

# **Natural Attenuation of MTBE**

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Tim Buscheck  
Senior Staff Hydrogeologist  
ChevronTexaco Energy Research and Technology Company

# Natural Attenuation

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## Multiple Lines of Evidence

- Tier 1 - Is the plume stable or shrinking?
- Tier 2 - Do the geochemical indicator parameters suggest ongoing bioactivity?
- Tier 3 - How significant is biodegradation of the target constituents under site conditions?

# Natural Attenuation of MTBE

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- **Oxygen** - Aerobic biodegradation has been demonstrated in mixed (Salanitro et al., 1994) and pure (Mo et al., 1997) cultures.
- **Methanogenesis** - EPA has found a link between methanogenesis and MTBE degradation in the lab and field (Wilson et al., 2000).
- **Nitrate** - USGS lab work suggests a link between nitrate reduction and MTBE transformation (Bradley et al., 2001a).
- **Sulfate** - USGS studies in sediments show MTBE-degrading microorganisms under a range of terminal electron-accepting processes including sulfate-reducing conditions (Bradley et al., 2001b).
- **Iron** - API funded laboratory study suggests MTBE transformation in presence of available iron (Finneran and Lovley, 2001).

# MTBE Plume Conceptual Model

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**There are four conceptual models for a MTBE plume:**

- + Shrinking - evidence of natural attenuation and a limited source
- + Stable - few plumes truly “stable”; natural attenuation rate approximately equal to the dissolution rate
- + Expanding - NAPL source may persist
- + Detached - source no longer contributing mass to the dissolved plume; only occur in highly transmissive groundwater (rare)

# Tier 1 Methods

| <b>Method</b>                                                                      | <b>Interpretation</b>                                    |
|------------------------------------------------------------------------------------|----------------------------------------------------------|
| MTBE (and other contaminants) concentration vs. time for multiple monitoring wells | Contaminant trends throughout the plume; plume stability |
| Concentration and depth to water vs. time                                          | Hydrologic influences on contaminant trends              |
| Contaminant contour maps for multiple monitoring events                            | Spatial plume behavior                                   |

# API Natural Attenuation Study

## Evaluation of Field Data

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- 18 sites varied in redox state
- Developed criteria for identifying terminal electron-accepting process (TEAP)
- Used criteria to evaluate each site
- Sites recommended for microcosm testing to give range of TEAP conditions.

# API Natural Attenuation Study

## Definition of Plume Geochemistry

| Analyte         | Concentration in Impacted Wells               | Designation              |
|-----------------|-----------------------------------------------|--------------------------|
| Maximum Methane | > 0.5 mg/L                                    | Methanogenic (M)         |
|                 | < 0.5 mg/L                                    | Weakly Methanogenic (WM) |
| Minimum Sulfate | Non-detect<br>or<br><< maximum sulfate        | Sulfate depleted (SD)    |
|                 | Detectable sulfate<br>or<br>< maximum sulfate | Sulfate available (SA)   |
| Minimum Nitrate | Non-detect<br>or<br><< maximum nitrate        | Nitrate depleted (ND)    |

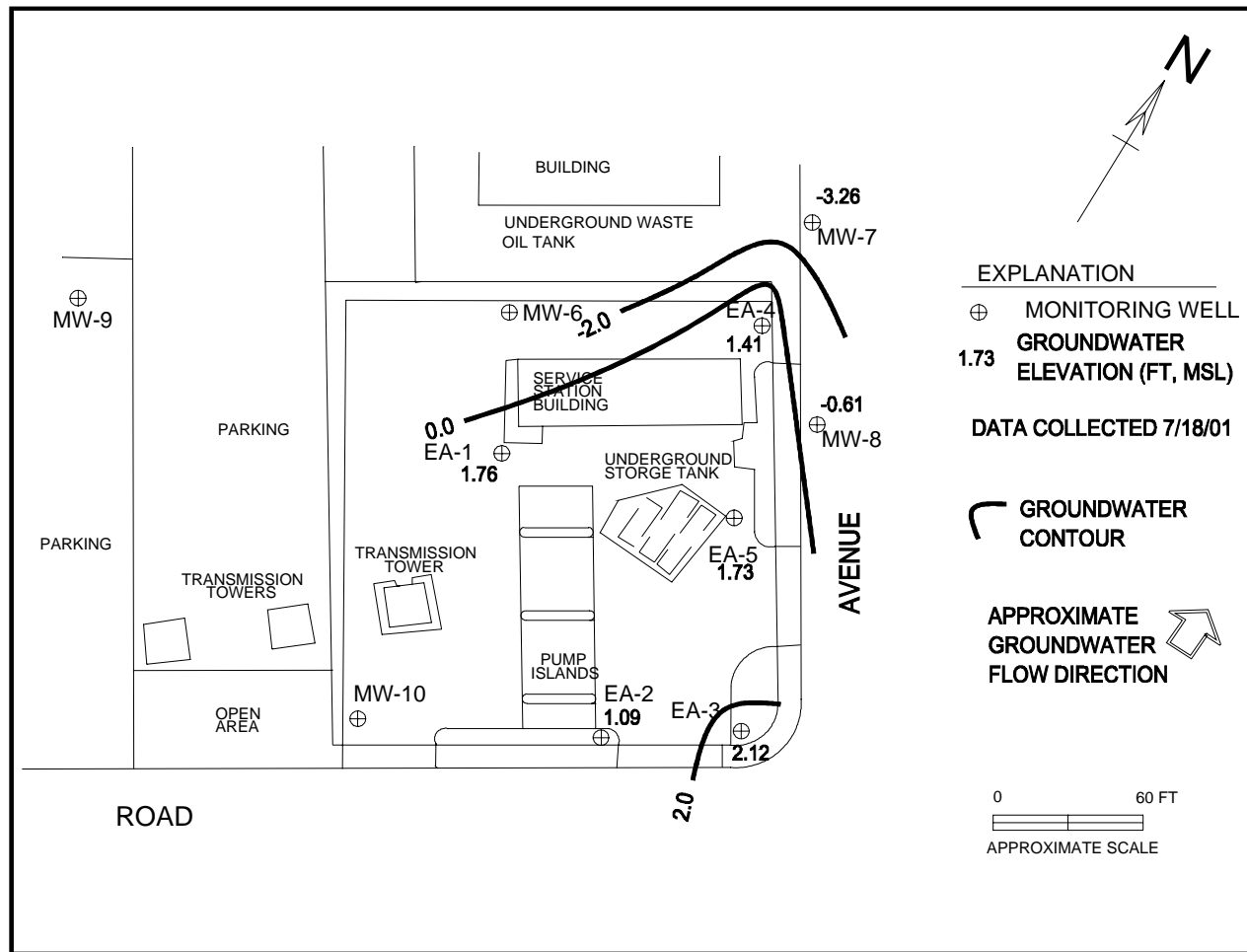
## Tier 2 Methods

| <b>Method</b>                               | <b>Interpretation</b>                           |
|---------------------------------------------|-------------------------------------------------|
| MTBE, TBA, and nitrate/sulfate vs. distance | Demonstration of various geochemical conditions |
| MTBE, TBA, and methane vs. distance         | Demonstration of methanogenic conditions        |
| MTBE/TBA ratio vs. distance                 | Evidence of MTBE transformation                 |

# API Natural Attenuation Study Site Evaluation

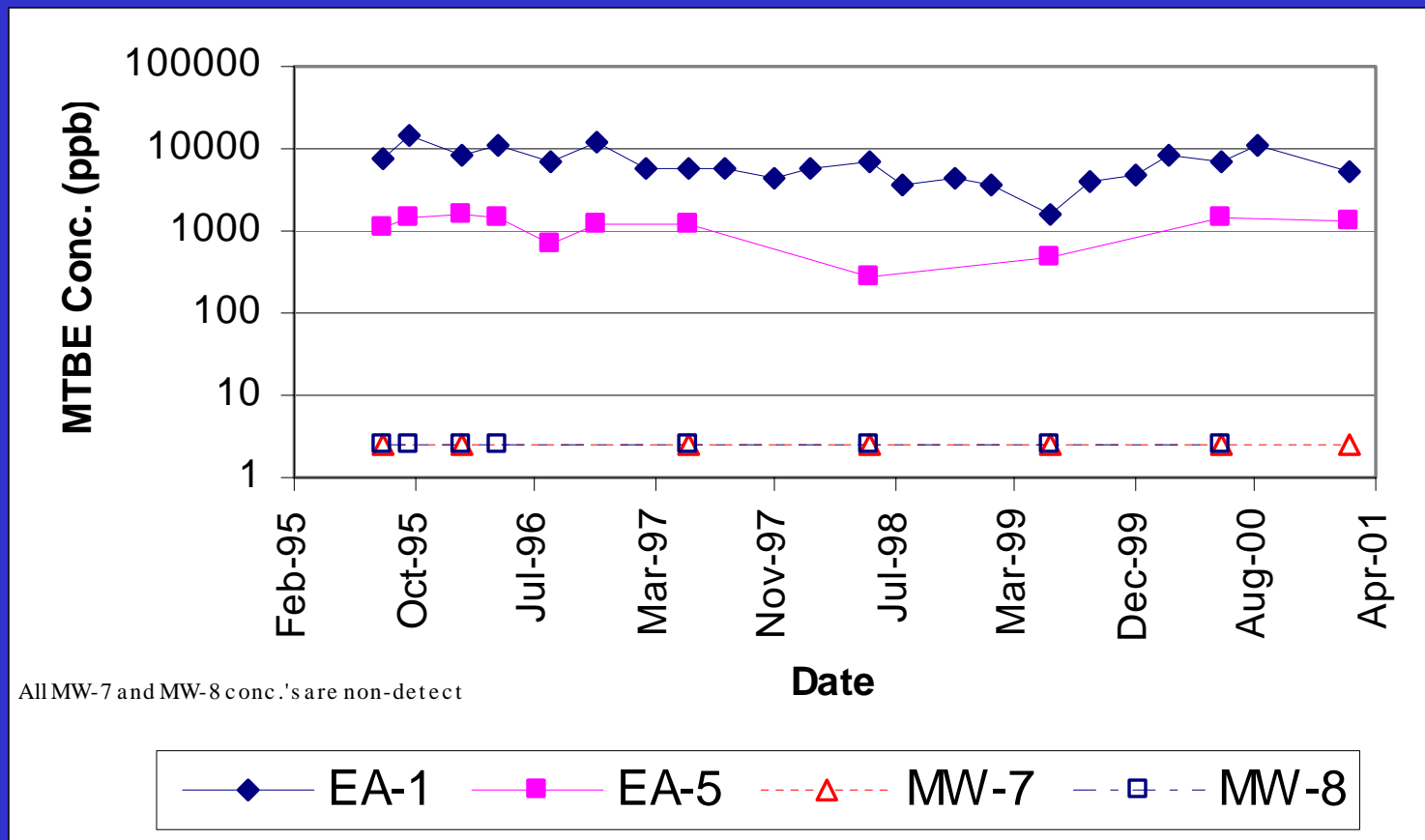
| Site Location                              |                       | Sulfate (mg/L) |     | Methane (µg/L) |       | Plume Geochemistry | Maximum Hydrogen (nM) | Maximum Ethane (ng/L) |
|--------------------------------------------|-----------------------|----------------|-----|----------------|-------|--------------------|-----------------------|-----------------------|
|                                            |                       | Min            | Max | Min            | Max   |                    |                       |                       |
|                                            | Max. Nitrate-N (mg/L) |                |     |                |       |                    |                       |                       |
| <b>Sites recommended for further study</b> |                       |                |     |                |       |                    |                       |                       |
| Millbrae, CA                               | <0.05                 | 12             | 120 | 2400           | 15000 | M+SA               | 51                    | 1100                  |
| Westlake, CA                               | 6.7                   | 240            | 770 | 1.7            | 7100  | M+SA               | 1.7                   | 3200                  |
| Redding, CA                                | <0.05                 | <5             | 24  | 42             | 3400  | M+SD               | 5.5                   | 2700                  |
| Monessen, PA                               | 32                    | <5             | 370 | 4.5            | 9300  | M+SD               | 1.4                   | 59000                 |
| San Mateo, CA                              | 3.5                   | <5             | 40  | 11             | 2900  | M+SD               | 8.1                   | 2300                  |
| San Jose, CA 2                             | 2.9                   | 23             | 150 | 1.4            | 9300  | M+SA               | 2.8                   | 110,000               |
| Agoura Hills, CA                           | 32                    | 14             | 250 | 0.08           | 120   | ND+SA              | 1.0                   | 130                   |
| San Jose, CA 1                             | 0.44                  | 280            | 680 | 0.23           | 5.1   | ND+SA              | 2.8                   | 9                     |
| Petaluma, CA                               | 5.0                   | <5             | 77  | 5.8            | 5600  | M+SD               | 6.2                   | 110,000               |
| Belle Meade, NJ                            | 3.2                   | <5             | 14  | 0.29           | 140   | WM+SD              | 2.0                   | 8                     |

# Site 1: Millbrae, CA



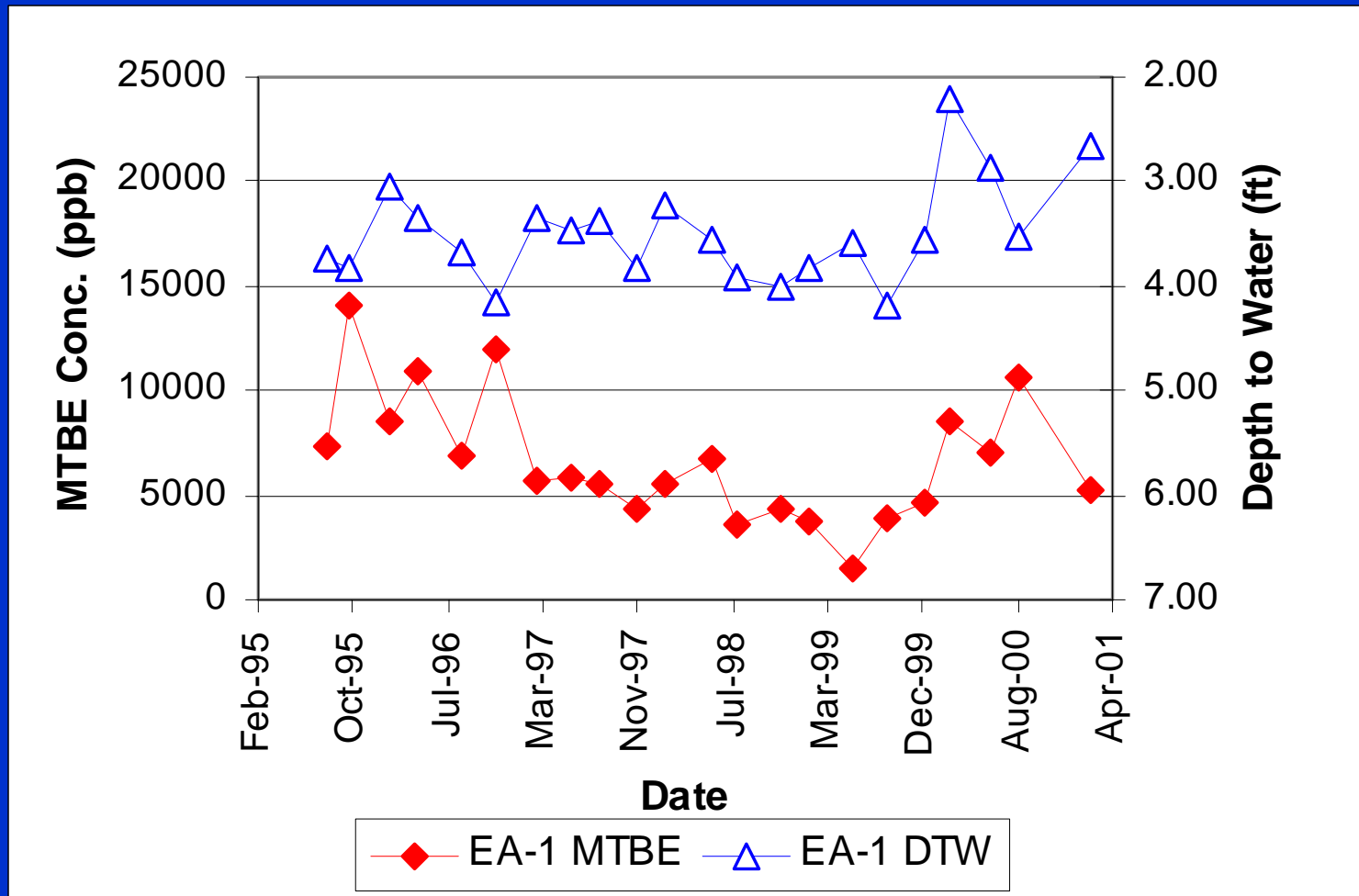
# Millbrae, CA

## MTBE Concentration vs. Time



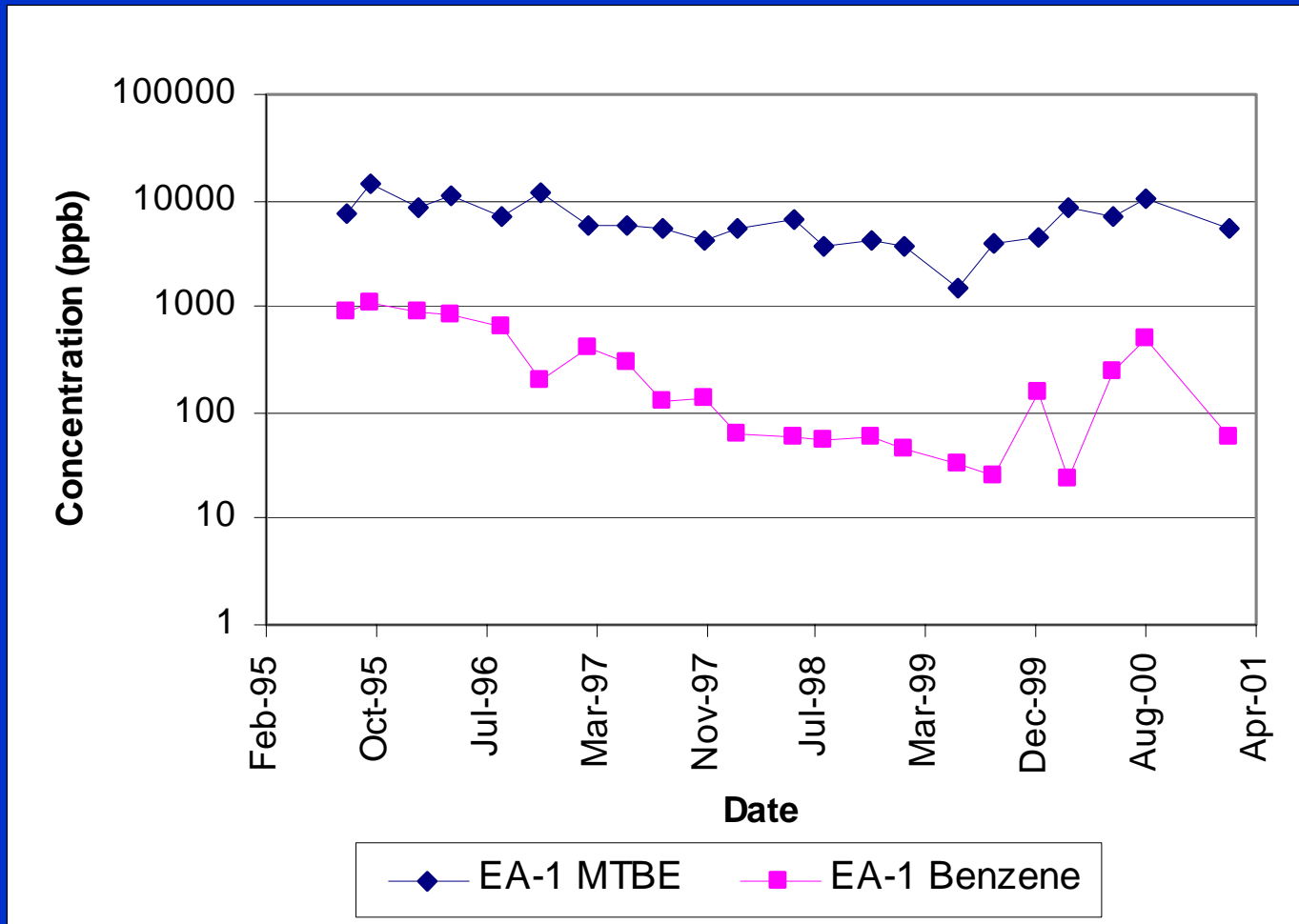
# Millbrae, CA

## EA-1 MTBE Concentration and Depth to Water vs. Time



# Millbrae, CA

## EA-1 MTBE and Benzene vs. Time



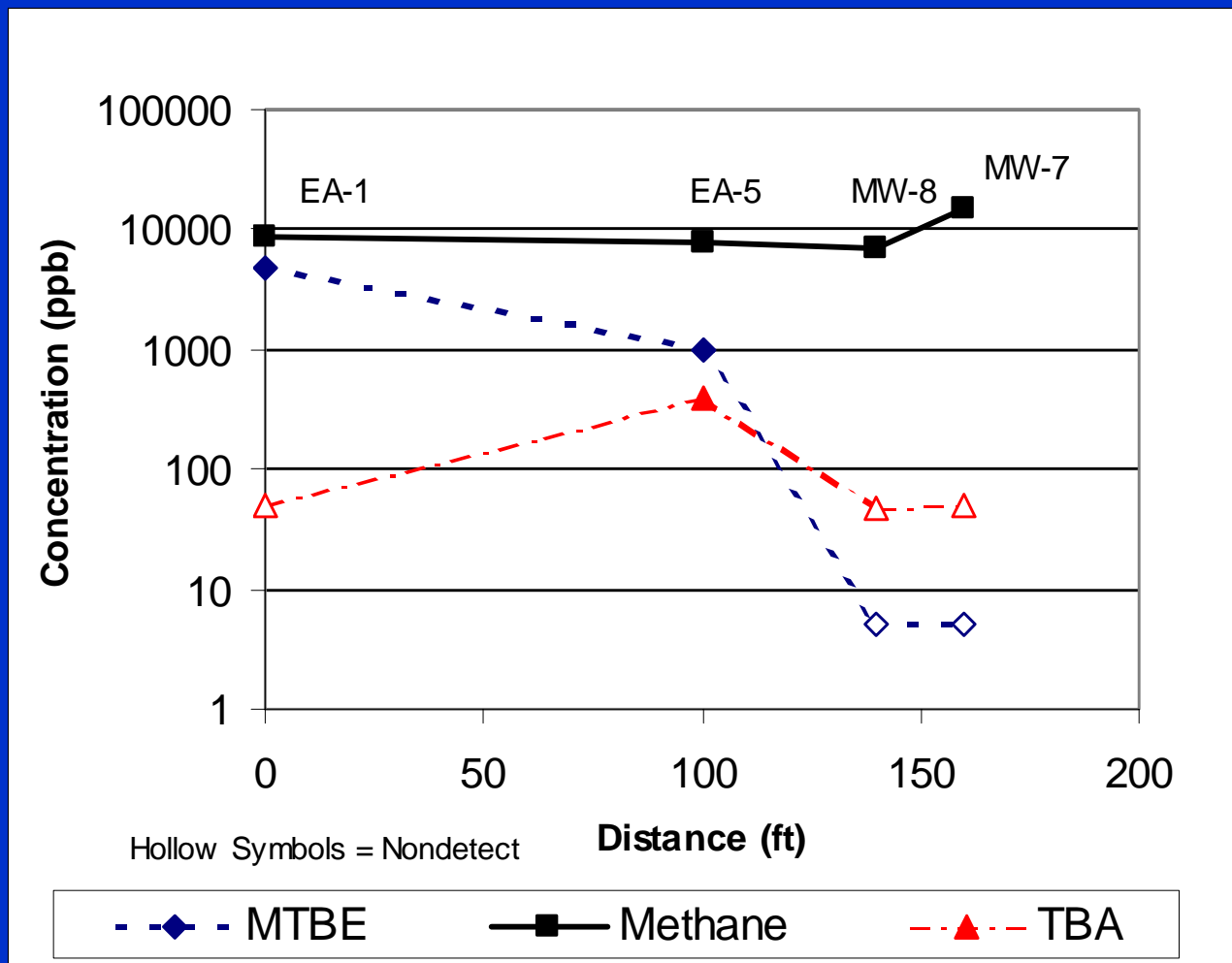
# Millbrae, CA

## Plume Geochemistry (8/9/00)

| Well | Distance (ft) | MTBE (ppb) | BTEX (ppb) | TBA (ppb) | DO (ppm) | Methane (ppb) | Sulfate (ppm) |
|------|---------------|------------|------------|-----------|----------|---------------|---------------|
| EA-3 | upgradient    |            | <25        | 96        | 0.44     | 2400          | 120           |
| EA-1 | 0             | 4900       | 75.5       | <50       | 0.15     | 8600          | 13            |
| EA-5 | 100           | 1000       | <25        | 390       | 0.15     | 7800          | 12            |
| MW-8 | 140           | <5         | <25        | <50       | 0.15     | 7000          | 55            |
| MW-7 | 160           | <5         | <25        | <50       | 0.15     | 15000         | 13            |

# Millbrae, CA

## MTBE, Methane, and TBA vs. Distance

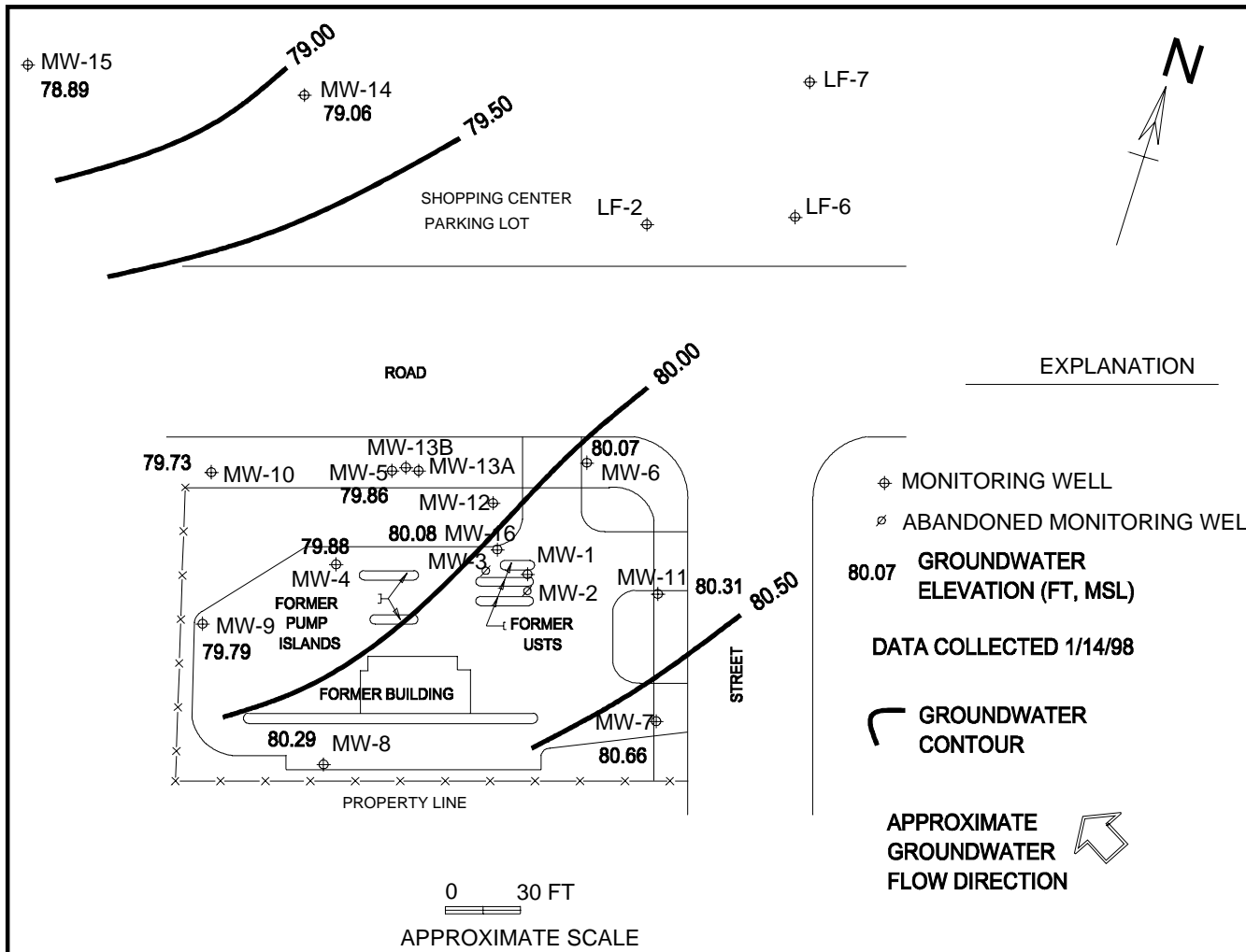


# Millbrae, CA Site Summary

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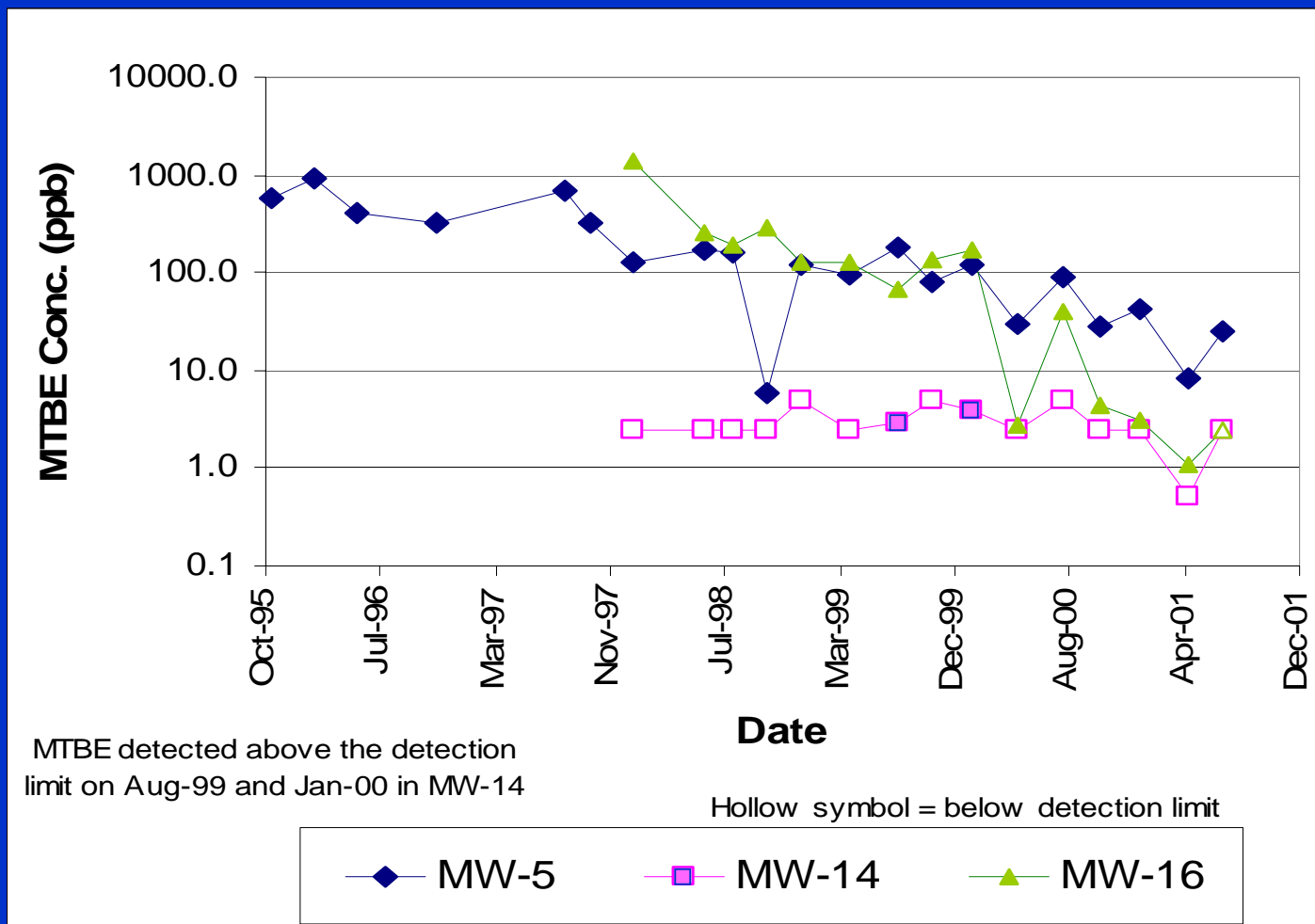
- Tier 1 analysis provides evidence of a “stable” plume
- Tier 2 geochemical analysis demonstrates elevated methane concentrations, evidence for a strongly anaerobic, methanogenic plume; there is also evidence of sulfate utilization
- Tier 3 studies, including anaerobic microcosms and isotopic ratio evaluation, are ongoing for this site

# Site 2: San Jose, CA



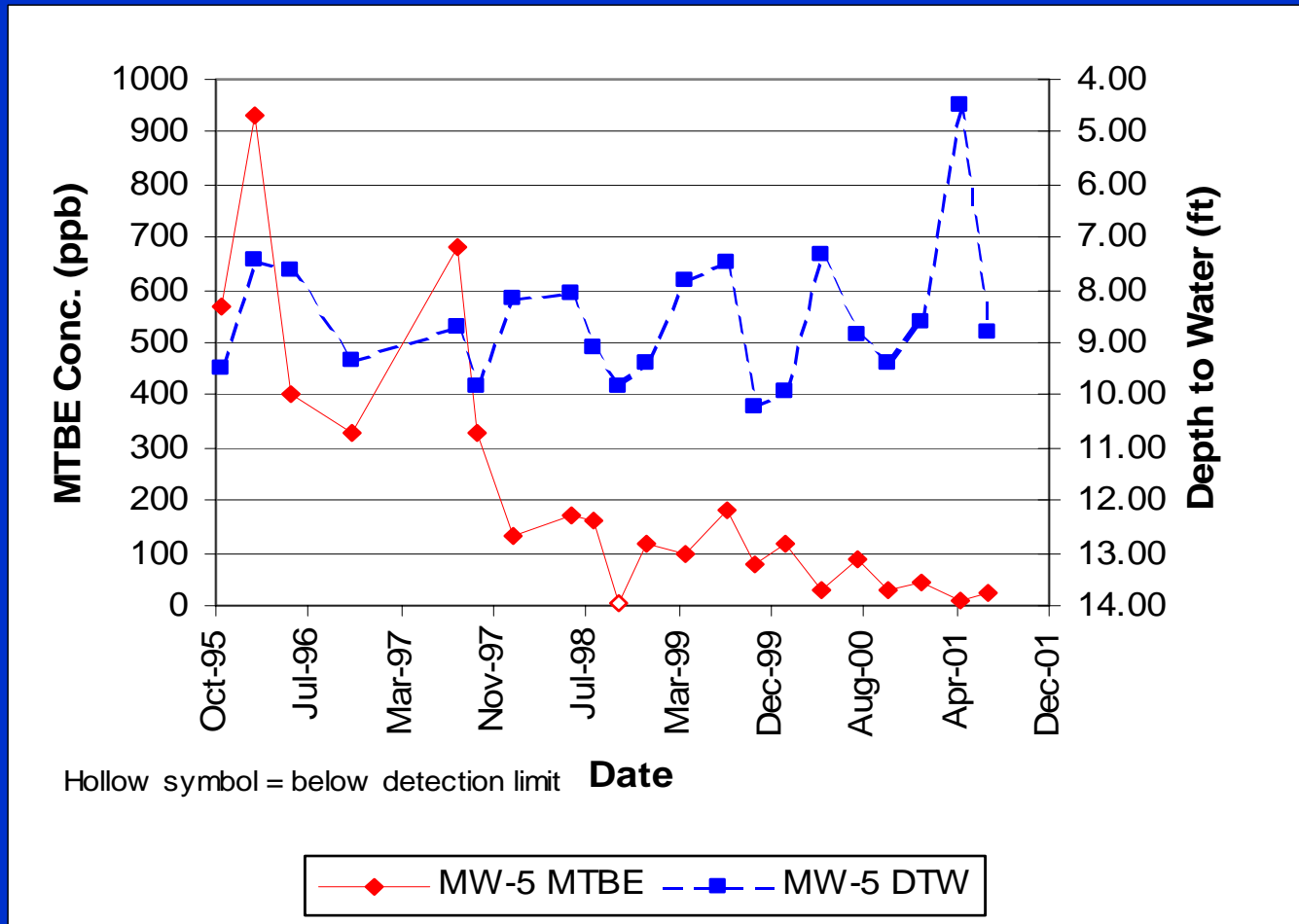
# San Jose, CA

## MTBE Concentration vs. Time



# San Jose, CA

## MW-5 MTBE Concentration and Depth to Water vs. Time



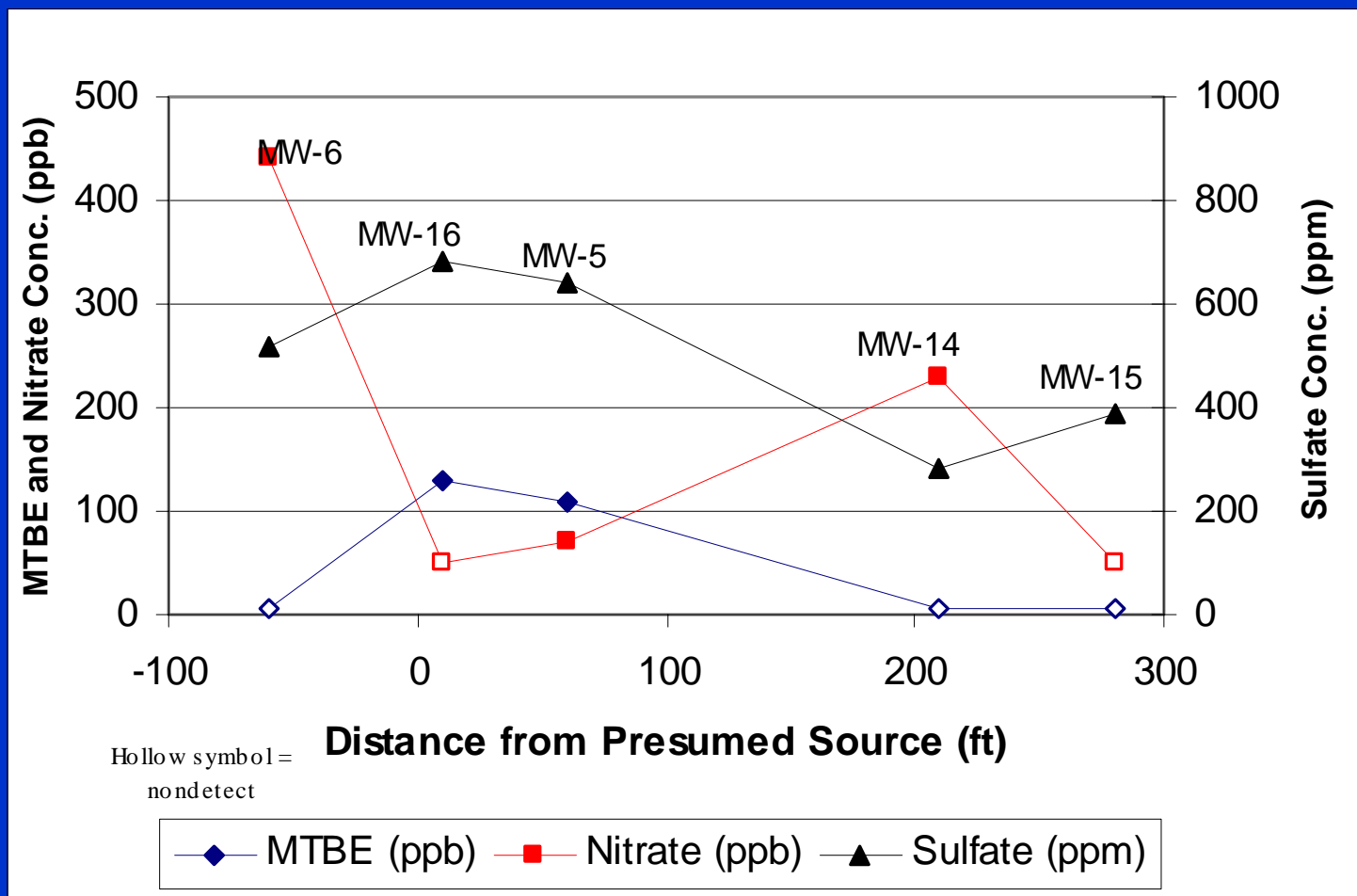
# San Jose, CA

## Plume Geochemistry (8/15/00)

| Well  | Distance (ft)           | MTBE<br>(ppb) | BTEX<br>(ppb) | DO<br>(ppm) | Nitrate<br>(ppb) | Sulfate<br>(ppm) | Methane<br>(ppb) |
|-------|-------------------------|---------------|---------------|-------------|------------------|------------------|------------------|
| MW-6  | -60<br>(cross-gradient) | <5            | <25           | 2           | 440              | 520              | 0.23             |
| MW-16 | 10                      | 130           | <25           | 2           | <50              | 680              | 4.2              |
| MW-5  | 60                      | 110           | <25           | 1.8         | 70               | 640              | 5.1              |
| MW-14 | 210                     | <5            | <25           | 2.2         | 230              | 280              | 1.5              |
| MW-15 | 280                     | <5            | <25           | 1.6         | <50              | 390              | 1.3              |

# San Jose, CA

## MTBE, Nitrate, and Sulfate vs. Distance



# San Jose, CA Site Summary

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- Tier 1 analysis demonstrates the plume is depleted of BTEX, the source is depleted of MTBE, and the plume is shrinking
- Tier 2 designation is a nitrate-depleted, sulfate available, “mildly” aerobic plume
- Tier 3 studies, including anaerobic microcosms and isotopic ratio evaluation, are ongoing for this site

# Natural Attenuation of MTBE Recommendations

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- Field sampling and analytical program for geochemical indicator parameters:
  - dissolved oxygen, nitrate, sulfate, and iron
  - methane and TBA
- MTBE, electron acceptors, methane, and TBA concentration versus distance plots

## Research Findings

# MTBE Natural Attenuation

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- Field evidence for degradation under aerobic and strongly reducing, anaerobic conditions.
- Laboratory data suggests degradation under other anaerobic conditions.
- More detailed geochemical evaluation may be required.
- Highest published attenuation rates similar to benzene. Many sites may have slower rates.
- Stable isotope approach shows promise as an indicator of in-situ activity.

# References

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- Bradley, P.M., F.H. Chapelle, and J.E. Landmeyer. 2001. *Methyl t-Butyl Ether Mineralization in Surface-Water Sediment Microcosms under Denitrifying Conditions*. Applied and Environmental Microbiology, 67(4):1975-1978.
- Bradley, P.M., F.H. Chapelle, and J.E. Landmeyer. 2001. *Effect of Redox Conditions on MTBE Biodegradation in Surface Water Sediments*. Environmental Science and Technology 35:4643 –4647.
- Finneran, K.T. and D.R. Lovley. 2001. *Anaerobic Degradation of Methyl tert-Butyl Ether (MTBE) and tert-Butyl Alcohol (TBA)*. Environmental Science and Technology 35:1785-1790.
- Kolhatkar, R., J. Wilson, and L.E. Dunlap. 2000. *Evaluating Natural Biodegradation of MTBE at Multiple UST Sites*. In Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water. National Ground Water Association/API, Houston, TX, November 15-17. pp. 32-49

# References

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- McLoughlin, P., R. Pirkle, T.E. Buscheck, R. Kolhatkar, and N. Novick. 2001. *Redox Conditions at Fuel Oxygenate Release Sites*. In *Bioremediation of MTBE, Alcohols, and Ethers*. Magar, V.S., J.T. Gibbs, K.T. O'Reilly, M.R. Hyman, and A. Leeson (Editors). Battelle Press, Columbus, OH, pp. 35-42.
- Mo, K., C.O. Lora, A.E. Wanken, M. Javanmardian, X. Yang, and C.F. Kulpa. 1997. *Biodegradation of Methyl Tert-Butyl Ether by Pure Bacterial Cultures*. *Applied Microbiology Biotechnology*, 47:69-72.
- Salanitro, J.P., L.A. Diaz, M.P. Williams, and H.L. Wisniewski. 1994. *Isolation of a Bacterial Culture that Degrades Methyl tert-Butyl Ether*. *Applied and Environmental Microbiology*, 60:2593-2596.
- Wilson, J.T., J.S. Cho, B.H. Wilson, and J.A. Vardy. 2000. *Natural Attenuation of MTBE in the Subsurface Under Methanogenic Conditions*. EPA/600/R-00/006.