known current manufacturing practices for intentional addition of TBA to gasoline. TBA was offered commercially as a blending component by ARCO Chemical under the trade name Arconol, which was synonymous with gasoline-grade TBA (GTBA) beginning in 1969. The use of TBA in this application ceased in 1987. The authors of this report have found no available information on the use of GTBA or Arconol in California.

There are several commercial processes for production of MtBE. The processes are based on the reaction of isobutylene with methanol in the presence of catalysts. The reaction is selective to isobutylene, allowing for the use of varying refinery streams (steam and fluid catalytic cracker effluent streams, for example) that contain isobutylene. Water present in the reaction mixture may lead to the formation of TBA. Thus, TBA may be present in MtBE either as a co-product, an impurity, or as an unreacted initial component, depending on the manufacturing process. Manufacturing process designs vary depending on product specifications, desired isobutylene conversion, MtBE purity, and the reactant stream composition. Typical gasoline-grade MtBE contains 96 to 99% MTBE by weight. [Reference: CEH Marketing Research Report, Gasoline Octane Improvers – 1999 Chemical Economics Handbook – SRI International].

Shell has never manufactured MTBE in any of its California refineries. All MtBE added to gasoline in California to meet Federal and State regulatory requirements has been purchased by Shell from commercial sources. The MtBE batches are analyzed to determine product quality. Review of these data shows detectable TBA levels in many of the MTBE shipments. This data set of TBA in MtBE has been used to estimate a range of TBA in gasoline (with MtBE added at required regulatory levels). When mixed into oxygenated gasoline at a nominal regulated concentration of 0.111 g-MtBE/g-gasoline (11.1% by weight), this data indicates a nominal concentration of TBA in MtBE-oxygenated gasoline as follows:

Fraction of samples at less than indicated concentration	Measured Concentration of TBA in MtBE (mg-TBA/kg-MtBE)	Estimated Concentration of TBA in Gasoline [at 11.1%w/w MTBE] (mg-TBA/kg-gasoline)
5%	370	40
50%	1300	140
95%	4700	520
99%	8000	890

The California Air Resources Board (CARB) specifies an analysis method for the determination of oxygenates in gasoline [CARB, 1996: Procedure for the Determination

of Ethers and Alcohols in Gasoline by Gas Chromatography, SOP NO. MLD 115], including TBA, with a method reporting limit of 0.1% mass, or 1000 mg-TBA/kg-gasoline. The CARB analysis method is similar to ASTM D4815 and ASTM D5599 methods. All of the estimated TBA levels in MtBE-oxygenated gasoline shown in the above table would not have been detected if analyzed at the CARB method detection limit.

Equilibrium partitioning factors between gasoline and water for a number of oxygenates, including TBA, have been measured by Shell in a series of batch gasoline-water partitioning tests. Measured partitioning values ($K_{gasoline\text{-}water}$) for TBA fall in the range of 0.05 to 0.26 (mg/L-gasoline)/(mg/L-water), with a nominal geometric mean of 0.11 (mg/L-gasoline)/(mg/L-water). This range of partitioning factors is in reasonable agreement with factors estimated from physical properties. Variation in the measured partitioning factor is due a number of influences, including experimental variability, tests of multiple gasoline compositions, and tests of multiple concentration ranges for mixtures of oxygenates.

An estimate of the concentration of TBA in water in contact with gasoline is given by:

$$C_{TBA-water} = \frac{C_{TBA-gasoline} \cdot \rho_{gasoline}}{K_{gasoline-water}}$$

Using nominal values of:

$\rho_{gasoline}$ = 0.91 (kg-gasoline/L-gasoline), density of gasoline

$K_{gasoline-water}$ = 0.11 (mg-TBA/L-gasoline)/(mg-TBA/L-water), partitioning factor

and

$C_{TBA-water}$ (mg-TBA/L-water), calculated.

$C_{TBA-gasoline}$ (mg-TBA/kg-gasoline), initial estimate.

yields a range of calculated TBA concentrations in water.

For estimating concentrations of MTBE in water in contact with unweathered gasoline, we use Raoult's law partitioning:

$$C_{MtBE-water} = C_{MtBE-gasoline} \cdot \left(10^{-6}\ \frac{kg}{mg}\right) \cdot \frac{MW_{gasoline}}{MW_{MtBE}} \cdot S$$

with

$MW_{gasoline}$ = 90.1 g/g-mole nominal average molecular weight of gasoline

MW_{MtBE} = 88.15 g/g-mole molecular weight of MTBE

S = 42000 mg/L-water pure chemical aqueous solubility limit of MTBE and

$C_{MTBE-water}$ (mg-MTBE/L-water), calculated.

$C_{MTBE-gasoline}$ (mg-MTBE/kg-gasoline), initial estimate

A plot of partitioning for TBA and MTBE between gasoline and water is shown in Figure 4.1. This plot indicates that, for water in contact with MTBE-gasoline, in approximately less than one out of twenty instances (cumulative probability, P=0.95 or greater), aqueous TBA concentrations can be similar or greater than the MTBE concentration levels in water.

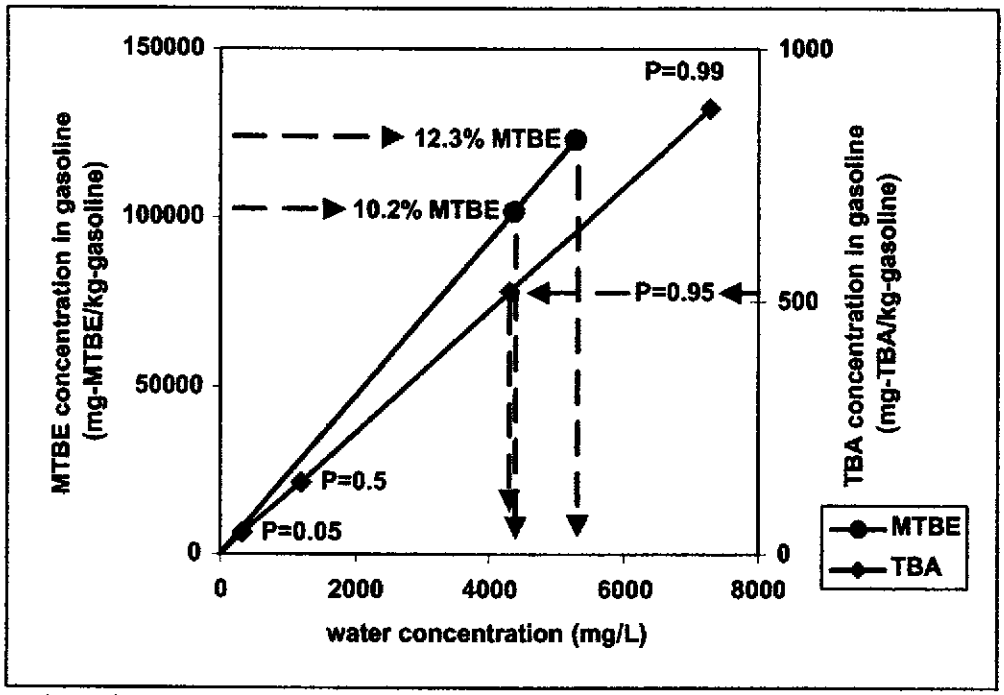

Figure 4.1 Estimated partitioning of MTBE and TBA from gasoline to water. A large gasoline to water ratio is presumed. The 10.2% to 12.3% range for MTBE is based on the reported range of MTBE in oxygenated gasoline. The plotted values for TBA, P = 0.05, 0.5, 0.95, and 0.99 refer to the confidence levels of finding TBA in gasoline at or lower than the referred concentration, in unweathered MTBE-gasoline.

Actual occurrence of TBA concentrations in groundwater at a remediation site would depend on a number of factors dependent on site conditions, geology, and hydrogeology. At the sites listed in Table 3.1, preliminary review shows nominal high-range measured TBA concentrations in groundwater that are (in some cases) of the same order as the calculated gasoline/water equilibrium-partitioning estimates of Figure 4.1. These estimates, based on ranges of TBA concentration, indicate that some fraction of TBA in groundwater may possibly originate from gasoline.

MTBE and TBA are soluble and volatile constituents of gasoline that, in a release, are depleted as the gasoline mixes with increasing volumes or water or air (or both). Concentrations in the water (or air) phase will decrease with increasing dilution of the gasoline, and will be less than the equilibrium partitioning estimates of Figure 4.1.

Calculated estimates of this depletion show that water-washing of gasoline will deplete TBA from gasoline faster than MTBE. In volatilization, MTBE will deplete from gasoline faster than TBA. It is, however, difficult to model a reasonable scenario that matches site observed measurements (high TBA, low MTBE, low BTEX) based solely on the physical mechanisms of dissolution, partitioning, mixing, and dilution. A transformation loss of MTBE, with intermediate generation of TBA, is a possible explanation. Biological transformation, as a possible source of site measured TBA in groundwater, is discussed in Section 5 of this report.

5. Biological Transformation of MtBE to TBA in the groundwater environment

Task 3 of the work plan included investigation of the possibility of biological transformation of TBA and MTBE, and potential identification of TBA as an intermediate degradation product of MTBE. The plan included microcosm studies using samples of the native soil and groundwater, under aerobic and anaerobic conditions. A revision to the initial work plan has been to extend the period of study from 60 days to approximately 150 days for the anaerobic microcosms.

5.1. Review of Potential Biological Degradation Mechanisms for MTBE and TBA

Natural attenuation (ASTM E1943-98; Wiedemeier et al. 1995, 1997) of chemicals in groundwater may be indicated by multiple lines of evidence including:

- *Plume stability*: direct measurement that concentrations in the groundwater plume are stable or decreasing in time and extent;
- *Geochemical indicators*: monitoring of electron acceptors (sulfate, nitrate, oxygen); mineralization products (methane, carbon dioxide); or intermediate metabolites (chemical-specific) as evidence of biological activity; or
- *Biological indicators*: demonstration that the activity is due to biological activity with laboratory microcosm studies of site media samples.

Laboratory microcosm analyses conducted as part of this work plan are intended to determine biological activity under a range of environmental conditions (aerobic, anaerobic) for the sites under study, and in particular, to identify if TBA may be an intermediate metabolite of MTBE.

Biodegradation of MTBE has been reported in the literature for aerobic conditions (Bradley et al., 1999a, 1999b; Landmeyer et al., 2001; Mo et al., 1997; Salanitro et al., 1994) and described in summary reviews (Deeb, et al., 2000). MTBE degradation has been reported in anaerobic conditions (Kolhatkar et al., 2002) and in specific reducing conditions including nitrate-reducing (Bradley et al., 2001a), sulfate-reducing (Bradley et al., 2001b), iron-reducing (Finneran and Lovley, 2001), and methanogenic (Wilson, et al., 2000) conditions. TBA degradation has been reported in aerobic conditions (Bradley et al., 1999a, 1999b) and anaerobic conditions (Bradley et al., 2002; Finneran and Lovley,

2001). TBA has been identified in some cases as an intermediate metabolite of MTBE biodegradation (Deeb, et al., 2000; Rittmann, 2003).

Several hydrocarbon degraders have been identified that can transform MtBE to TBA fortuitously during their growth phase (in co-metabolism) using propane or cyclohexane as growth substrate (Steffan, et al., 1997). In many other cases, degradation is observed with either TBA or MTBE as a sole-carbon source. In aerobic conditions, we note that almost all known MtBE degraders can also use TBA as their sole-carbon source for growth, although the individual organism may have different relative rates of MtBE and TBA degradation.

In direct microbial metabolism of a chemical, part of the chemical is converted to an increase in biomass. In a number of studies of biomass growth on either MTBE or TBA in aerobic conditions, reported maximum growth rate and yield for both TBA and MTBE is significantly less than that for a number of other readily biodegradable chemicals. This can lead to relatively long acclimation times before degradation of MTBE or TBA is observed, either in laboratory microcosms or field observations. Observed reduction of the TBA or MTBE substrate will occur only after a critical active biomass concentration is reached.

Observed acclimation times and degradation rates for TBA and MTBE may be different, depending on initial active biomass concentrations in the soil. In some cases, TBA can be a temporary intermediate product, particularly during the initial acclimation period of the biodegradation process. No routine measurements are available to directly measure active biomass levels in soil. For TBA and MTBE degradation, the active biomass is a small fraction of the total biomass in soil.

5.2. Laboratory Microcosm Experiments

As noted previously, three Shell remediation project sites in Orange County, California were selected for laboratory microcosm experiments. These sites include:

30011 Crown Valley Parkway, Laguna Niguel.
16969 Brookhurst, Fountain Valley.
27101 Ortega Highway, San Juan Capistrano.

Saturated soil cores were collected from three locations within selected regions of the groundwater plume at each site, along with site groundwater, for microcosm analysis. The spatial location of these samples is indicated in the figures of Appendix 1.

For three soil samples from each site, a test series of six microcosms were prepared, each in duplicate, as indicated in Table 5.1

Table 5.1. Microcosm test series for each soil sample.

test	solid phase:	liquid phase (in water):	vapor phase headspace:	notes and comments
1	soil	MTBE, TBA, sodium azide	oxygen	abiotic control test, no biological degradation
2	soil	MTBE, TBA	oxygen	test of aerobic MTBE, TBA degradation in native soils
3	soil, MC-100	MTBE, TBA	oxygen	positive control test of aerobic MTBE and TBA degradation, with added culture (MC-100) known to degrade these chemicals
4	soil	MTBE, TBA	oxygen, propane	test of co-metabolism conditions
5	soil	MTBE, TBA	nitrogen	test of anaerobic or low-oxygen conditions
6	soil	MTBE, TBA, Methanol	nitrogen	anaerobic test with methanol added to deplete available electron acceptors

The nominal setup for an individual microcosm consisted of a 160mL glass vial with a septum-seal, 50g of soil and 75 mL of water. The remaining vapor headspace was purged with either GC-grade oxygen or nitrogen (as applicable), respectively, for either 5 minutes or 30 minutes. Each microcosm in the set was then spiked with MTBE and TBA to bring the initial aqueous phase concentration to a level of approximately 10 mg/L. For the abiotic control (Table 5.1, test 1), sodium azide was added to bring aqueous concentrations to a level of 2%. For the positive control (Table 5.1, test 3), a bacterial culture known to degrade both TBA and MTBE was added at a level of approximately 400 ug-culture/g-soil. The samples were incubated at room temperature (20-22°C) for the test duration.

In analysis, water samples were taken through the vial septa with a syringe and analyzed for MTBE, TBA, and methanol by purge and trap with GC/MS. The initial analysis schedule was planned for either a 70 day duration or when detection limits were reached for the aerobic tests, and up to 150 days for the anaerobic tests. The implemented sampling schedule is included in the data tables of Appendix 2, along with measured test results over time. While microcosms were set up in duplicate, analysis was in most cases performed from one microcosm in each test series. Duplicate analyses were performed in only selected sampling events.

At the test conclusion, the vapor headspace of selected microcosms was sampled with a syringe and analyzed for oxygen and methane concentrations. The liquid phase was analyzed for nitrate and sulfate.

5.3. Data Analysis

Data results from the microcosm tests are included in Appendix 2, including plots of concentration versus time. In each case, both TBA and MTBE are monitored within the same microcosm. A summary table of results is also included in the appendix and identifies:

- whether the microcosm showed evidence of degradation for either MTBE or TBA (yes or no);
- whether an intermediate increase in TBA concentration is noted over the test duration (yes); and

- the percent change in measured concentration over the test duration. For TBA, if a peak concentration was noted, the percentage is calculated from the peak level, not the initial level.

Each time series of data includes an observed lag time, or acclimation time, prior to an observed decrease in monitored concentration levels (if any). The range of acclimation time is noted in the summary tables of Appendix 2. For TBA where an intermediate increase in TBA concentration is noted, the noted lag time is of longer duration than the peak time.

Conservation equations are used in estimating degradation rates from the microcosm data results, consistent with DeVaull, G. E., et al., 1997. For each microcosm, we fit an overall observed rate parameters to the active period of decrease in monitored concentration. Presuming zero-order kinetics (concentration change independent of concentration),

$$\Lambda_{w,i} = -\left(\frac{V_{eff}}{V_w}\right) \cdot \frac{dc_{w,i}}{dt}$$

or, given data at specific time increments, t_1 and t_2,

$$\Lambda_{w,i-observed_{1-2}} = -\left(\frac{V_{eff}}{V_w}\right) \cdot \frac{(c_{w,i,2} - c_{w,i,1})}{(t_2 - t_1)}$$

Presuming first-order kinetics (concentration change linearly dependent on concentration),

$$k_{w,i} = \left(\frac{\Lambda_{w,i}}{\phi_{w,i}}\right) = -\left(\frac{V_{eff}}{V_w}\right) \cdot \frac{1}{c_{w,i}} \cdot \frac{dc_{w,i}}{dt} = -\left(\frac{V_{eff}}{V_w}\right) \cdot \frac{d\ln(c_{w,i})}{dt}$$

or, given data at specific time increments,

$$k_{w,i-observed_{1-2}} = -\frac{V_{eff}}{V_w} \cdot \frac{\ln(c_{w,i,2}) - \ln(c_{w,i,1})}{(t_2 - t_1)}$$

In the above equations,

$\Lambda_{w,i\text{-}observed}$ [mg/(hr - L-water)] observed maximum rate constant for chemical i.
$k_{w,i\text{-}observed}$ (1/hr) observed first-order rate constant for chemical i
$c_{w,i}$ (mg/L-water) water-phase chemical concentration
t (hr) elapsed time

and

$$V_{eff} = V_w + V_a \cdot H_i + m_s \cdot f_{oc} \cdot K_{oc,i}$$

with

V_w (L-water) water volume within the microcosm
V_a (L-air) air volume within the microcosm
H_i (L-water/L-air) chemical-specific Henry's law coefficient
m_s (kg) total mass of soil in the microcosm
f_{oc} (g-oc/g-soil) organic carbon fraction of the soil
$K_{oc,i}$ (L-water/kg-oc) chemical-specific organic carbon to water partition coefficient

Calculated values for the zero-order rate estimate and first-order rate estimate are taken as averages over the applicable time increments in a given test. The results are tabulated in Appendix 2 for each test.

Half-life is also included in the tables of Appendix 2, and is defined as

$$t_{1/2} = \ln(2) / k_{w,i\text{-}observed}$$

A concise summary of test results is included in Table 5.2.

Table 5.2 Summary of microcosm test results.

		MTBE				TBA			
	maximum test duration	degradation indicated	in tests with degradation identified:			degradation indicated	in tests with degradation identified:		
Microcosm Test / Site Location	(days)	(no. tests)	range of mass change	lag time range (days)	half-life range (hours)	(no. tests)	range of mass change	lag time range (days)	half-life range (hours)
Aerobic, native soil									
30011 Crown Valley Parkway	56	3 of 3	-100%	0 to 14	95 to 157	3 of 3	-100%	7 to 28	82 to 357
16969 Brookhurst	56	5 of 5	-100%	0 to 49	174 to 1263	5 of 5	-100%	0 to 14	15 to 184
27101 Ortega Highway	154	3 of 3	-39% to -100%	7 to 140	684 to 2965	3 of 3	-100%	14 to 35	169 to 840
Anaerobic transformation									
30011 Crown Valley Parkway	196	3 of 3	-29% to -100%	21 to 145	167 to 3976	2 of 3	-100%	0 to 14	345 to 1129
16969 Brookhurst	161	3 of 3	-100%	7 to 70	116 to 1362	3 of 3	-50% to -78%	21 to 145	239 to 2689
27101 Ortega Highway	154	1 of 3	-100%	14 to 56	657	2 of 3	-100%	14 to 70	1227 to 1974
Anaerobic with methanol									
30011 Crown Valley Parkway	196	3 of 3	-99% to -100%	56 to 145	87 to 777	1 of 3	-20%	142	3720
16969 Brookhurst	161	3 of 3	-100%	21 to 111	90 to 264	0 of 3	--	>161	--
27101 Ortega Highway	154	2 of 3	-100%	56 to 114	179 to 448	0 of 3	--	>154	--
Co-metabolism, propane									
30011 Crown Valley Parkway	196	1 of 3	-100%	125 to 145	160	0 of 3	--	>196	--
16969 Brookhurst	161	3 of 3	-100%	14 to 70	127 to 281	1 of 3	-27%	70 to 91	4556
27101 Ortega Highway	154	1 of 3	-40%	56 to 70	2414	1 of 3	-84%	0 to 7	113
Control Tests:		(for all tests):				(for all tests):			
Abiotic control									
30011 Crown Valley Parkway	196	0 of 3	-8% to -15%	(negative control)		0 of 3	-8% to -16%	(negative control)	
16969 Brookhurst	161	0 of 5	-9% to 10%			0 of 5	5% to -10%		
27101 Ortega Highway	154	0 of 3	0%			0 of 3	11% to 0%		
Aerobic, soil with MC-100									
30011 Crown Valley Parkway	28	3 of 3	-100%	(positive control)		3 of 3	-100%	(positive control)	
16969 Brookhurst	14	5 of 5	-100%			5 of 5	-100%		
27101 Ortega Highway	7	3 of 3	-100%			3 of 3	-100%		

5.4. Discussion of Microcosm Data Results

5.4.1. Aerobic microcosms

Both MTBE and TBA showed significant degradation in all aerobic soil microcosms, at all three investigated sites. For MTBE in 8 of 11 microcosms, with all three sites represented, the observed acclimation time was 14 days or less. For TBA, all samples showed acclimation times less than 35 days, but with an observed trend of increased acclimation time, respectively, for 16969 Brookhurst, 30011 Crown Valley Parkway, and 27101 Ortega Highway. Calculated degradation rates for TBA and MTBE were in similar

range at each site, with a geometric mean half-life for MTBE and TBA respectively, of 340 hrs and 90 hrs.

In 4 of 9 microcosms (3 of 3 from 30011 Crown Valley Parkway and 1 of 3 from San Juan Capistrano), an initial increase of TBA was observed, commensurate with a decrease in MTBE concentration. In all of these cases, TBA concentrations later decreased.

Positive observation of MTBE and TBA degradation, and relatively short observed acclimation times in all of these microcosms, are indicative of a relatively significant indigenous biomass capable of degrading both MTBE and TBA at these sites in aerobic conditions.

5.4.2. Anaerobic microcosms with methanol addition

The anaerobic microcosms with added methanol were intended to evaluate degradation of MTBE and TBA in methanogenic conditions. The added methanol, in excess, initially depletes the microcosm of available electron acceptors (oxygen, nitrate, sulfate, etc.), allowing methanogenesis to proceed.

MTBE showed degradation in 8 of 9 of these microcosms, with, in the same 8 of 9 cases, an observed increase in TBA as the MTBE degraded. Elevated methane in headspace was measured at the conclusion of the monitoring period for the same 8 of 9 microcosms, indicating methanogenic conditions. TBA showed degradation in 1 of 9 of these microcosms, with an observed lag time of 145 days (in a microcosm test of 196 days duration).

In the single microcosm for which MTBE did not show degradation (M-3d42, #18, 27101 Ortega Highway), neither TBA nor methanol was degraded, and methane was not detected in headspace vapor at the test conclusion.

Acclimation times for MTBE degradation in these microcosms ranged from 56 to 145 days. Observed half-life, ranged from 87 to 777 hours. This range is similar in magnitude to that observed for aerobic MTBE degradation in the same native soils (95 to 2965 hours).

The sole observation of TBA degradation in this set of microcosms (MS3A, #18, 30011 Crown Valley Parkway) occurred between days 145 and 196 in a set of microcosms that were originally scheduled for a 150-day incubation period. A longer incubation period may have increased the fraction of microcosms with observed TBA degradation.

Reported ancillary data for these three sites [personal communication by Seth Daugherty to George DeVaull, 23 July 2003, of data collected and measured by John Wilson of USEPA] showed dissolved methane levels in groundwater at these three sites as follows:

	Well	Methane (ml/L)	Methane (ug/L)
16969 Brookhurst, Fountain Valley	MW-6	0.0982	64.4
	MW-15	0.0293	19.2
	MW-13	0.535	351
30011 Crown Valley Parkway, Laguna Niguel	MW-7	1.02	669
	MW-10	0.953	663
	MW-11	0.0176	11.5
27101 Ortega Highway, San Juan Capistano	W-2	4	2620
	MW-8	1.56	1020
	MW-11	0.835	547
(unit conversion at nominal temperature of 25°C)			

The observed concentration levels and gradients across the sites are indicative of methanogenic conditions over at least a portion of the groundwater plume(s) at all three sites.

5.4.3. Anaerobic microcosms - nitrogen sparged

The anaerobic microcosms sparged with nitrogen were intended to evaluate degradation of MTBE and TBA in oxygen-depleted conditions, but with other electron acceptors, if present in the native soil and groundwater, remaining available.

Individually, MTBE showed observed degradation in 7 of 9 of these microcosms, and TBA showed observed degradation 7 of 9 of these microcosms. Both TBA and MTBE in the same microcosm were degraded in 5 of 9 cases. For the 7 microcosms in which MTBE was observed to degrade, a commensurate increase in TBA concentration was observed in 5 of 7 microcosms.

The mechanism of anaerobic degradation was not identified in these microcosms. Sulfate and nitrate were measured in the initial groundwater and in a water sample from these microcosms at the test conclusion, however no conclusions could be drawn from changes in levels of these electron acceptors over the test period.

5.4.4. Co-metabolism

The aerobic microcosms with added propane were intended to evaluate the potential for co-metabolism of MTBE and propane, compared with negative results from the aerobic microcosms with only added MTBE and TBA.

MTBE and TBA showed significant degradation in every aerobic microcosm (discussed in Section 5.4.1) with only these chemicals added. Given this, the results from the co-metabolism tests are inconclusive.

5.4.5. Controls

The sodium azide -spiked microcosms showed relatively stable TBA and MTBE levels over the test duration, with variability on the order of +10% to -15% or less. Exceeding this range of variability was an initial indication in the active tests that a change in MTBE or TBA concentration was occurring.

The positive controls, spiked with a culture known to degrade both MTBE and TBA, provided an indication that procedures would be adequate and able to determine if degradation was occurring in other cases, as well as a qualitative comparison of relative degradation rates.

6. Evaluate possible abiotic transformation of TBA from MTBE

Task 4 of the work plan included investigation of possible abiotic transformation mechanisms. Significant hydrolysis of MtBE to TBA is unlikely at normal environmental conditions. The potential for hydrolysis at low pH levels is discussed below as part of Task 5. The potential for other possible abiotic transformations from MtBE to TBA is not likely to be significant. No significant changes were noted in the abiotic control tests included in the microcosm tests series.

7. Evaluation of the possibility of TBA detections being an artifact of sample collection and/or laboratory analytical methods

Task 5 of the work plan included identifying and quantifying the possibility of measured TBA in groundwater originating as a sampling and analysis artifact from conversion of MTBE to TBA. White et al. (2003) and O'Reilly et al. (2001) have indicated the potential for TBA detection as an artifact of sample collection and/or analysis. Further comment on these papers is discussed following.

The aqueous hydrolysis rate of MTBE is dependent upon temperature, pH, and the presence of other ions (i.e. salts). Roughly, a 10°C increase in temperature increases the rate by a factor of 2.5. A decrease in pH by one pH unit will increase the reaction rate by about one order of magnitude. The influence of other ions is little understood, but probably of less significance than temperature and pH.

O'Reilly et al. (2001) examined these variables, but not in enough detail to permit an extrapolation of data for accurate prediction under various conditions. However, the data do confirm the existence of hydrolysis at pH = 1 and 20 to 30°C, with half-lives from weeks to months. Approximate extrapolation indicates potential half-lives in the range of minutes to hours at approximately pH=1 and 80°C. However, a survey of the laboratories doing the majority of MTBE analyses for Shell in California shows that purge temperatures used are actually between 40 to 45°C and purge times are approximately 11 minutes. Under these conditions, at pH=1, TBA production would likely be less than 1% of the original MTBE concentration. The transformation would be less if dilution of the sample prior to analysis results in a pH increase.

White et al. (2003) reported EPA data showing a half-life of about 22 minutes at pH=1 and 80°C, and about 154 minutes at pH=2 and 80°C. Within the limits of the data, this roughly represents an order of magnitude difference in rate with a difference of one pH unit.

These data indicate that under conditions of pH near 2 and temperature near 80°C, hydrolysis of MTBE in samples is possible. These conditions will not occur in the subsurface, nor during sample storage. As noted (White et al., 2003), some analytical procedures may include a step of heating an acid-treated sample to about 80°C for between 3 to 30 minutes, depending upon the specific method. If the sample is at pH=1, this could potentially be a cause for concern.

Given this review, it is apparent that hydrolysis can occur in storage and heating of aqueous MtBE samples under low pH conditions and high temperature. Additional testing with field and controlled samples would be required to establish a range of measured hydrolysis data with a sufficient accuracy to predict MtBE hydrolysis under a broad range of arbitrary conditions. Within the scope of this project, however, we have instead focused directly on examining and testing the range of conditions and analytical methods commonly used for analysis of groundwater samples.

7.1. Potential Conversion of MtBE to TBA Under Storage Conditions:

Studies done to date indicate that there is no significant contribution to formation of TBA from hydrolysis of MtBE under normal sample preservation and storage conditions (pH <2 and 4°C). A recent study performed by Shell indicates no conversion of MtBE to TBA during the time of the study (14 days). A modest conversion of MTBE to TBA (~0.4%) was observed when the sample was kept below pH 1. The study was done with an MtBE concentration of 20,000 mg/L.

It must be emphasized that samples are acidified in the field directly by having the acid already placed in the laboratory provided Volatile Organic Analysis (VOA) vials, or by adding the acid in the field. Typically, 4 drops of 1:1 hydrochloric acid:water are added for this purpose. The pH achieved by this acid addition is in the range of 1.5 to 2. It is our experience that to reach a pH level less than 1, more than twice the number of drops would be required. It is unlikely that the pH would be near 1 in groundwater samples preserved using this method.

7.2. Potential Conversion of MtBE to TBA During Analysis

Because alcohols such as TBA are not readily stripped (or volatilized) from water, it is common for laboratories to heat samples to improve detection sensitivity. This raises the concern for potential hydrolysis of ethers such as MtBE while heating under acidic conditions. It is expected that MtBE can hydrolyze and form TBA at low pH and high temperature. Because of this conversion possibility and the observance of TBA in groundwater, there has been a great deal of speculation and interest in this issue.

EPA/ORD has recently completed a two-part study of the effect of heating and acidification on MtBE in groundwater samples (White et al., 2002, 2003). The first part dealt with the rate of hydrolysis of MtBE at 80°C at pH 1 and pH 2, using headspace analysis where the sample is heated statically for 30 minutes (EPA Method 8021). They found that at pH 2, 6% of the MtBE hydrolyzed to TBA and that 57% of the MtBE hydrolyzed to TBA at pH 1. The second part of the study involved analysis of diluted and undiluted replicate samples from an MTBE plume in California. The samples were acidified in the field to a pH of <2 and analyzed using the same static headspace sampler. As expected, diluted samples with corresponding diluted acid reduced the rate of MtBE hydrolysis to TBA. In undiluted samples, 22 to 89% hydrolysis of MTBE was reported. In diluted samples (1:10 dilution), the fraction of MtBE hydrolyzed ranged from 1 to 18%. These studies have prompted EPA/ORD to consider proposing addition of trisodium phosphate (TSP) to raise the pH of groundwater samples for preservation instead of acid addition. No studies have been done to determine potential impact of this preservation change to analysis of VOAs.

In further study (Lin, et al., 2003) acid hydrolysis was identified when samples at pH < 2 were heated in headspace sampling at 80°C. No acid hydrolysis was seen in storage (28 d at 4°C), and none was seen if the pH of the stored samples was adjusted prior to heating.

It is important to state that, to the best of our knowledge, there are no commercial laboratories that are currently using EPA Methods 5021 (static headspace) for the analysis of VOAs (including oxygenates). The static headspace method is seldom used for water samples.

All of the California laboratories that we surveyed used purge and trap procedures (EPA Method 5030) where the samples are either not heated, or are heated to a maximum of 45°C while purged with helium at 40mL/min for 11 minutes. Some labs have a preheat time which is typically less than 3 minutes. The maximum concentration of MtBE that can be analyzed without dilution is typically <200 µg/L. These conditions are markedly different from the static headspace analysis where the samples are heated at 80°C in the presence of acid with no purge for 30 minutes.

Recent studies using typical field and laboratory conditions indicate that acid hydrolysis of MtBE in properly handled groundwater samples do not compromise the integrity of dissolved MtBE and TBA analysis:

- A recent study done by Handex using EPA Method 624 (purge and trap with GC/MS) found no conversion of MtBE to TBA. Water samples were spiked with 200, 2000, 20000 µg/L MtBE, stored at 4°C and acidified to a pH ≤2 with various holding times of up to 31 days. Unpreserved control samples were also analyzed. No TBA concentrations were detected.
- A study done by SPL at the request of Marvin Katz (Shell Oil Products US) consisted of analysis of 200 µg/L MtBE in HCl preserved, unpreserved and heated and unheated samples showed no detectable TBA.

- Preliminary results of an ongoing study at Shell Global Solutions (US) Environmental Chemistry laboratory indicate that no significant hydrolysis of MtBE is observed, even when the samples are heated to 70°C at pH 1 in a purge and trap system. This study varied the preheat time (0, 3, 10 and 30 minutes) prior to purging to mimic the static headspace procedure used by EPA/ORD. Hydrolysis of MtBE to TBA (<6%) was only somewhat significant when the samples were preheated for 30 minutes at the lower than typical pH of 1. These studies were done at an MtBE concentration of 500 µg/L.

In summary, it is our opinion that hydrolysis of MtBE to TBA is not of concern during storage and analysis of acid-preserved samples. Samples are typically analyzed by purge and trap GC methods that minimize the time that MtBE is heated (usually at temperatures 45°C or lower), the pH is 1 to 2, and samples with significant MtBE concentrations are diluted.

Although it is possible that a small portion of TBA found in groundwater could be due to analytical artifacts, it is extremely unlikely that the significant concentrations of TBA found in groundwater samples collected from some UST remediation project sites are attributable to lab methodology problems.

8. Summary and Conclusions

This study was initiated to determine the potential source of TBA in groundwater at selected LUST sites in Orange County, California. A number of potential TBA sources were identified and investigated.

The most plausible explanation is that the TBA at these sites is predominately an intermediate biological degradation product, produced from MTBE primarily in either low-oxygen or methanogenic environmental conditions. This is supported by laboratory microcosm studies under methanogenic conditions, using soils from selected sites in Orange County. These tests showed degradation of MTBE, and a commensurate increase in TBA while the MTBE was decreasing. Field data indicates that at least a portion of groundwater at the sites under study is methanogenic, based on measured dissolved methane concentrations in groundwater.

MTBE-gasoline has also been investigated as a potential source of TBA in groundwater. Estimated water concentrations of TBA in dissolution from MTBE-gasoline are consistent with measured soluble concentrations of TBA in groundwater at the investigated sites. Dissolution from gasoline as a sole source of TBA in groundwater cannot, however, explain high measured levels of TBA with low (or non-detect) co-located measurement of either MTBE or BTEX constituents. Dilution, partitioning, and transport alone cannot explain the observed relative concentration levels of these chemicals. Transformation, (in this case laboratory confirmation of biological degradation and transformation), helps explain the measured site data.

Other possible sources of measured TBA in groundwater, including abiotic transformation in the environment, or presence of TBA as an artifact of chemical analysis methods, for the conditions investigated, are likely insignificant contributors for the levels of TBA observed at the investigated sites.

Microcosm analyses conducted on soils (collected below the water table) as part of this work showed degradation of MTBE and TBA in both aerobic and anaerobic conditions. Investigation of co-metabolism of TBA or MTBE in the presence of propane was inconclusive, since degradation had been observed without the presence of the selected (propane) co-metabolic substrate.

In further conclusion, the identified prevalence of observed biodegradation of MTBE and TBA at the investigated sites is encouraging evidence for either a monitored natural attenuation or enhanced natural attenuation solution for these sites, as well as other similar underground storage tank remediation project sites. Either existing natural attenuation guidance (ASTM E1943-98; Wiedemeier et al. 1995, 1997) or a modified guidance to-be-developed would aid in this application. As a preliminary proposal, along the lines of evidence commonly used in natural attenuation studies:

- *To establish plume stability*: Continued groundwater monitoring of MTBE, TBA, and other chemicals of concern in quarterly monitoring events. Evaluation of trends in data using statistical or other methods to establish that concentrations in the groundwater plume are stable or decreasing in time and extent.
- *Geochemical indicators*: Monitoring of relevant electron acceptors, primarily dissolved oxygen, sulfate, and nitrate, as well as methane, as evidence of biological activity.
- *Biological indicators*: In selected cases, laboratory microcosm studies of site media samples to establish the level and type of biological transformation occurring at a site.

Finally, we note that the selected sites exhibited low groundwater gradients and inferred low groundwater seepage velocities. We would expect the effects of biological degradation to be more significant and observable at these types of sites, than at sites with higher groundwater flow rates (high permeability/high recharge sites). This is especially true if degradation in anaerobic conditions is the significant transformation and removal mechanism.

9. References

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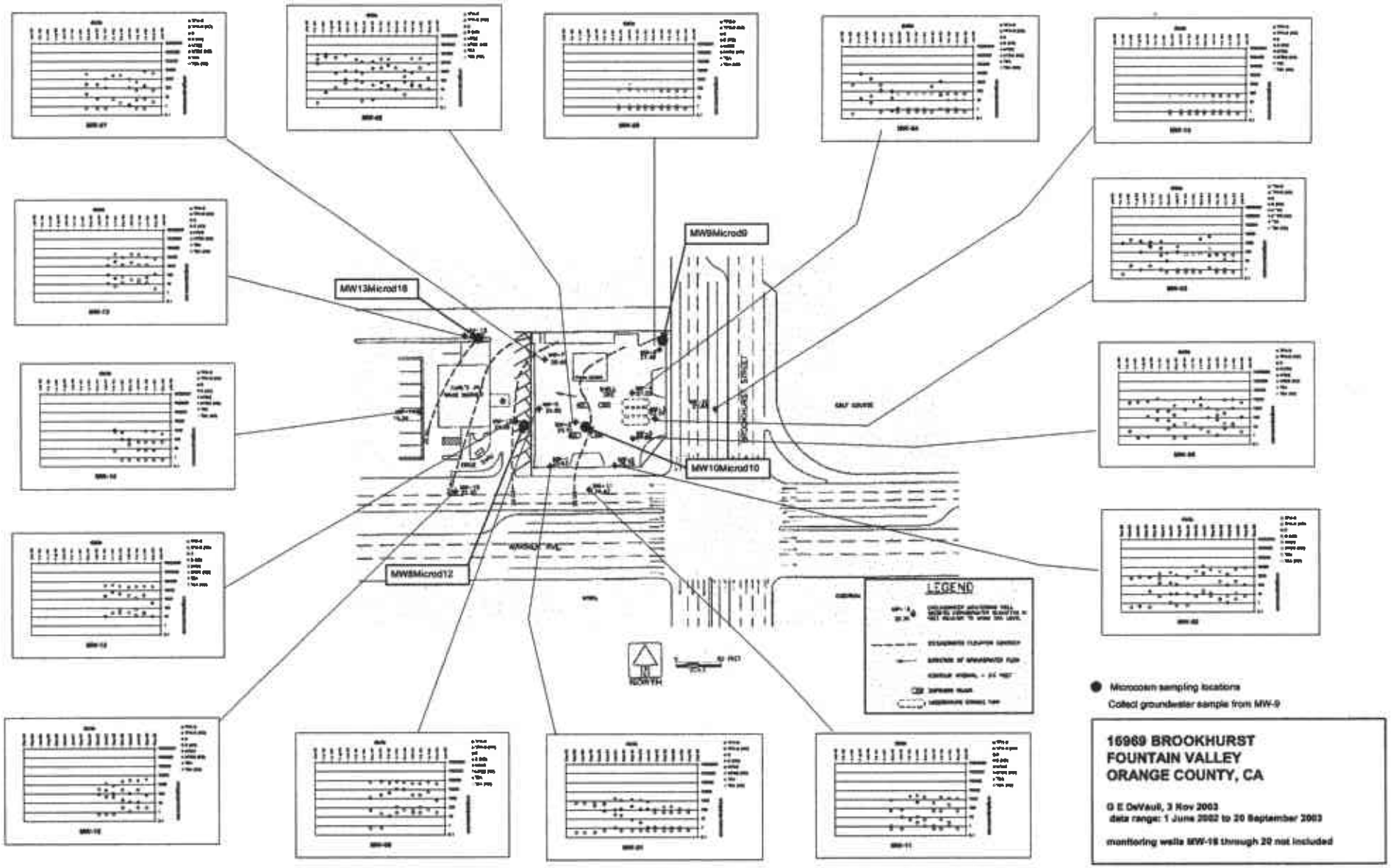
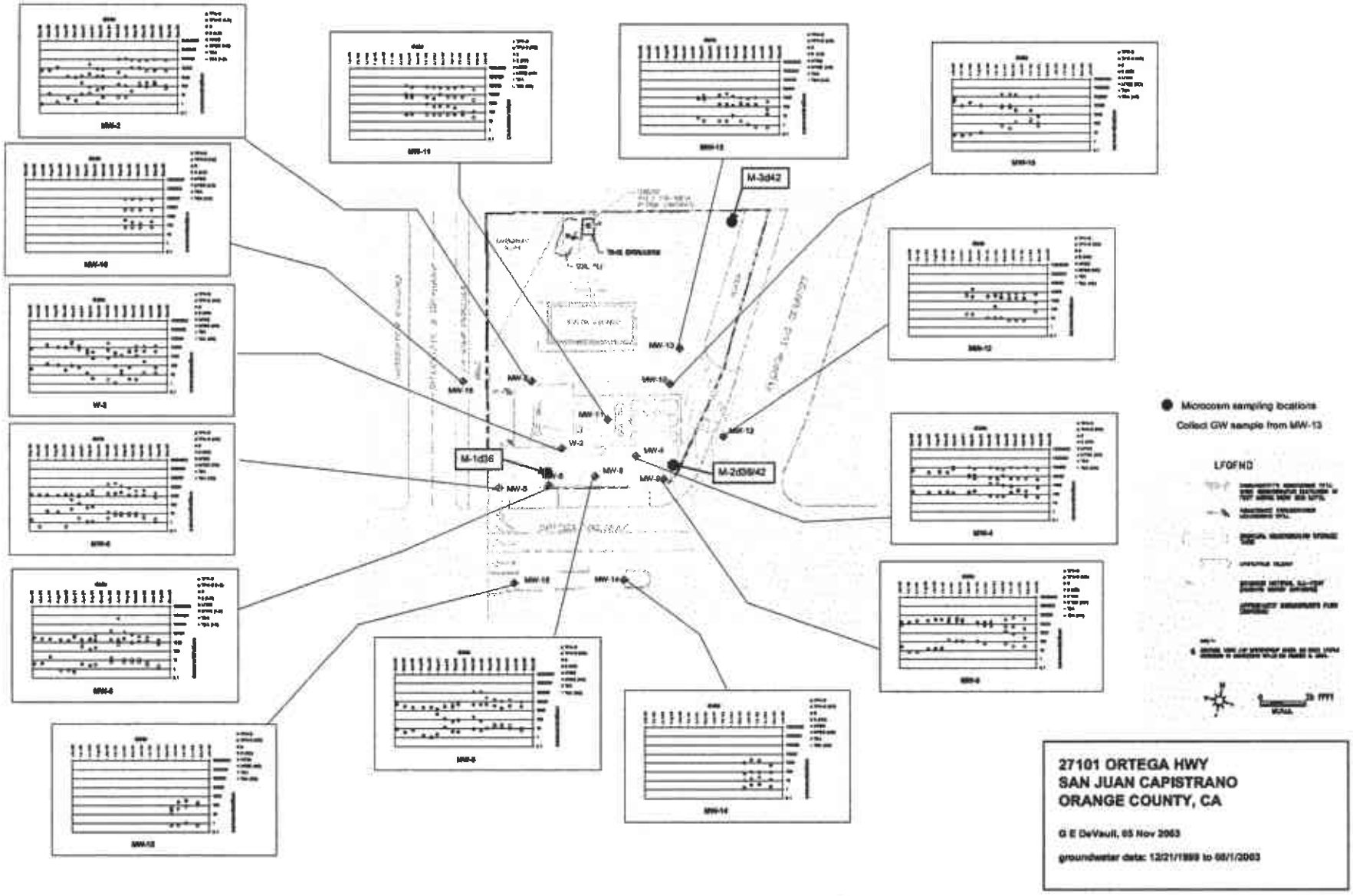
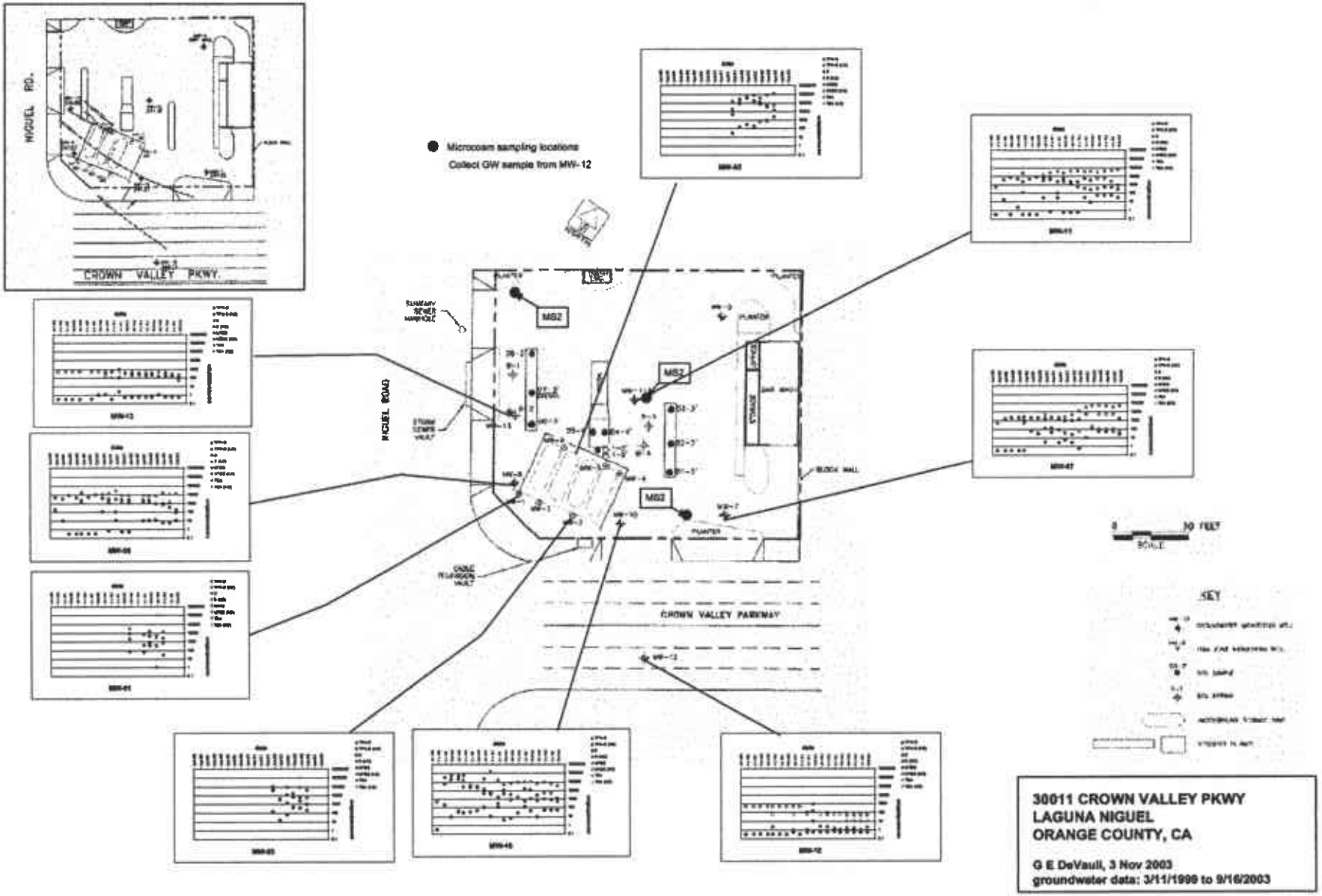
Appendix 1

Plan view maps for Orange County Sites, including time-series plots on monitored groundwater concentrations.

30011 Crown Valley Parkway, Laguna Niguel.
16969 Brookhurst, Fountain Valley
27101 Ortega Highway, San Juan Capistrano


MW13Microd13
MW9Microd9
MW10Microd10
MW8Microd12
LEGEND
Microcosm sampling locations
Collect groundwater sample from MW-9
16969 BROOKHURST
FOUNTAIN VALLEY
ORANGE COUNTY, CA
G E DeVaull, 3 Nov 2003
data range: 1 June 2002 to 20 September 2003
monitoring wells MW-16 through 20 not included


M-3d42
M-1d36
M-2d36/42
MW-13
MW-12
MW-11
MW-10
MW-9
MW-8
MW-6
MW-5
MW-4
MW-3
W-2
MW-14
Microcosm sampling locations
Collect GW sample from MW-13
LEGEND
27101 ORTEGA HWY
SAN JUAN CAPISTRANO
ORANGE COUNTY, CA
G E DeVault, 05 Nov 2003
groundwater data: 12/21/1999 to 08/1/2003


NIGUEL RD.
CROWN VALLEY PKWY.
Microcoam sampling locations
Collect GW sample from MW-12
NIGUEL ROAD
MS2
MS2
MS2
CROWN VALLEY PARKWAY
BLOCK WALL
PLANTER
SCALE
KEY
30011 CROWN VALLEY PKWY
LAGUNA NIGUEL
ORANGE COUNTY, CA
G E DeVaull, 3 Nov 2003
groundwater data: 3/11/1999 to 9/16/2003

Appendix 2

Soil microcosm data results.

Plots of time versus concentration of microcosm data.

30011 Crown Valley Parkway
Laguna Niguel
Orange County, CA

sample ID	index	test description	initial vapor headspace	analyte	conc units	measured concentration data start date: 02/27/2003 elapsed hours 0	96	168	336	504	672	816	1176	1344	1680	2016	2160	2520	3000	3480	3984	4704
						elapsed days 0	4	7	14	21	28	34	49	56	70	84	90	105	125	145	166	196
MS1 A	#1	Abiotic control	Oxygen	MTBE	mg/L	13		12	12	12		11	12	11		12		9.3	12	11	11	11
				TBA	mg/L	12		11	11	11		10	11	11		11		9	12	10	11	11
MS1 A	#2	Aerobic, native soil	Oxygen	MTBE	mg/L	13		11	7	1.8	0.096	<.02	<.005									
				TBA	mg/L	13		13	14	15	16	12	2.4	<.02								
MS1 A	#3	Aerobic, soil with MC-100	Oxygen	MTBE	mg/L	14	0.054	<.005	<.005													
				TBA	mg/L	13	8.3	0.083	<.02													
MS1 A	#4	Co-metabolism, propane	O2/Propane	MTBE	mg/L	14		12	12	12		10	11	12		12		13	12	2.2	0.02	<.02
				TBA	mg/L	12		12	10	11		9.7	10	11		11		13	13	18	19	19
MS1 A	#5	Anaerobic transformation	Nitrogen	MTBE	mg/L	14		13		13		12		5.5	0.18	0.012	<.005					
				TBA	mg/L	12		12		11		11		18	23	21	23	24	23	20	19	21
MS1 A	#6	Anaerobic with methanol	Nitrogen	MTBE	mg/L	14		13		13		12		12		0.049	0.016	<.005				
				TBA	mg/L	13		12		11		11		12		22	23	23	22	19	19	21
				MeOH	mg/L	1672		1755		719		10		<1								
MS2 A	#7	Abiotic control	Oxygen	MTBE	mg/L	13		12	14	13		12	11	12		12		9.8	13	10	9.9	12
				TBA	mg/L	12		13	11	11		11	10	12		11		9.8	12	10	9.8	11
MS2 A	#8	Aerobic, native soil	Oxygen	MTBE	mg/L	12		12	10	5.1	5	0.44	<.005									
				TBA	mg/L	13		12	14	12	11	5.2	<.02									
MS2 A	#9	Aerobic, soil with MC-100	Oxygen	MTBE	mg/L	15	0.14	<.02														
				TBA	mg/L	14	1.2	<.005														
MS2 A	#10	Co-metabolism, propane	O2/Propane	MTBE	mg/L	14		12	14	12		12				12		15	13	10	10	12
				TBA	mg/L	13		13	12	12		11				12		14	12	11	9.9	11
MS2 A	#11	Anaerobic transformation	Nitrogen	MTBE	mg/L	14		12		12		11	13	12	12	13	12	7.4	8.6	9.5	9.1	9.1
				TBA	mg/L	13		13		11		7.2	4.9	2.9	1.8	0.14	<.005				<.02	
MS2 A	#12	Anaerobic with methanol	Nitrogen	MTBE	mg/L	14		13		12		12		12		12		8.3	12	9.7	8.5	0.12
				TBA	mg/L	13		13		12		12		13		12		9.7	12	10	9.6	21
				MeOH	mg/L	1881		1985		2047		2012		<1								
MS3 A	#13	Abiotic control	Oxygen	MTBE	mg/L	12		13	15	12		12	12	12		12			6.7	9.2	8.9	11
				TBA	mg/L	8.9		8.5	8.5	8.2		7.9	7.5	8.5		8.1			9	7	6.3	7.5
MS3 A	#14	Aerobic, native soil	Oxygen	MTBE	mg/L	12		10	1.4	<.005	<.005											
				TBA	mg/L	9.2		9.6	13	1.3	<.02											
MS3 A	#15	Aerobic, soil with MC-100	Oxygen	MTBE	mg/L	14	<0.005															
				TBA	mg/L	9	<0.02															
MS3 A	#16	Co-metabolism, propane	O2/Propane	MTBE	mg/L	13		13	14	12		10	12	11		11			12	9.5	11	9.8
				TBA	mg/L	8.6		7.9	8.7	7.8		7.1	8	8.2		8			8.6	7	8.7	7.3
MS3 A	#17	Anaerobic transformation	Nitrogen	MTBE	mg/L	14		12		12		12		12		12			13	14	12	10
				TBA	mg/L	8.2		8		7.3		7.3		7.7		7.2		5.8	1.8	<.5	<.02	
MS3 A	#18	Anaerobic with methanol	Nitrogen	MTBE	mg/L	13		12		12		10		12		12		9.9	3.5	<0.1	<.02	
				TBA	mg/L	8.3		8.3		7.8		6.9		8		7.5		7.3	6	20	18	16
				MeOH	mg/L	1788		1751		1823		1908		<1								

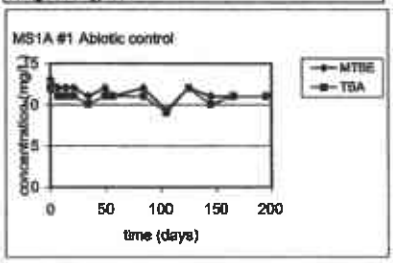
30011 Crown Valley Parkway
Laguna Niguel
Orange County, CA

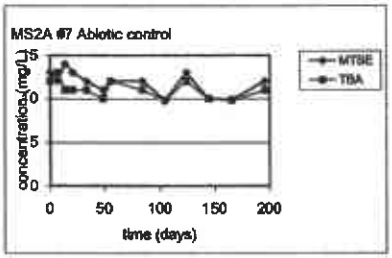
notes:
aerobic criteria for dissolved oxygen > 1 mg/L
methanogenic criteria for dissolved methane > 0.5 mg/L

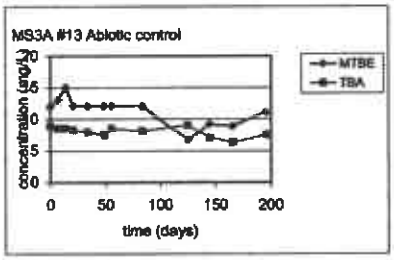
sample ID	index	test description	analyte	noted TBA accum-ulation	concentration change initial	final	percent	final dissolved oxygen (mg/L)	final dissolved methane (mg/L)	degrad. evident	lag time range (hrs)	zero-order rate est. λ (mg/L)/hr	first-order rate est. k (1/hr)	half life $t_{1/2}$ (hrs)	average conc. c_w (mg/L)	$k \cdot c_w$ (mg/L)/hr
MS1 A	#1	Abiotic control	MTBE		13	11	-15%			no						
			TBA		12	11	-8%			no						
MS1 A	#2	Aerobic, native soil	MTBE		13	0.005	-100%	2.5	0	yes	0 to 168	0.021	0.0073	95	6.5	0.048
			TBA	[yes]	16	0.02	-100%			yes	504 to 672	0.019	0.0019	357	12.1	0.023
MS1 A	#3	Aerobic, soil with MC-100	MTBE		14	0.005	-100%			yes						
			TBA		13	0.02	-100%			yes						
MS1 A	#4	Co-metabolism, propane	MTBE		14	0.02	-100%	2	0	yes	3000 to 3480	0.010	0.0043	160	4.7	0.021
			TBA	[yes]	19	19	0%			no	>4704	--	--	--	13.0	--
MS1 A	#5	Anaerobic transformation	MTBE		14	0.005	-100%	1.7	0	yes	504 to 816	0.012	0.0042	167	6.1	0.025
			TBA	[yes]	23	21	-9%			no	>4704	--	--	--	18.2	--
MS1 A	#6	Anaerobic with methanol	MTBE		14	0.005	-100%	0.2	14	yes	1344 to 2016	0.010	0.0060	87	4.0	0.032
			TBA	[yes]	23	21	-9%			no	>4704	--	--	--	17.3	--
			MeOH		1672	1	-100%			yes						
MS2 A	#7	Abiotic control	MTBE		13	12	-8%			no						
			TBA		12	11	-8%			no						
MS2 A	#8	Aerobic, native soil	MTBE		12	0.005	-100%	20.3	0	yes	168 to 336	0.020	0.0044	157	5.1	0.023
			TBA	[yes]	13	0.02	-100%			yes	168 to 336	0.039	0.0045	155	10.6	0.047
MS2 A	#9	Aerobic, soil with MC-100	MTBE		15	0.02	-100%			yes						
			TBA		14	0.005	-100%			yes						
MS2 A	#10	Co-metabolism, propane	MTBE		14	12	-14%	1.9	0.1	no	>4704	--	--	--	12.4	--
			TBA		13	11	-15%			no	>4704	--	--	--	11.9	--
MS2 A	#11	Anaerobic transformation	MTBE		14	9.1	-35%	2.6	0	yes	2016 to 2160	0.006	0.0005	1397	9.3	0.005
			TBA		13	0.02	-100%			yes	0 to 168	0.008	0.0020	345	6.7	0.014
MS2 A	#12	Anaerobic with methanol	MTBE		14	0.12	-99%	0.2	14.6	yes	3000 to 3480	0.007	0.0009	777	8.9	0.008
			TBA	[yes]	21	21	0%			no	>4704	--	--	--	12.5	--
			MeOH		1861	1	-100%			yes						
MS3 A	#13	Abiotic control	MTBE		12	11	-8%			no						
			TBA		8.9	7.5	-16%			no						
MS3 A	#14	Aerobic, native soil	MTBE		12	0.005	-100%	16.5	0.1	yes	0 to 168	0.035	0.0064	108	7.8	0.050
			TBA	[yes]	13	0.02	-100%			yes	168 to 336	0.049	0.0084	82	8.0	0.067
MS3 A	#15	Aerobic, soil with MC-100	MTBE		14	0.005	-100%			yes						
			TBA		9	0.02	-100%			yes						
MS3 A	#16	Co-metabolism, propane	MTBE		13	9.8	-25%	1.8	0.1	no	>4704	--	--	--	11.5	--
			TBA		8.6	7.3	-15%			no	>4704	--	--	--	8.0	--
MS3 A	#17	Anaerobic transformation	MTBE		14	10	-29%	0.4	0	yes	3000 to 3480	0.002	0.0002	3976	10.1	0.002
			TBA		8.2	0.02	-100%			yes	1344 to 2016	0.004	0.0006	1129	6.7	0.004
MS3 A	#18	Anaerobic with methanol	MTBE		13	0.02	-100%	0.2	14.1	yes	2016 to 2520	0.006	0.0013	544	8.5	0.011
			TBA	[yes]	20	16	-20%			yes	3408	0.003	0.0002	3720	18.0	0.003
			MeOH		1788	1	-100%			yes						

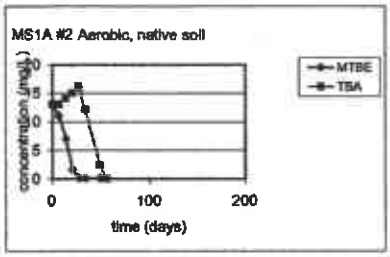
A2.3

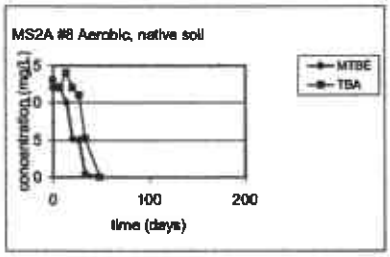
30011 Crown Valley Parkway
Laguna Niguel
Orange County, CA

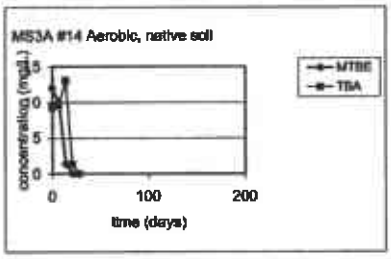


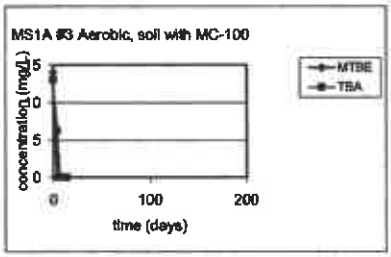


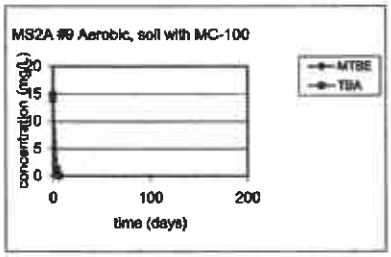


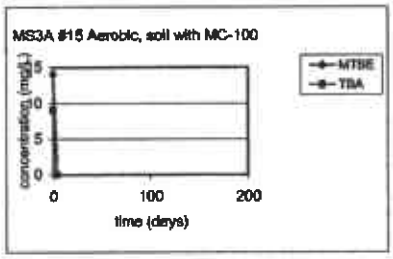


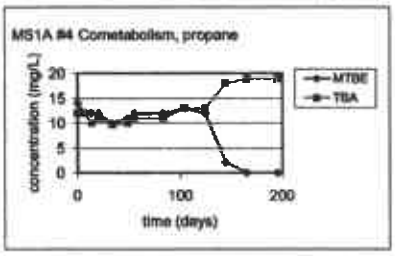


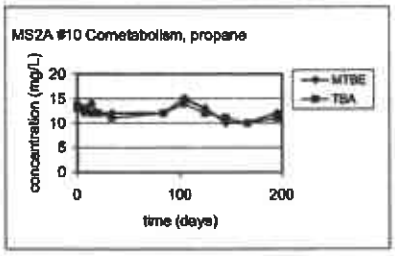


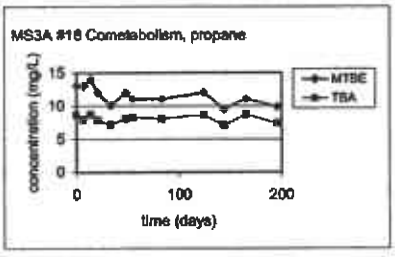


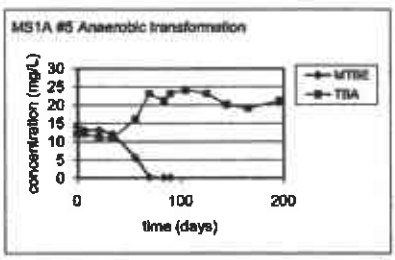


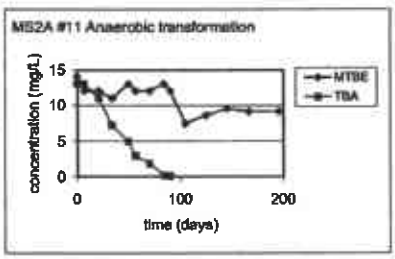


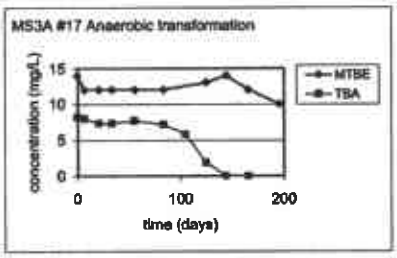


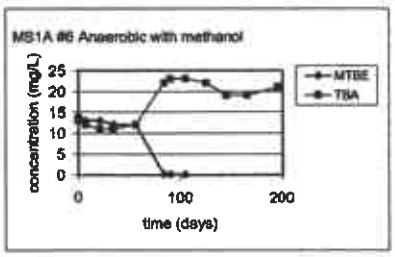


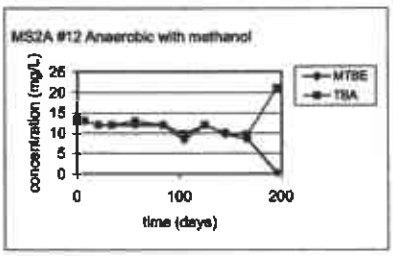


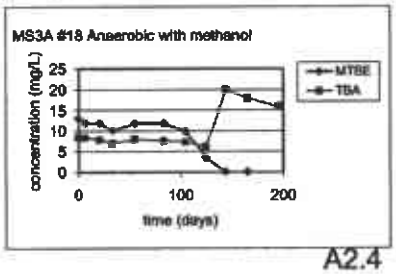












16869 Brookhurst
Fountain Valley, CA
Orange County, CA

sample ID	index	test description	initial vapor headspace	analyte	conc units	measured concentration data start date: 02/04/2003													
						elapsed hours													
						0	96	168	336	504	840	1176	1344	1680	2184	2664	3216	3480	3864
						elapsed days													
						0	4	7	14	21	35	49	56	70	91	111	134	145	161
mw6microd12	#1	Abiotic control	Oxygen	MTBE	mg/L	11		12	10	10	9.9	12		9.6	9.6	12	11		10
				TBA	mg/L	9.1		9.2	8	8.8	9.2	9.5		7.9	8.3	10	9		8.4
mw6microd12	#2	Aerobic, native soil	Oxygen	MTBE	mg/L	11		11	9.6	10	10	2.7	<.005						
				TBA	mg/L	9.8		9.6	0.024	0.018	<.005								
mw6microd12	#3	Aerobic, soil with MC-100	Oxygen	MTBE	mg/L	12	0.067	<.005											
				TBA	mg/L	8.9	3.4	<.02											
mw6microd12	#4	Co-metabolism, propane	O2/Propane	MTBE	mg/L	11		11	9.8	9.5		0.74	0.19	0.017	<.005		<.02		
				TBA	mg/L	7.5		7.7	7	7.2		14	13	12	12	14	12		12
mw6microd12	#5	Anaerobic transformation	Nitrogen	MTBE	mg/L	11		12	11	9.6		1.6	0.37	<.005			<.02		
				TBA	mg/L	12		13	8.7	13		20	19	18	16	14	14		10
mw6microd12	#6	Anaerobic with methanol	Nitrogen	MTBE	mg/L	11		11		10		10		8.5	7.2	5	0.033		<.02
				TBA	mg/L	10		11		10		11		9.6	11	16	18		18
				MeOH	mg/L	1804		1701		1987		589		560	512	<1			
mw6microd9	#7	Abiotic control	Oxygen	MTBE	mg/L	10		12		10	11	10		9.9	9.6	10	10		11
				TBA	mg/L	8.6		8.6		9	9.6	9.1		8.4	8.5	8.9	8.9		9
mw6microd9	#8	Aerobic, native soil	Oxygen	MTBE	mg/L	10		12	9.1	8.7	7.5		0.01						
				TBA	mg/L	8.5		10	0.68	0.013	<.005								
mw6microd9	#9	Aerobic, soil with MC-100	Oxygen	MTBE	mg/L	11	<.005	<.005											
				TBA	mg/L	9.1	1	<.02											
mw6microd9	#10	Co-metabolism, propane	O2/Propane	MTBE	mg/L	11		12	11	10		10		8.5	0.83	<0.1	<.02		
				TBA	mg/L	8.8		10	8.3	9		8.8		8.2	14	14	16		15
mw6microd9	#11	Anaerobic transformation	Nitrogen	MTBE	mg/L	11		12		11		12		0.59	<.005				
				TBA	mg/L	8.6		8.2		9.5		10		17	17	16	1	0.74	0.28
mw6microd9	#12	Anaerobic with methanol	Nitrogen	MTBE	mg/L	10		11		11		13		10	10	12	2.7		<.02
				TBA	mg/L	8.4		8.8		9.9		10		8.4	8.7	11	15		17
				MeOH	mg/L	2986		2513		2180		4		<1					
mw6microd10	#13	Abiotic control	Oxygen	MTBE	mg/L	12		11	11	11	11	12		11	11	11	11		11
				TBA	mg/L	7.9		7.2	7.3	7.6	7.6	7.9		7	7	7.2	7.1		7.1
mw6microd10	#14	Aerobic, native soil	Oxygen	MTBE	mg/L	12		11	10	9.7	7.1	<.005							
				TBA	mg/L	9.1		5.6	0.026	0.01	<.005								
mw6microd10	#15	Aerobic, soil with MC-100	Oxygen	MTBE	mg/L	11	1.3	<.005	<.005										
				TBA	mg/L	8.7	3	0.067	<.02										
mw6microd10	#16	Co-metabolism, propane	O2/Propane	MTBE	mg/L	11		11	11	11		2.9	0.65	<.005					
				TBA	mg/L	9.1		7.6	7.8	8.1		16	15	15	13	11	12		11
mw6microd10	#17	Anaerobic transformation	Nitrogen	MTBE	mg/L	12		11		9.3		<.005							
				TBA	mg/L	10		9.3		11		18		17	16	18	15		3.9
mw6microd10	#18	Anaerobic with methanol	Nitrogen	MTBE	mg/L	13		13		12		2.2	0.26	<.005					
				TBA	mg/L	9.7		9.3		9.6		18	19	19	18	20	20		18
				MeOH	mg/L	1800		1704		1271		<1							

16969 Brookhurst
Fountain Valley, CA
Orange County, CA

notes:
aerobic criteria for dissolved oxygen > 1 mg/L
methanogenic criteria for dissolved methane > 0.5 mg/L

sample ID	index	test description	analyte	noted TBA accum-ulation	concentration change initial	final	percent	final dissolved oxygen (mg/L)	final dissolved methane (mg/L)	degrad. evident	lag time range (hrs)	zero-order rate est. λ (mg/L)/hr	first-order rate est. k (1/hr)	half life $t_{1/2}$ (hrs)	average conc. c_w (mg/L)	$k \cdot c_w$ (mg/L)/hr
mw8microd12	#1	Abiotic control	MTBE		11	10	-9%			no	-- abiotic (sterile) control --					
			TBA		9.1	8.4	-8%			no	-- abiotic (sterile) control --					
mw8microd12	#2	Aerobic, native soil	MTBE		11	0.005	-100%	8.8	0	yes	840 to 1176	0.024	0.0039	178	6.4	0.026
			TBA		9.8	0.005	-100%			yes	168 to 336	0.021	0.0450	15	4.9	0.218
mw8microd12	#3	Aerobic, soil with MC-100	MTBE		12	0.005	-100%			yes	-- active (amended) control --					
			TBA		8.9	0.02	-100%			yes	-- active (amended) control --					
mw8microd12	#4	Co-metabolism, propane	MTBE		11	0.02	-100%	3.8	0	yes	336 to 504	0.005	0.0046	144	2.8	0.013
			TBA	[yes]	14	12	-14%			no	>3000	--	--	--	10.8	--
mw8microd12	#5	Anaerobic transformation	MTBE		11	0.005	-100%	0.6	0	yes	336 to 504	0.009	0.0032	218	5.6	0.018
			TBA	[yes]	20	10	-50%			yes	504 to 1176	0.003	0.0003	2889	13.5	0.003
mw8microd12	#6	Anaerobic with methanol	MTBE		11	0.02	-100%	0.2	12.1	yes	1176 to 1680	0.005	0.0026	264	5.1	0.016
			TBA	[yes]	18	18	0%			no	>3864	--	--	--	12.8	--
			MeOH		1804	1	-100%			yes						
mw9microd9	#7	Abiotic control	MTBE		10	11	10%			no	-- abiotic (sterile) control --					
			TBA		8.6	9	5%			no	-- abiotic (sterile) control --					
mw9microd9	#8	Aerobic, native soil	MTBE		10	0.01	-100%	9.3	0.1	yes	168 to 336	0.010	0.0039	178	7.5	0.029
			TBA		8.5	0.005	-100%			yes	0 to 168	0.039	0.0240	29	3.6	0.086
mw9microd9	#9	Aerobic, soil with MC-100	MTBE		11	0.005	-100%			yes	-- active (amended) control --					
			TBA		9.1	0.02	-100%			yes	-- active (amended) control --					
mw9microd9	#10	Co-metabolism, propane	MTBE		11	0.02	-100%	4.7	0	yes	1176 to 1680	0.010	0.0025	281	6.4	0.016
			TBA	[yes]	16	15	-6%			no	>3864	--	--	--	11.3	--
mw9microd9	#11	Anaerobic transformation	MTBE		11	0.005	-100%	0.4	0	yes	1176 to 1680	0.025	0.0060	116	6.3	0.038
			TBA	[yes]	17	0.28	-98%			yes	2184 to 2664	0.010	0.0029	239	4.5	0.013
mw9microd9	#12	Anaerobic with methanol	MTBE		10	0.02	-100%	0.2	19.3	yes	2664 to 3216	0.019	0.0027	257	6.4	0.017
			TBA	[yes]	17	17	0%			no	>3864	--	--	--	10.8	--
			MeOH		2986	1	-100%			yes						
mw8microd10	#13	Abiotic control	MTBE		12	11	-8%			no	-- abiotic (sterile) control --					
			TBA		7.9	7.1	-10%			no	-- abiotic (sterile) control --					
mw8microd10	#14	Aerobic, native soil	MTBE		12	0.005	-100%	14	0.2	yes	0 to 168	0.006	0.0005	1263	10.0	0.005
			TBA		9.1	0.005	-100%			yes	0 to 168	0.022	0.0421	16	3.7	0.155
mw8microd10	#15	Aerobic, soil with MC-100	MTBE		11	0.005	-100%			yes	-- active (amended) control --					
			TBA		8.7	0.02	-100%			yes	-- active (amended) control --					
mw8microd10	#16	Co-metabolism, propane	MTBE		11	0.005	-100%	5.2	0	yes	504 to 1176	0.014	0.0054	127	4.9	0.026
			TBA	[yes]	15	11	-27%			yes	1680 to 2184	0.002	0.0002	4556	11.8	0.002
mw8microd10	#17	Anaerobic transformation	MTBE		12	0.005	-100%	1.3	0	yes	168 to 504	0.006	0.0005	1362	10.2	0.005
			TBA	[yes]	18	3.9	-78%			yes	2664 to 3480	0.018	0.0019	372	13.2	0.025
mw8microd10	#18	Anaerobic with methanol	MTBE		13	0.005	-100%	0.1	13.3	yes	504 to 1176	0.014	0.0077	90	4.8	0.037
			TBA	[yes]	20	18	-10%			no	>3864	--	--	--	14.5	--
			MeOH		1800	1	-100%			yes						

16969 Brookhurst
Fountain Valley, CA
Orange County, CA
(continued)

sample ID	index	test description	initial vapor headspace	analyte	conc units	measured concentration data start date: 02/04/2003													
						elapsed hours													
						0	96	168	336	504	840	1176	1344	1680	2184	2664	3216	3480	3864
						elapsed days													
						0	4	7	14	21	35	49	56	70	91	111	134	145	161
mw13microd16	#19a	Abiotic control		MTBE	mg/L	9		11	9.6	9.6	9.5	10		9.6					
				TBA	mg/L	8.1		8.7	8.3	9	9	9		8.2					
mw13microd16	#19b	Abiotic control		MTBE	mg/L	11		11	10	10	10	12		11					
				TBA	mg/L	8.7		8.6	8.3	9.1	9	9.4		8.6					
mw13microd16	#20a	Aerobic, native soil		MTBE	mg/L	11		11	9.3	3.1	< 005								
				TBA	mg/L	9.4		8.3	0.022	0.01	< 005								
mw13microd16	#20b	Aerobic, native soil		MTBE	mg/L	8.6		10	10	8.3	7	4.6	0.12	< 005					
				TBA	mg/L	7.7		8.2	0.017	< 005									
mw13microd16	#21a	Aerobic, soil with MC-100		MTBE	mg/L	11	1.5	<.005	<.005										
				TBA	mg/L	8.7	4.3	0.22	<.02										
mw13microd16	#21b	Aerobic, soil with MC-100		MTBE	mg/L	9.4	0.031	<.005	<.005										
				TBA	mg/L	8.7	2.7	0.14	<.02										

10969 Brookhurst
Fountain Valley, CA
Orange County, CA
(continued)

notes:
aerobic criteria for dissolved oxygen > 1 mg/L
methanogenic criteria for dissolved methane > 0.5 mg/L

sample ID	index	test description	analyte	noted TBA accum-ulation	concentration change: initial	concentration change: final	concentration change: percent	final dissolved: oxygen (mg/L)	final dissolved: methane (mg/L)	degrad. evident	lag time range (hrs)	zero-order rate est. λ (mg/L·hr)	first-order rate est. k (1/hr)	half life $t_{1/2}$ (hrs)	average conc. C_{av} (mg/L)	$k \cdot C_{av}$ (mg/L·hr)
mw13microd16	#19a	Abiotic control	MTBE		9	9.6	7%			no	– abiotic (sterile) control –					
			TBA		8.1	8.2	1%			no	– abiotic (sterile) control –					
mw13microd16	#19b	Abiotic control	MTBE		11	11	0%			no	– abiotic (sterile) control –					
			TBA		9.4	8.6	-9%			no	– abiotic (sterile) control –					
mw13microd16	#20a	Aerobic, native soil	MTBE		11	0.005	-100%			yes	168 to 336	0.026	0.0038	184	7.8	0.029
			TBA		9.4	0.005	-100%			yes	0 to 168	0.033	0.0166	42	4.4	0.074
mw13microd16	#20b	Aerobic, native soil	MTBE		8.8	0.005	-100%			yes	0 to 168	0.008	0.0040	174	7.0	0.028
			TBA		7.7	0.005	-100%			yes	0 to 168	0.025	0.0182	38	5.3	0.097
mw13microd16	#21a	Aerobic, soil with MC-100	MTBE		11	0.005	-100%			yes	– active (amended) control –					
			TBA		8.7	0.02	-100%			yes	– active (amended) control –					
mw13microd16	#21b	Aerobic, soil with MC-100	MTBE		9.4	0.005	-100%			yes	– active (amended) control –					
			TBA		8.7	0.02	-100%			yes	– active (amended) control –					

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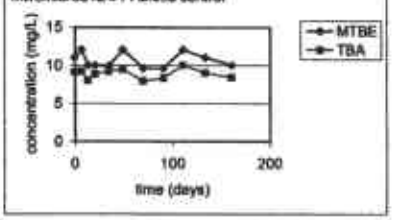
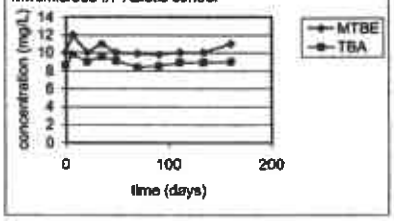
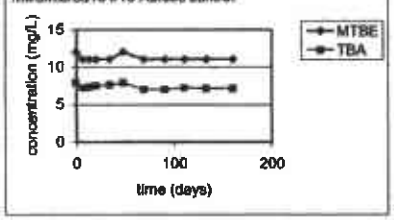
mw8microd12 #1 Abiotic control



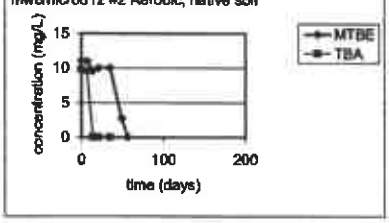
mw9microd9 #7 Abiotic control



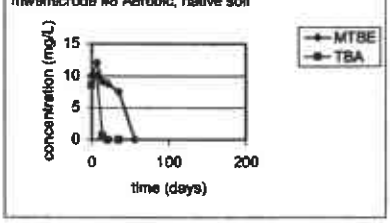
mw8microd10 #13 Abiotic control



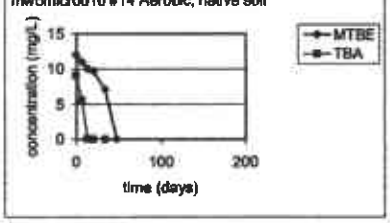
mw8microd12 #2 Aerobic, native soil



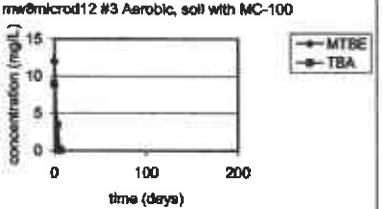
mw9microd9 #8 Aerobic, native soil



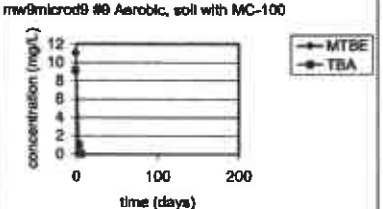
mw8microd10 #14 Aerobic, native soil



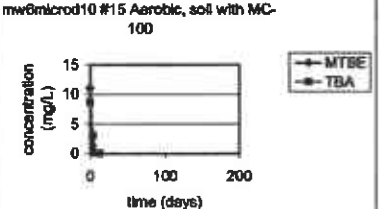
mw8microd12 #3 Aerobic, soil with MC-100



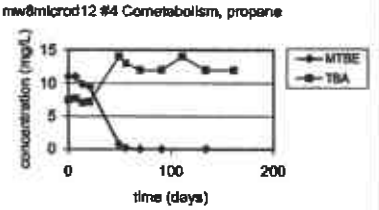
mw9microd9 #9 Aerobic, soil with MC-100



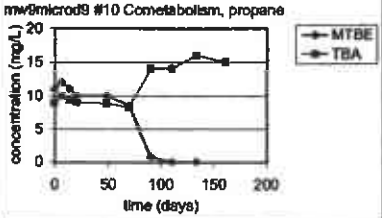
mw8microd10 #15 Aerobic, soil with MC-100



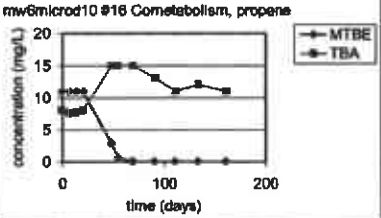
mw8microd12 #4 Cometabolism, propane



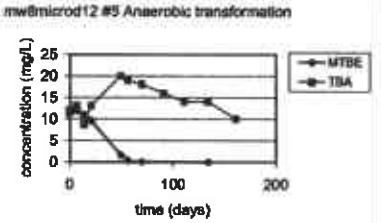
mw9microd9 #10 Cometabolism, propane



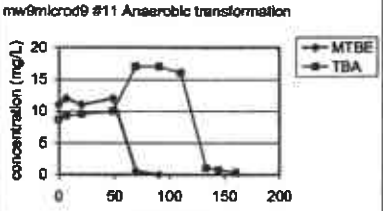
mw8microd10 #16 Cometabolism, propane



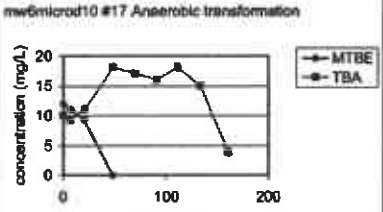
mw8microd12 #5 Anaerobic transformation



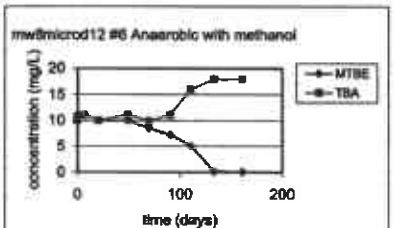
mw9microd9 #11 Anaerobic transformation



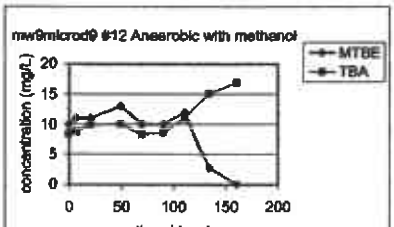
mw8microd10 #17 Anaerobic transformation



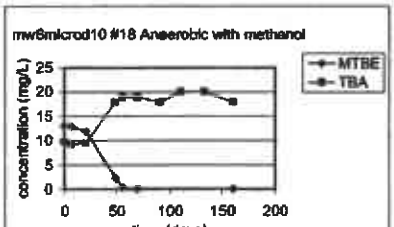
mw8microd12 #6 Anaerobic with methanol



mw9microd9 #12 Anaerobic with methanol



mw8microd10 #18 Anaerobic with methanol



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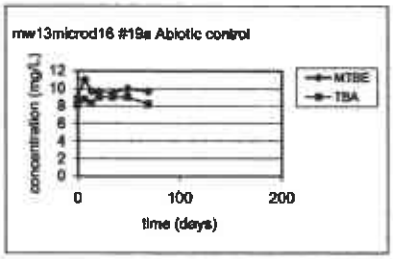
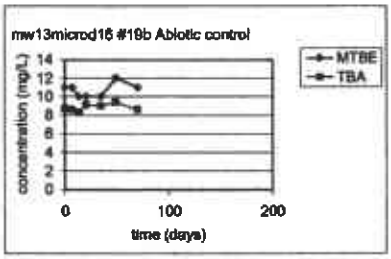
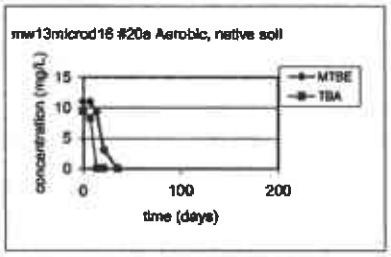
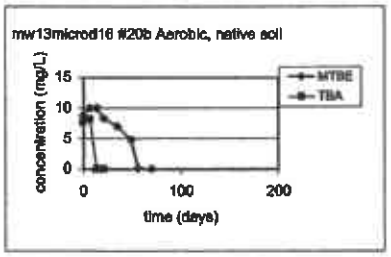
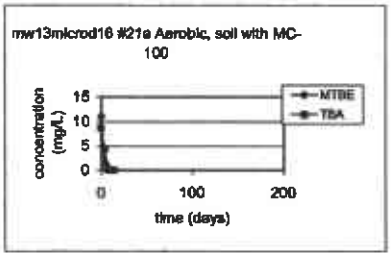
Orange County, CA
(continued)

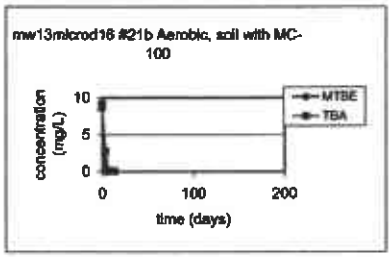












27101 Ortega Highway
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sample ID	index	test description	initial vapor headspace	analyte	conc units	measured concentration data start date: 04/22/2003 elapsed hours 0	72	168	336	840	1032	1344	1680	2088	2184	2736	3360	3696
						elapsed days 0	3	7	14	35	43	56	70	87	91	114	140	154
M-1d36 Ortega	#1	Abiotic control	Oxygen	MTBE	mg/L	11		11	10	11		10	10		11	10	9.8	11
				TBA	mg/L	8.9		11	11	11		10	11		11	8.8	10	11
M-1d36 Ortega	#2	Aerobic, native soil	Oxygen	MTBE	mg/L	11		10	11	11	12	9.7	8.9		9	7	6.1	6.6
				TBA	mg/L	11		11	11	6.6	5.3	2.1	<.005			0.02	< 02	
M-1d36 Ortega	#3	Aerobic, soil with MC-100	Oxygen	MTBE	mg/L	10	1.4	<.005										
				TBA	mg/L	10	5.9	< 02										
M-1d36 Ortega	#4	Co-metabolism, propane	O2/Propane	MTBE	mg/L	10		11	10	12		9.9	9.3		9.1	7.8	8.1	8
				TBA	mg/L	9.5		4.7	1.2	< 02		0.036	0.2		0.48	0.51	1	1.5
M-1d36 Ortega	#5	Anaerobic transformation	Nitrogen	MTBE	mg/L	10		11	11			3.8	< 005					
				TBA	mg/L	11		12	13			16	20		18	15	18	17
M-1d36 Ortega	#6	Anaerobic with methanol	Nitrogen	MTBE	mg/L	11		12	12			9.2	0.86		0.1	<.02		
				TBA	mg/L	11		13	14			13	21		20	19	22	21
				MeOH	mg/L	1783		2150	1874			<1						
M-2d36/42	#7	Abiotic control	Oxygen	MTBE	mg/L	10		10	10	10		8.8	10		8.6	8.6	11	10
				TBA	mg/L	11		12	13	12		11	12		9.3	9.3	12	12
M-2d36/42	#8	Aerobic, native soil	Oxygen	MTBE	mg/L	11		8.8	10	6	<.005							
				TBA	mg/L	11		11	13	13	8.1			<0.02				
M-2d36/42	#9	Aerobic, soil with MC-100	Oxygen	MTBE	mg/L	10	0.011	<.005										
				TBA	mg/L	11	0.009	< 02										
M-2d36/42	#10	Co-metabolism, propane	O2/Propane	MTBE	mg/L	10		10	9.7	9		7.5	10		11	9	9.8	9.1
				TBA	mg/L	11		12	13	11		9.6	12		12	11	13	12
M-2d36/42	#11	Anaerobic transformation	Nitrogen	MTBE	mg/L	10		10	11				9.9		10	9.5	10	9.5
				TBA	mg/L	11		12	13			9.7	<.005			<.02		
M-2d36/42	#12	Anaerobic with methanol	Nitrogen	MTBE	mg/L	11		11	11			8.6	9.1		8.7	3.7	<.02	
				TBA	mg/L	11		12	13			11	12		12	14	21	20
				MeOH	mg/L	1882		2166	2087			<1						
M-3d42	#13	Abiotic control	Oxygen	MTBE	mg/L	11		11	11	12		10	10		11	10	11	11
				TBA	mg/L	12		12	13	13		11	12		13	10	12	12
M-3d42	#14	Aerobic, native soil	Oxygen	MTBE	mg/L	12		11	11	12		10	10		13	9.5	8.2	7.3
				TBA	mg/L	11		12	13	12		5.6	0.17		<.1	<.02		
M-3d42	#15	Aerobic, soil with MC-100	Oxygen	MTBE	mg/L	12	0.55	<.005										
				TBA	mg/L	11	2.1	< 02										
M-3d42	#16	Co-metabolism, propane	O2/Propane	MTBE	mg/L	11		11	11	11		10	11		14	12	12	11
				TBA	mg/L	10		11	11	11		9.9	10		13	10	10	11
M-3d42	#17	Anaerobic transformation	Nitrogen	MTBE	mg/L	11		10	11			10	9.8		8.6	10	11	11
				TBA	mg/L	11		11	12			9	4.7		3.7	<.02		
M-3d42	#18	Anaerobic with methanol	Nitrogen	MTBE	mg/L	11		10	10			10	10		9.1	8.9	12	11
				TBA	mg/L	11		12	12			12	12		11	9.9	11	12
				MeOH	mg/L	2079		2341	2172				2423		2094	2006	2225	2048

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notes:
aerobic criteria for dissolved oxygen > 1 mg/L
methanogenic criteria for dissolved methane > 0.5 mg/L

sample ID	index	test description	analyte	noted TBA accum-ulation	concentration change: initial	final	percent	final dissolved: oxygen (mg/L)	methane (mg/L)	degrad. evident	lag time range (hrs)	zero-order rate est. λ (mg/L)/hr	first-order rate est. k (1/hr)	half life $t_{1/2}$ (hrs)	average conc. c_w (mg/L)	$k \cdot c_w$ (mg/L)/hr
M-1d36 Ortega	#1	Abiotic control	MTBE		11	11	0%			no	– abiotic (sterile) control –					
			TBA		9.9	11	11%			no	– abiotic (sterile) control –					
M-1d36 Ortega	#2	Aerobic, native soil	MTBE		11	6.5	-41%	15.6	0	yes	1032 to 1344	0.002	0.0002	2965	8.5	0.002
			TBA		11	0.02	-100%			yes	336 to 840	0.009	0.0020	343	6.3	0.013
M-1d36 Ortega	#3	Aerobic, soil with MC-100	MTBE		10	0.005	-100%			yes	– active (amended) control –					
			TBA		10	0.02	-100%			yes	– active (amended) control –					
M-1d36 Ortega	#4	Co-metabolism, propane	MTBE		10	6	-40%	2.8	0	yes	1344 to 1680	0.003	0.0003	2414	8.4	0.002
			TBA		9.5	1.5	-84%			yes	0 to 168	0.027	0.0062	113	3.0	0.018
M-1d36 Ortega	#5	Anaerobic transformation	MTBE		10	0.005	-100%	1.4	0	yes	336 to 1344	0.008	0.0011	657	7.4	0.008
			TBA	[yes]	20	17	-15%			no	336 to 1344	–	–	–	15.6	–
M-1d36 Ortega	#6	Anaerobic with methanol	MTBE		11	0.02	-100%	1.1	8.7	yes	1344 to 1680	0.011	0.0039	179	5.5	0.021
			TBA	[yes]	21	21	0%			no	>3696	–	–	–	17.1	–
			MeOH		1783	1	-100%			yes						
M-2d36/42	#7	Abiotic control	MTBE		10	10	0%			no	– abiotic (sterile) control –					
			TBA		11	12	9%			no	– abiotic (sterile) control –					
M-2d36/42	#8	Aerobic, native soil	MTBE		11	0.005	-100%	7.1	0	yes	168 to 336	0.009	0.0010	684	8.0	0.008
			TBA	[yes]	13	0.02	-100%			yes	336 to 840	0.009	0.0008	840	10.7	0.009
M-2d36/42	#9	Aerobic, soil with MC-100	MTBE		10	0.005	-100%			yes	– active (amended) control –					
			TBA		11	0.02	-100%			yes	– active (amended) control –					
M-2d36/42	#10	Co-metabolism, propane	MTBE		10	9.1	-9%	7.8	0	no	>3696	–	–	–	9.5	–
			TBA		11	12	9%			no	>3696	–	–	–	11.7	–
M-2d36/42	#11	Anaerobic transformation	MTBE		10	9.5	-5%	2.5	0	no	>3696	–	–	–	10.0	–
			TBA	[yes]	13	0.02	-100%			yes	1344 to 1680	0.004	0.0004	1974	11.4	0.004
M-2d36/42	#12	Anaerobic with methanol	MTBE		11	0.02	-100%	1.6	3.6	yes	2184 to 2736	0.010	0.0015	448	7.4	0.011
			TBA	[yes]	21	20	-5%			no	>3696	–	–	–	14.0	–
			MeOH		1882	1	-100%			yes						
M-3d42	#13	Abiotic control	MTBE		11	11	0%			no	– abiotic (sterile) control –					
			TBA		12	12	0%			no	– abiotic (sterile) control –					
M-3d42	#14	Aerobic, native soil	MTBE		12	7.3	-39%	24.1	0	yes	2736 to 3360	0.004	0.0004	1861	10.2	0.004
			TBA		11	0.02	-100%			yes	336 to 840	0.011	0.0041	169	7.7	0.032
M-3d42	#15	Aerobic, soil with MC-100	MTBE		12	0.005	-100%			yes	– active (amended) control –					
			TBA		11	0.02	-100%			yes	– active (amended) control –					
M-3d42	#16	Co-metabolism, propane	MTBE		11	11	0%	13.7	0	no	>3696	–	–	–	11.4	–
			TBA		10	11	10%			no	>3696	–	–	–	10.7	–
M-3d42	#17	Anaerobic transformation	MTBE		11	11	0%	1.1	0	no	>3696	–	–	–	11.0	–
			TBA		11	0.02	-100%			yes	336 to 1344	0.003	0.0006	1227	8.6	0.005
M-3d42	#18	Anaerobic with methanol	MTBE		11	11	0%	2.3	0	no	>3696	–	–	–	11.0	–
			TBA		11	12	9%			no	>3696	–	–	–	11.4	–
			MeOH		2079	2048	-1%			no						

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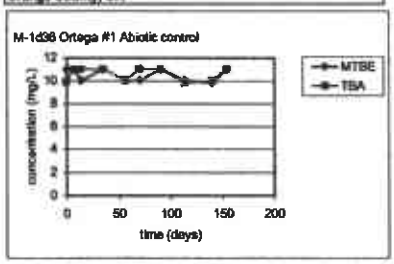
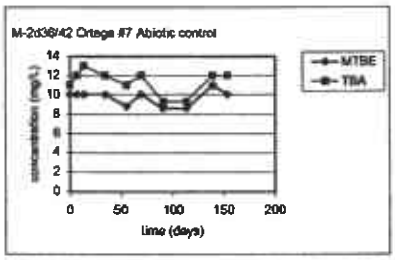
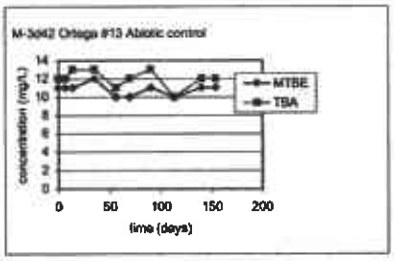
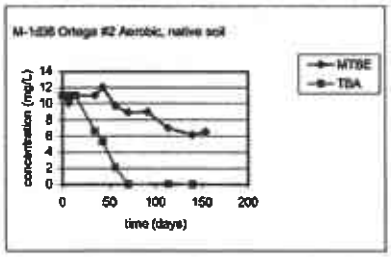
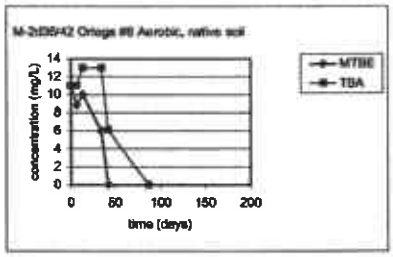
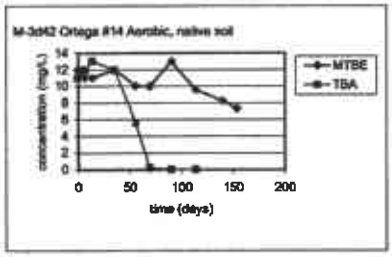


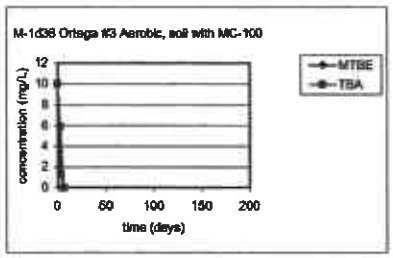


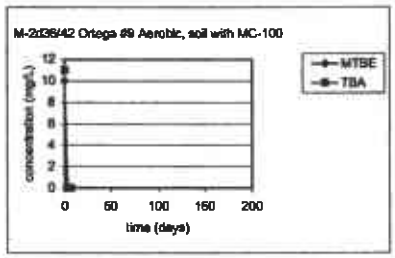


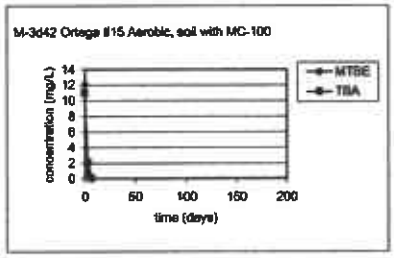


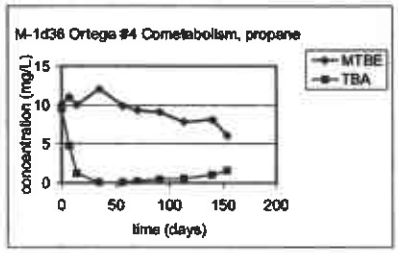


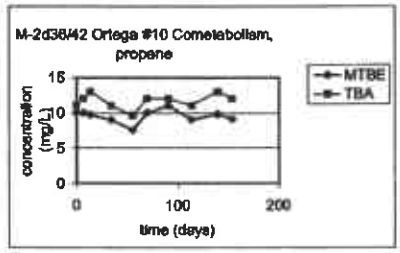


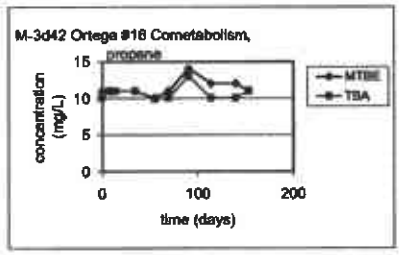


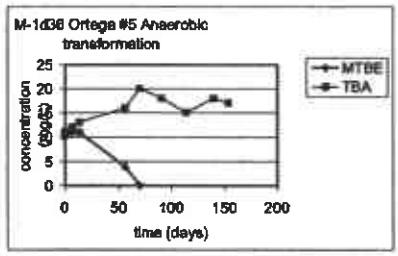


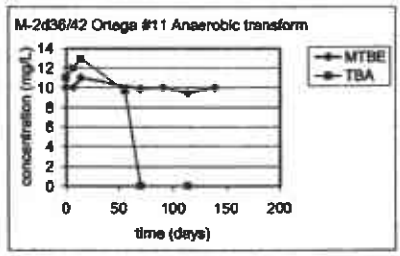


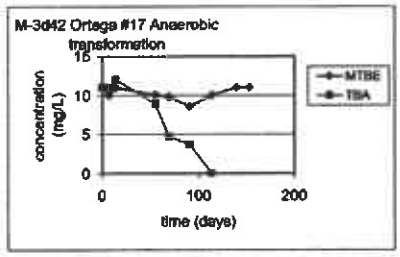


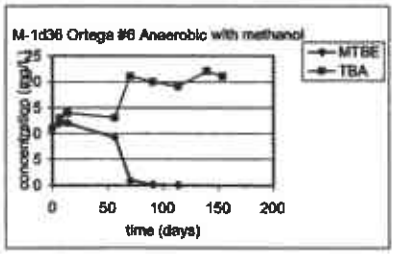


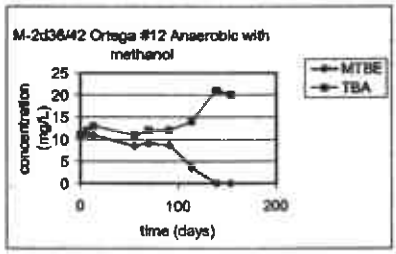


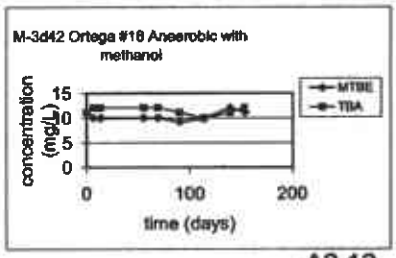












Shell Global Solutions

Study of Tert-Butyl Alcohol (TBA) at Selected Underground Storage Tank Remediation Project Sites in Orange County, California

January 2004
Presentation of study results to OCHCA

George DeVaull, Dan Walsh, Karen Lyons, Marvin Katz

Timeline / Background

- OCHCA - May-Sept 2002:
  - Tell us the source of the TBA
  - Shell received letters on 6 sites with TBA in groundwater at >30ppm
- WTC Work Plan to OCHCA
  - plan approval - Aug 2002 - phased approach
- Study updates
  - Nov 2002, May 2003, Report completed 14 Nov 2003
    (~5 to 7 months of incubation for some microcosms)
- Other companies receiving letters:
  - Exxon-Mobil
  - BP (Arco)
  - ConocoPhillips (Tosco)

Summary of Orange County TBA Study

Requested Study to Evaluate:

- Is TBA due to presence in gasoline product?
- Is TBA the result of MTBE biodegradation?
- Is TBA the result of abiotic transformation?
- Is TBA an artifact of sample handling or analytical methods?

Shell work plan parallels the study request:

- screen available sites, select a subset for microcosm analyses
- evaluate gasoline composition as possible source of TBA in groundwater via dissolution
- evaluate the potential abiotic transformation pathway
- evaluate sample preservation and lab analytical methods as possible contributing source of elevated TBA

Site Conditions at Study Initiation

Shell - Six Sites with OCHCA letters

- TBA max range: (2.6 to 390 ppm)
  - At high end of TBA distribution in Los Angeles *(Shih, et al., 2004, ES&T, 38 (1), 42 -48).*
- MTBE max range: (0.22 to 250 ppm)
  - Generally lower than TBA
- BTEX max range: (non-detect to 36 ppm)

Shell Sites Selected for Detail Study

- Chose 3 sites for detailed testing:
  - *30011 Crown Valley, Laguna Niguel*
  - *16969 Brookhurst, Fountain Valley*
  - *27101 Ortega Hwy, San Juan Capistrano*
- *For these three sites:*
  - TBA generally higher than MTBE; BTEX is low or nil
  - MTBE & TBA well concentrations stable / decreasing / selectively increasing
  - Depth to groundwater: 9, 24, 35 ft (site average) - *shallow water table*
  - Water table gradient: 0.01 to 0.02 ft/ft, - *relatively flat gradient*
  - Methane: 0.35, 0.67, 2.6 mg/L (site max), *methanogenic to weakly methanogenic*
  - Sulfate: 130 to 2700 (upgradient), *depletion measured in some wells*
  - Carbon isotope ratio: δ^{13}C-MTBE: -0.7 to 57.8 (max), source: ~ -28
    - *[site data: John Wilson, USEPA]*

TBA directly from gasoline dissolution

Interpretation of data and calculations:

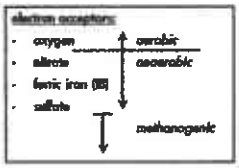
- Measured TBA concentration levels *could* originate from MTBE-gasoline dissolution
  - Skewed distribution of trace TBA concentration levels in MTBE-gasoline
  - 140 mg-TBA/kg-gasoline (median); 890 mg/kg (P=99%).
  - Alcohol partitions preferentially to the water phase
- BUT, Can't easily explain concentrations of TBA >> MTBE (and low/no BTEX) in groundwater by physical mechanisms alone:
  - oil/water/air partitioning and source depletion / mass balance
  - TBA should deplete faster from water-washed gasoline than would MTBE
  - difficult to see how high TBA, low MTBE, and low BTEX could occur based on dissolution, partition, mixing, and dilution alone....TBA generation from MTBE degradation is a very likely explanation.

Shell Orange County TBA Study
evaluation of potential biodegradation mechanisms

- Sampling Plan
  - For each site, soil cores collected at three locations
    - Two soil samples in/along the plume
    - one background
  - Microcosm tests
    - Identify the presence/absence of MTBE and TBA degraders
    - Aerobic, anaerobic, potential cometabolic effects
    - Should provide indication of possible pathway of TBA formation from MBE
    - Yield yes/no for degradation and a rate estimate
    - Total of 60 microcosms including controls, plus duplicates

Reported MTBE, TBA Biodegradation

- Literature Reported MTBE degradation:
  - aerobic and anaerobic conditions
  - direct metabolism and as a co-metabolite
  - Some complete degradation of MTBE; some with intermediate metabolites, such as TBA.
- Literature Reported TBA degradation:
  - aerobic and anaerobic conditions



- Both MTBE and TBA are indicated in literature as "recalcitrant" to biological degradation, slow biomass growth
- Microcosms used in this study are one (of several) lines of evidence for natural attenuation

Microcosm Test Series

Aerobic: (70 day incubation)
- soil, water, oxygen-sparged,

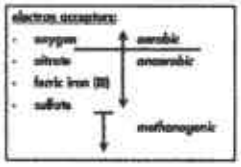
Anaerobic: (150 day incubation)
- soil, water, nitrogen-sparged,

Anaerobic + MeOH: (150 day)
- methanol added to deplete electron acceptors

Co-metabolism:
- aerobic, propane added, 70 day

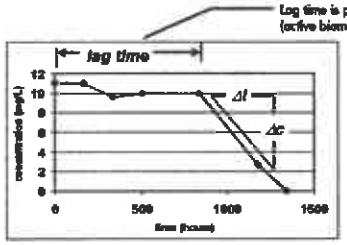
Negative control: aerobic, sodium azide

Positive control: aerobic, culture (MC-100) spiked

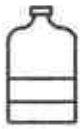


- All spiked to approx. 10 ppm for both TBA and MTBE in same bottles
- Septum syringe withdrawal of water; Purge and trap GC/MS analysis

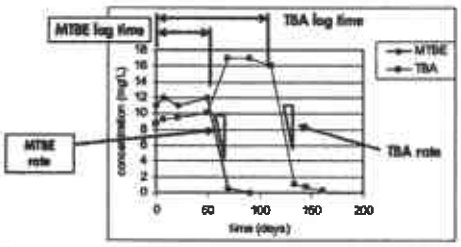
Soil microcosm data interpretation: general



- No easy direct measurement of active biomass in soil
- Therefore we measure
  - Substrate - MTBE and TBA, or
  - Electron Acceptors, or
  - Products

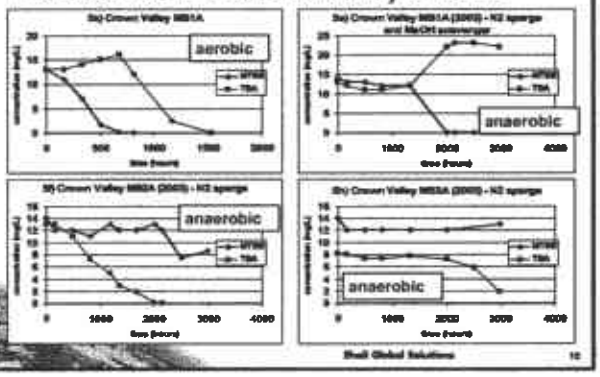


Microcosm Data Analysis: Specific Example



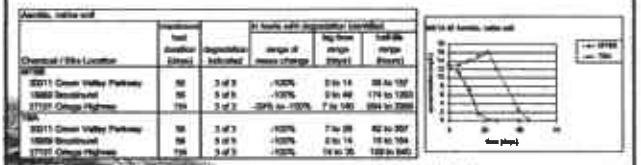
16969 Breakhurst, Fountain Valley, CA
mw9microd9 #11, Anaerobic transformation

microcosm data - a selected variety of results



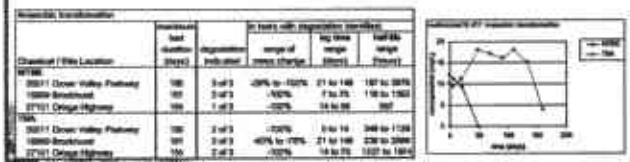
aerobic biodegradation, native soils

- Sparged with oxygen prior to sealing
- *All sites, all samples, showed aerobic degradation of both MTBE and TBA!*
- In 4 of 9 samples, TBA initially increased as MTBE decreased, with TBA tailing afterward.
- Compared to other, similar soil microcosms showing positive results:
  - Lag times are relatively short in these microcosms
  - Measured first-order rates are in a similar range



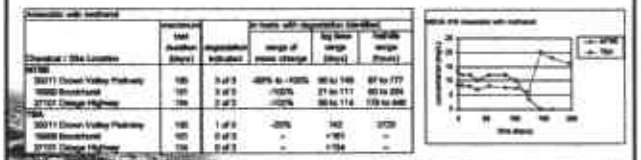
anaerobic biodegradation, native soils

- nitrogen sparge of microcosm (30 min) prior to sealing depletes oxygen
- Remaining electron acceptors (primarily sulfate) still available
- *All sites showed anaerobic degradation of both MTBE and TBA*
  - *degradation indicated in 7 of 9 microcosms for MTBE, and a different 7 of 9 for TBA*



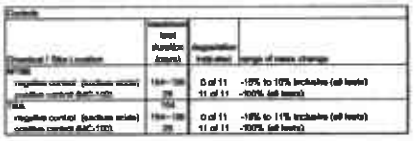
aerobic biodegradation, methanol added

- Methanol (MeOH) addition intended to deplete any electron acceptors
  - **Methanol depletion in 8 of 9 samples; Methane detected in same 8 of 9 at test end**
- All sites showed degradation of MTBE in methanogenic conditions
  - Degradation in 8 of 9 microcosms
- TBA degradation indicated in only 1 of 9 microcosms
  - **at a long lag time (>150 days)**
  - **more anaerobic TBA degradation may occur given sufficient time.**



controls

- indicate microcosm test variability and viability (±10% ~15%)
- A change greater than this level is interpreted as significant in active tests
- There is no apparent abiotic generation of TBA from MTBE in controls



cometabolism

- inconclusive, as MTBE and TBA degradation was seen in both the absence and presence of propane substrate

Summary / Interpretation of Orange County TBA Study (1)

- TBA *at these sites* is predominantly:
  - **an intermediate biological degradation product from MTBE under low-oxygen/anaerobic conditions (typical of plume core, near sources)**
  - **More significant under increasingly reduced conditions**
- Some TBA:
  - **may be due to dissolution from gasoline product, but observed levels are not fully explained via this mechanism alone (especially considering low/ND values for MTBE and BTEX in some samples)**
- Abiotic generation of TBA is unlikely (not observed)
  - **TBA generation as an analytical artifact is insignificant at these sites.**

Summary / Interpretation of Orange County TBA Study (2)

- **Positive note: MTBE & TBA biodegradation found at each site in study!**
- **In both aerobic & anaerobic conditions; MTBE in methanogenic conditions**
- **What does this mean for remediation options?**

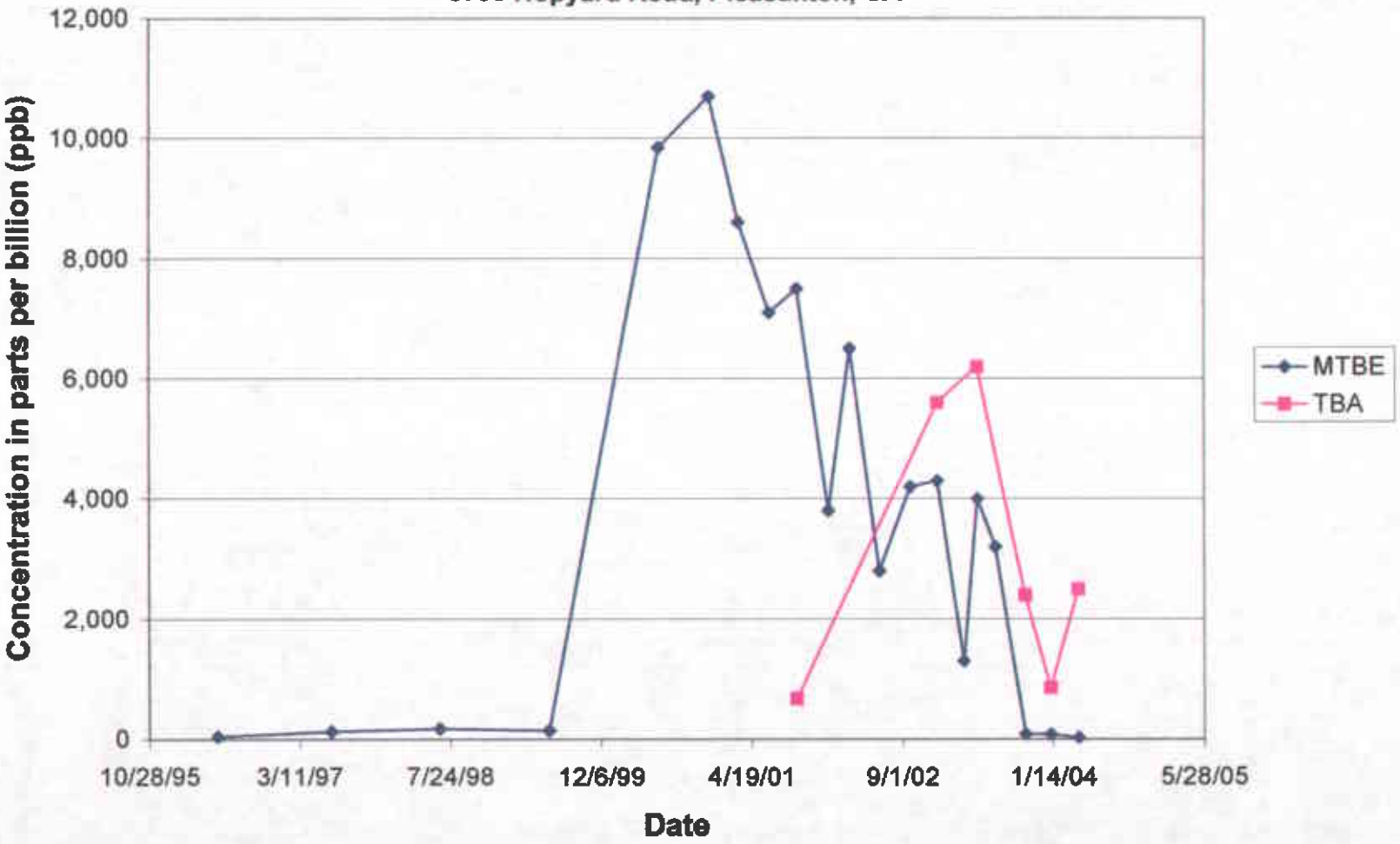
Bio-attenuation more significant with:	⇔	*Less significant with:*
• Low MTBE & TBA loadings		• Higher MTBE & TBA concentrations
• Adapted biomass present		• Higher seepage velocities
• Lower seepage velocities		• Higher threat to close receptor

- **Electron acceptor availability (oxygen, sulphate), if limiting, could be addressed with amendment**
- **Site remedial viability w.r.t. biodegradation improves over time:**
  - **Biomass growth**
  - **Dissolution Source depletion**

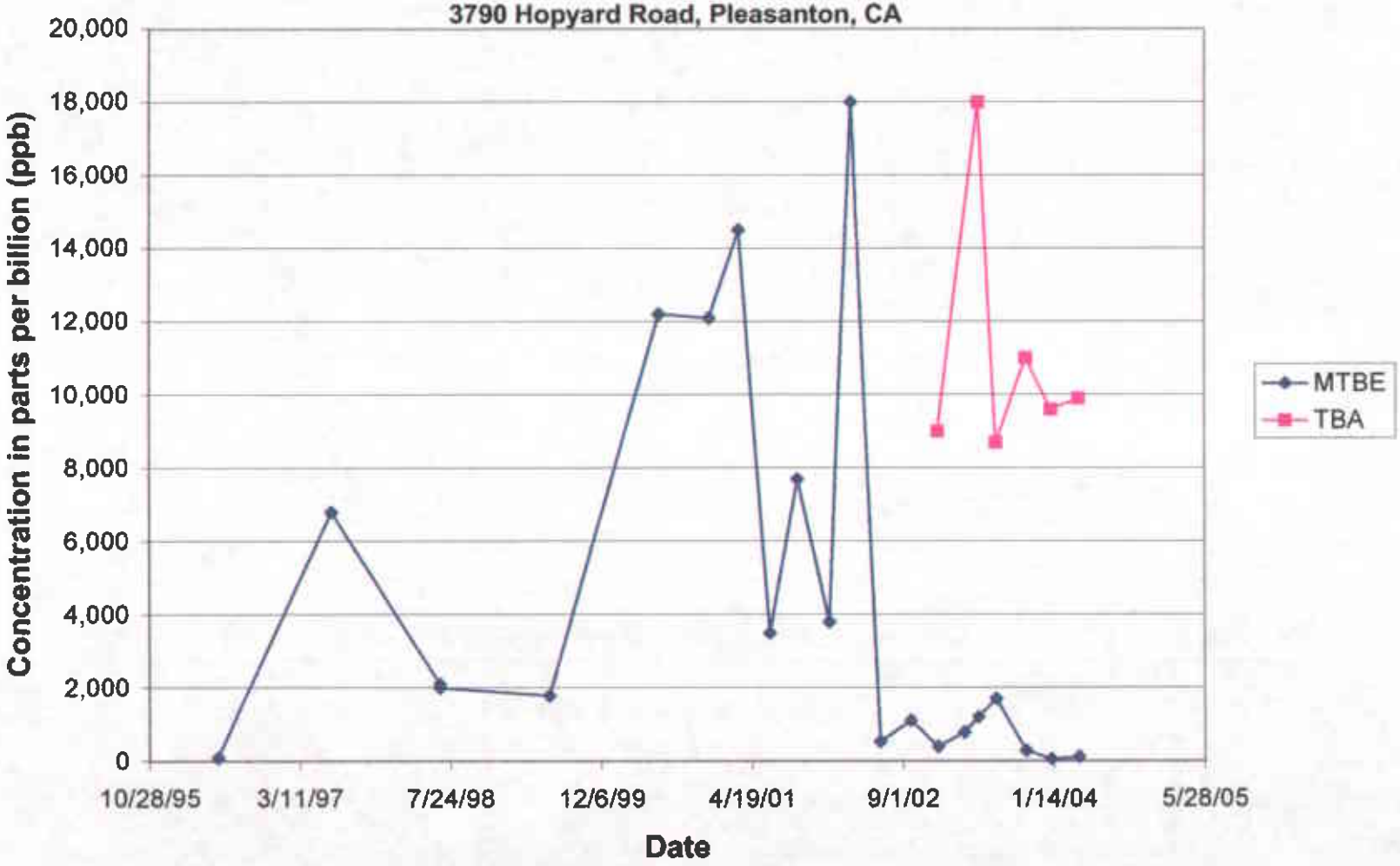
ATTACHMENT B

MTBE and TBA Concentration versus Time Graphs

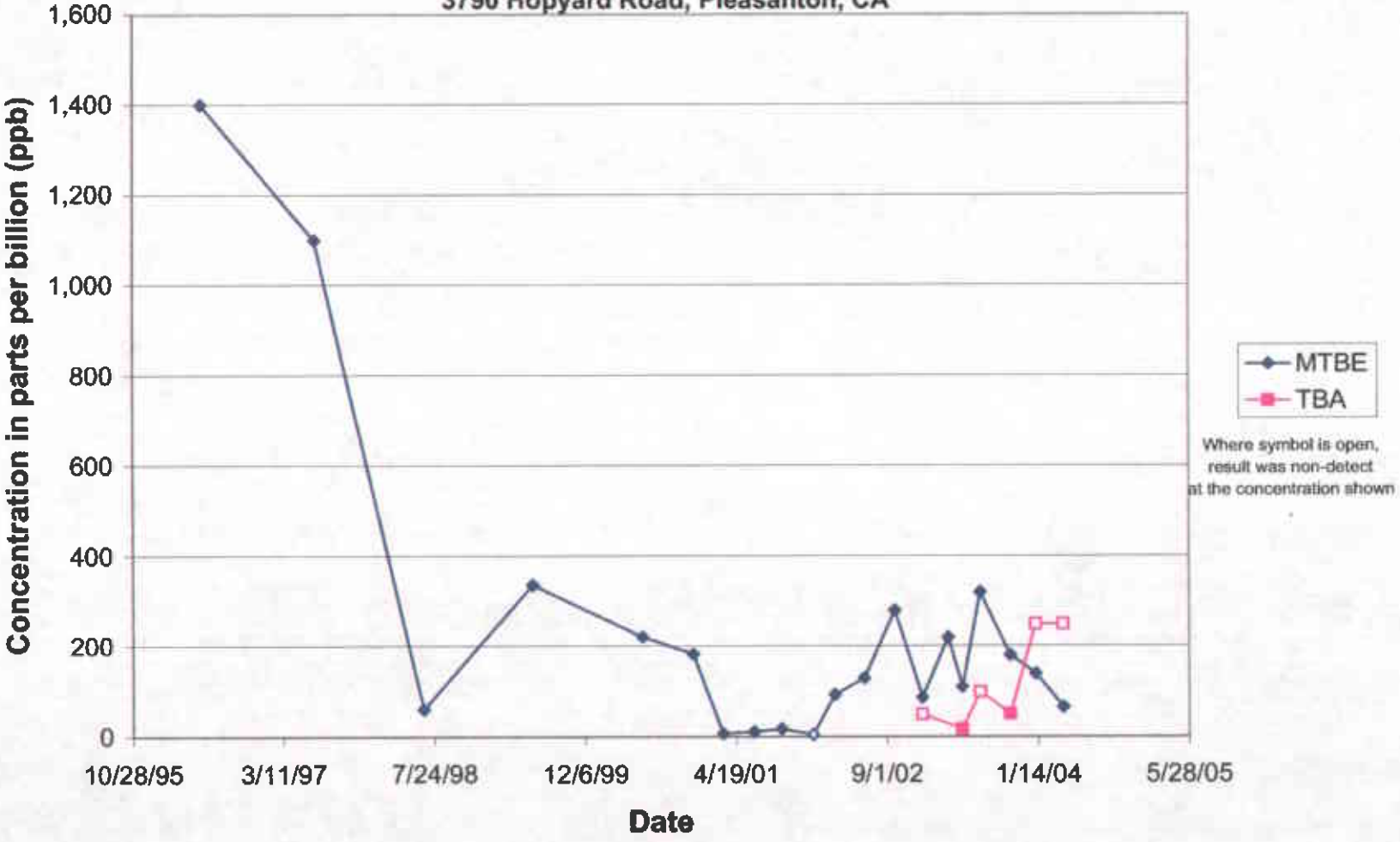
Graph 1 - MTBE & TBA Concentration vs. Time - Well S-2
Shell-branded Service Station
3790 Hopyard Road, Pleasanton, CA



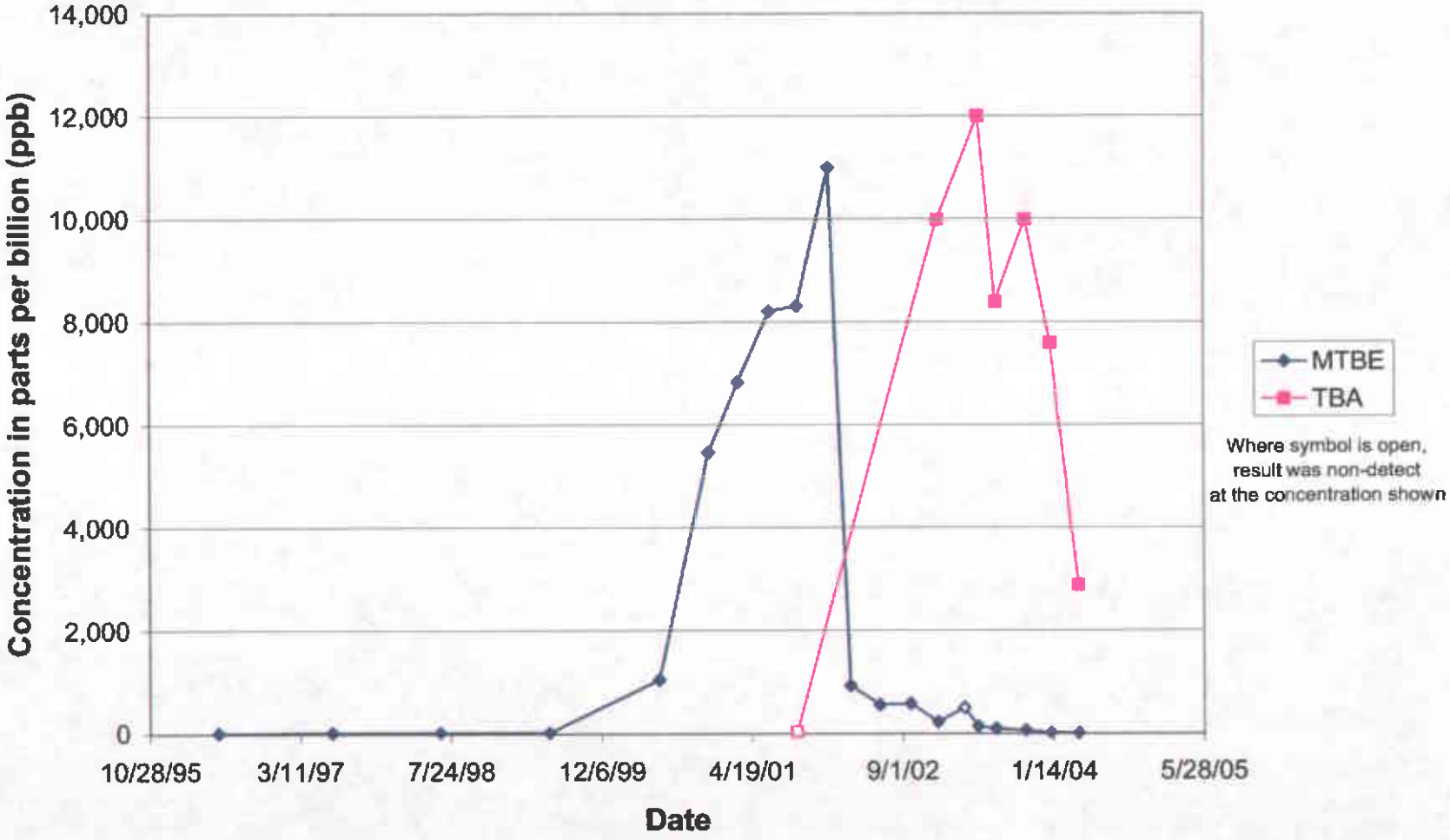
Graph 2 - MTBE & TBA Concentration vs. Time - Well S-4
Shell-branded Service Station
3790 Hopyard Road, Pleasanton, CA



Graph 3 - MTBE & TBA Concentration vs. Time - Well S-5
Shell-branded Service Station
3790 Hopyard Road, Pleasanton, CA



Graph 4 - MTBE & TBA Concentration vs. Time - Well S-6
Shell-branded Service Station
3790 Hopyard Road, Pleasanton, CA



ATTACHMENT C

MTBE and TBA Isoconcentration Contour Maps - Second Quarter 2004

21-Jun-04

MTBE Isoconcentration Contour Map

April 7, 2004

EXPLANATION

- Proposed CPT boring
- Shell groundwater monitoring well
- Groundwater recovery well
- Tank backfill well
- Creek gauging location
- MTBE isoconcentration contour - dashed where inferred.
- *(150)* MTBE concentration in parts per billion (ppb)

Note: Map features not a product of survey

LAS POSITAS BOULEVARD

Municipal Well
Located 1,500 ft. SE
of Shell site

Las Positas
Office Plaza

Groundwater Flow Direction
(2Q97 to 2Q03)

planter
walkway
planter

S-10
(<0.50)

S-11
(1.4)

S-12
(0.76)

invert elevation = 315'

fence
bike path

Storm Drain
culvert flows
to creek

ARROYO
MOCHO
CANAL

fence
creek bridge

S-6
(15)

250

S-7
(380)

HOPYARD ROAD

creek bridge

C-1

planter
former
USTs

T-1
T-2
(5.6)
T-3
T-4
(6.1)

USTs

S-4
(110)

SR-2
(280)

250

dispensers

fire hydrant

PG&E vault

Shell-branded
Service Station
3790 Hopyard

S-5
(66)

SR-3
(4.4)

SR-1

CPT-3

S-2
(28)

former dispensers

7-Eleven
3760 Hopyard

S-9
(250)

CPT-4

bike path

fence

S-3
(<0.50)

planter

W/O
UST

former
W/O UST

Exploratory
excavation
~6' deep

Exploratory
excavation
~6.5' deep

S-8
(33)

25

2.5

DMV
6280 Las Positas

Business Center
3730 Hopyard

ARROYO
MOCHO
CANAL

fence

Scale (ft)
0 30 60 120

FIGURE
5

Shell-branded Service Station
3790 Hopyard Road
Pleasanton, California

CAMBRIA

0497

21-Jun-04

TBA Isoconcentration Contour Map

April 7, 2004

EXPLANATION

- Proposed CPT boring
- Shell groundwater monitoring well
- Groundwater recovery well
- Tank backfill well
- Creek gauging location
- TBA isoconcentration contour - dashed where inferred.
- *(150)* TBA concentration in parts per billion (ppb)

Note: Map features not a product of survey

Municipal Well
Located 1,500 ft. SE
of Shell site

Groundwater Flow Direction
(2Q97 to 2Q03)

LAS POSITAS BOULEVARD

Las Positas
Office Plaza

ARROYO MOCHO CANAL

HOPYARD ROAD

creek bridge

fence

bike path

planter

walkway

Shell-branded
Service Station
3790 Hopyard

7-Eleven
3760 Hopyard

Business Center
3730 Hopyard

DMV
6280 Las Positas

former USTs

former dispensers

former W/O UST

dispensers

Storm Drain culvert flows to creek

Exploratory excavation ~6' deep

Exploratory excavation ~6.5' deep

S-1 (<5.0)
S-2 (2,500)
S-3 (<5.0)
S-4 (9,900)
S-5 (<250)
S-6 (2,900)
S-7 (130)
S-8 (<5.0)
S-9 (<10)
S-10 (<5.0)
S-11 (<5.0)
S-12 (<5.0)
SR-1
SR-2 (10,000)
SR-3 (370)
T-1
T-2 (11)
T-3
T-4 (<5.0)
CPT-3
CPT-4
C-1

5
50
500
5,000

Scale (ft)
0 30 60 120

FIGURE
6

Shell-branded Service Station
3790 Hopyard Road
Pleasanton, California

CAMBRIA

0497

ATTACHMENT D

Updated Site Conceptual Model

SITE CONCEPTUAL MODEL
Revised June 2004
Cambria Environmental Technology, Inc.

Site Address:	3790 Hopyard Road	Incident Number:	98995842
City:	Pleasanton, CA	Regulator:	Alameda County Health Care Services Agency

Item	Evaluation Criteria	Comments/Discussion
1	Hydrocarbon Source	
1.1	Identify/Describe Release Source and Volume (if known)	Release source and volume is unknown. Contamination has been detected in the vicinity of the former underground storage tanks (USTs), and near the former and current dispensers and piping.
1.2	Discuss Steps Taken to Stop Release	The previous USTs at the site were removed and replaced in 1988. In July 2002, Shell voluntarily initiated upgrades at the service station. Paradiso Mechanical of San Leandro upgraded the fuel dispensers and the product, vapor and vent lines. In addition, Paradiso added dispenser pans under the new dispensers and replaced the UST fuel fill port sumps and all associated piping in the tank pit areas above the USTs. MTBE-containing gasoline is no longer dispensed at the station, effective 1/1/03.
2	Site Characterization	
2.1	Current Site Use/Status	The site is an active Shell-branded service station located at the southwest corner of the intersection of Hopyard Road and Las Positas Boulevard in Pleasanton, California. The service station layout includes a station building, two dispenser islands on the eastern side of the property, a waste oil UST and three gasoline USTs. The surrounding property use is primarily commercial and residential property.
2.2	Soil Definition Status	Prior to 2002, no soil samples collected from the site were analyzed for MTBE. Soil contamination is defined in the upgradient direction by non-detection of TPHg and BTEX in soil samples from well S-3. Soil contamination is defined in the cross- and downgradient directions by non-detection of TPHg and BTEX in wells S-7, S-8, S-9 and S-10, and by non-detection of TPHg, BTEX and MTBE in wells S-11 and S-12. TPHg and benzene was detected at concentrations of up to 80 ppm and 4.8 ppm, respectively, in soil samples collected from the former UST pit following tank removal and over-excavation. Up to 260 ppm TPHg, 0.079 ppm benzene and no MTBE were detected beneath the dispensers and piping during 2002 upgrades at the site. Vertical extent is defined down to the groundwater table.
2.3	Separate-Phase Hydrocarbon Definition Status	No SPH has been detected at the site.
2.4	Groundwater Definition Status (BTEX)	Groundwater monitoring has been conducted at the site since 1987. The downgradient extent of BTEX is defined by non-detect results in monitoring wells S-6, S-7, S-8, S-9, S-10, S-11 and S-12. The upgradient (northeastern) extent is delineated by well S-3. The vertical extent of BTEX in groundwater has not been defined other than in borings CPT-1 and CPT-2. Depth discrete groundwater samples collected at depths ranging from 26 fbg to 88 fbg during CPT-1 and CPT-2 boring installation did not contain any TPHg, benzene or MTBE (analyzed by EPA Method 8260).
2.5	BTEX Plume Stability and Concentration Trends	Currently, BTEX concentrations exhibit a decreasing trend in site wells, with the exception of a recent spike in well S-5 observed in the January 2004 sample event that significantly declined during the April 2004 event.

Item	Evaluation Criteria	Comments/Discussion
2.6	Groundwater Definition Status (MTBE)	The southeastern (downgradient extent of MTBE in groundwater is defined by non-detection (at 5.0 ppb) in monitoring wells S-10, S-11 and S-12. The downgradient extent of MTBE in groundwater has not been defined south-southeast or southeast of monitoring wells S-8 and S-9. The vertical extent of MTBE in groundwater has not been defined other than in borings CPT-1 and CPT-2. Depth discrete groundwater samples collected at depths ranging from 26 fbg to 88 fbg during CPT-1 and CPT-2 boring installation did not contain any TPHg, benzene or MTBE (analyzed by EPA Method 8260).
2.7	MTBE Plume Stability and Concentration Trends	MTBE concentrations in all onsite and some offsite wells currently show a decreasing trend since 2001. MTBE concentrations in the tank backfill have decreased from 100,000 ppb to less than 10 ppb between June 2002 and April 2004. MTBE concentrations in downgradient well S-9 are fairly stable and in S-7 are increasing. Wells S-7 and S-9 are located beyond the remediation systems radius of influence.
2.8	Groundwater Definition Status (TBA)	TBA occurance in site wells has followed a pattern similar to the MTBE concentrations, but on a delayed time frame. It is thought that the increase in TBA observed in site wells is a result of biological degradation of the MTBE in the vicinity of the well. Thus, as MTBE concentrations decline and the microbial population more efficiently degrades MTBE, TBA concentrations increase as a by-product. Once the MTBE concentrations are depleted at that location, the microbial population appears to rapidly degrade the residual TBA. Graphs of MTBE and TBA concentrations versus time in source area (S-2 and S-4) and near down-gradient (S-5 and S-6) wells are included as Attachment B of the June 30, 2004 Agency Response document prepared by Cambria. Delineation of the TBA plume to concentrations less than 5 ppb is achieved by wells S-10, S-11, S-12, S-9, S-8 and S-3. The vertical extent of TBA has not been assessed.
2.9	TBA Plume Stability and Concentration Trends	TBA concentrations appear to be declining in source area and near-downgradient wells, with a slight increase observed in downgradient well S-7, which has increased from less than a dection limit of 5 ppb to 130 ppb in the past three quarters.
2.10	Groundwater Flow Direction, Depth Trends and Gradient Trends	Groundwater flow at the site has ranged from southeast to south-southeast since monitoring began in 1987. Depth to water in site monitoring wells has ranged from 11.59 to 19.59 feet below grade (fbg) since 1991; although it was initially encountered in the well borings at a depth of approximately 25 fbg.
2.11	Stratigraphy and Hydrogeology	The site subsurface consists of a relatively low permeability zone underlain by a relatively higher permeability zone, underlain by another low permeability zone. The uppermost low permeability zone consists of interbedded layers of sandy clay, clayey sand, silty clay and clay from the surface to approximately 43 to 53 fbg. The first groundwater encountered at this site and screened by the monitoring wells occurs in a relatively thin sandy lens within a relatively low permeability zone at a depth of approximately 24 fbg. The deeper, higher permeability zone consists of silt and sand interbeds to approximately 75 fbg. The lowermost low permeability zone consists of silts and clays to approximately the total explored depth of 120 fbg. A sandy layer was encountered at approximately 117 fbg in one boring installed downgradient of the site.

Item	Evaluation Criteria	Comments/Discussion
2.12	Preferential Pathways Analysis	Identified utilities downgradient of the site include water, electrical and gas lines, as well as storm drain lines. The majority of the lines in the downgradient direction from the site run approximately north to south, which approximates the natural groundwater flow direction at the site. The invert elevations of the storm drains in the site vicinity range from 315.81 to 315.29 feet above mean sea level (msl). The deepest identified point of the water lines in the site vicinity is 9 fbg, and the gas line was identified to be approximately 5 fbg. While exact depths to the electrical lines could not be determined, they are typically buried between 3 and 8 fbg. Measured depths-to-groundwater at the site have ranged from approximately 11.52 fbg to 19.59 fbg, which corresponds to a range of elevations of 318.14 to 308.65 feet above msl. Based on the information that the utilities in the site vicinity parallel natural groundwater flow and are more shallow than historical groundwater table, the identified utilities are not able to serve as preferential pathways for chemical migration in groundwater. The water-bearing sand lens which is monitored by the site wells appears to have varying degrees of clay content from location to location, which could allow for preferential migration of contaminants in directions that vary from the predominant gorundwater flow direction.
2.13	Other Pertinent Issues	
3	Remediation Status	
3.1	Remedial Actions Taken	Following tank removal in 1988, the former UST pit was over-excavated to approximately 20 fbg. The fuel-related equipment at the service station was upgraded in July 2002, including the addition of secondary containment to the dispensers, and the replacement of fuel fillport sumps and all associated piping above the USTs. Weekly groundwater extraction (GWE) from monitoring wells S-1 and S-4 and tank backfill well T-2 was conducted during May 2001 and August 2001. Twice-monthly GWE from either wells S-4, T-2 or T-4 was conducted at the site between April 2002 and March 2003. A fixed GWE system was installed and has been operating fairly continuously since July 2003. Since wells S-7 and S-9 lie outside of the capture zone of the GWE system, Cambria is going to attempt periodic GWe using vacuum trucks from wells S-7 and S-9 in an effort to capture some of the residual mass downgradient of the capture zone.
3.2	Area Remediated	Remediation at the site has concentrated on the current and former tank pit complexes and in the downgradient direction from both the current and former UST pits. The radius of influence of the current GWE system is approximately 150 feet in the downgradient direction.

Item	Evaluation Criteria	Comments/Discussion
3.3	Remediation Effectiveness	Through the performance of periodic GWE (between May 2001 and March 2003), a total of approximately 71,500 gallons of groundwater had beer removed, with an estimated mass removal of 0.96 pounds of TPHg, 0.01 pounds of benzene and 9.3 pounds of MTBE. From the continuous operation of the GWE system, over 1,167, 698 gallons of groundwater have been extracted at the site through June 4, 2004. This calculates to an estimated 5.90 pounds of TPHg, 0.059 pounds of benzene, and 15.4 pounds of MTBE removed by GWE system between July 1, 2003 and June 4, 2004. MTBE concentrations in well S-2 decreased from 10,700 ppb in November 2000 to 28 ppb in April 2004. MTBE concentrations in well S-4 decreased from 14,500 ppm in March 2001 to 110 ppb in April 2004. MTBE concentrations in tank backfill well T-2 decreased from 100,000 ppb in June 2002 to 5.6 ppb in April 2004. As of the April 2004 sample event, the highest concentration of MTBE at this site is 380 ppb in downgradient well S-7.The maximum TBA concentration is 9,900 ppb in onsite well S-4, and the maximum benzene concentration is 70 ppb in onsite well S-5.
4	Well and Sensitive Receptor Survey	
4.1	Designated Beneficial Groundwater Use	The San Francisco Bay Region RWQCB Basin Plan identifies the following existing beneficial uses for groundwater in this region: Municipal and domestic water supply, Industrial process water supply, Industrial service water supply, and Agricultural water supply.
4.2	Shallow Groundwater Use	No pumping wells that draw from shallow groundwater were identified within a half-mile radius of the site.
4.3	Deep Groundwater Use	An active municipal well (Hop-6) is located approximately 1,500 feet southeast of the site. This well is screened from 215 to 235 fbg, 275 to 305 fbg, 355 to 375 fbg, and 400 to 490 fbg.
4.4	Well Survey Results	An April 2002 well survey conducted by Cambria identified six wells within a 1/2-mile radius, including one active municipal well (Hop-6, noted above), one destroyed municipal well (Hop-1), one abandoned irrigation well located between the site and the Arroyo Mocho Canal, one destroyed irrigation well and two wells of unknown use located in the former military yard southeast of the site. Based on a review of the Department of Water Resources Well Driller's Report form for the identified abandoned irrigation well, as well as a review of aerial photographs and historical utility maps, the abandoned irrigation well is likely located beneath the commercial building at 3730 Hopyard Road south of the site.
4.5	Likelihood of Impact to Wells	Impact to the municipal well is unlikely considering the low estimated permeability of the subsurface soils, and the distance to the well of 1,500 feet. Potential impact to the abandoned irrigation well depends on the screened interval of the well and its location, which has not yet been accurately determined, and the existence of downward vertical groundwater gradients. Results from downgradient vertical sampling at CPT-2 suggest that the lateral and vertical extent of the plumes originating from the subject site is less than 400 feet in the downgradient direction.

Item	Evaluation Criteria	Comments/Discussion
4.6	Likelihood of Impact to Surface Water	Based on a review of the USGS topographic maps of the site vicinity and site reconnaissance, the nearest survey water body to the site is the Arroyo Mocho Canal located approximately 400 feet south of the site. The Arroyo Mocho Canal is an unlined, losing canal. Well S-12 is located downgradient of the site on the northern bank of the Arroyo Mocho Canal, and groundwater samples collected from well S-12 have not contained MTBE since installation in September 2002. Further, vertical groundwater analyses from CPT-2 indicate that deeper groundwater is also not impacted at this distance. Based on this information, impact to the Arroyo Mocho Canal is not likely.
5	Risk Assessment	
5.1	Site Conceptual Exposure Model (current and future uses)	Onsite land use is commercial. There is an operating Shell-branded service station with an enclosed station building onsite. Offsite land use in the immediate vicinity is commercial. Residential use land is located southwest of the site south of the Arroyo Mocho Canal.
5.2	Exposure Pathways	Soil and/or groundwater volatilization to outdoor and/or indoor air, commercial exposure.
5.3	Risk Assessment Status	No formal risk assessment has been performed.
5.4	Identified Human Exceedances	No exceedances have been identified or evaluated.
5.5	Identified Ecological Exceedances	No exceedances have been identified or evaluated.
6	Additional Recommended Data or Tasks	
6.1		

Attached:
The attachments to this document were submitted with the original document dated April 2003
The most recent quarterly monitoring report was submitted on June 28, 2004 (2Q04)
A corrected version of the Historical Soil Analytical Table is included as Attachment E of the main submittal
No additional subsurface work has been performed since the last iteration, and therefore, there are no new boring logs and no edits to the cross sections.

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Environmental Documents Available to Cambria Environmental		
Date	Title/Subject	Company
03/21/86	Investigation report	Emcon Associates
12/04/87	Investigation report	Kaprealian Engineering Inc.
01/25/88	Request for remedial action	Zone 7
03/10/88	Investigation report	Kaprealian Engineering Inc.
03/25/88	Work Plan	Shell Oil Company
08/11/88	Soil Sampling Report	Kaprealian Engineering Inc.
01/18/89	Environmental Assessment Report	Woodward-Clyde Consultants
05/11/89	Phase II Environmental Assessment	Woodward-Clyde Consultants
07/18/89	Work Plan	Geostrategies Inc.
09/19/89	Addendum to Work Plan	Geostrategies Inc.
11/06/89	Groundwater Sampling Report	Gettler-Ryan Inc.
12/04/89	Quarterly Report - July to September 1989	Geostrategies Inc.
03/01/90	Quarterly Report - October to December 1989	Geostrategies Inc.
03/25/90	Aquifer Test Report	Geostrategies Inc.
08/16/90	Site Update	Geostrategies Inc.
12/07/90	Site Update	Geostrategies Inc.
02/15/91	Site Update	Geostrategies Inc.
05/16/91	Site Update	Geostrategies Inc.
08/12/91	Site Update	Geostrategies Inc.
11/08/01	Site Update	Geostrategies Inc.
02/07/92	Site Update	Geostrategies Inc.
05/08/92	Quarterly Report	Geostrategies Inc.
08/04/92	Quarterly Report	Geostrategies Inc.
11/06/92	Quarterly Report	Geostrategies Inc.
11/08/93	Quarterly Report	Geostrategies Inc.
05/07/93	Quarterly Report	Geostrategies Inc.
09/22/93	Quarterly Report	Geostrategies Inc.
10/30/93	Quarterly Report	Geostrategies Inc.
02/08/94	Fourth Quarter 1993 Groundwater Sampling	Hydro Environmental Technologies, Inc.
05/20/94	First Quarter 1994 Activities	Weiss Associates
08/22/94	Second Quarter 1994 Activities	Weiss Associates
11/17/94	Third Quarter 1994 Activities	Weiss Associates
07/31/95	Second Quarter 1995	Weiss Associates
06/18/96	Second Quarter 1996	Weiss Associates
07/31/96	Letter requesting interpretation of historical GW data	ACHCSA
01/15/97	Response to 7/31/96 ACHCSA letter	Cambria Environmental
08/14/97	Second Quarter 1997 Monitoring Report	Cambria Environmental
09/01/98	Second Quarter 1998 Monitoring Report	Cambria Environmental
09/22/98	1998 Upgrade Site Inspection Report	Cambria Environmental
09/15/99	Second Quarter 1999 Monitoring Report	Cambria Environmental

Environmental Documents Available to Cambria Environmental		
Date	Title/Subject	Company
08/24/00	Second Quarter 2000 Monitoring Report	Cambria Environmental
09/14/00	Request for quarterly monitoring schedule	ACHCSA
02/05/01	Fourth Quarter 2000 Monitoring Report	Cambria Environmental
04/09/02	Sensitive Receptor Survey Report	Cambria Environmental
04/30/01	First Quarter 2001 Monitoring Report	Cambria Environmental
06/12/02	Subsurface Investigation Work Plan	Cambria Environmental
07/22/02	Work plan addendum submitted via e-mail to ACHCSA	Cambria Environmental
07/31/01	Second Quarter 2001 Monitoring Report	Cambria Environmental
11/30/01	Third Quarter 2001 Monitoring Report	Cambria Environmental
03/25/02	Fourth Quarter 2001 Monitoring Report	Cambria Environmental
06/11/02	First Quarter 2002 Monitoring Report	Cambria Environmental
07/25/02	Second Quarter 2002 Monitoring Report	Cambria Environmental
08/28/02	Interim Remediation Work Plan	Cambria Environmental
09/09/02	Interim Remediation Work Plan Approval	ACHCSA
10/22/02	Request for Total Fuel Oxygenate Analysis	ACHCSA
11/12/02	Third Quarter 2002 Monitoring Report	Cambria Environmental
01/21/03	Dispenser and Piping Upgrade Soil Sampling Report	Cambria Environmental
02/27/03	SWI, SCM and CAP request letter	ACHCSA
03/28/03	Subsurface Investigation Report	Cambria Environmental
04/09/03	Agency Response and Extension Request	Cambria Environmental
04/29/03	Fourth Quarter 2002 Monitoring Report	Cambria Environmental

ATTACHMENT E

Historical Soil Analytical Data Table (revised)

Table 1. Historical Soil Analytical Data, Shell-branded Service Station - 3790 Hopyard Road, Pleasanton, California

Sample ID	Date	Depth (fbg)	TPHg (ppm)	MTBE (ppm)	Benzene (ppm)	Toluene (ppm)	Ethylbenzene (ppm)	Xylenes (ppm)
S-2	10/28/87	33.5 - 35.0	<5	---	<0.05	<0.1	---	<0.4
S-3	01/26/88	19.0 - 20.5	<5	---	<0.05	<0.1	---	<0.4
S-4	01/26/88	19.0 - 20.5	41	---	6.2	<0.1	---	5.9
S-5	01/26/88	19.0 - 20.5	4,700	---	50	170	---	900
A1	08/03/88	14	1300	---	13	110	45	230
A1X	08/03/88	20	<1.0	---	<0.1	<0.1	<0.1	<0.1
A2	08/03/88	14	2100	---	11	32	72	350
A2X	08/03/88	20.5	80	---	1.3	2.6	3.4	16
B-1	08/03/88	14	11	---	0.2	<0.1	<0.1	<0.1
B-2	08/03/88	14	120	---	5.9	5.8	3.7	19
B2X	08/03/88	20.5	1.5	---	<0.1	<0.1	<0.1	<0.1
C-1	08/03/88	14	110	---	2.8	0.4	7.8	31
C-1X	08/03/88	16	9.1	---	0.8	<0.1	1.1	0.6
C-2	08/03/88	14	52	---	4.8	0.1	4.4	3.9
Comp A	08/03/88	---	<1	---	<0.1	<0.1	<0.1	<0.1
Comp B	08/03/88	---	8.7	---	<0.1	0.2	0.1	0.6

Table 1. Historical Soil Analytical Data, Shell-branded Service Station - 3790 Hopyard Road, Pleasanton, California

Sample ID	Date	Depth (fbg)	TPHg (ppm)	MTBE (ppm)	Benzene (ppm)	Toluene (ppm)	Ethylbenzene (ppm)	Xylenes (ppm)
Comp C	08/03/88	---	35	---	0.5	2.1	1.9	11
Comp D	08/03/88	---	32	---	0.3	0.1	0.1	5.9
A5	08/05/88	5	3.0	---	1.3	<0.1	<0.1	<0.1
A10	08/05/88	10	3.5	---	0.5	<0.1	0.2	0.2
A15	08/05/88	15	4.4	---	0.7	<0.1	0.5	0.3
S-6-2A	10/04/88	9 - 10.5	<5	---	0.05	<0.1	<0.1	<0.3
S-6-3A	10/04/88	14 - 15.5	9	---	<0.05	<0.1	<0.1	<0.3
S-6-4A	10/04/88	19 - 20.5	6	---	0.05	<0.1	0.1	<0.3
S-6-5A	10/04/88	24 - 25.5	<5	---	<0.05	<0.1	<0.1	<0.3
S-7-2A	10/04/88	9 - 10.5	<5	---	<0.05	<0.1	<0.1	<0.3
S-7-3A	10/04/88	14 - 15.5	<5	---	<0.05	<0.1	<0.1	<0.3
S-7-4A	10/04/88	19 - 20.5	<5	---	<0.05	<0.1	<0.1	<0.3
S-8-3A	02/24/89	14 - 15.5	<5	---	<0.05	<0.1	<0.1	<0.3
S-8-4A	02/24/89	19 - 20.5	<5	---	<0.05	<0.1	<0.1	<0.3
S-9-3A	02/24/89	14 - 15.5	<5	---	<0.05	<0.1	<0.1	<0.3
S-9-4A	02/24/89	19 - 20.5	<5	---	<0.05	<0.1	<0.1	<0.3
SR-1-15	08/09/89	15	<5	---	<0.1	<0.1	<0.1	<0.3
SR-1-20	08/09/89	20	40	---	5.4	<0.1	2.5	2.7

Table 1. Historical Soil Analytical Data, Shell-branded Service Station - 3790 Hopyard Road, Pleasanton, California

Sample ID	Date	Depth (fbg)	TPHg (ppm)	MTBE (ppm)	Benzene (ppm)	Toluene (ppm)	Ethylbenzene (ppm)	Xylenes (ppm)
S-10-15	08/09/89	15	<5	---	<0.05	<0.1	<0.1	<0.3
S-10-20	08/09/89	20	<5	---	<0.05	<0.1	<0.1	<0.3
SR-3-10	09/19/89	10	<5.0	---	0.98	<0.1	<0.1	<0.3
SR-3-15	09/19/89	15	54	---	3.9	<0.2	4.2	2.7
SR-3-20	09/19/89	20	<5.0	---	<0.05	<0.1	0.2	<0.3
SR-2-10	09/20/89	10	<5.0	---	0.05	<0.1	<0.1	<0.3
SR-2-15	09/20/89	15	67	---	0.11	0.1	0.1	<0.3
SR-2-20	09/20/89	20	8.4	---	<0.05	<0.1	1.0	<0.3
D-1	07/26/02	3.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005
D-2	07/26/02	3.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005
D-3	07/26/02	3.5	**4.0**	<0.5	<0.005	<0.005	**0.012**	**0.011**
D-4	07/26/02	3.5	**1.8**	<0.5	<0.005	<0.005	**0.053**	**0.018**
P-1	07/26/02	3.5	**260**	<0.5	**0.079**	**0.072**	**0.48**	**1.1**
P-2	07/26/02	3.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005
P-3	07/26/02	3.5	**10**	<0.5	**0.0083**	<0.005	**0.26**	<0.005
S-11-5.5	07/26/02	5.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005
S-11-10.5	07/26/02	10.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005
S-11-15.5	07/26/02	15.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005
S-11-20.5	07/26/02	20.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005
S-11-24.5	07/26/02	24.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005

Table 1. Historical Soil Analytical Data, Shell-branded Service Station - 3790 Hopyard Road, Pleasanton, California

Sample ID	Date	Depth (fbg)	TPHg (ppm)	MTBE (ppm)	Benzene (ppm)	Toluene (ppm)	Ethylbenzene (ppm)	Xylenes (ppm)
S-12-5.5	09/19/02	5.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005
S-12-10.5	09/19/02	10.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005
S-12-15.5	09/19/02	15.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005
S-12-20.5	09/19/02	20.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005
S-12-24.5	09/19/02	24.5	<1.0	<0.5	<0.005	<0.005	<0.005	<0.005

Notes and Abbreviations:

TPHg = Total petroleum hydrocarbons as gasoline analyzed by EPA Method 8015; analyzed by EPA Method 8260B starting August 26, 2002

MTBE = Methyl tert-butyl ether, analyzed by EPA Method 8260B

Benzene, ethylbenzene, toluene, and xylenes analyzed by EPA Method 8015/5030; analyzed by EPA Method 8260B starting August 26, 2002

fbg = feet below grade

ppm = parts per million

--- = Not analyzed

<x = Below laboratory detection limit of x

[a] = Result is for undifferentiated xylenes and ethylbenzene