Natural Attenuation of MTBE

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Natural Attenuation

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

- **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

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

Method	Interpretation
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

- 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 or << maximum sulfate	Sulfate depleted (SD)
	Detectable sulfate or < maximum sulfate	Sulfate available (SA)
Minimum Nitrate	Non-detect or << maximum nitrate	Nitrate depleted (ND)

Kolhatkar et al, 2000; McLoughlin et al., 2001

Tier 2 Methods

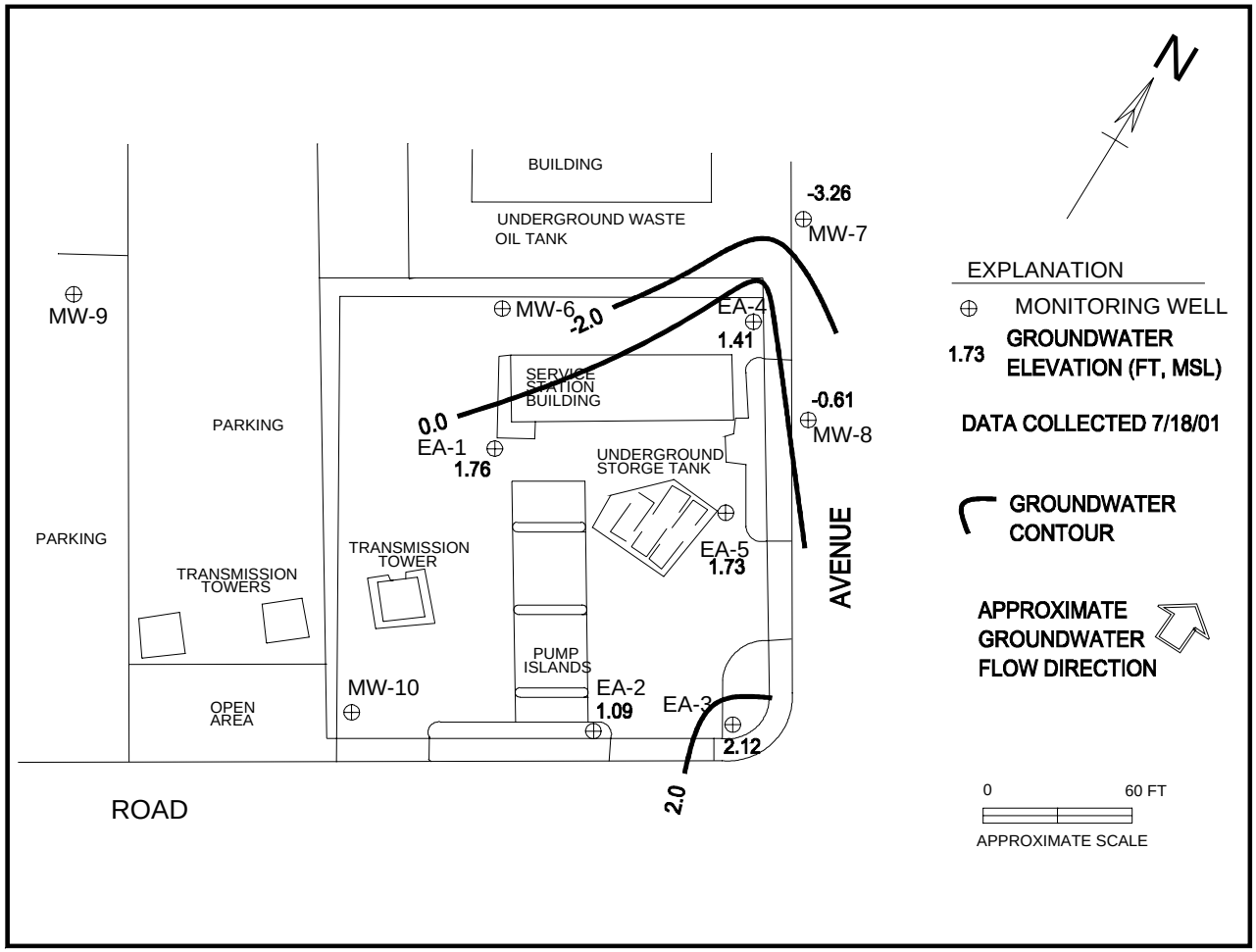
Method	Interpretation
MTBE, TBA, and nitrate/sulfate vs. distance	Demonstration of various geochemical conditions
MTBE, TBA, and methane vs. distance	Demonstration of methanogenic conditions
MTBE/TBA ratio vs. distance	Evidence of MTBE transformation

API Natural Attenuation Study
Site Evaluation

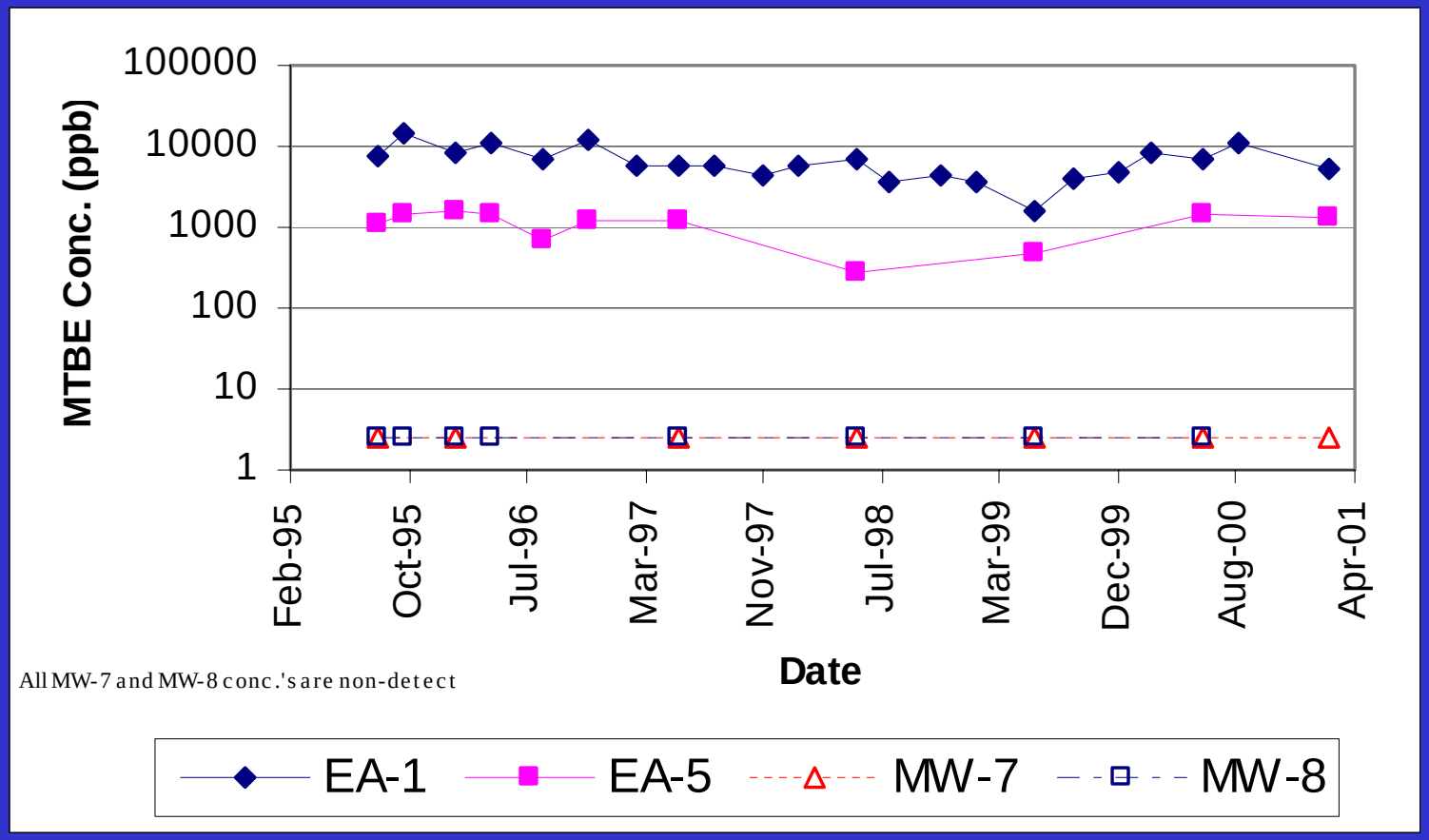
Site Location	Max. Nitrate-N (mg/L)	Sulfate (mg/L) Min	Sulfate (mg/L) Max	Methane (µg/L) Min	Methane (µg/L) Max	Plume Geochem-istry	Maximum Hydrogen (nM)	Maximum Ethane (ng/L)
Sites recommended for further study								
Millbrae, CA	<0.05	12	120	2400	15000	M+SA	51	1100
Westlake, CA	6.7	240	770	1.7	7100	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

McLoughlin et al., 2001

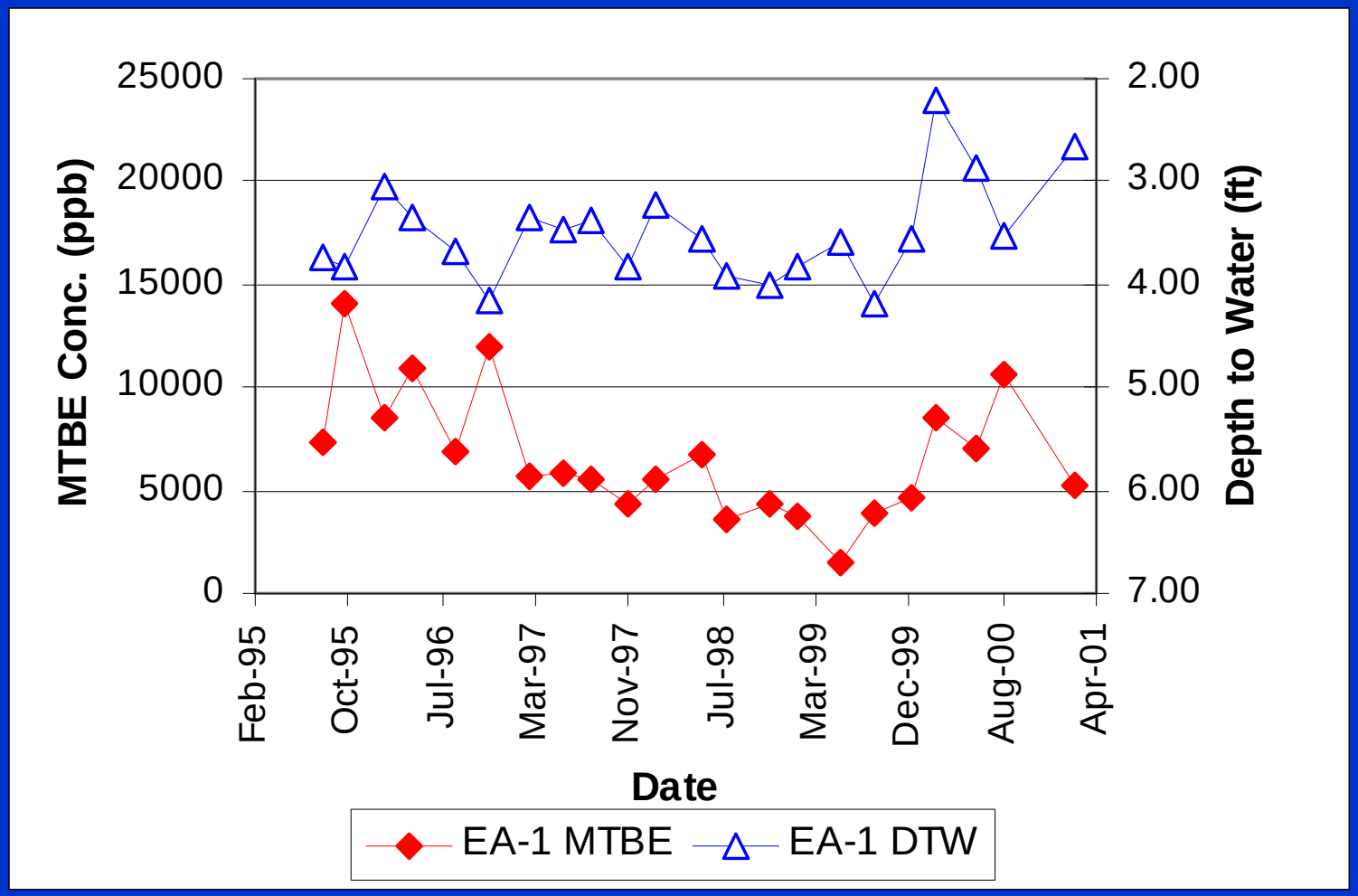
Site 1: Millbrae, CA



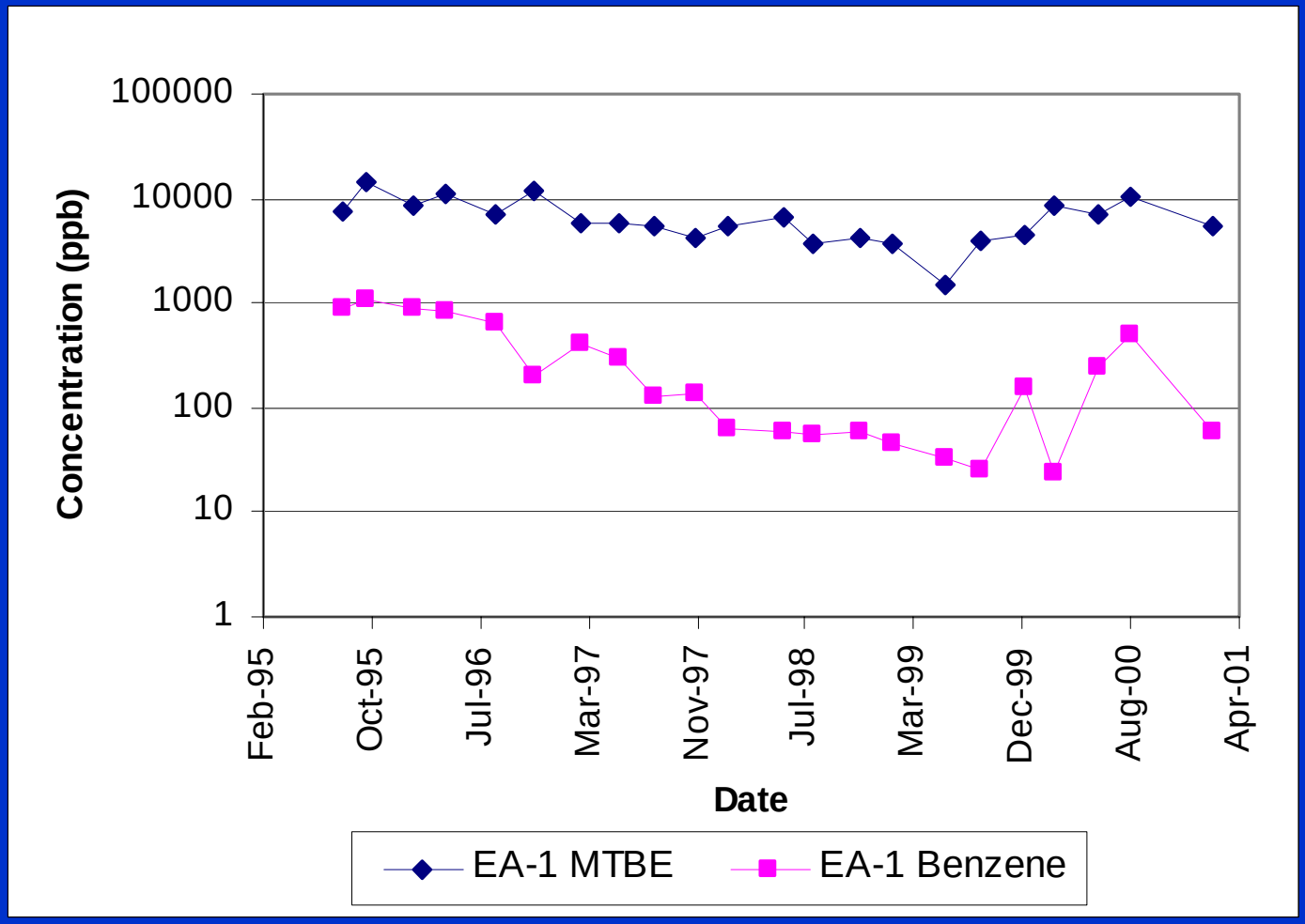
Millbrae, CA
MTBE Concentration vs. Time



Millbrae, CA
EA-1 MTBE Concentration and Depth to Water vs. Time



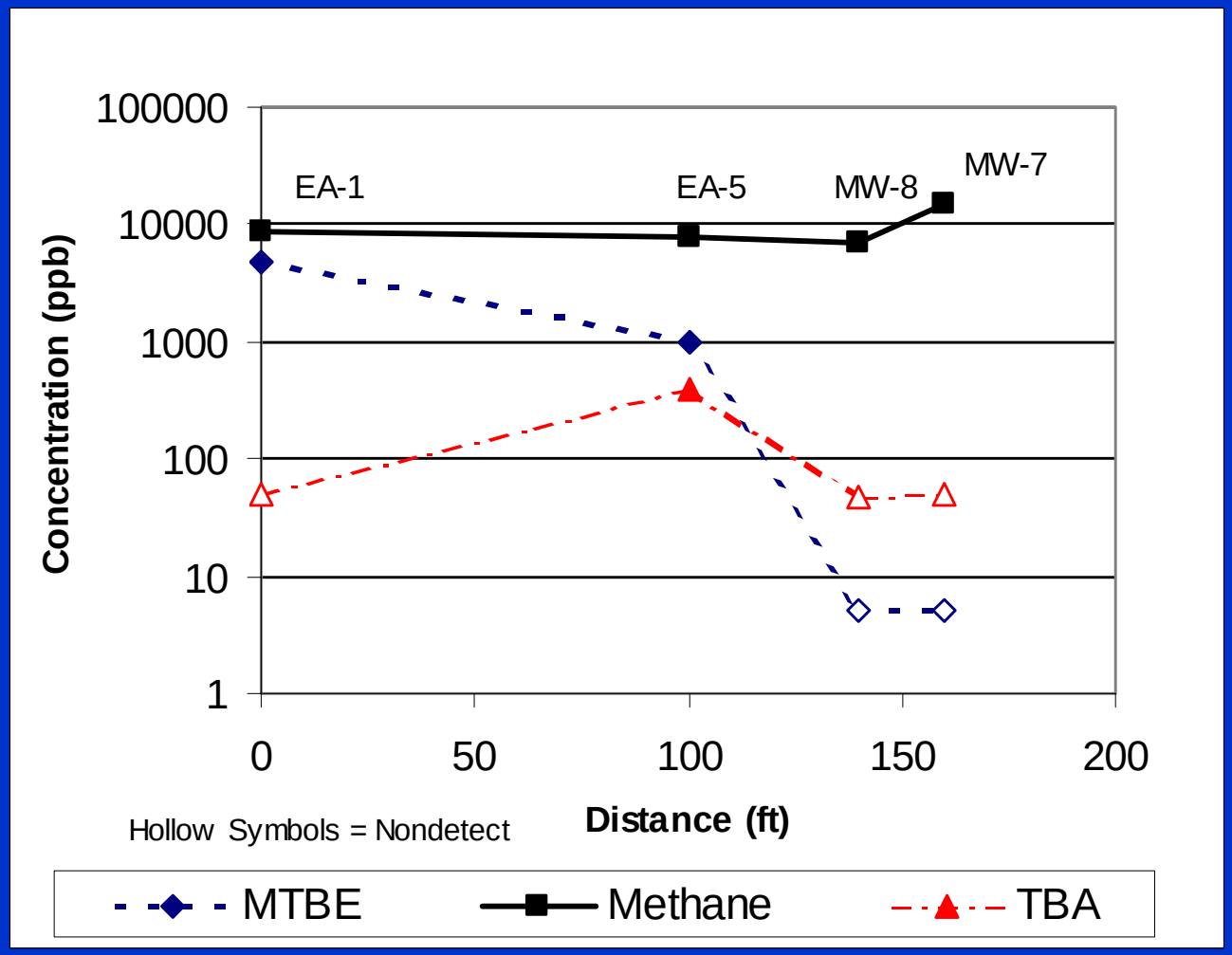
Millbrae, CA
EA-1 MTBE and Benzene vs. Time



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

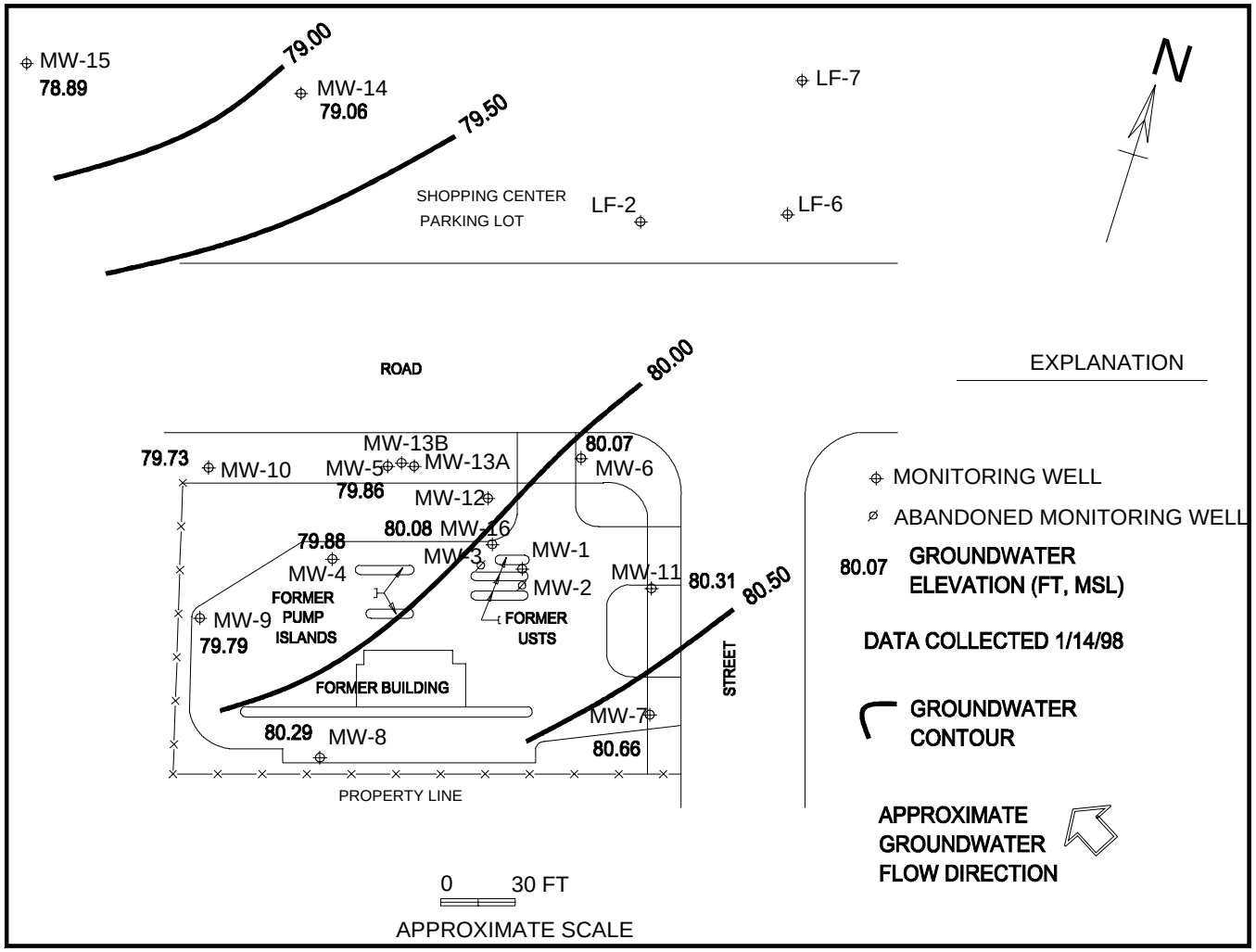
Millbrae, CA
MTBE, Methane, and TBA vs. Distance



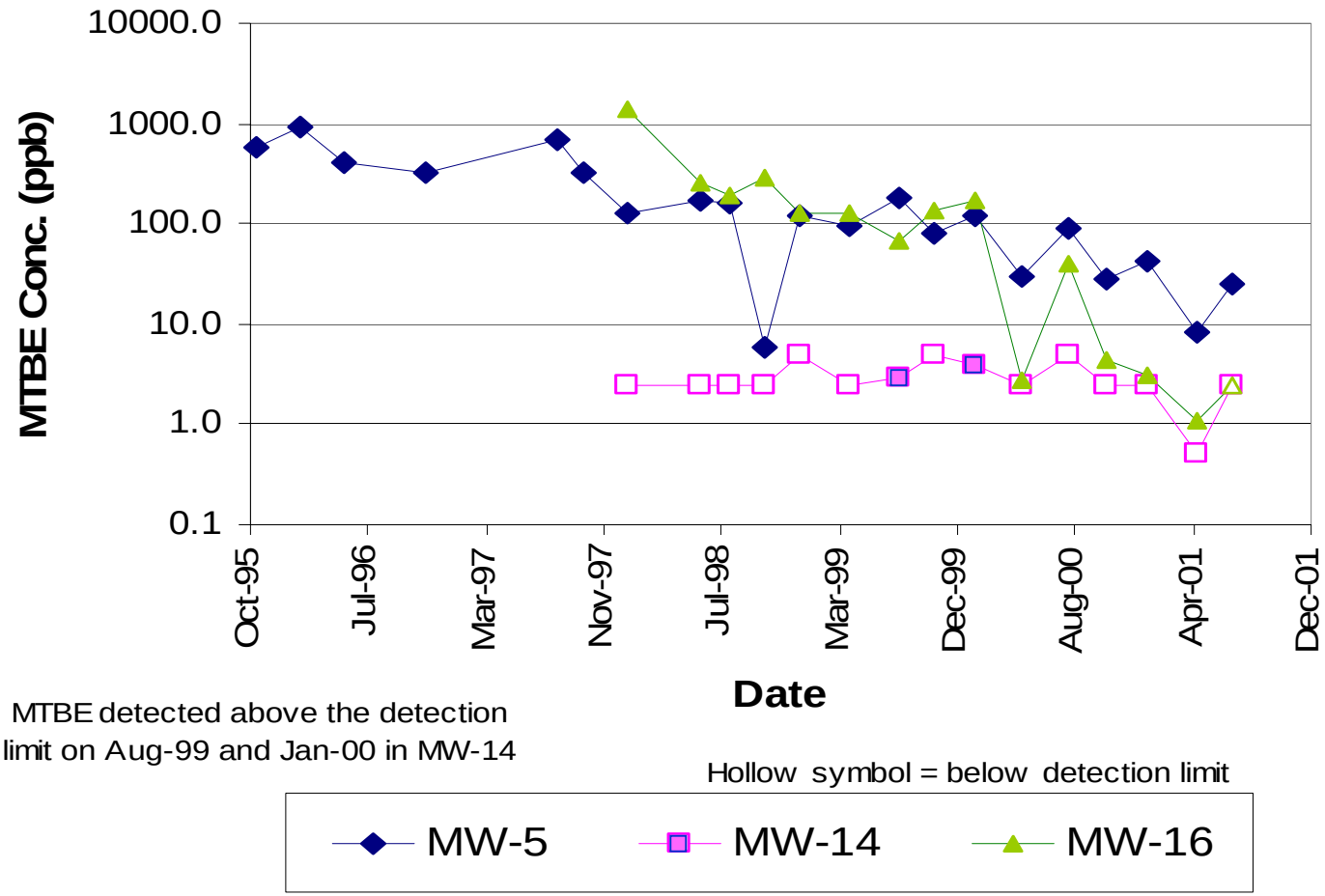
Millbrae, CA Site Summary

- 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



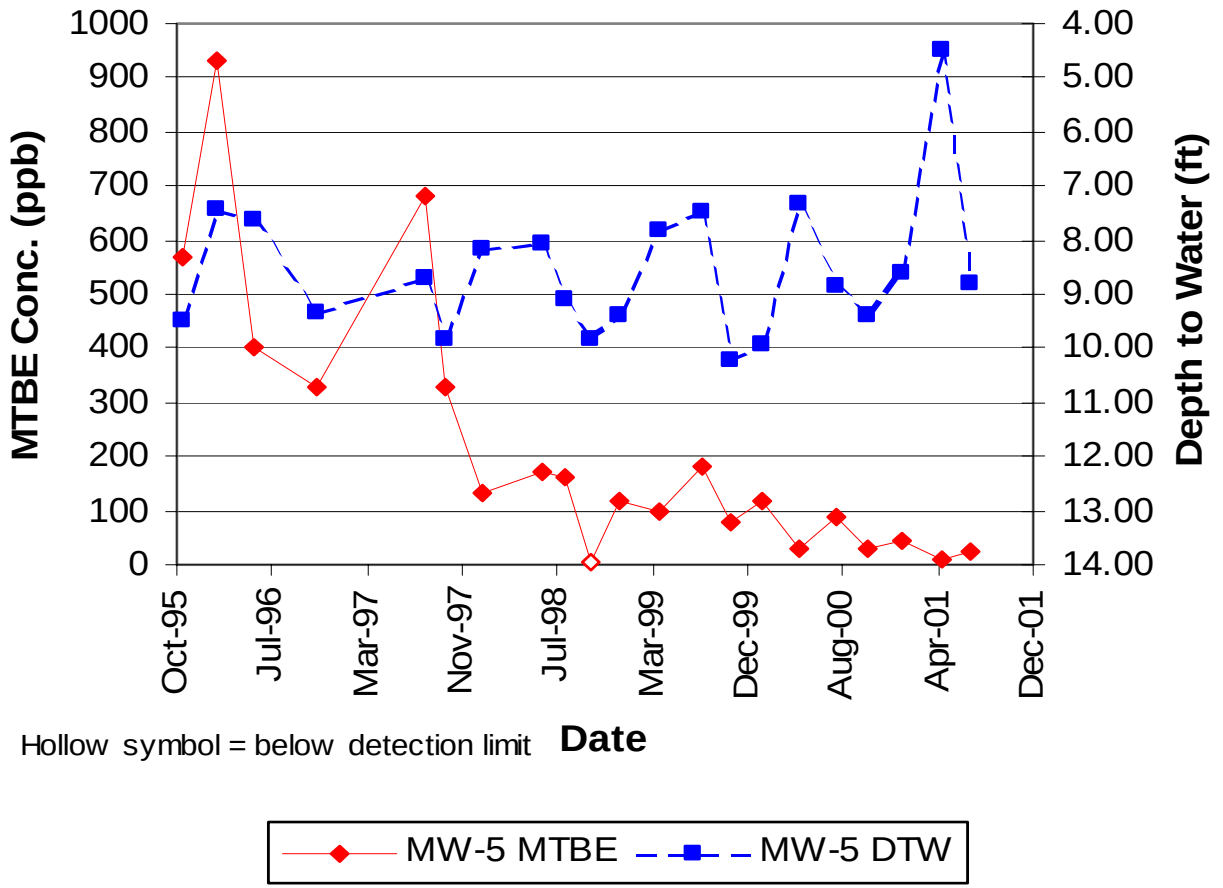
San Jose, CA
MTBE Concentration vs. Time



MTBE detected above the detection limit on Aug-99 and Jan-00 in MW-14

Hollow symbol = below detection limit

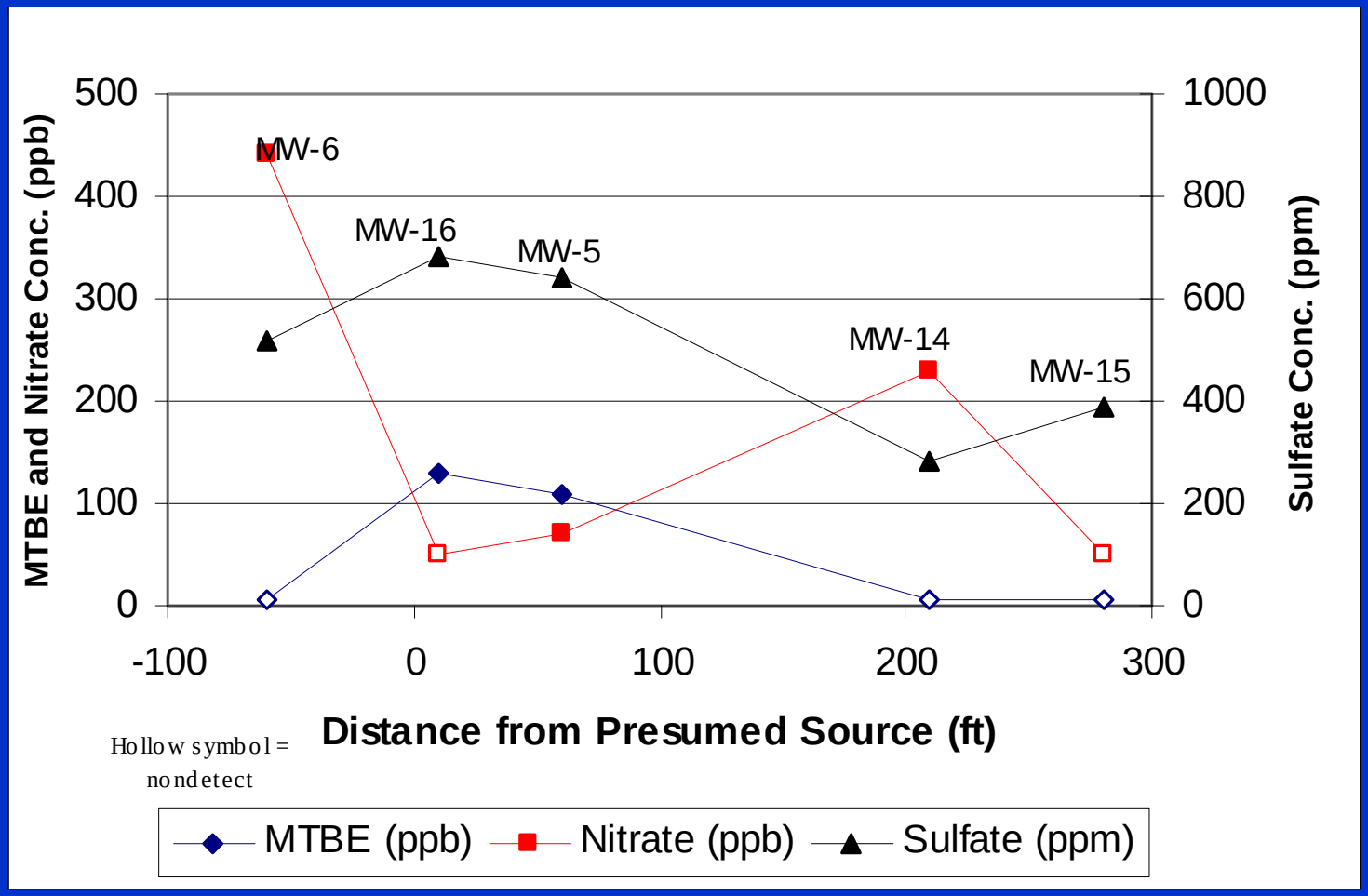
San Jose, CA
MW-5 MTBE Concentration and Depth to Water vs. Time



San Jose, CA
Plume Geochemistry (8/15/00)

Well	Distance (ft)	MTBE (ppb)	BTEX (ppb)	DO (ppm)	Nitrate (ppb)	Sulfate (ppm)	Methane (ppb)
MW-6	-60 (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

- 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

- 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

- 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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