Confirming Natural Attenuation of a Large MTBE and TBA Plume

SAM Fall Forum 2006
September 20

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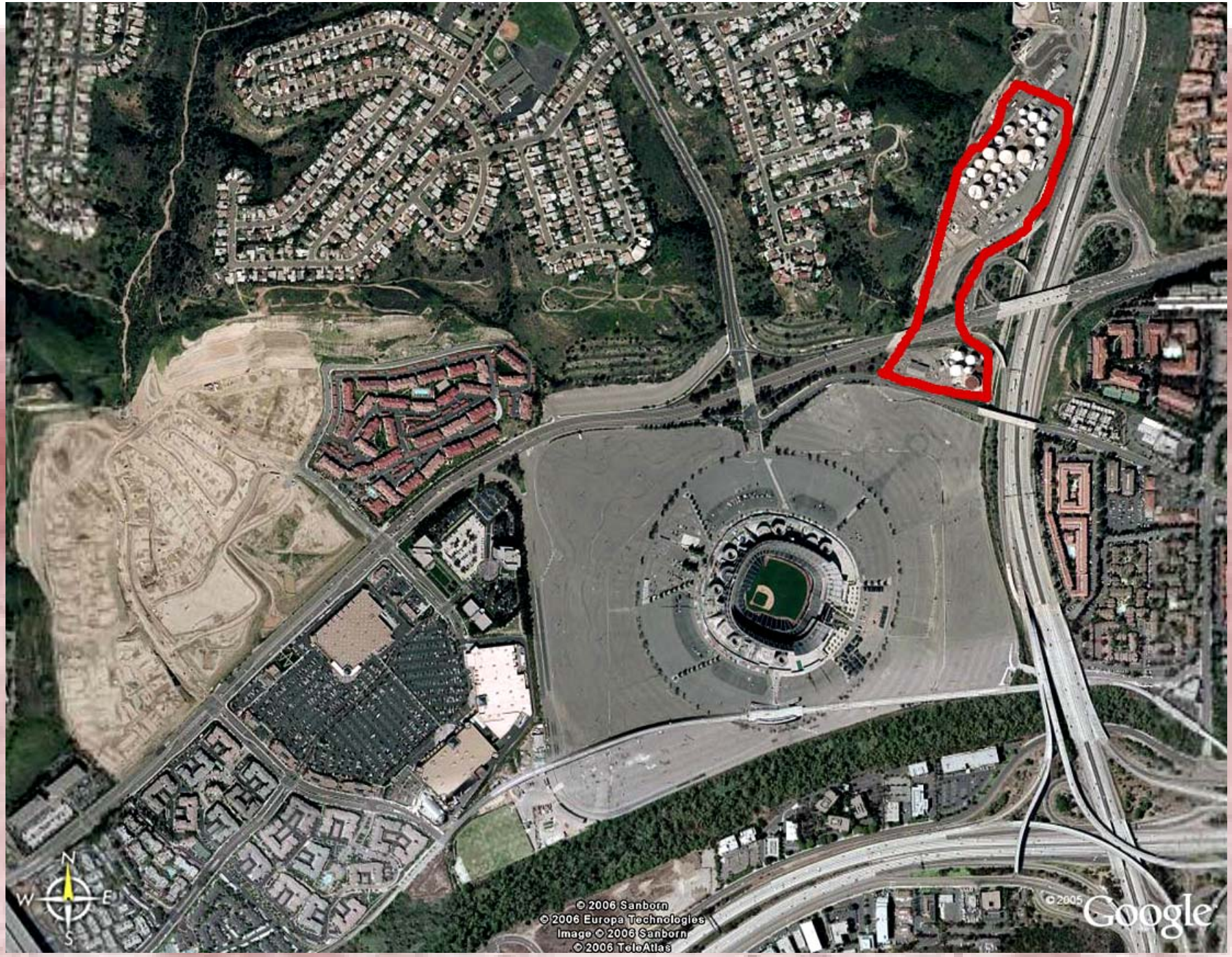
LFR

PM1 - ***Methylobium petroleophilum***
Department of Energy's Joint Genome Institute
University of California
http://genome.jgi-psf.org/finished_microbes/metpe/metpe.home.htm

Subject Site

- Southern California Petroleum Terminal
- 20 to 60 feet of complex, stratified, heterogeneous alluvium over Friars Formation bedrock
- Depth to groundwater ~15 to 25 feet
- Groundwater velocities 0.5 to 20 feet/day
- Poor water quality, high TDS, chlorides, bicarbonate, Fe, Mn
- Evidence of MTBE-degrading microbes (UCDavis study)


N
W
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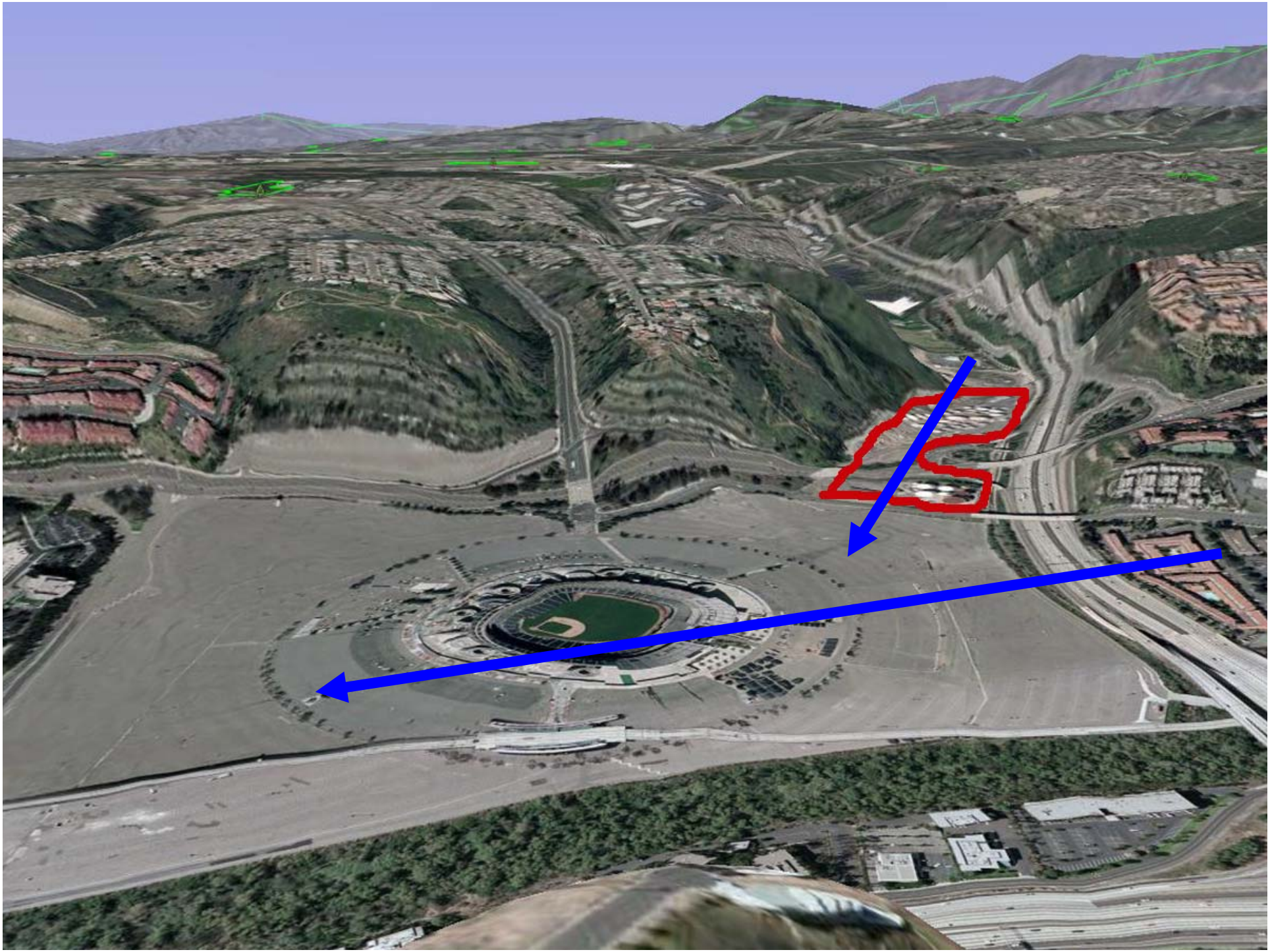
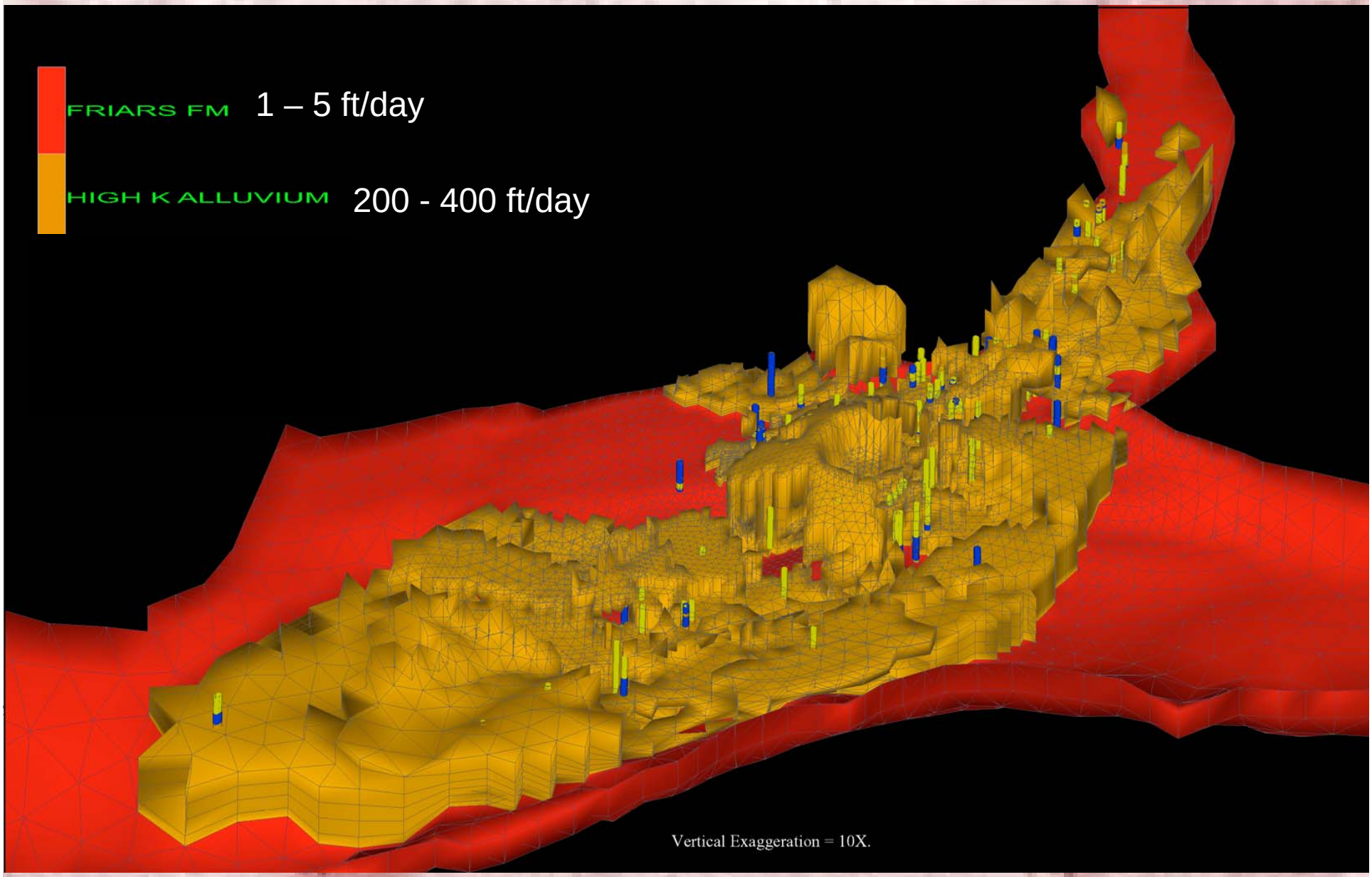
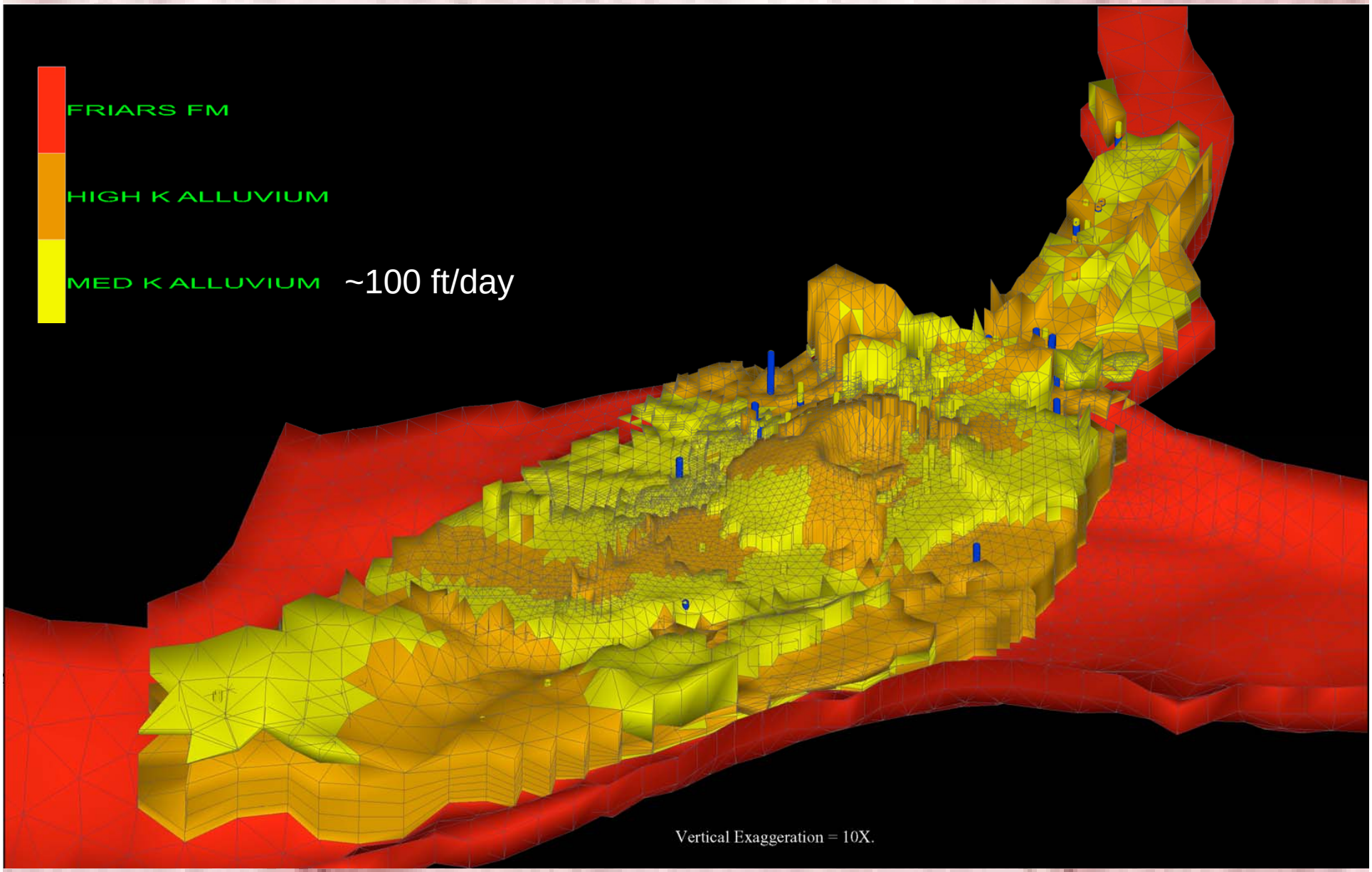
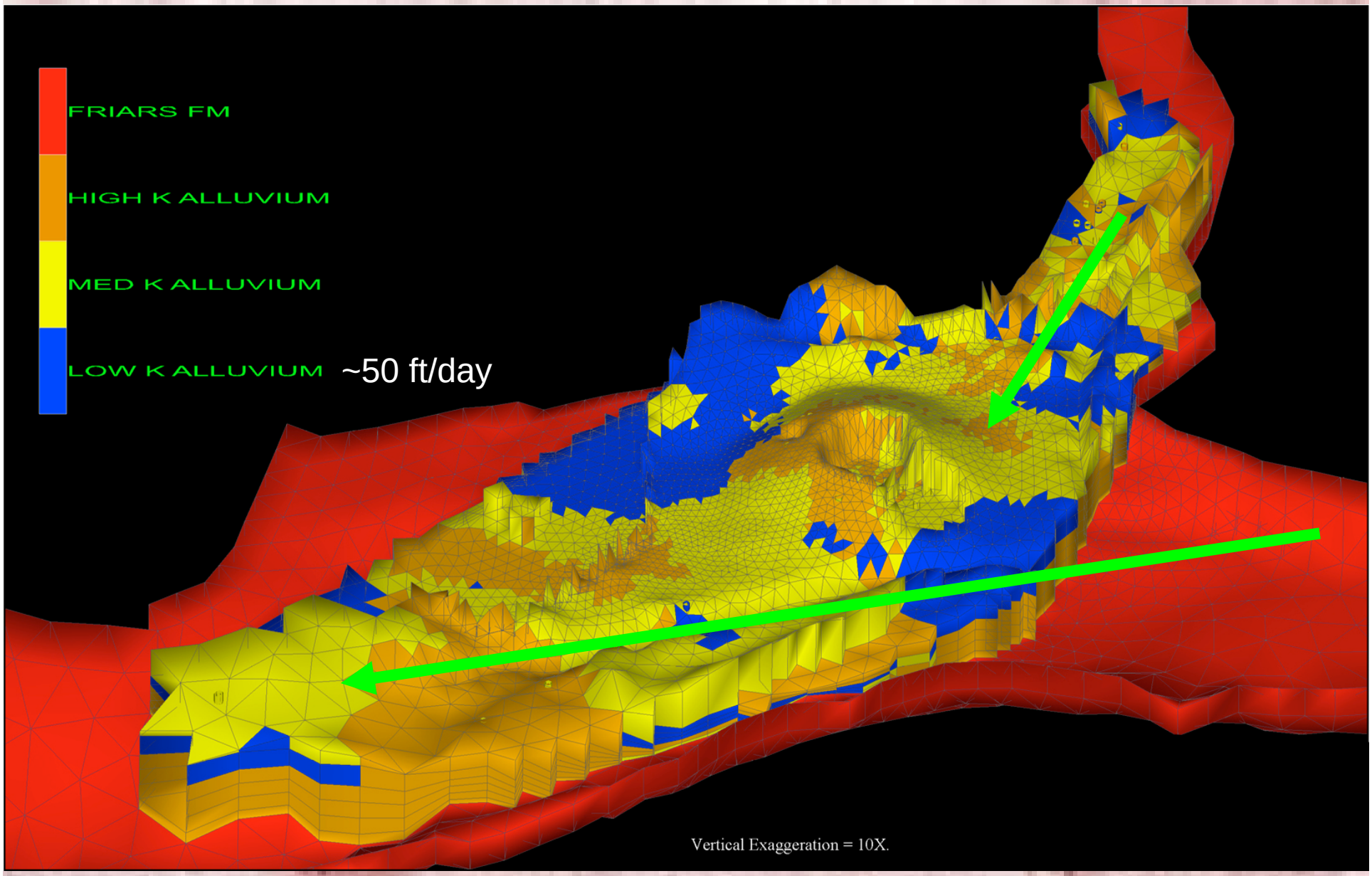
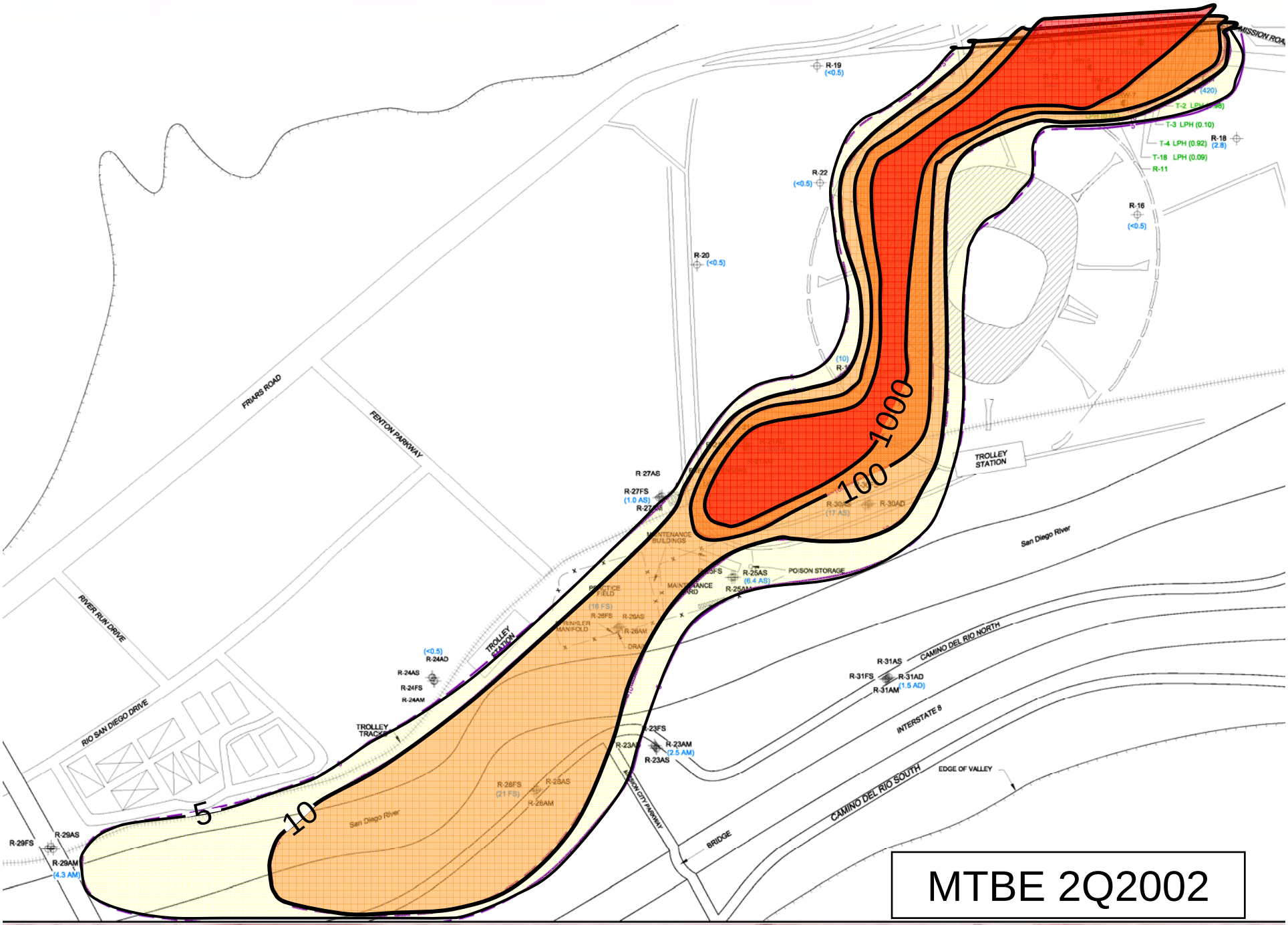
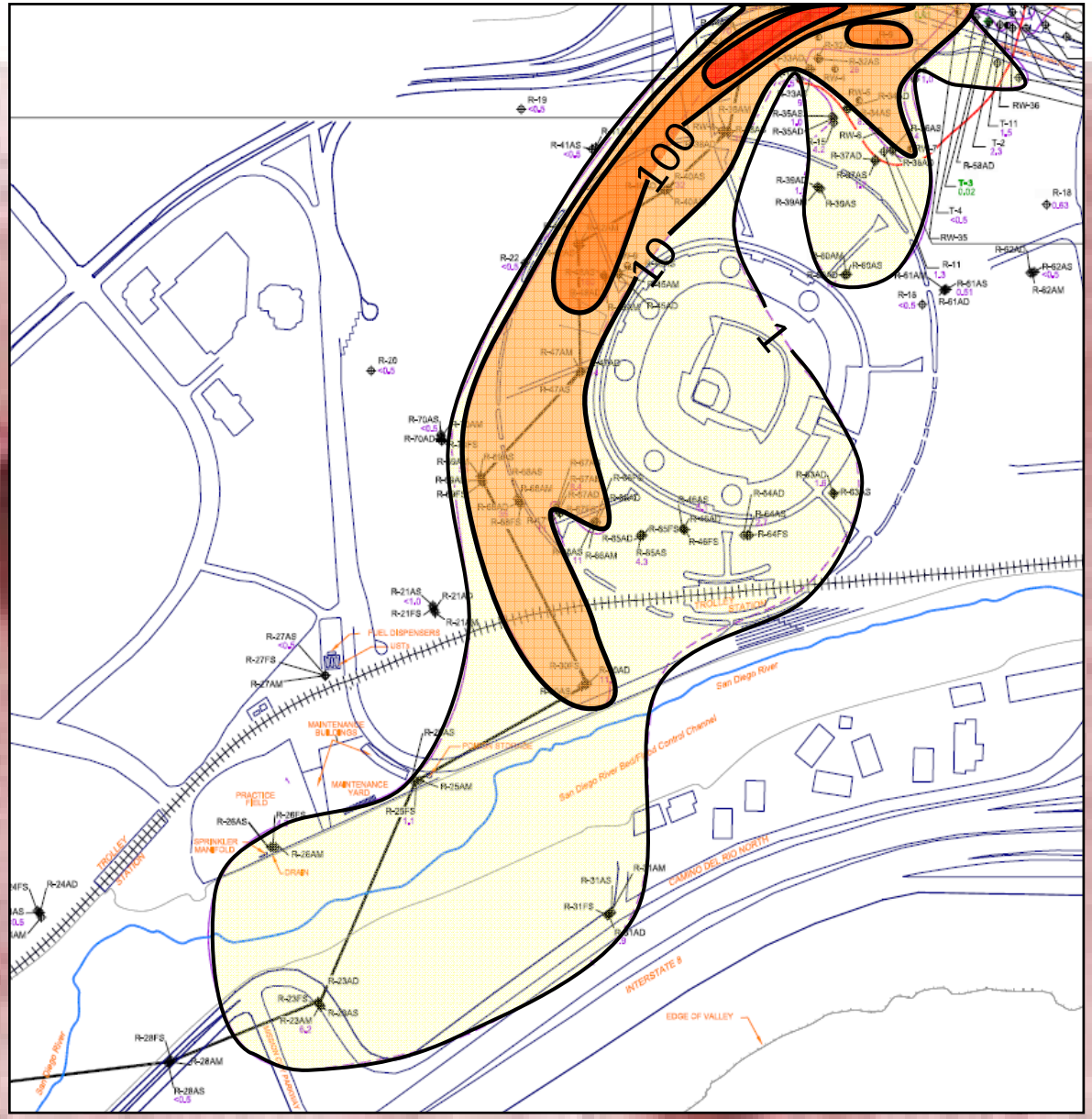



FRIARS FM
1 – 5 ft/day
HIGH K ALLUVIUM
200 - 400 ft/day
Vertical Exaggeration = 10X.

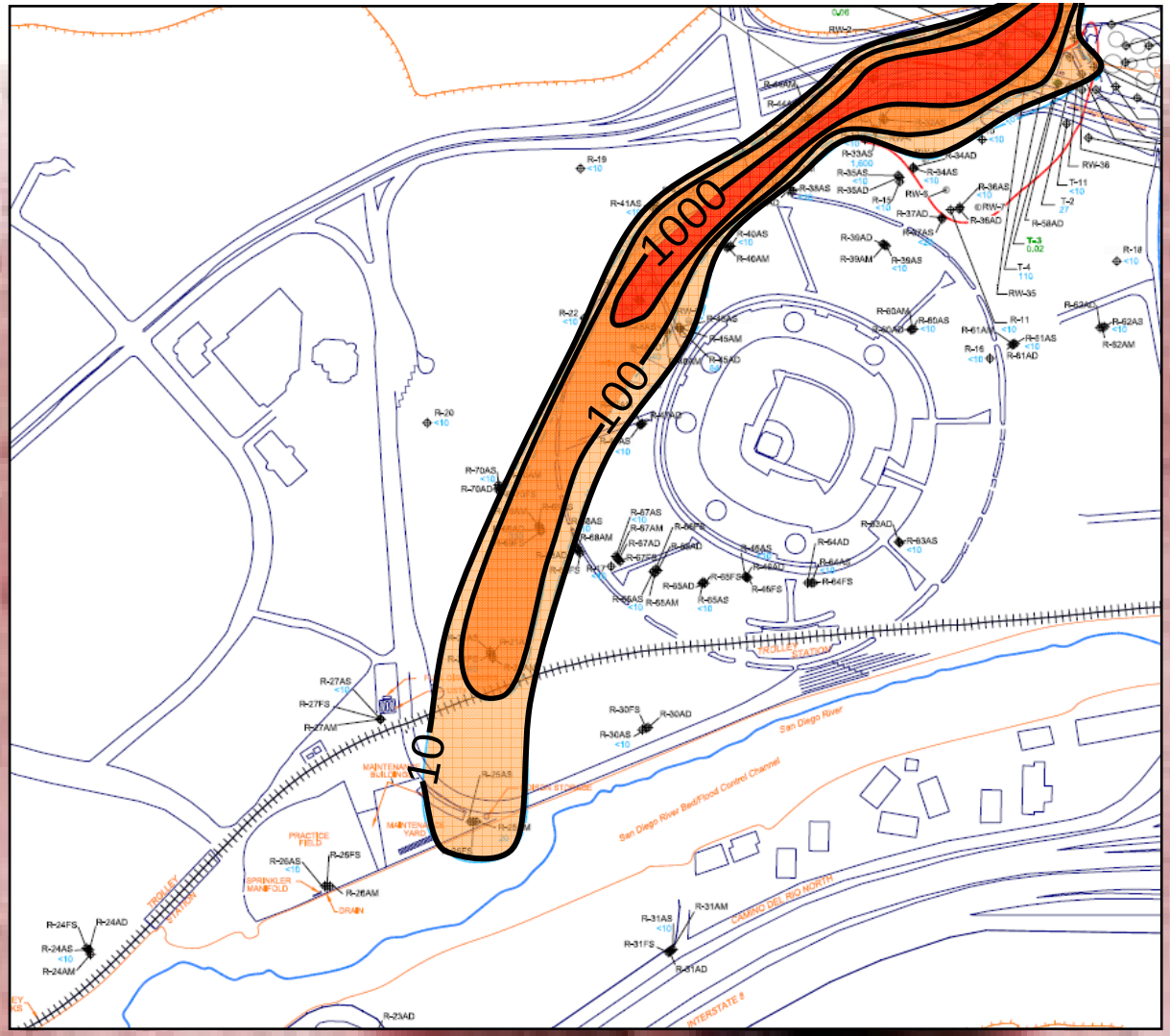

FRIARS FM
HIGH K ALLUVIUM
MED K ALLUVIUM
~100 ft/day
Vertical Exaggeration = 10X.


FRIARS FM
HIGH K ALLUVIUM
MED K ALLUVIUM
LOW K ALLUVIUM
~50 ft/day
Vertical Exaggeration = 10X.


MTBE 2Q2002
5
10
100
1000
FRIARS ROAD
FENTON PARKWAY
RIVER RUN DRIVE
RIO SAN DIEGO DRIVE
TROLLEY STATION
TROLLEY TRACKS
TROLLEY STATION
MISSION ROAD
San Diego River
POISON STORAGE
CAMINO DEL RIO NORTH
CAMINO DEL RIO SOUTH
INTERSTATE 8
EDGE OF VALLEY
BRIDGE
R-19 (<0.5)
R-22 (<0.5)
R-20 (<0.5)
R-16 (<0.5)
R-18 (2.8)
T-3 LPH (0.10)
T-4 LPH (0.92)
T-18 LPH (0.09)
R-11
R-27AS
R-27FS (1.0 AS)
R-25AS (6.4 AS)
R-24AD (<0.5)
R-24AS
R-24FS
R-24AM
R-23FS
R-23AM (2.5 AM)
R-23AS
R-31AS
R-31FS
R-31AD (1.5 AD)
R-31AM
R-29FS
R-29AS
R-29AM (4.3 AM)


100
10
1
FUEL DISPENSERS
MAINTENANCE BUILDINGS
MAINTENANCE YARD
PRACTICE FIELD
SPRINKLER MANIFOLD
DRAIN
TROLLEY STATION
San Diego River
San Diego River Bed/Flood Control Channel
CAMINO DEL RIO NORTH
INTERSTATE 8
EDGE OF VALLEY

MTBE 4Q2005


1000
100
10
San Diego River
San Diego River Bed/Flood Control Channel
LAMAR DEL RIO NORTH
INTERSTATE 8
TROLLEY STATION
PRACTICE FIELD
SPRINKLER MANIFOLD
DRAIN

TBA 4Q2005

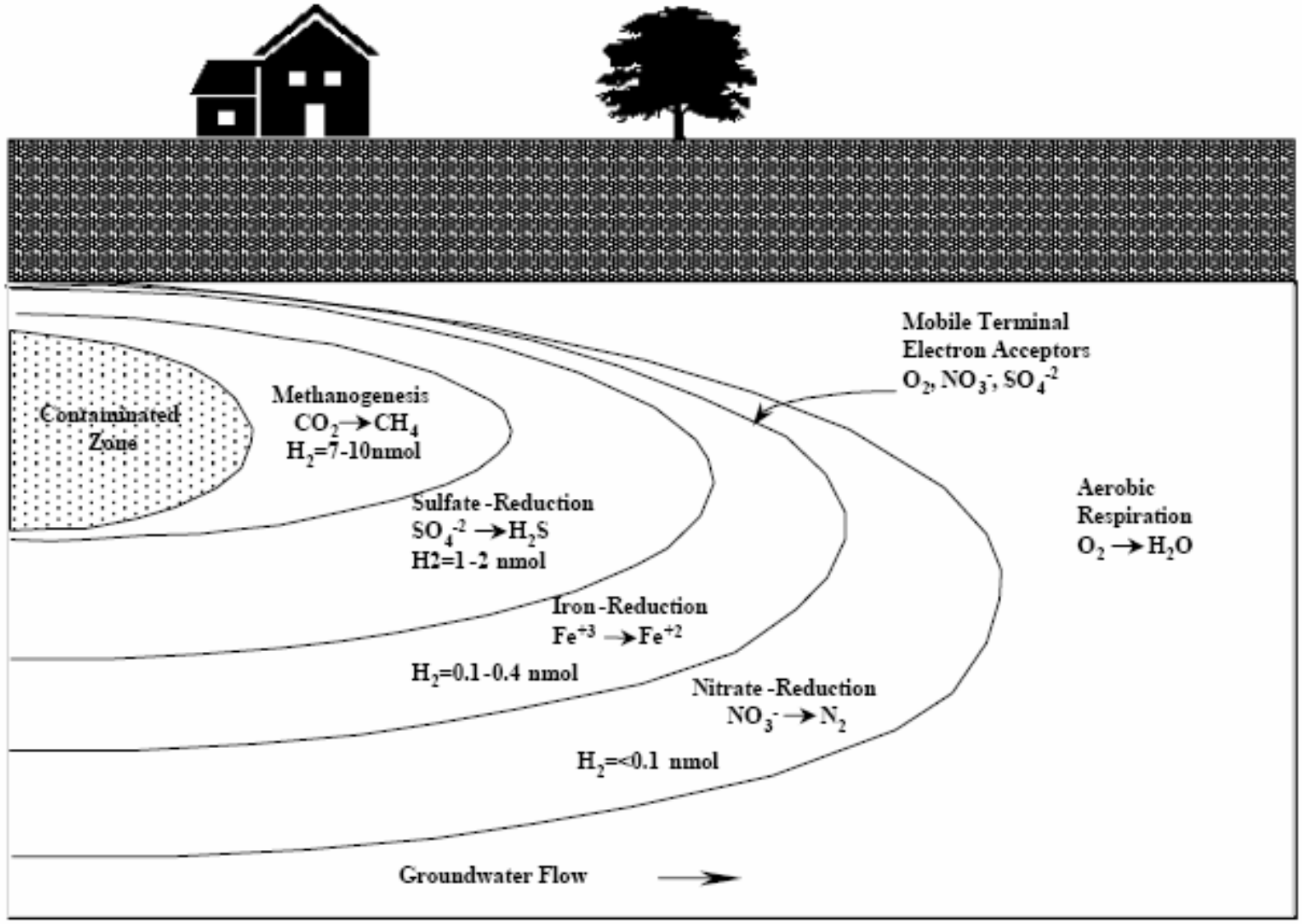


Figure 3-2. Idealized Terminal Electron Acceptor Process

ITRC, 2002 (http://www.itrcweb.org/Documents/ISB-8.pdf)

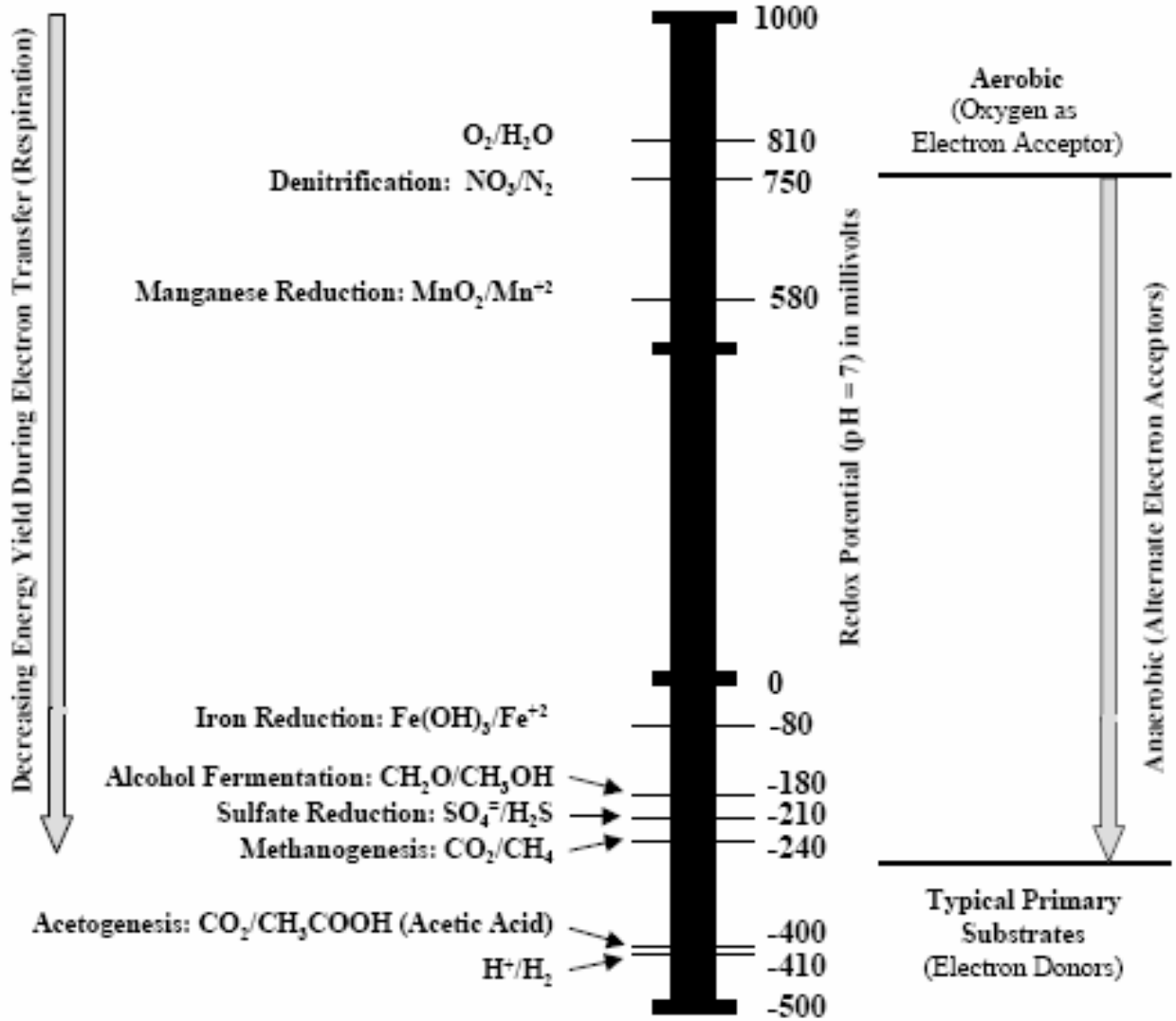
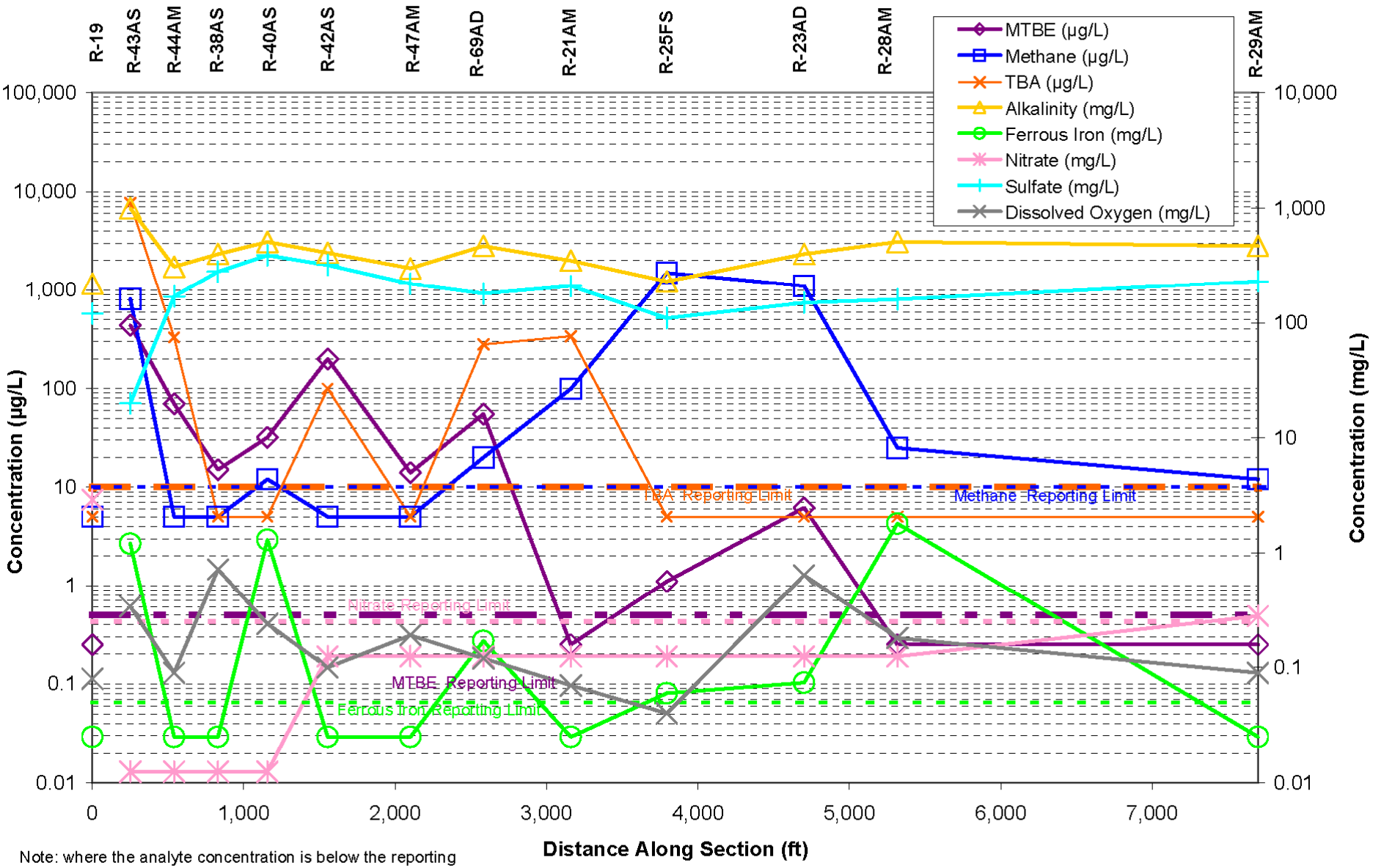


Figure 3-1. Estimated Oxidation-Reduction Potentials of Commonly Monitored Chemical Specie

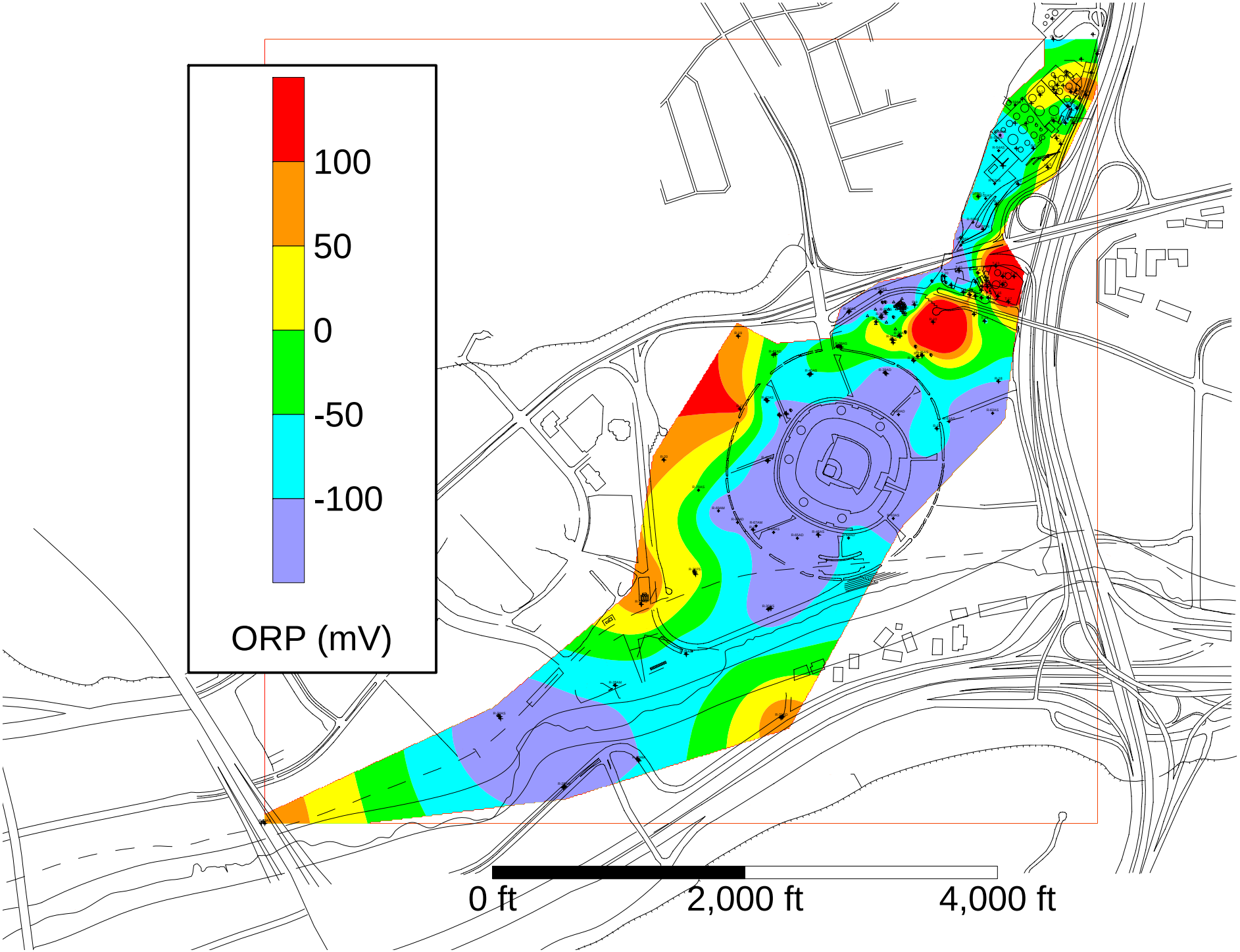
ITRC, 2002 (http://www.itrcweb.org/Documents/ISB-8.pdf)

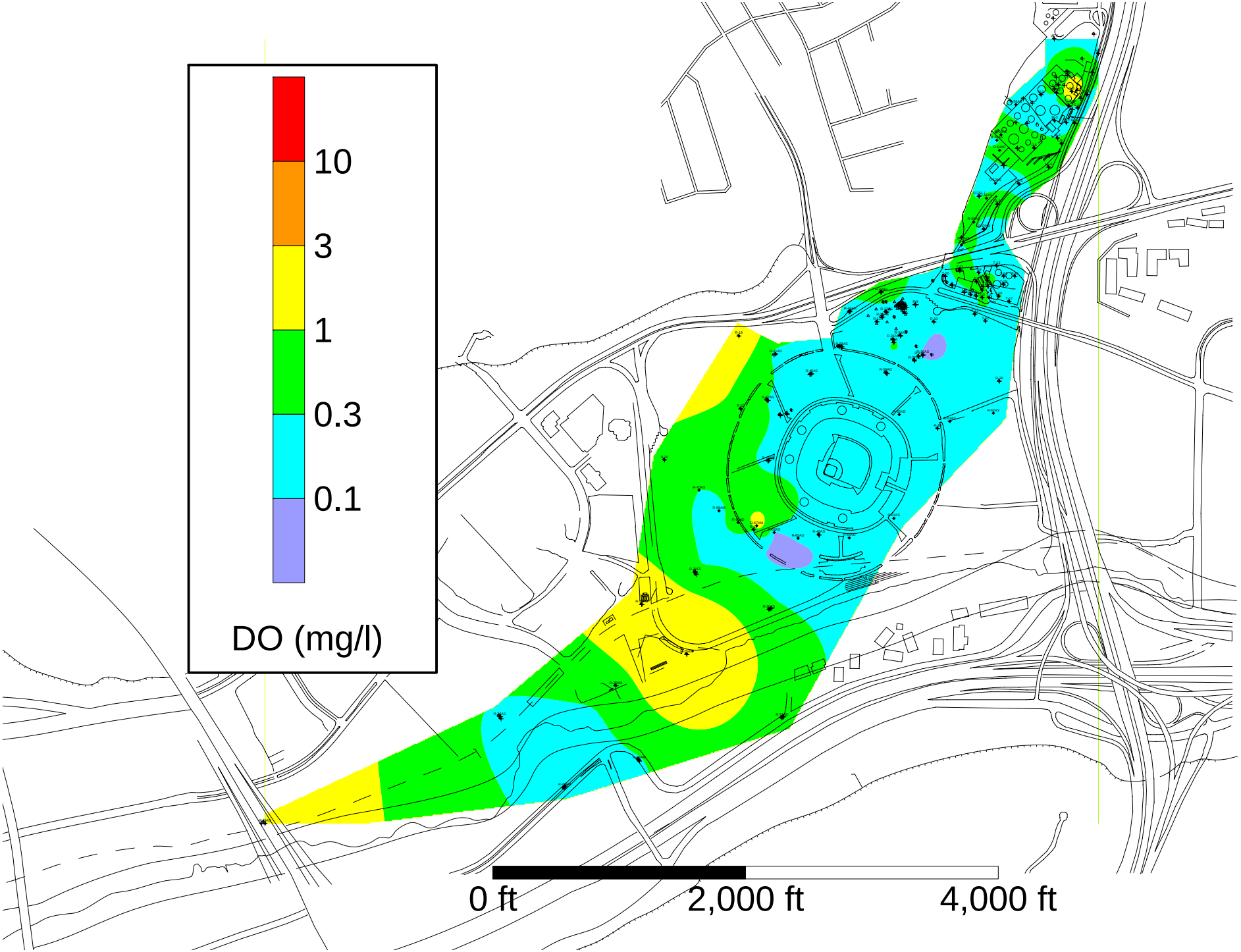


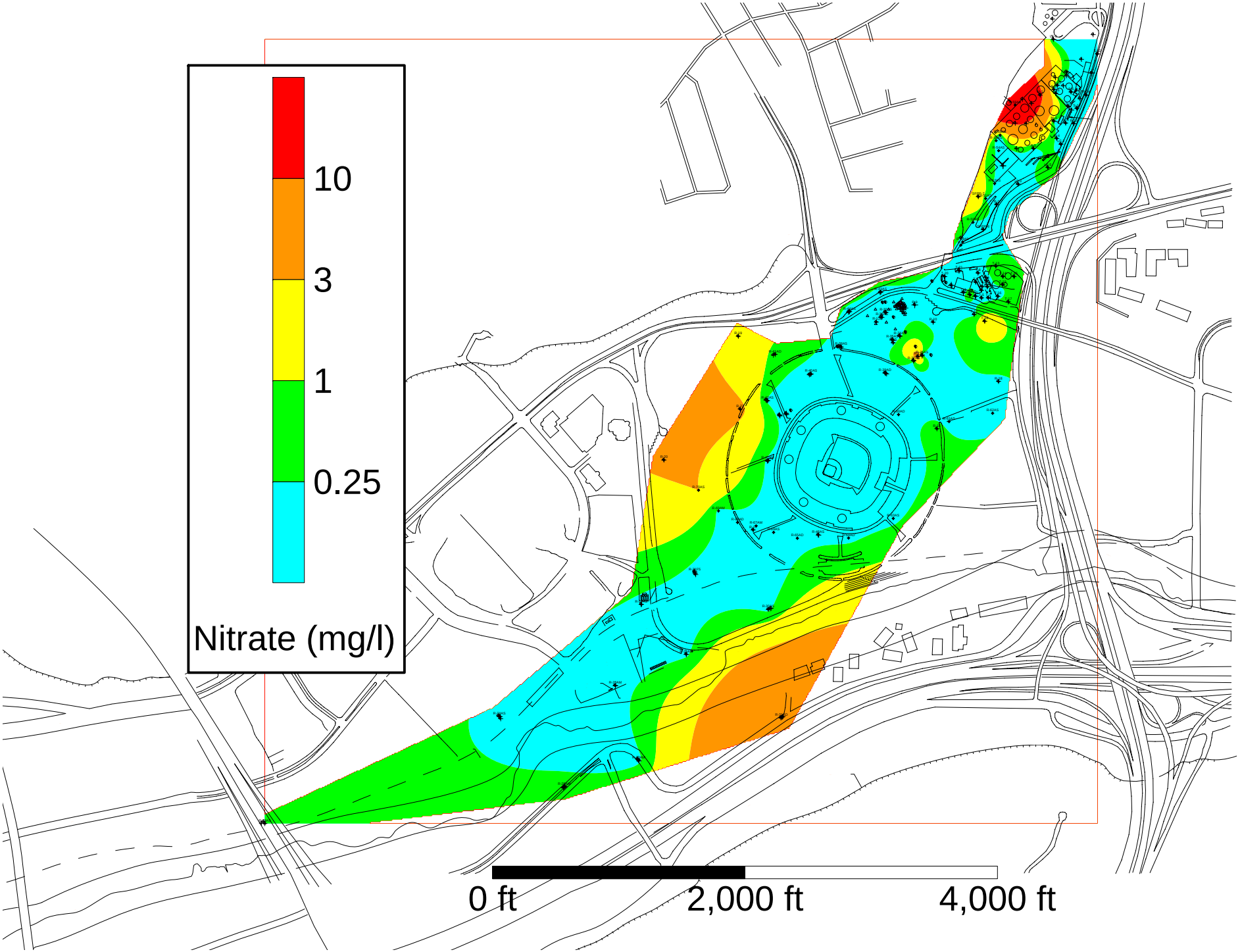
Note: where the analyte concentration is below the reporting limit, the value shown is one half the reporting limit

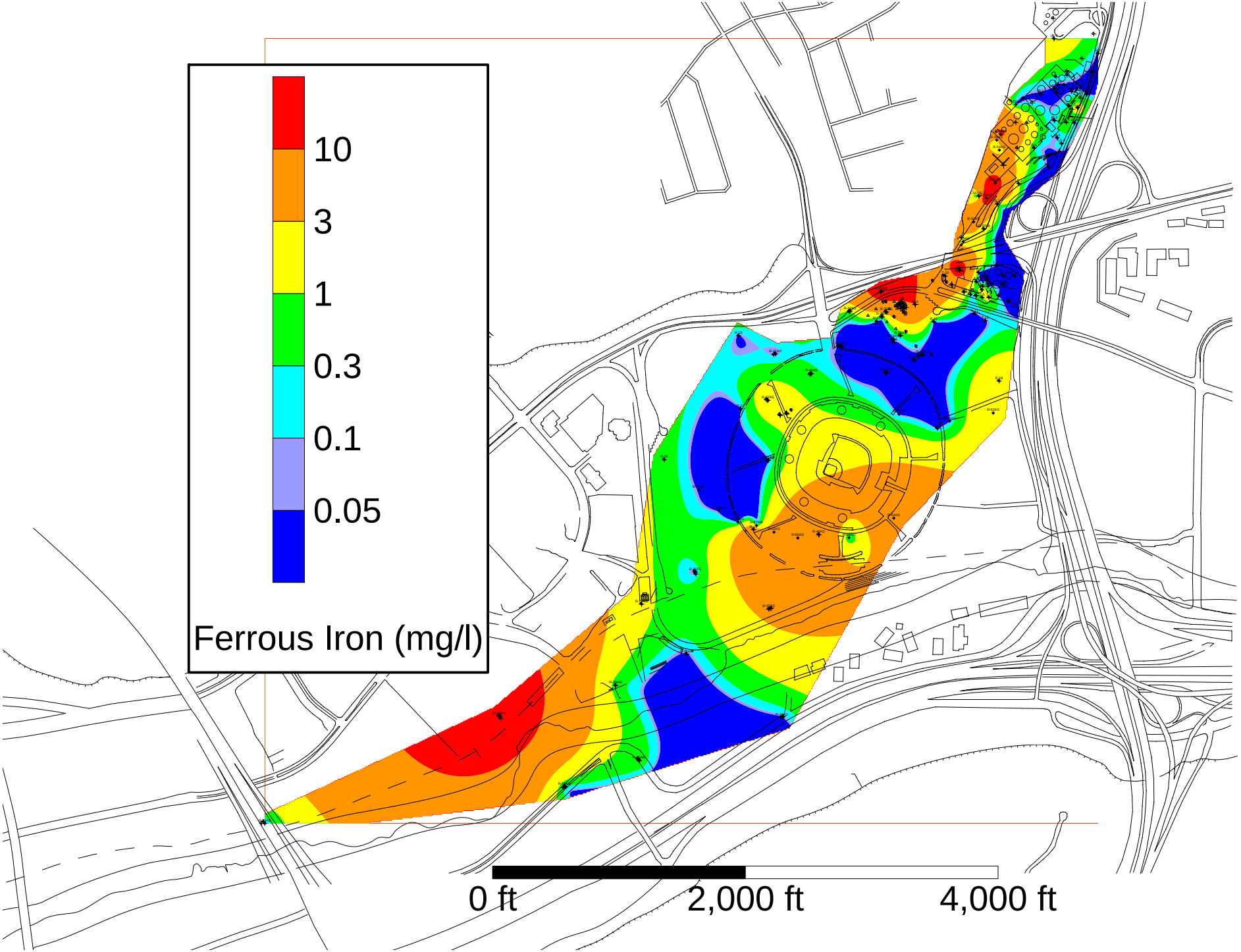
Biodegradation Assessment Activities

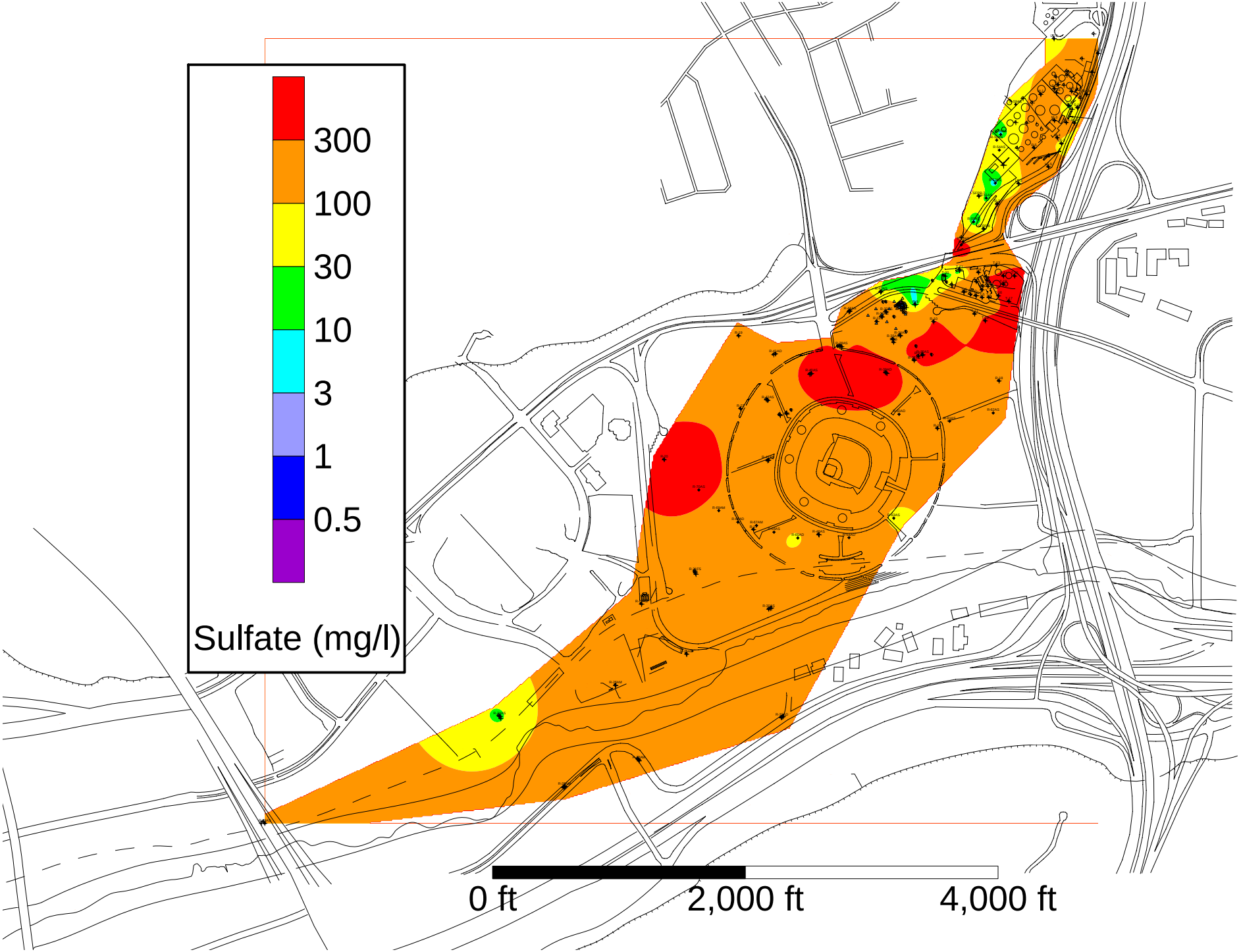
- Review of Historical Geochemical and Contaminant Data
- Field Microbial Assessment
- Aerobic and Anaerobic Microcosms
- Field Carbon and Hydrogen Isotope Data

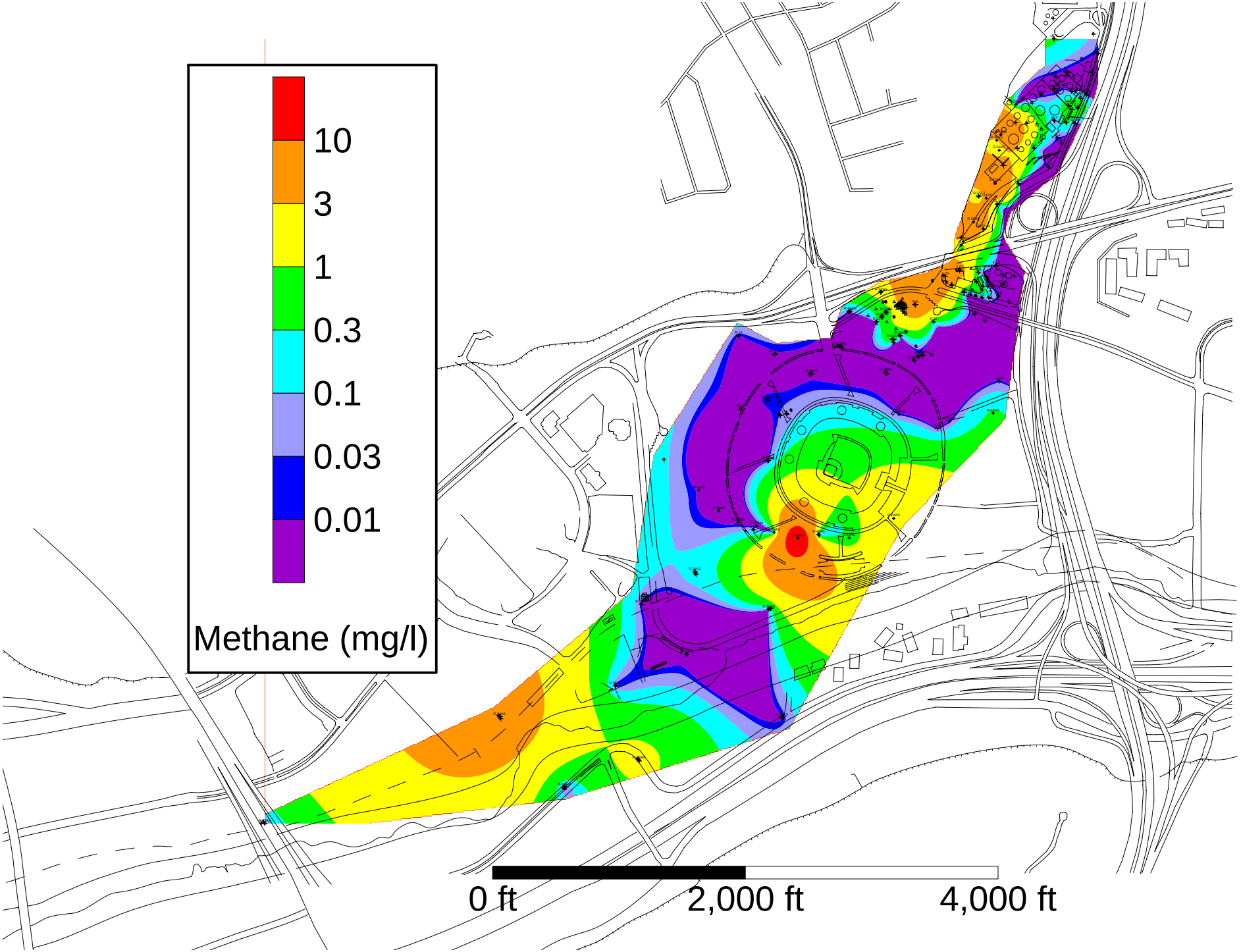

100
50
0
-50
-100
ORP (mV)
0 ft
2,000 ft
4,000 ft


10
3
1
0.3
0.1
DO (mg/l)
0 ft
2,000 ft
4,000 ft

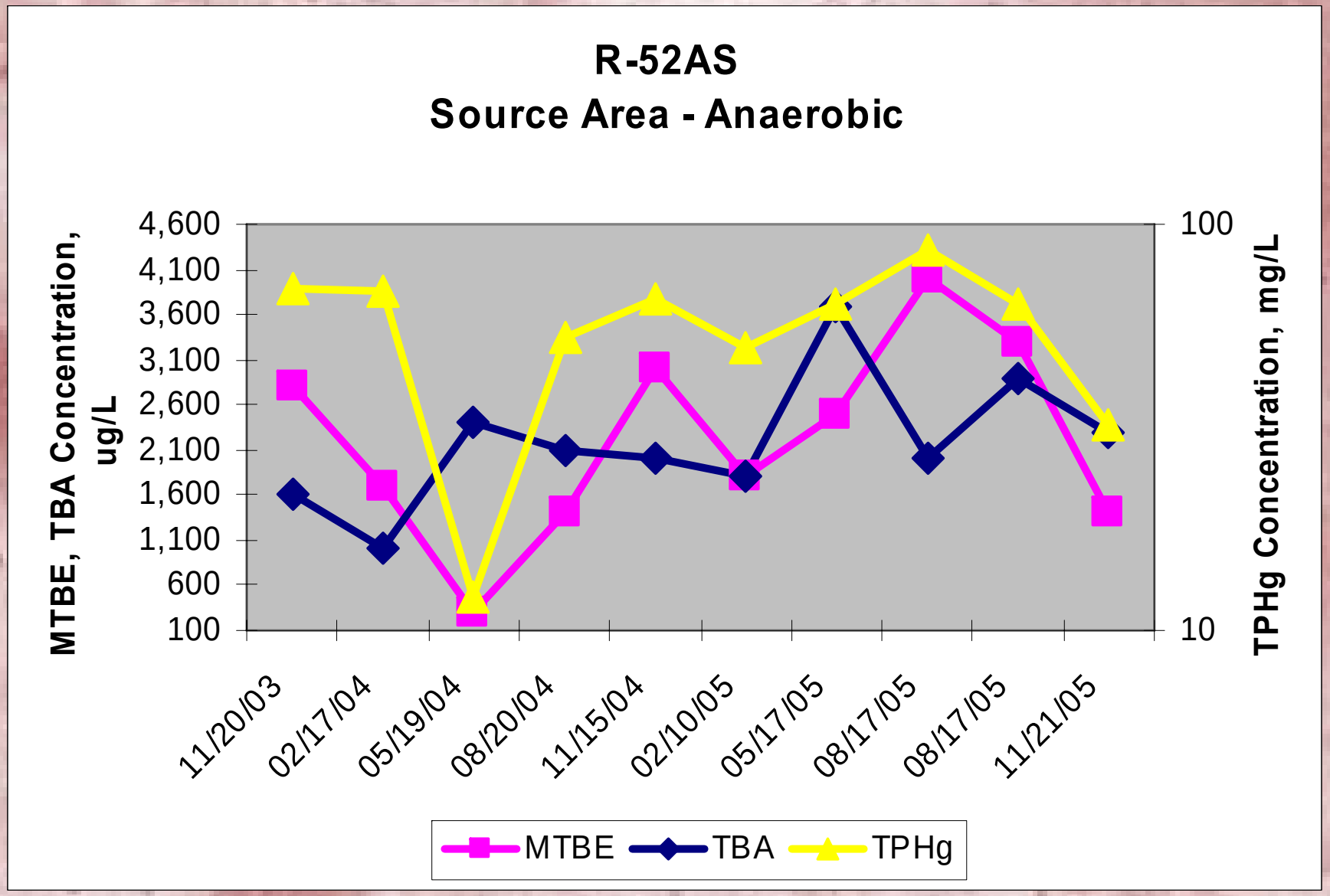

10
3
1
0.25
Nitrate (mg/l)
0 ft
2,000 ft
4,000 ft


10
3
1
0.3
0.1
0.05
Ferrous Iron (mg/l)
0 ft
2,000 ft
4,000 ft

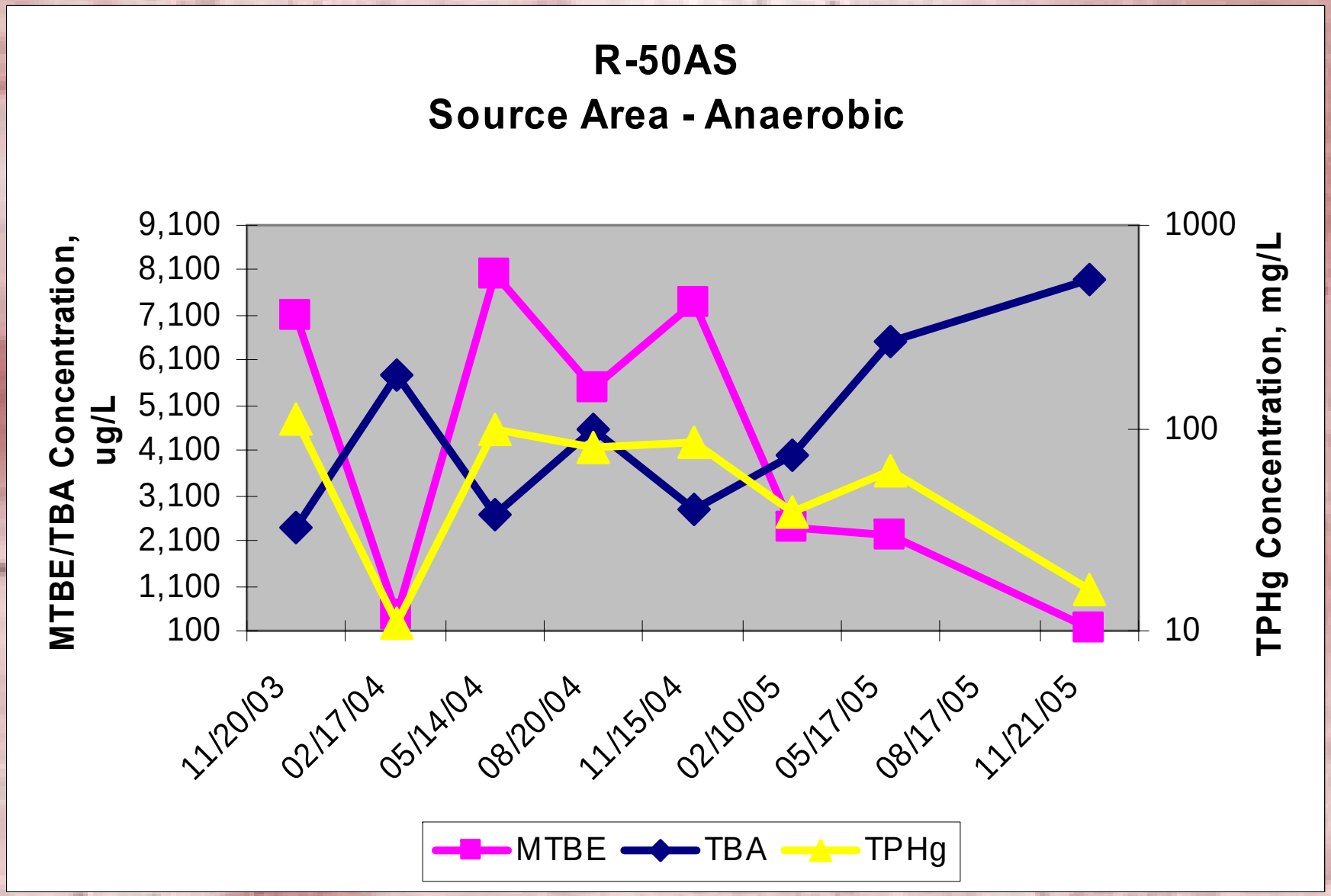

300
100
30
10
3
1
0.5
Sulfate (mg/l)
0 ft
2,000 ft
4,000 ft


10
3
1
0.3
0.1
0.03
0.01
Methane (mg/l)
0 ft
2,000 ft
4,000 ft

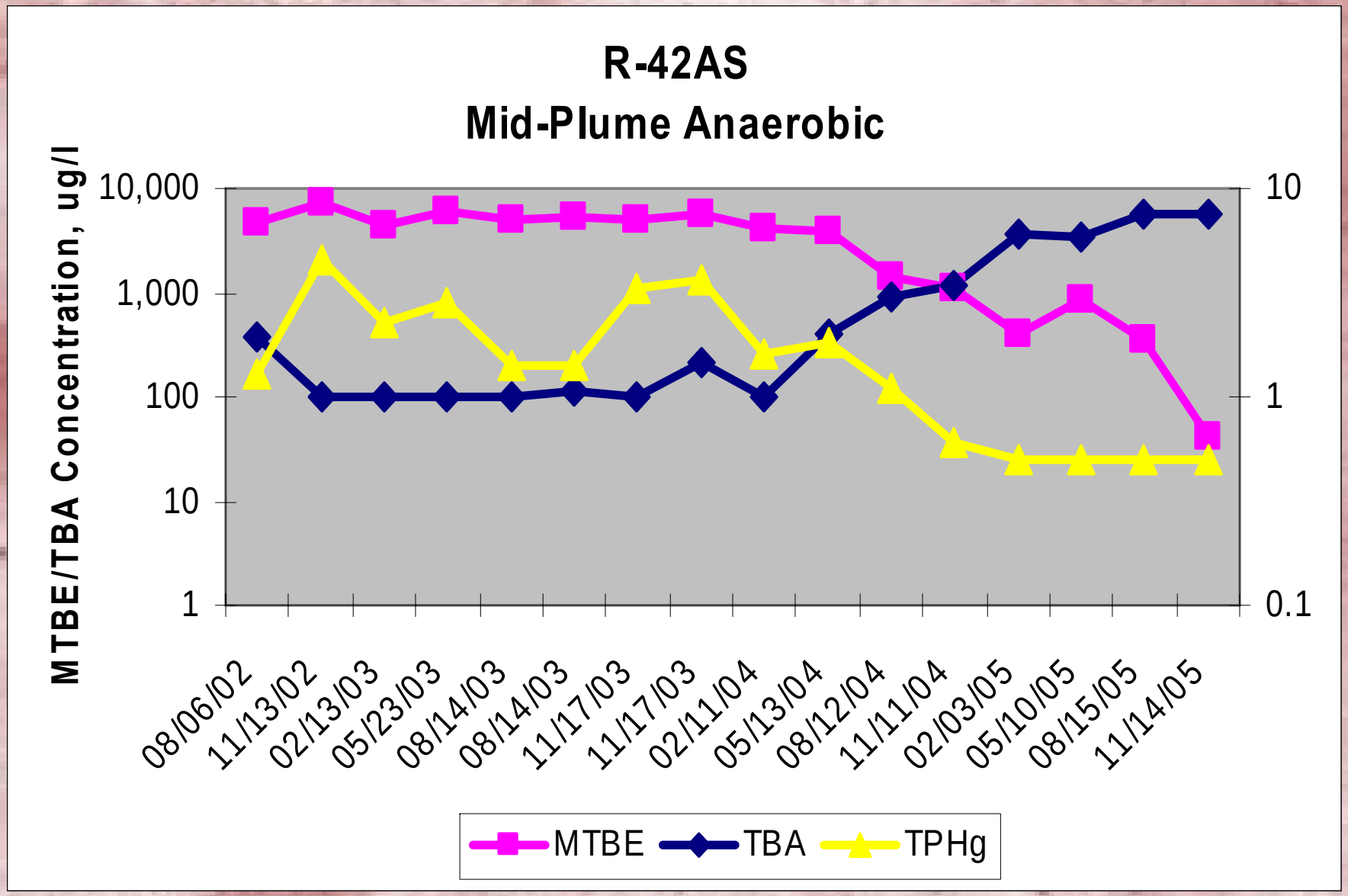
Time vs. Concentration Data



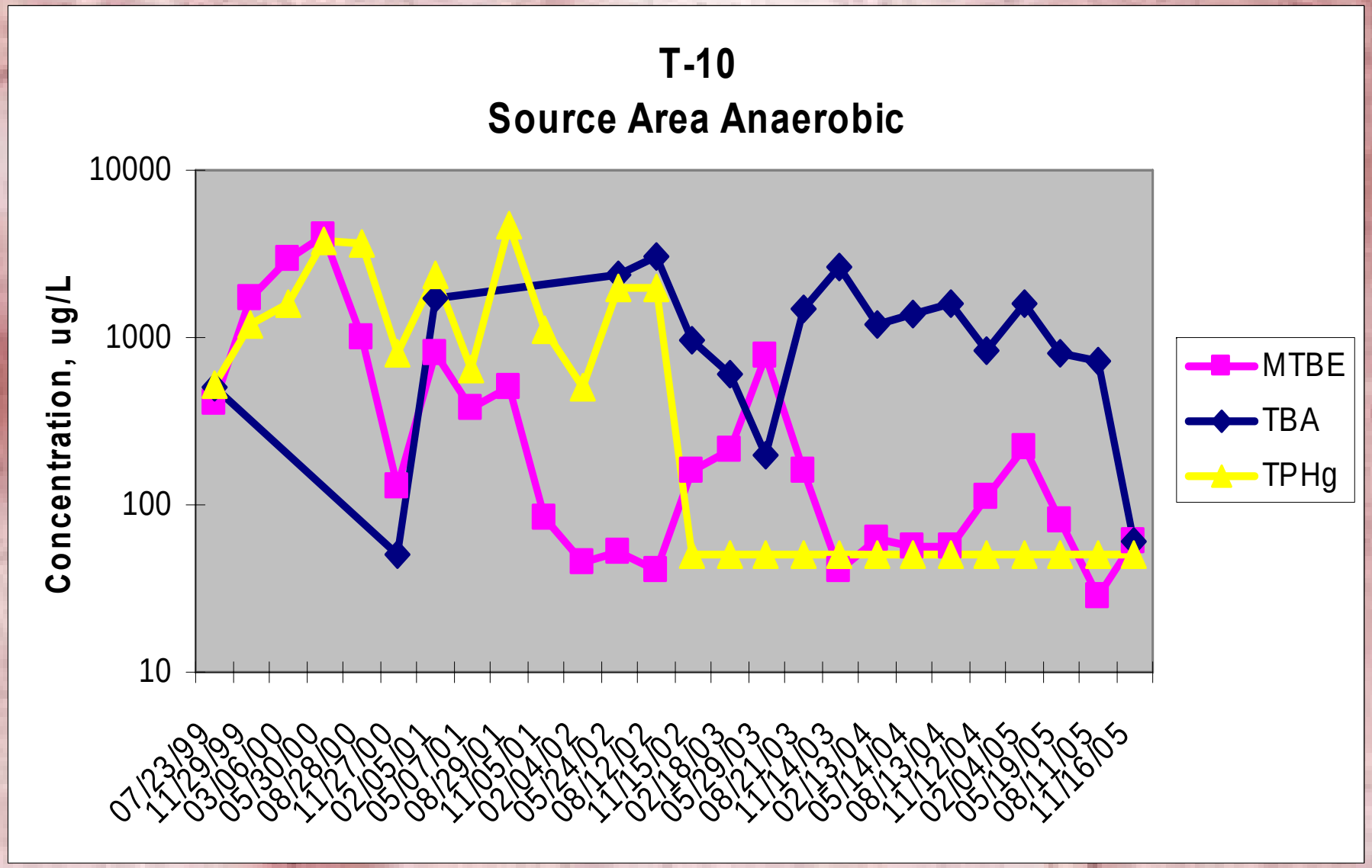
Time vs. Concentration Data



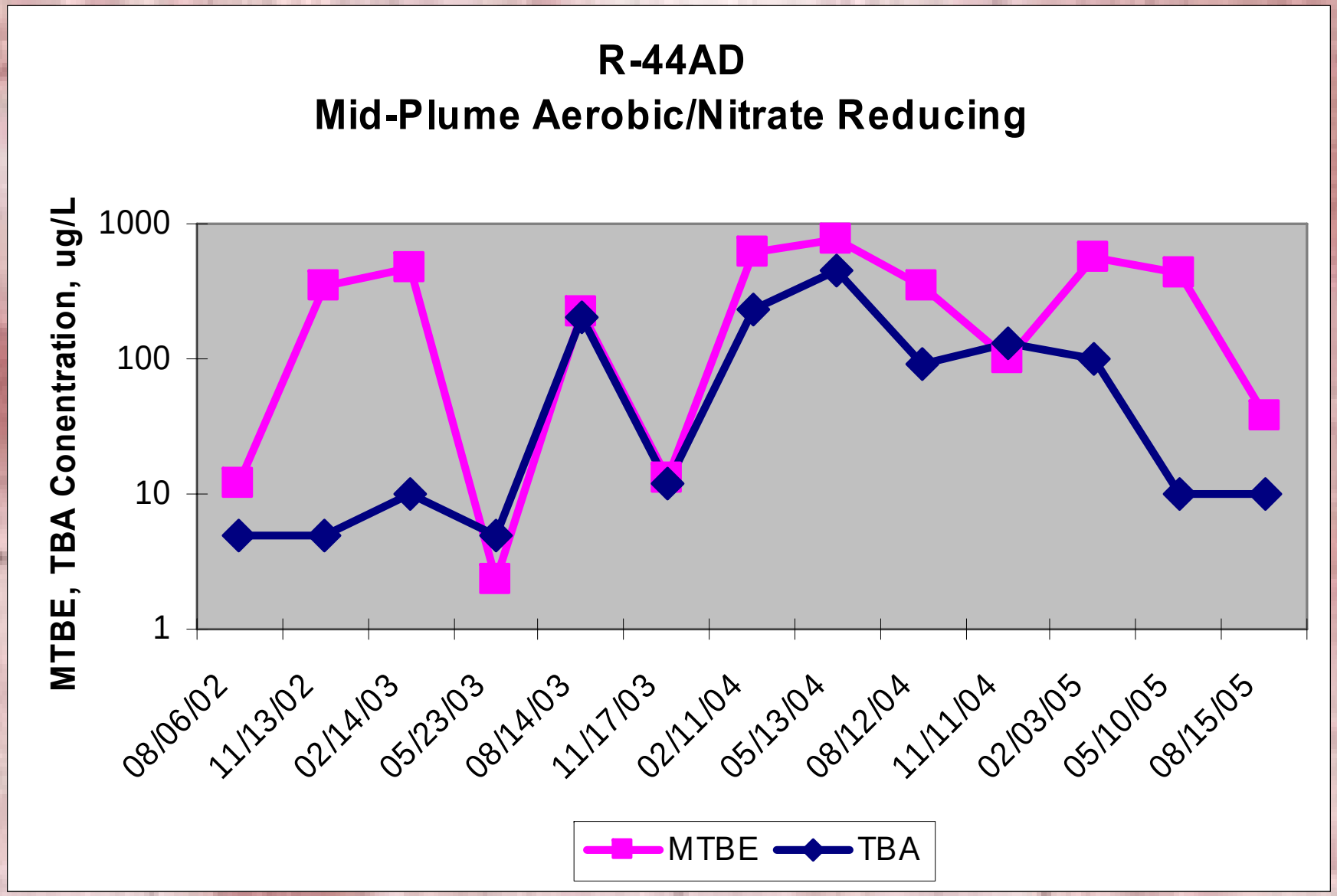
Time vs. Concentration Data



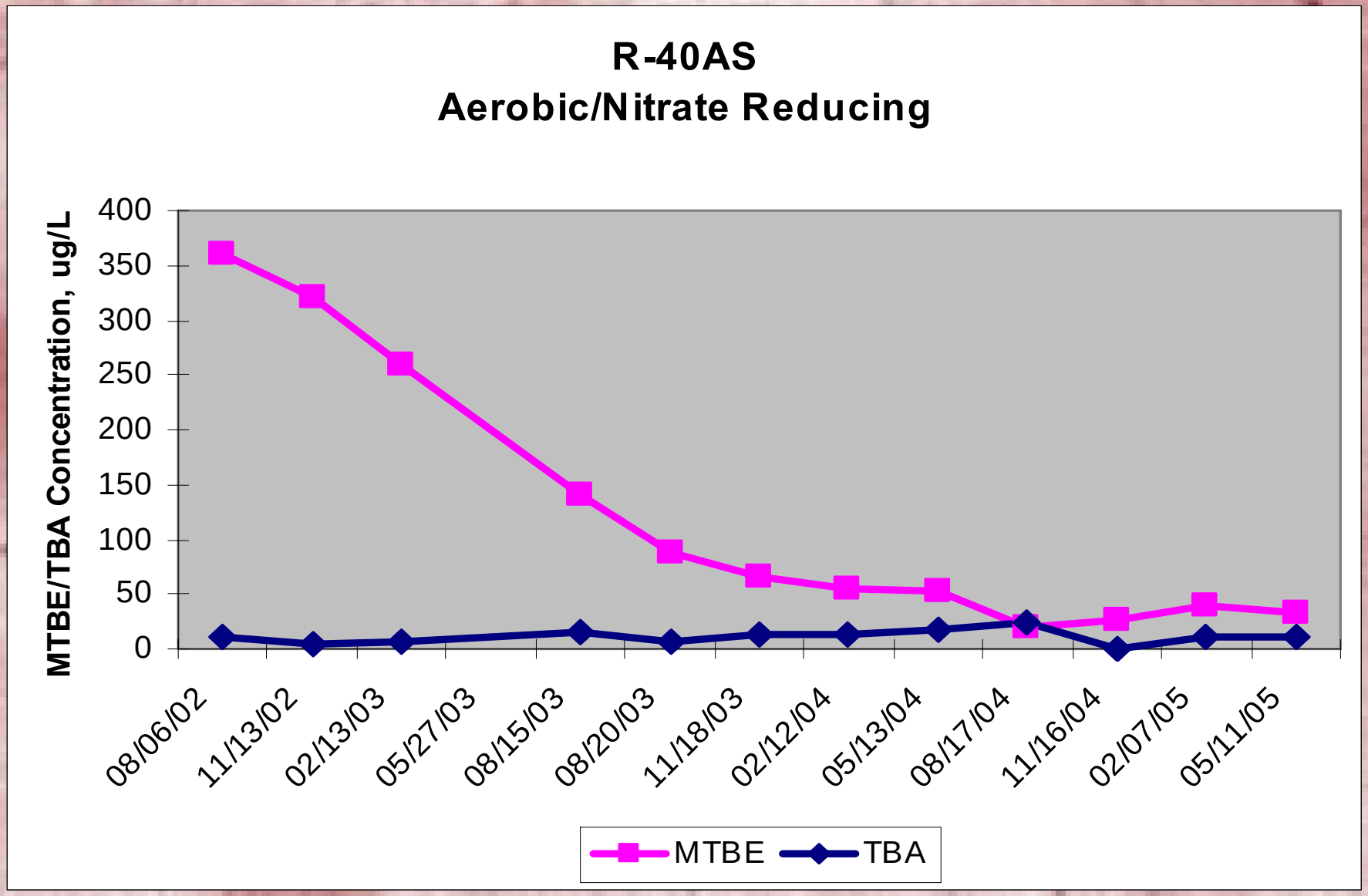
Time vs. Concentration Data



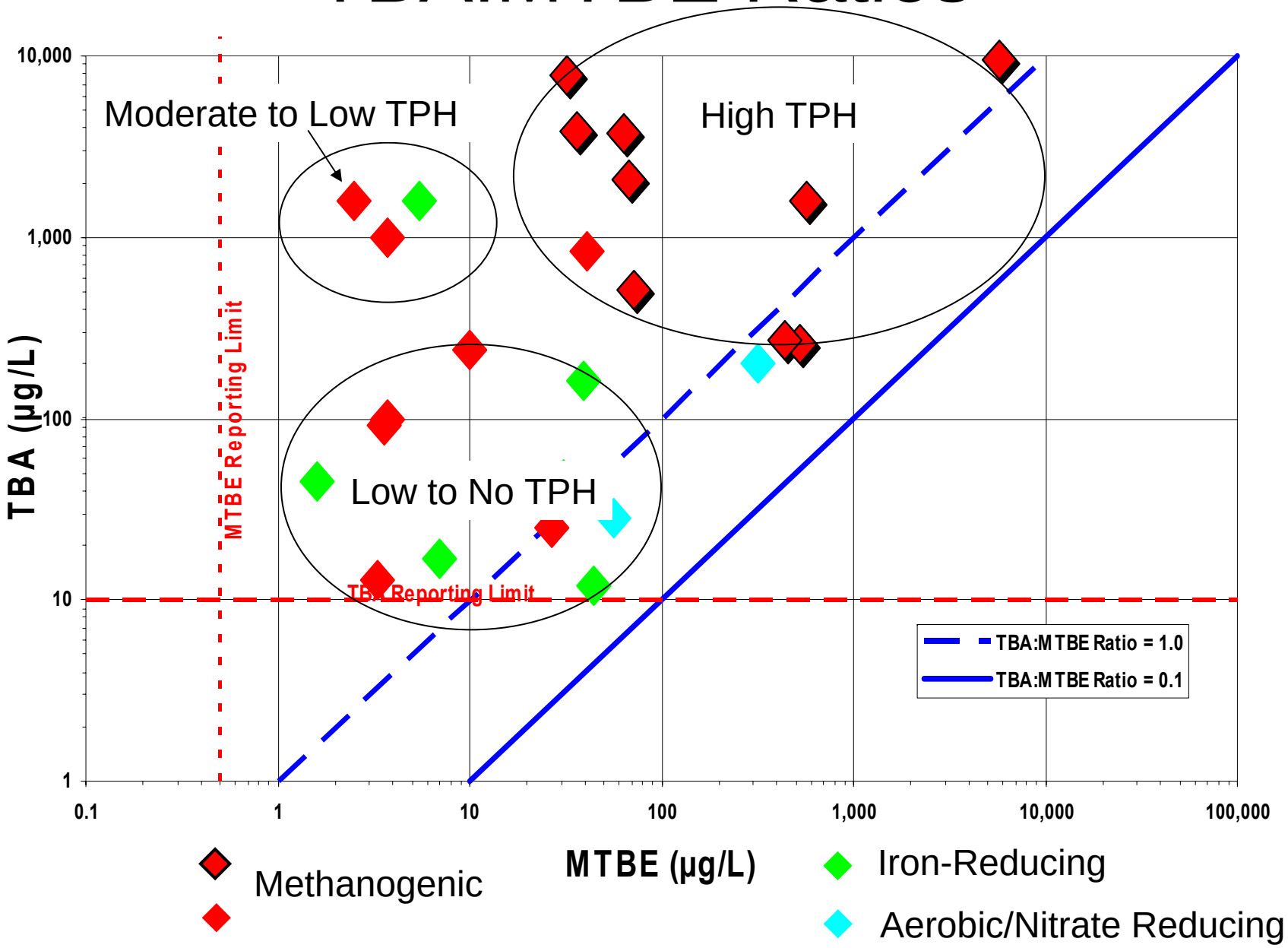
Time vs. Concentration Data

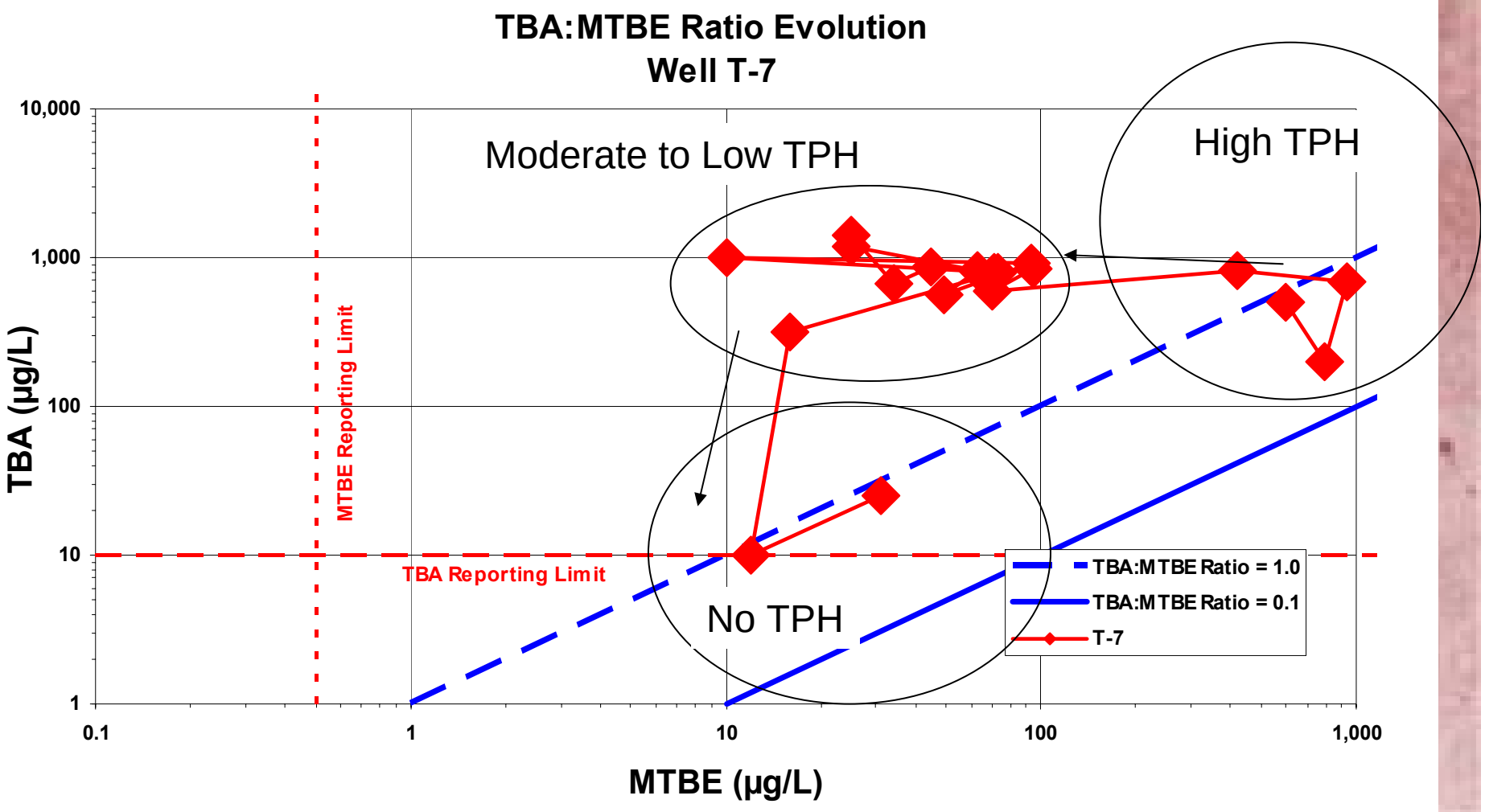


Time vs. Concentration Data



TBA:MTBE Ratios




TBA:MTBE Ratio Evolution
Well T-7
Moderate to Low TPH
High TPH
No TPH
MTBE Reporting Limit
TBA Reporting Limit
TBA:MTBE Ratio = 1.0
TBA:MTBE Ratio = 0.1
T-7
TBA (µg/L)
MTBE (µg/L)
10,000
1,000
100
10
1
0.1
1
10
100
1,000

Field Sample Plate Counts

Aerobic CFU/ml			
Sample ID	HPC/SD	Results	Specific Degrader Concentrations
R30AD	HPC	147,000-202,000	TBA: 0 ppb
R30AD	SD	192,000-197,000	MTBE: 15 ppb
R44AS	HPC	15,300-16,000	TBA: 500 ppb
R44AS	SD	11,700-25,400	MTBE: 20 ppb
R44AD	HPC	42,000-44,400	TBA: 50 ppb
R44AD	SD	89,000-151,000	MTBE: 70 ppb
T21	HPC	171,000-190,000	TBA: 2000 ppb
T21	SD	217,000-229,000	MTBE: 500 ppb

Anaerobic CFU/ml			
Sample ID	HPC/SD	Results	Specific Degrader Concentrations
R30AD*	HPC	880,000-2,140,000	TBA: 0 ppb
R30AD	SD	44,400-55,200	MTBE: 15 ppb
R44AS	HPC	22,000-35,600	TBA: 2000 ppb
R44AS*	SD	22,900	MTBE: 500 ppb
R44AD*	HPC	6,200-15,800	TBA: 50 ppb
R44AD	SD	11,500-16,200	MTBE: 70 ppb
T21	HPC	54,400-99,200	TBA: 2000 ppb
T21*	SD	21,400-88,000	MTBE: 500 ppb

Field Sample Microbe Speciation

DGGE Analytical Results

Hydrogenophaga spp. (ENV735?; MTBE degrader)

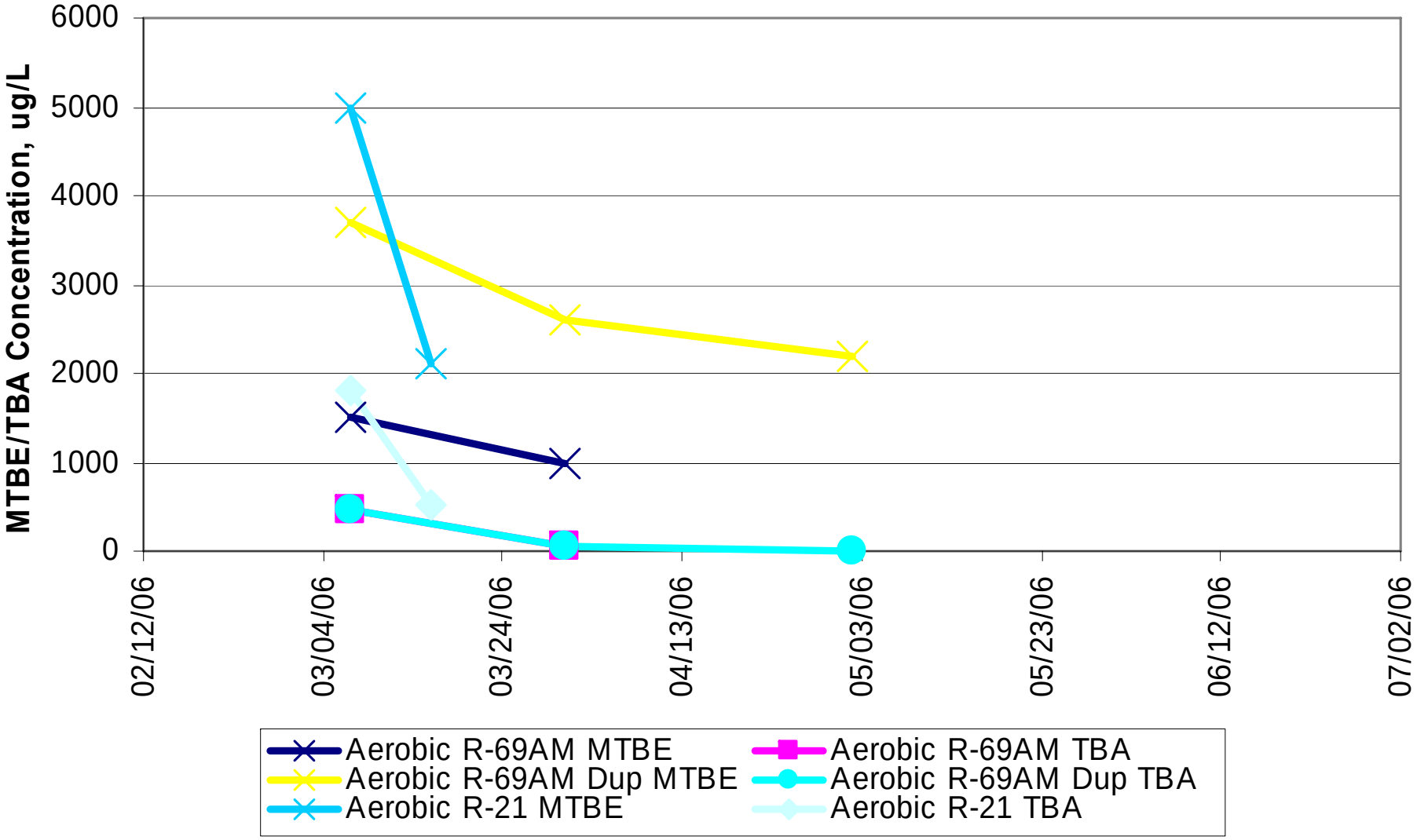
Rubrivivax (PM1-like; MTBE/TBA degrader)

Leptothrix (PM1-like; MTBE/TBA degrader)

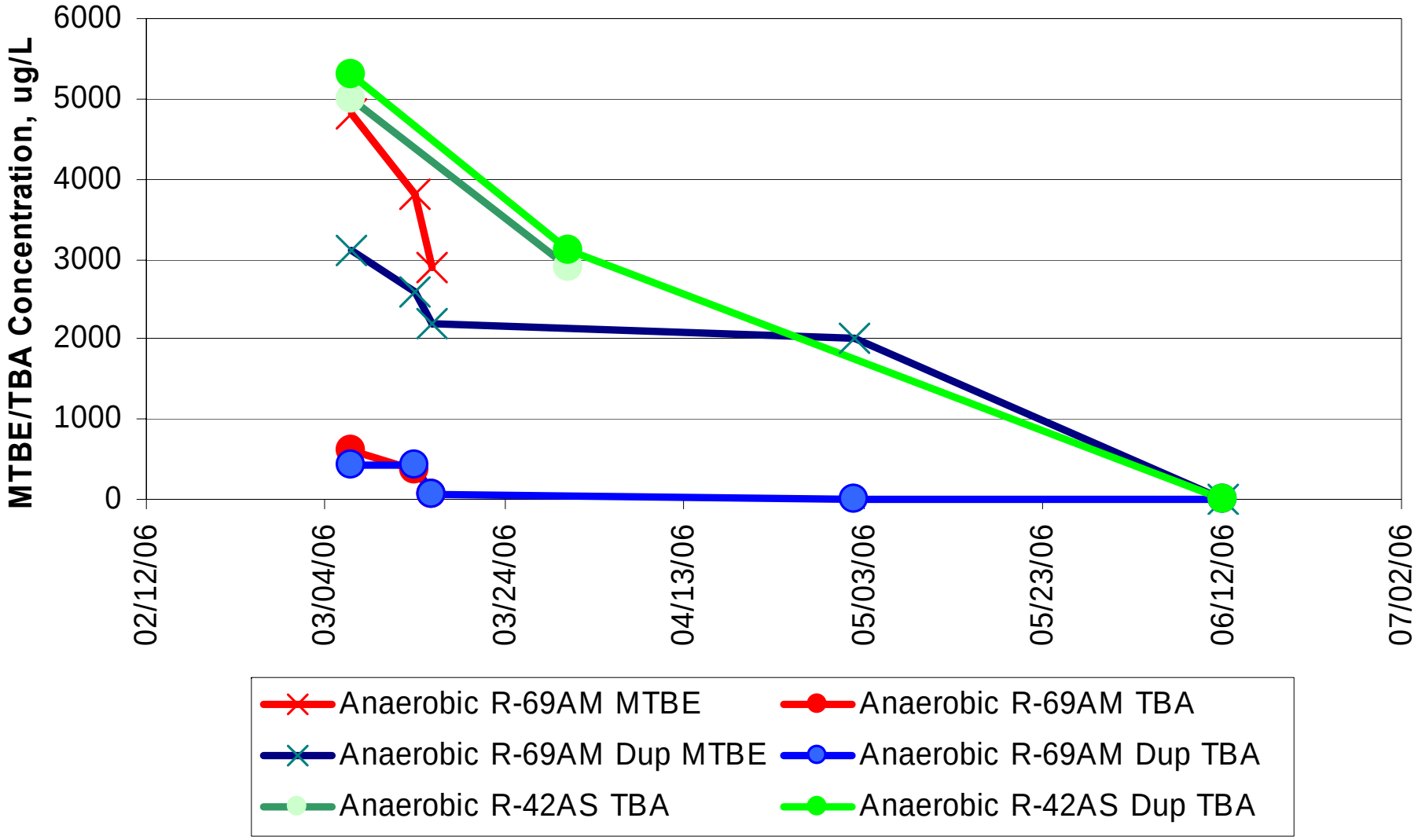
Ideonella (PM1-like; MTBE/TBA degrader)

Stenotrophomonas spp. (BTEX degraders)

Aerobic Microcosm Data



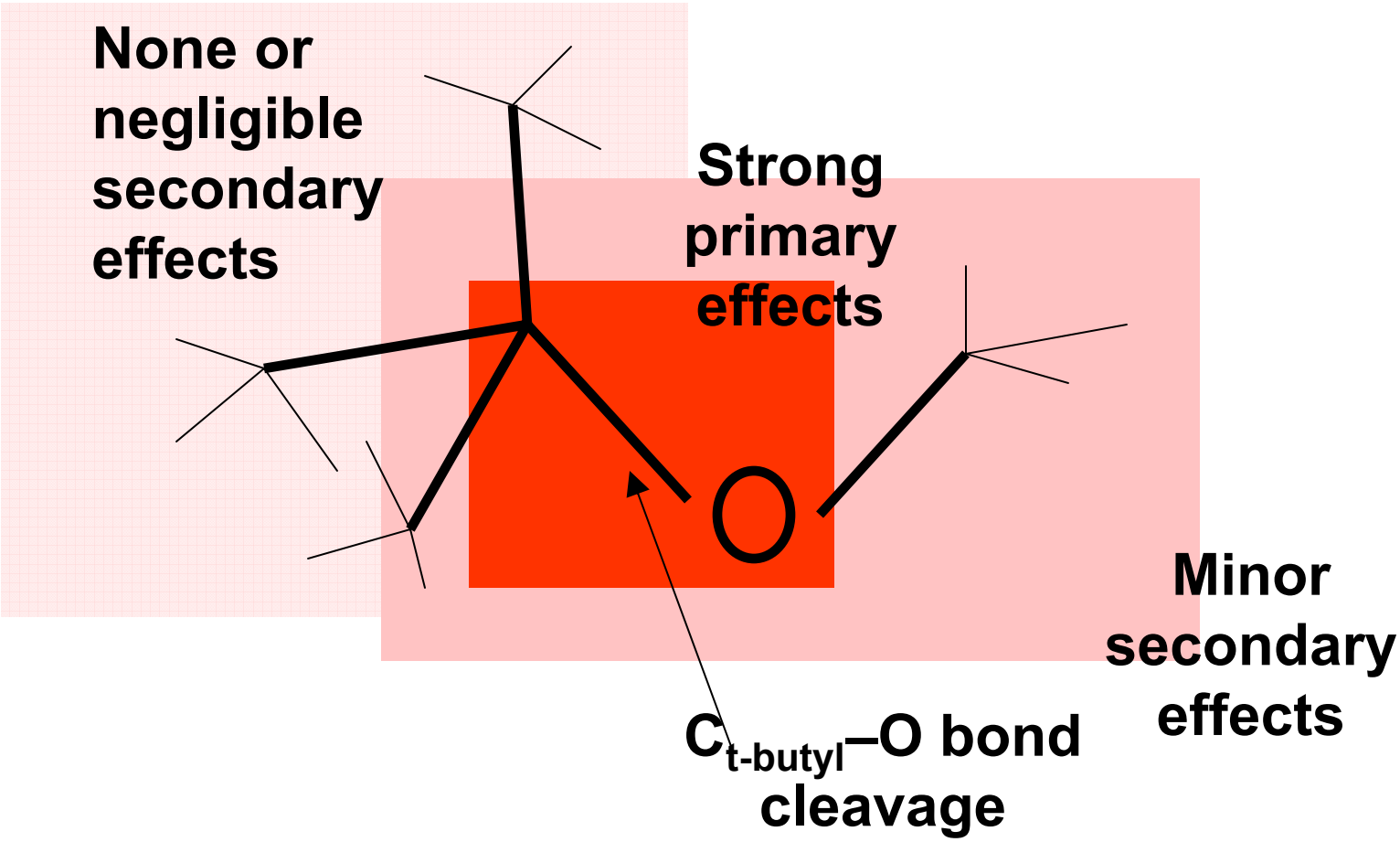
Anaerobic Microcosm Data



Microcosm Problems

- Reactors experienced formaldehyde poisoning!
  - Formaldehyde only degradation by-product detected in field, no HIBA or TBF. Could be producing mild inhibition

Isotope Fractionation

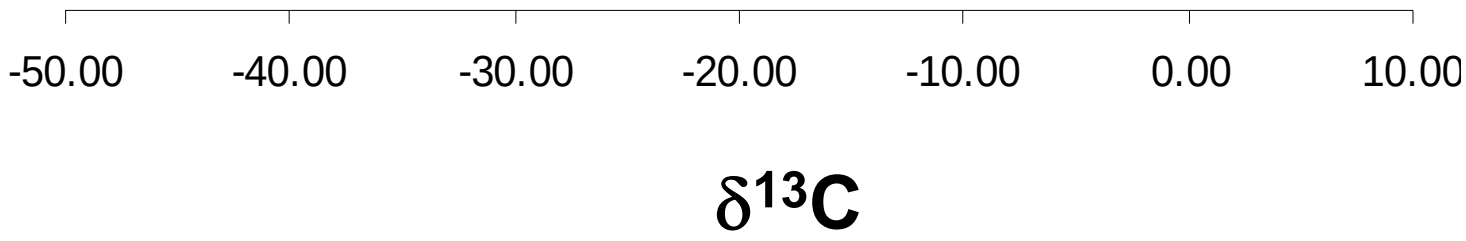


Delta Notation vs. Isotopic Ratio

Example: Anaerobic degr.

% MTBE remaining	$\delta^{13}C$	$^{13}C/^{12}C$
100.0	-30.0	0.010900
50.0	-24.5	0.010962
12.5	-13.4	0.011087
1.6	3.3	0.011274

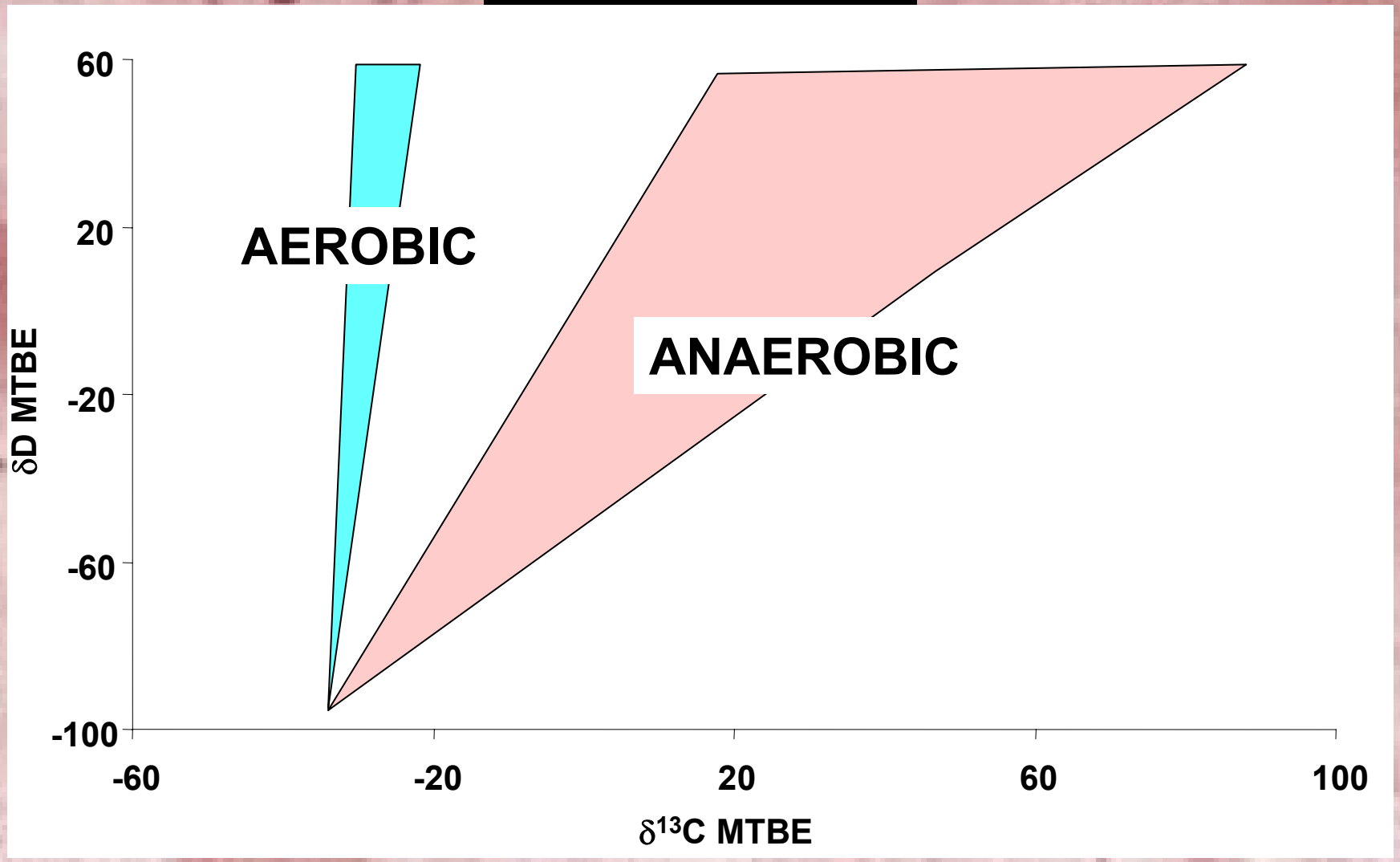
Data Output-Isotope Scale



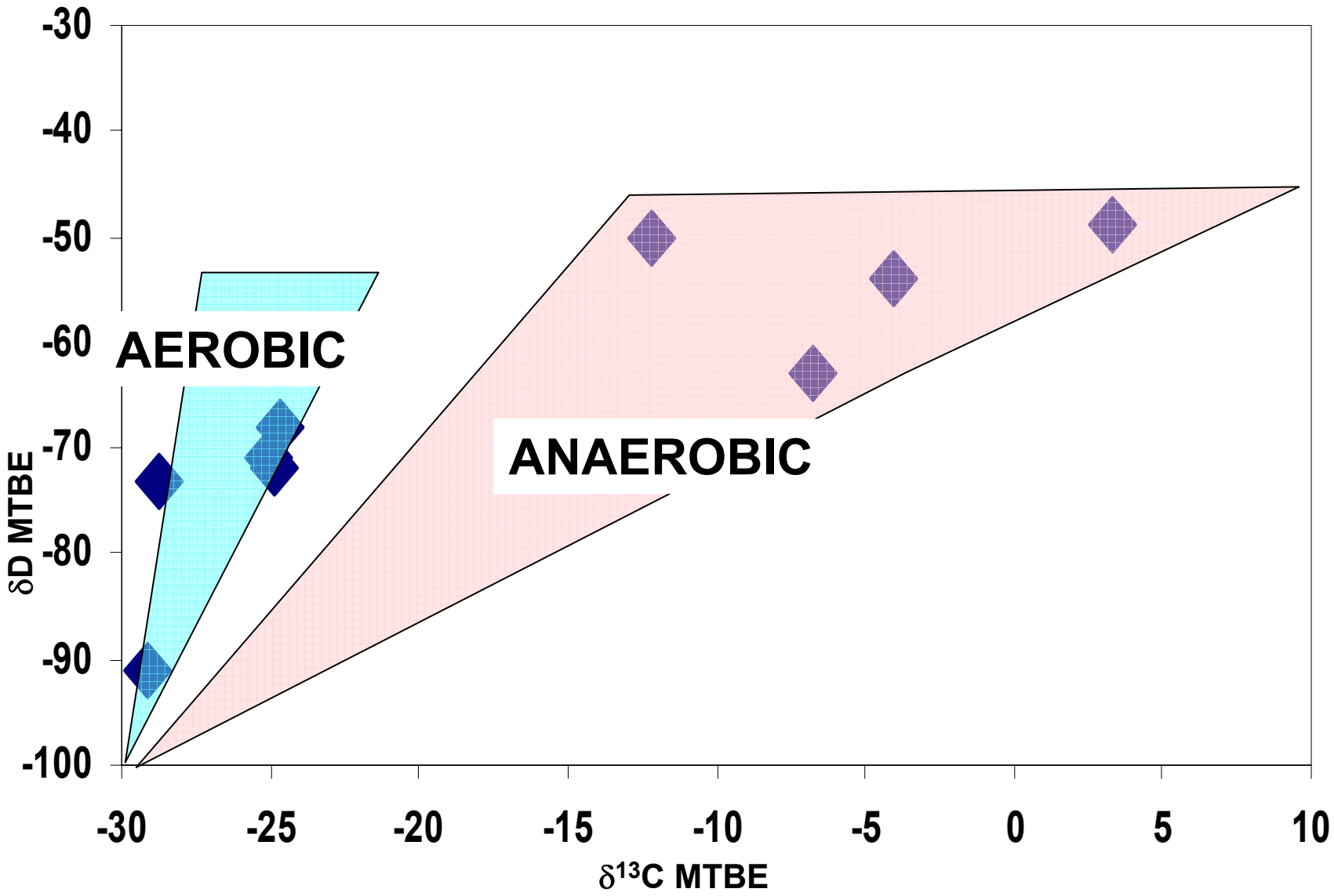
Isotopically enriched (biodegraded) →

Isotopically depleted ←

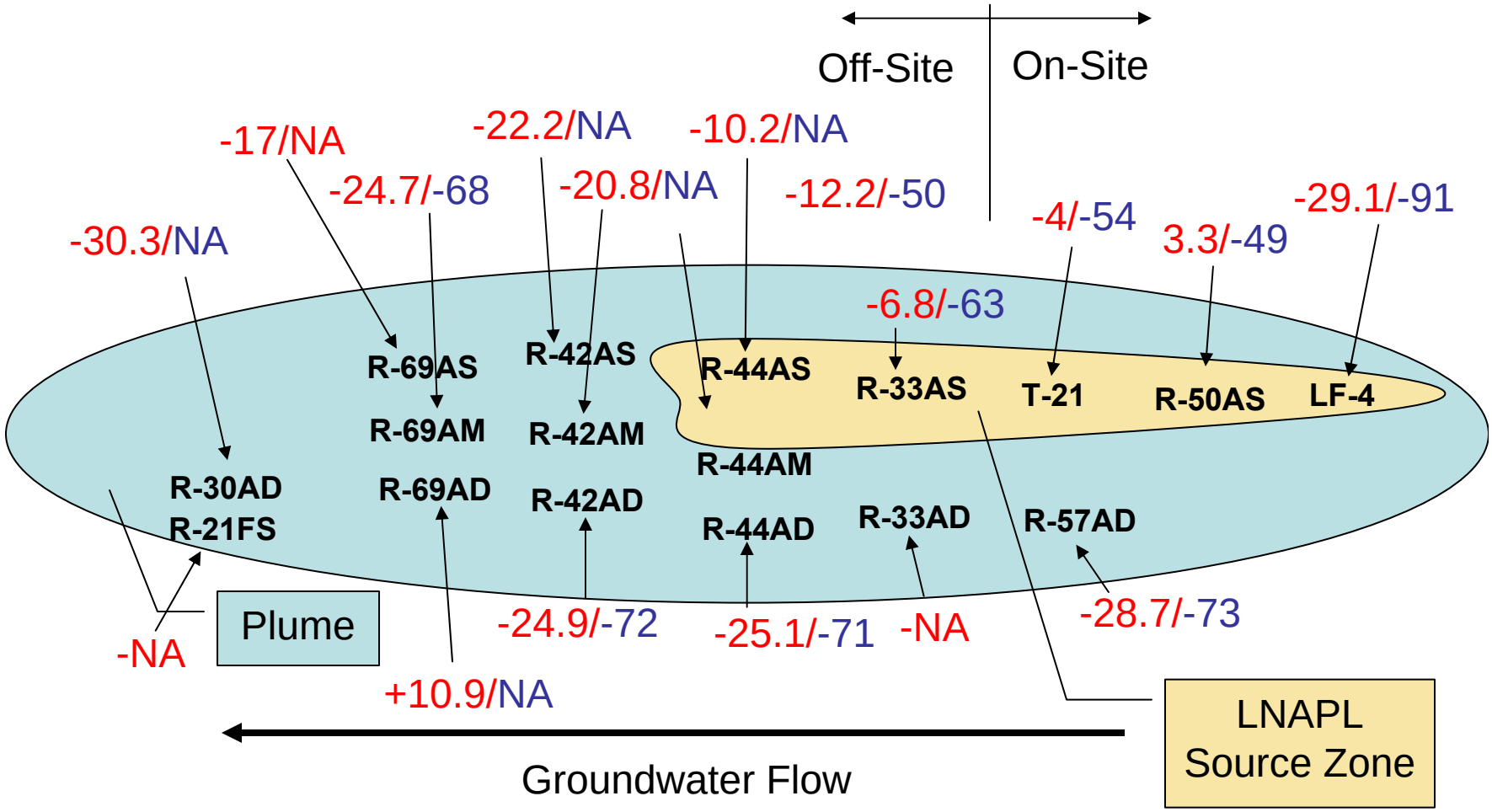
The Contrast in Aerobic and Anaerobic Isotope Fractionation



Field MTBE Carbon Isotope Data



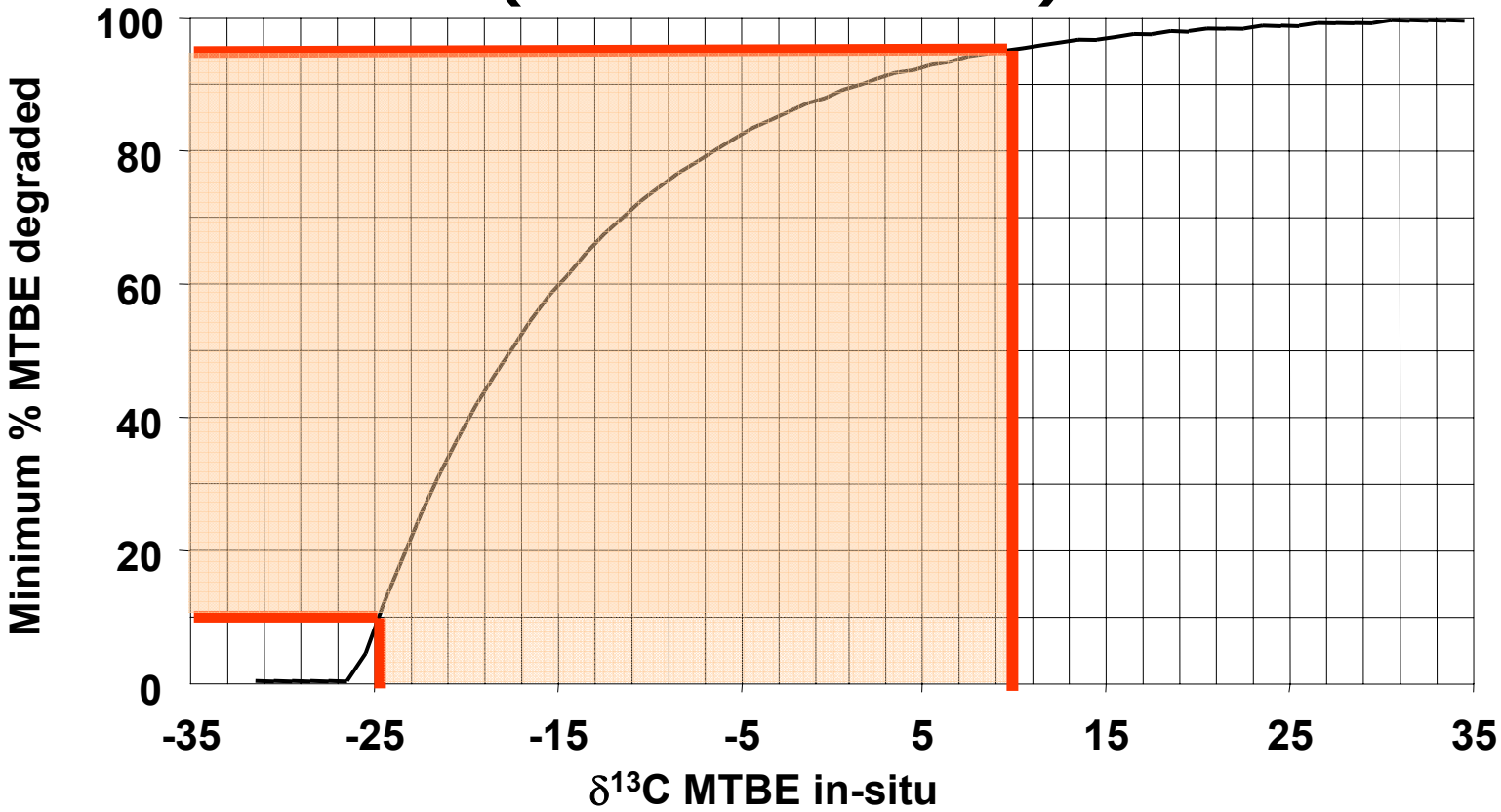
Schematic of MTBE Carbon and Hydrogen Isotope Data Results



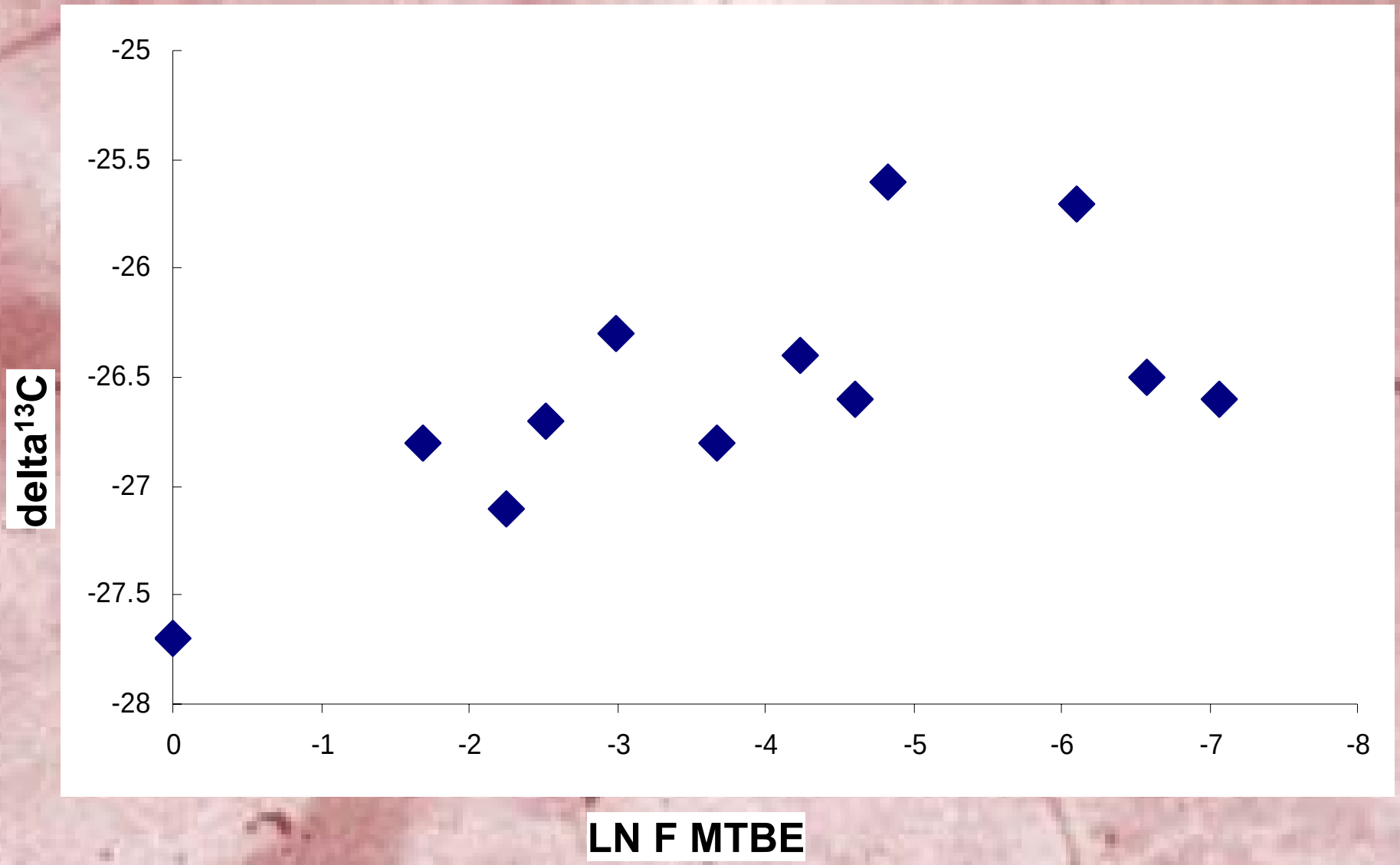
MTBE **δ13C**/MTBE **δD**

Estimate of Fraction MTBE Biodegraded

(Anaerobic)



Field TBA Carbon Isotope Data



Conclusions

- Microcosm data indicates MTBE and TBA biodegrading under both aerobic and anaerobic conditions.
- Field sample MTBE carbon and hydrogen isotope data supports both anaerobic and aerobic biodegradation of MTBE and TBA