

*Biodegradation - Monitored Natural Attenuation (MNA) for
Oxygenates:*

*How it evolved, why it occurs and
using stable carbon isotopes to predict plume behavior.*

Advanced Tools for In-situ Remediation Workshop

State University of New York at Stony Brook

July 29, 2008

John T. Wilson, U.S. EPA

Wilson.johnt@epa.gov

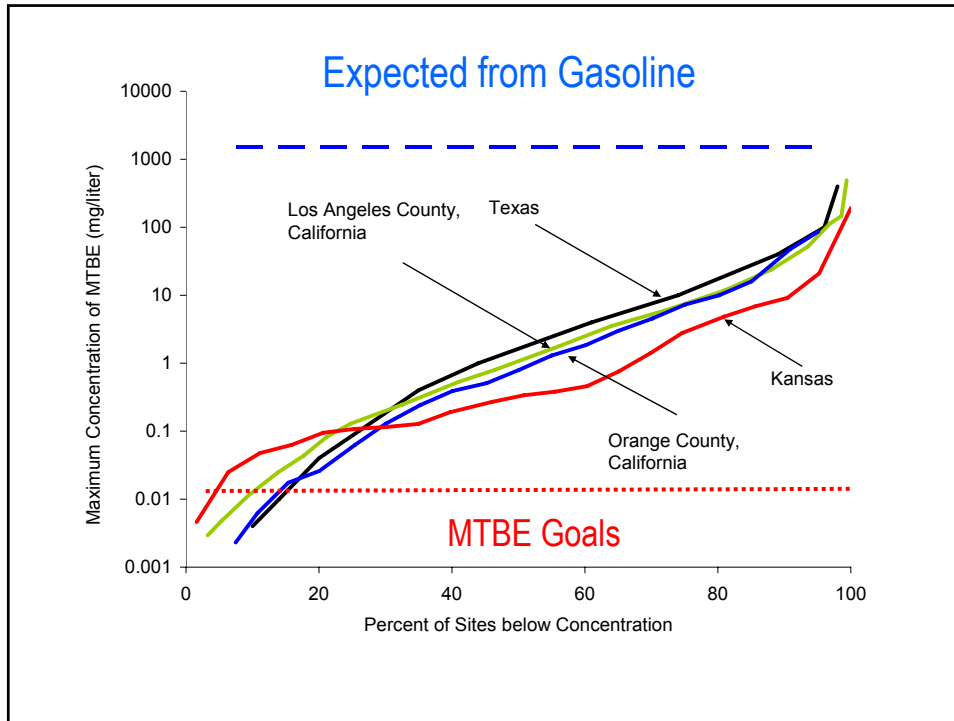
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What is the most important
criteria for successful
implementation of MNA?

The existing concentration of
MTBE in the source area of the
plume, and the concentration
goal for MTBE in ground water.



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For 25% of sites, only need a ten fold decrease

For 50% of sites need a one hundred fold decrease

Natural anaerobic biodegradation of MTBE is very site specific. It occurs in some plumes but not in others.

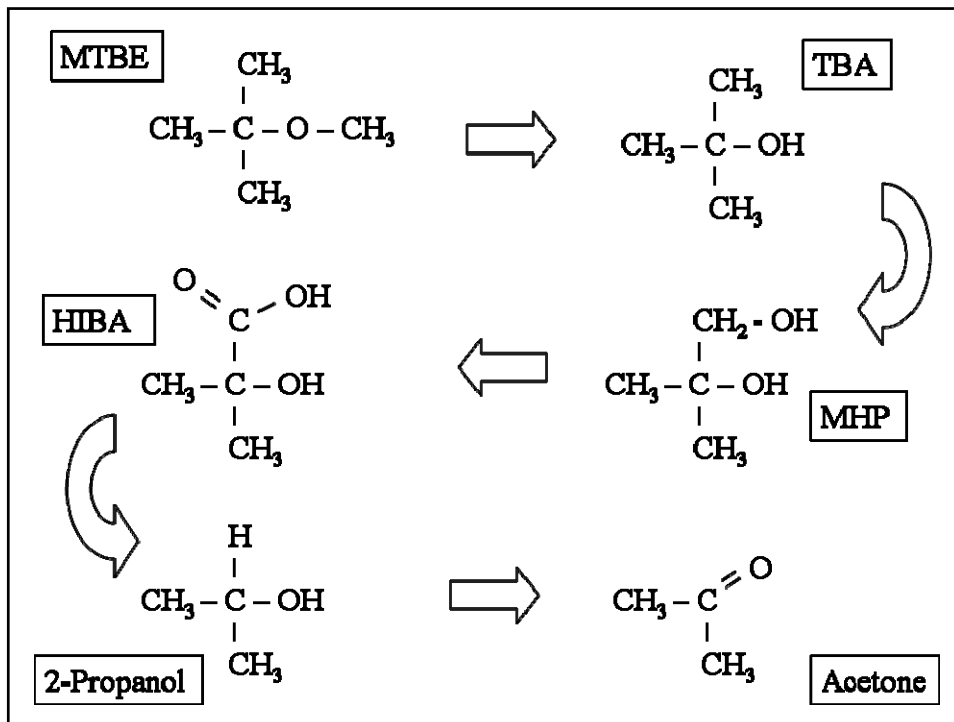
Natural anaerobic biodegradation of MTBE is very heterogeneous in plumes when it does occur.

Natural anaerobic biodegradation of MTBE leads in the short term to accumulation of TBA.

Natural anaerobic biodegradation of MTBE is probably carried out by acetogenic bacteria.

MTBE and TBA

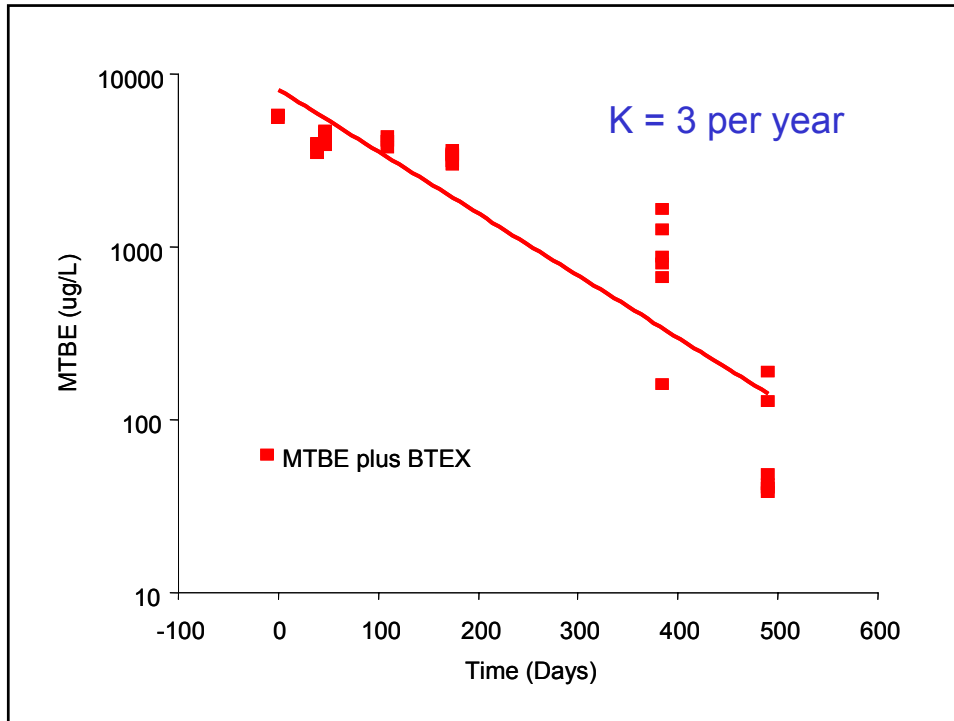
Biodegradation in Microcosms an Cultures



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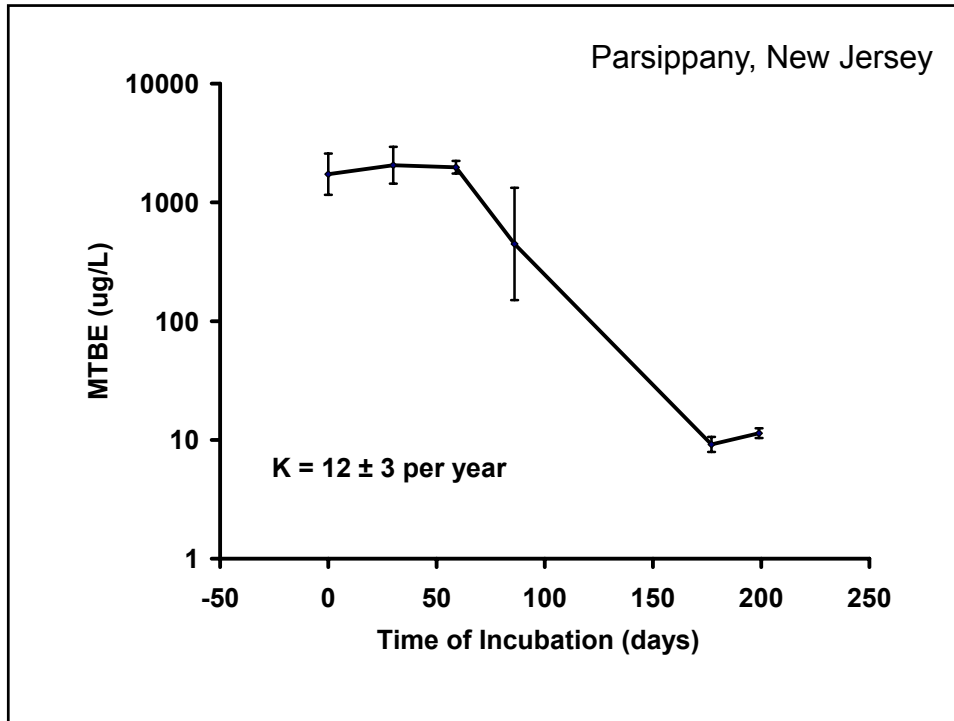
Biodegradation of MTBE in microcosms constructed with methanogenic aquifer material from Elizabeth City, North Carolina



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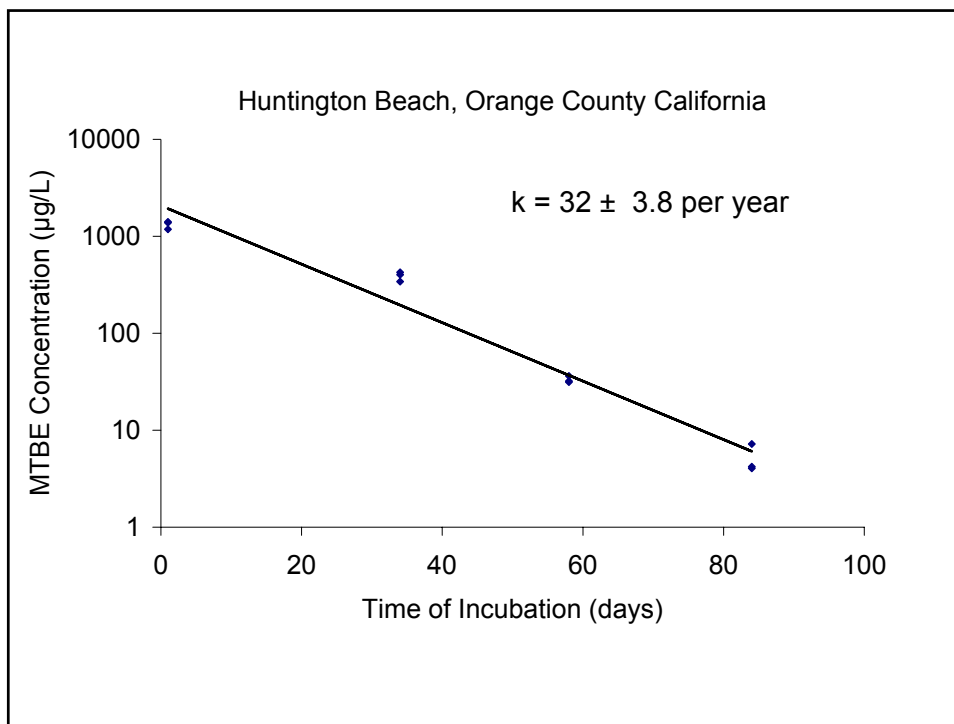
Biodegradation of MTBE in microcosms constructed with methanogenic aquifer material from Parsippany, New Jersey



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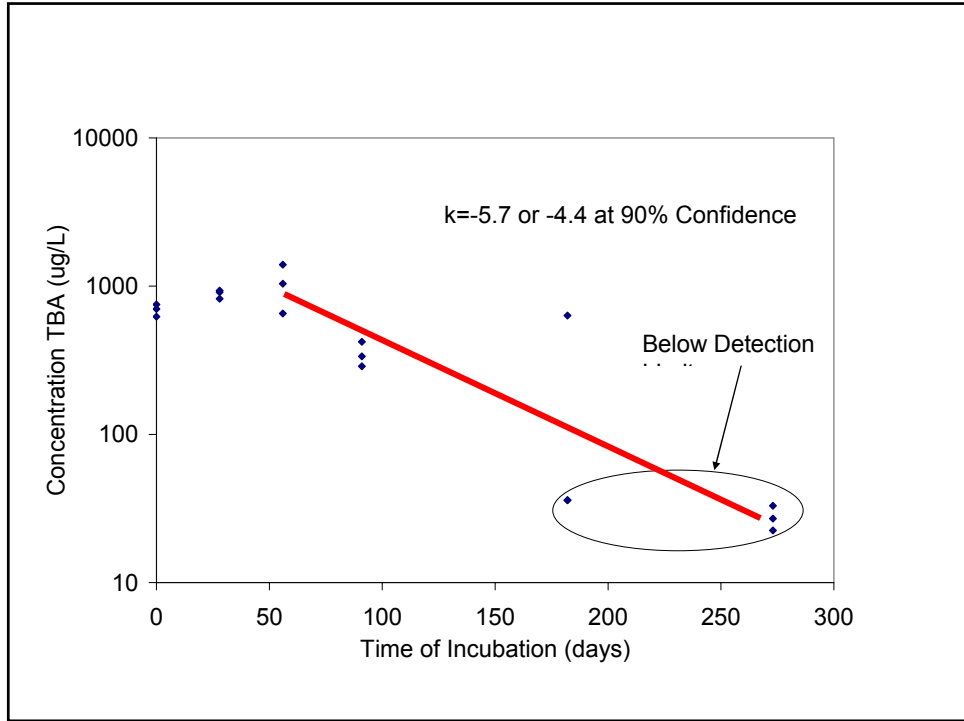
Biodegradation of MTBE in
microcosms constructed with sulfate
reducing aquifer material from
Huntington Beach, Orange County,
California



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Biodegradation of TBA
in microcosms for
Petaluma California



Location	MTBE Biodegradation (per year)	TBA Biodegradation (per year)
Petaluma, California	Not detected	5.7 ± 1.8
Elizabeth City, North Carolina	3.5 ± 0.65	Not detected
Parsippany, New Jersey	12 ± 3	Not detected
Huntington Beach California	32 ± 4	Not detected

The common wisdom teaches that the rate of anaerobic biodegradation of MTBE in ground water is slow.

Compared to the typical residence time of MTBE in plumes, rates of 3 to 20 per year are fast. MTBE can disappear from one quarter to the next, or from one monitoring well to the next.

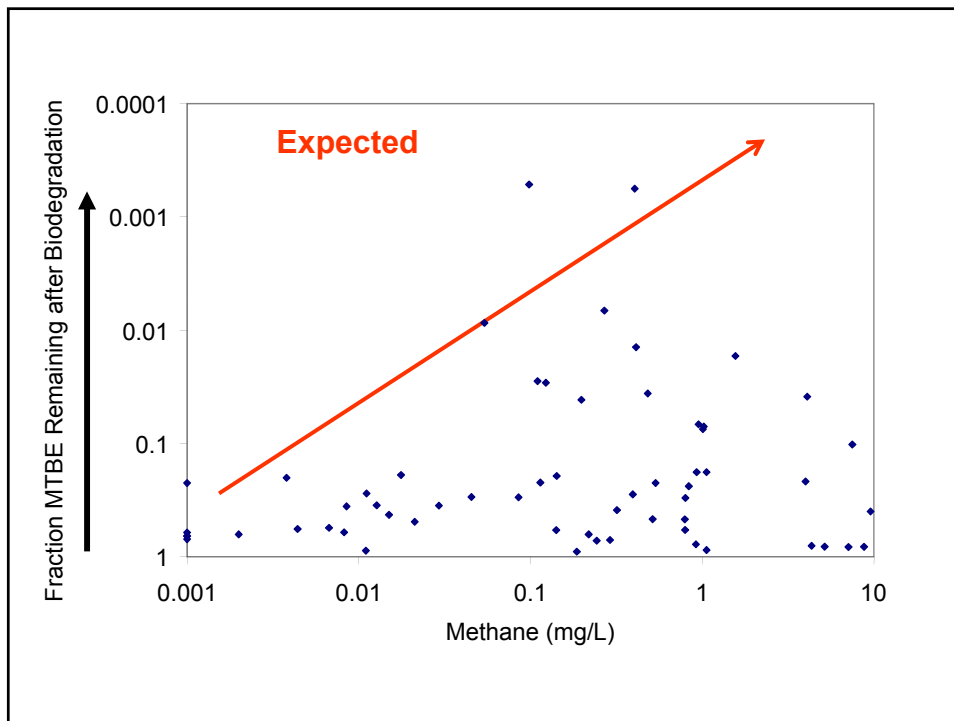
Biogeochemistry of the Ground Water supporting anaerobic biodegradation of MTBE.

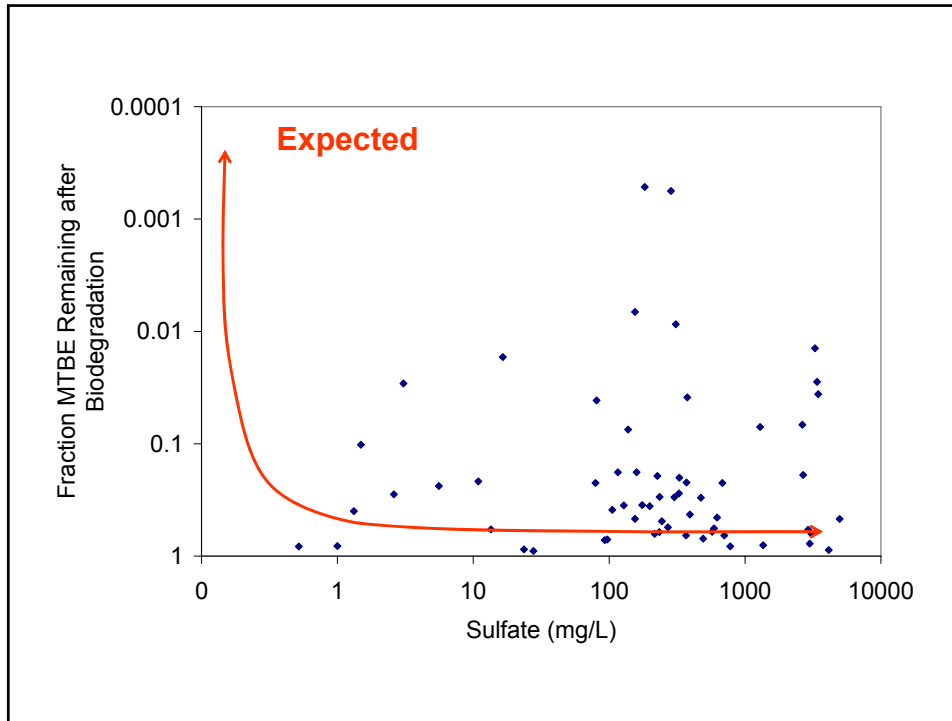
Earlier publications by John Wilson and Ravi Kolhatkar indicated that natural anaerobic biodegradation of MTBE to TBA was associated with methanogenic ground water

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In 61 wells at 13 gasoline spills in Orange County California, the fractionation of stable carbon isotopes in MTBE was used to predict the extent of biodegradation of MTBE to TBA. The fraction of MTBE remaining after biodegradation was compared to the concentrations of methane and sulfate in the ground water.





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Sulfate reduction or methane production in the ground water was not associated with natural biodegradation of MTBE. Biogeochemistry can not be used to predict TBA production.

Natural anaerobic biodegradation of MTBE is probably carried out by acetogenic bacteria.

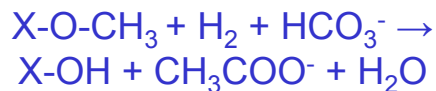
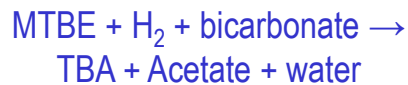
Carbon isotopic fractionation during anaerobic biotransformation of methyl tert-butyl ether and tert-amyl methyl ether. 2005. Somsamak, P. HH Richnow, and MM Haggblom. *Environ Sci Technol.* 39(1):103-9.

Their culture that degraded MTBE to TBA under anaerobic conditions was pre-acclimated to degrade TAME to TAA. These organisms metabolize the methyl ether (methoxy group) and discard the rest.

Methyl ethers are common in nature, occurring in substances such as pectin. One group of organisms called acetogens gain energy under anaerobic conditions by oxidizing carbon-oxygen bonds.

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Acetogenic bacteria are almost autotrophic organisms. They would metabolize MTBE as part of their energy metabolism, but not for food. They do not need a separate electron acceptor, but they do need a source of H_2 .

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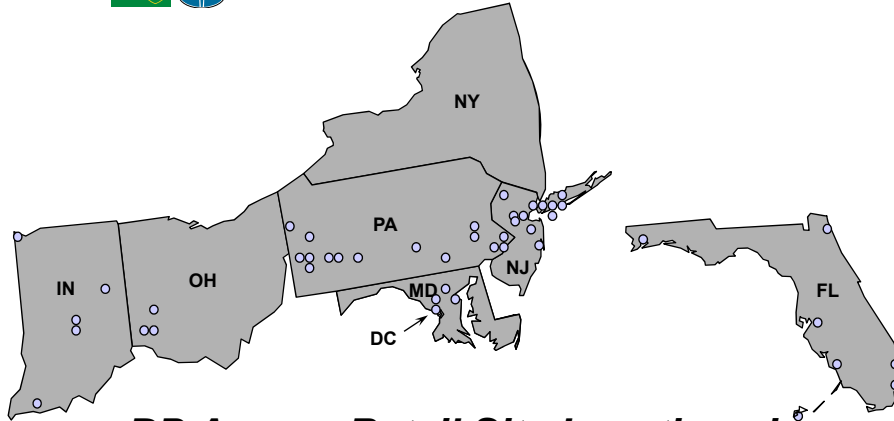
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In many old fuel spills, hydrogen is produced by a methane fermentation of the BTEX compounds.



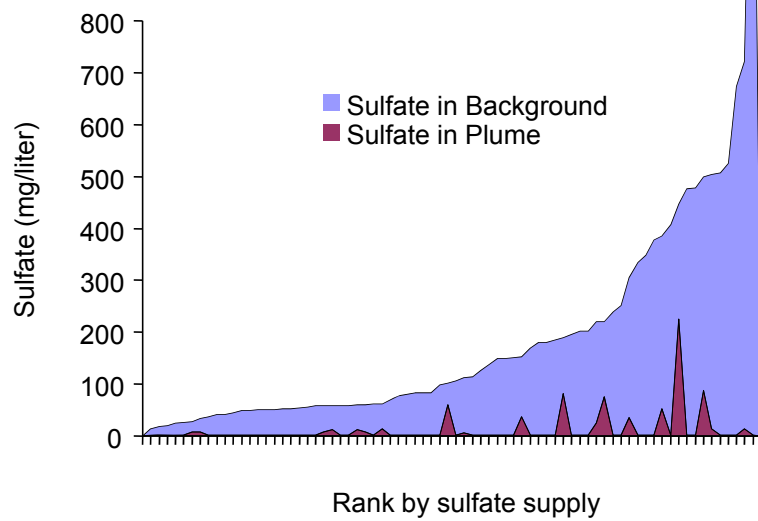
If acetogenic bacteria are the agents of natural anaerobic biodegradation, that would explain the association with BTEX fermentation, and the lack of association with sulfate reduction or methanogenesis.

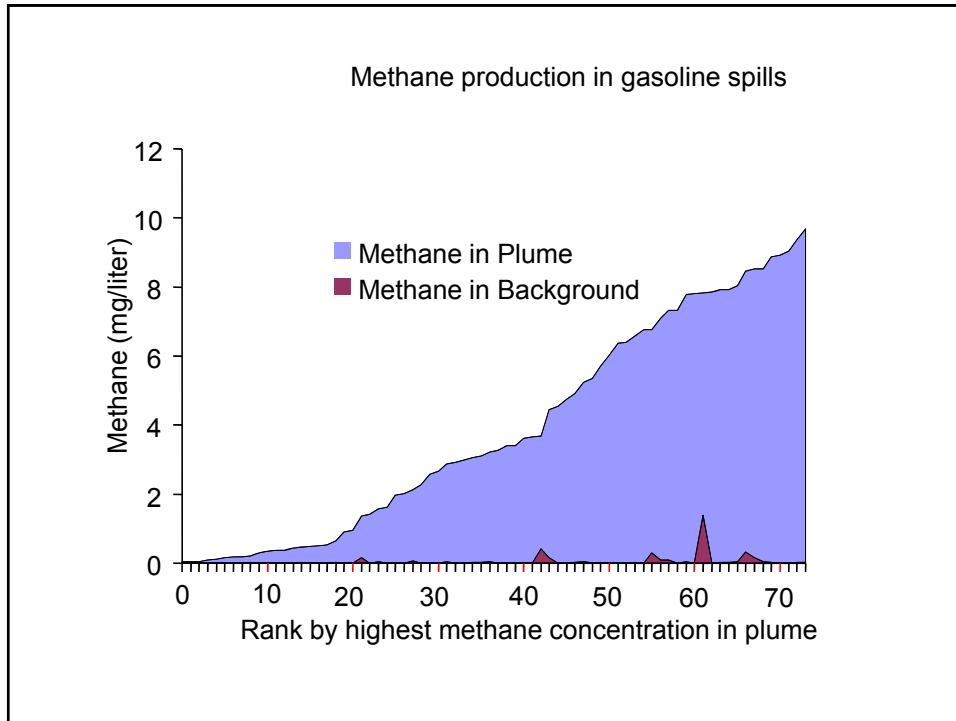
BP Amoco



BP Amoco Retail Site Locations in the MTBE NA Study

Sulfate supply in gasoline spills





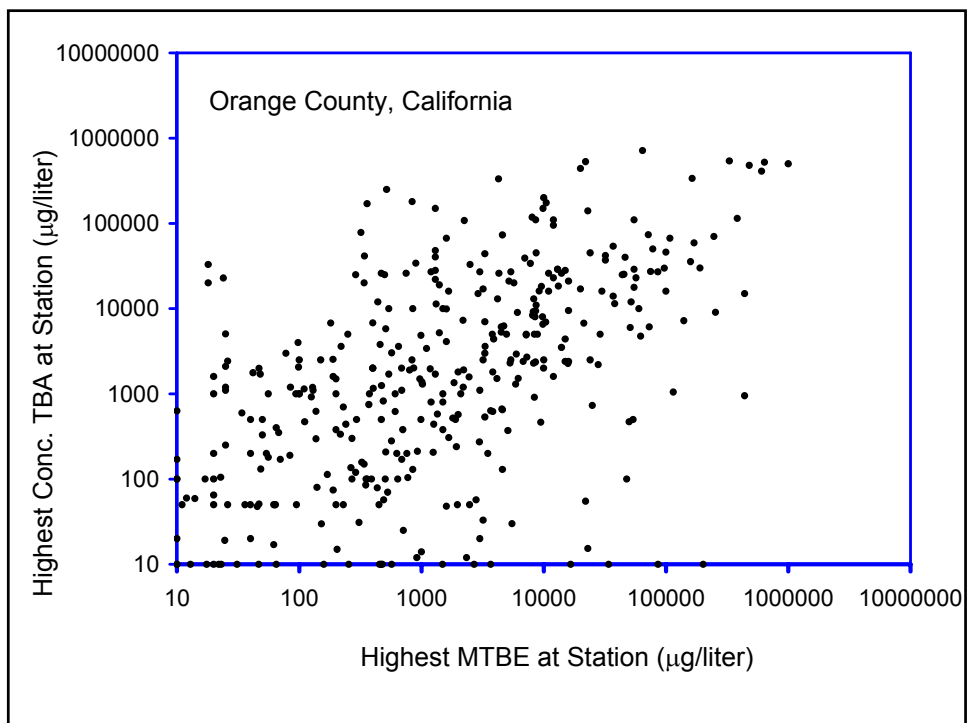
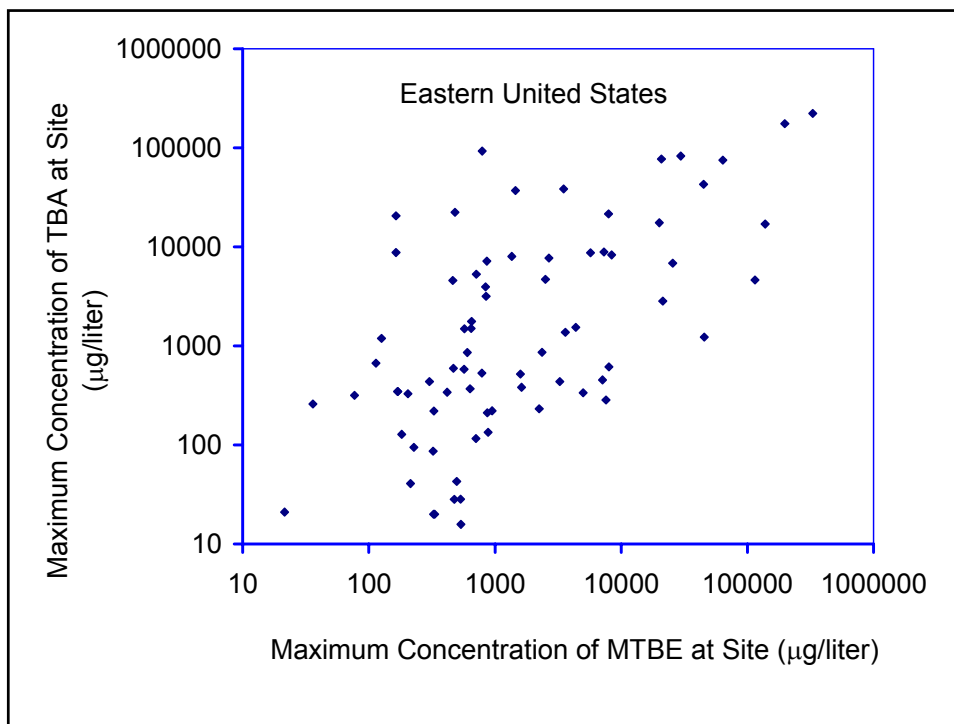
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How much TBA is there in ground water at gasoline spills?

How much TBA in ground water would we expect from the TBA in gasoline?

How much is coming from biodegradation of MTBE?



How much TBA in ground water
would we expect from the TBA
in gasoline?

**Predict the Ratio of TBA to MTBE
using equilibrium partitioning
theory**

$$C_w = \frac{C_{o,NAPL}}{K_{NAPL} + \frac{\theta_w}{\theta_{NAPL}}}$$

C_w is the concentration in the ground water

$C_{o,NAPL}$ is the concentration in the gasoline that was spilled

θ_{NAPL} is the porosity filled with gasoline

θ_w is the water-filled porosity

K_{NAPL} is the distribution coefficient between gasoline and water.

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Assume:

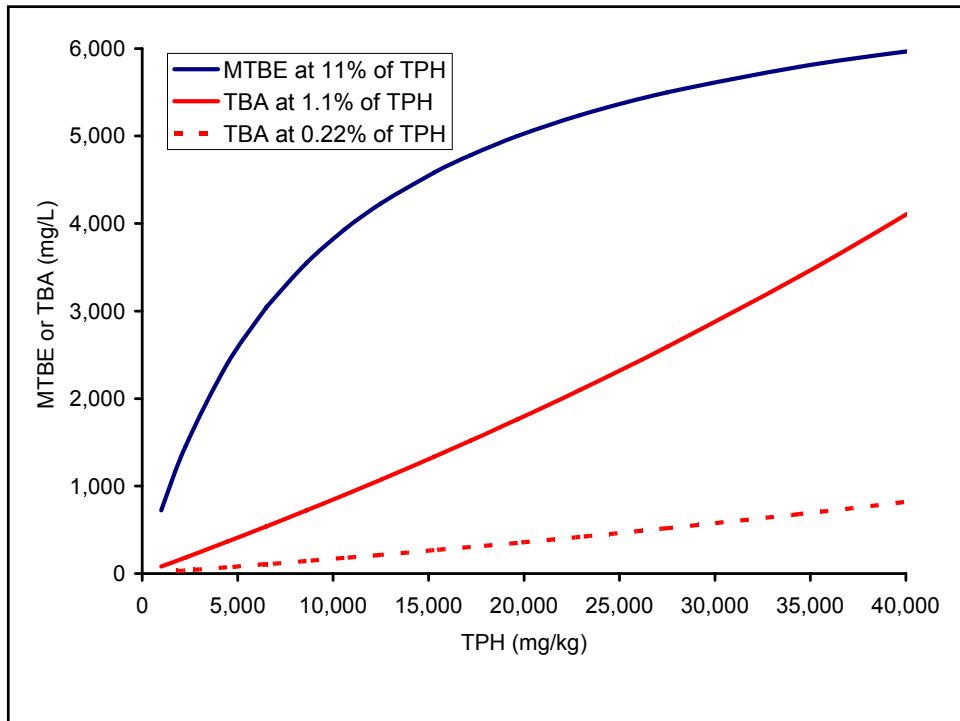
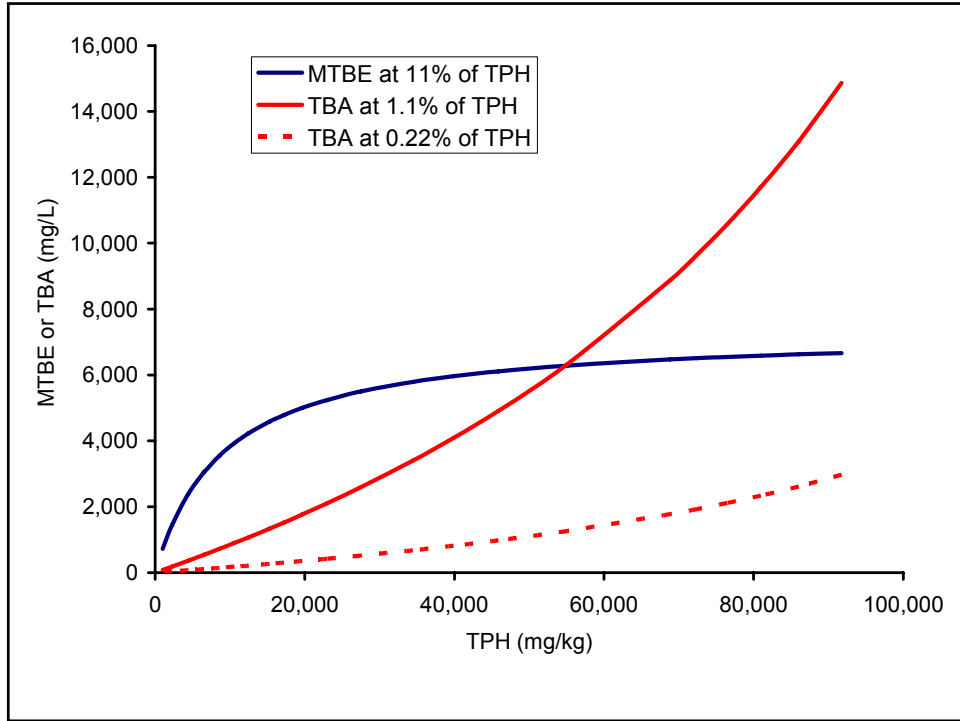
Bulk density of aquifer material = 1.7
gm/cm³

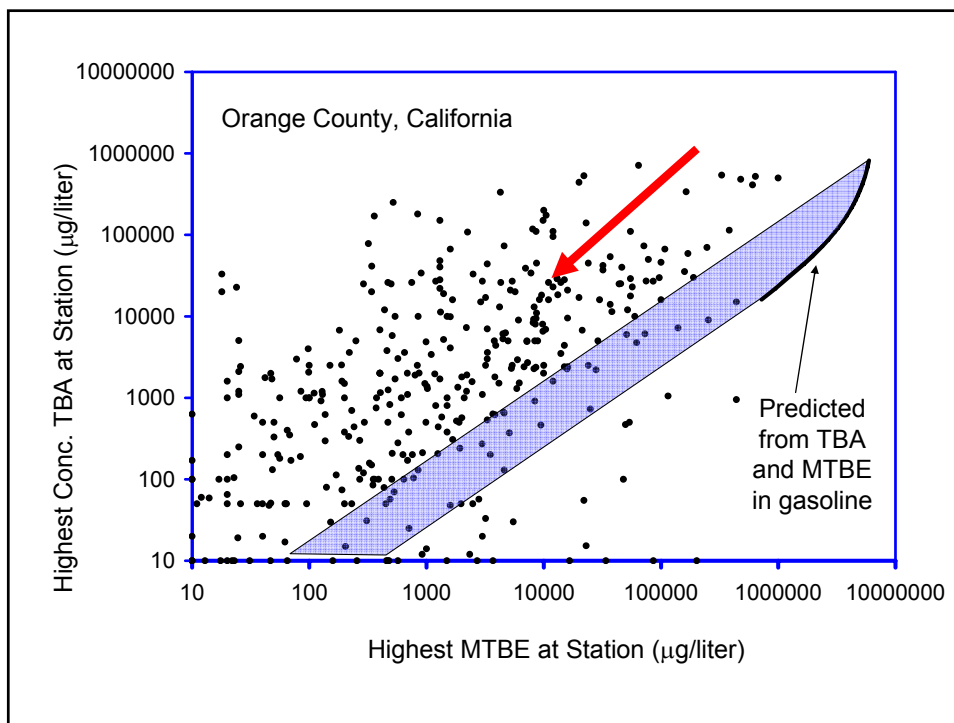
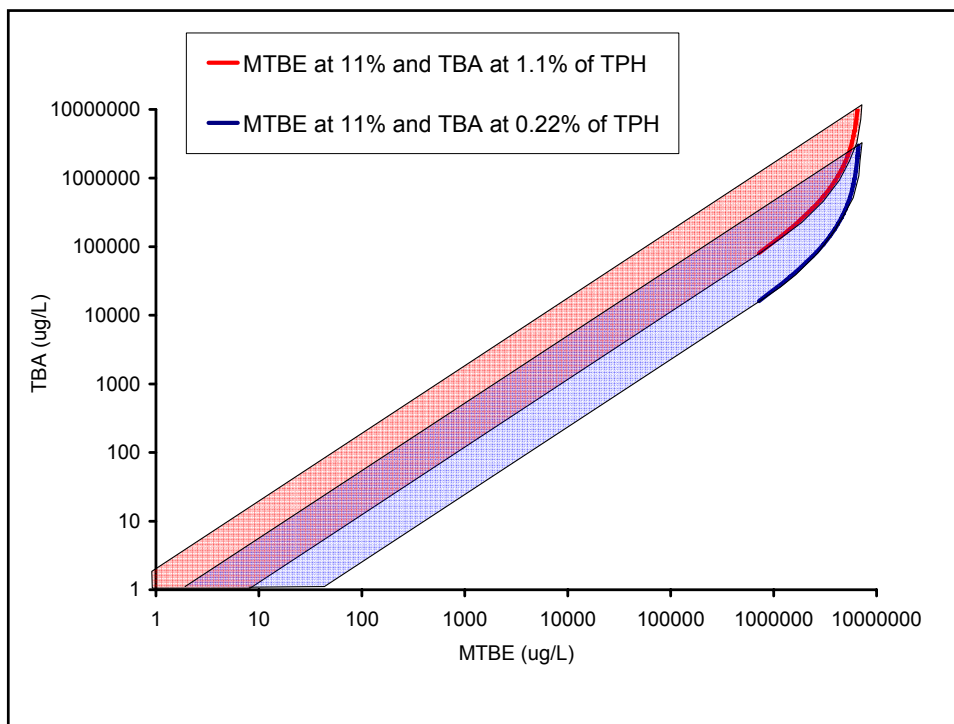
Bulk density of gasoline = 0.78 gm/cm³

$\theta = 0.30 = \theta_{NAPL} + \theta_w$

K_{NAPL} for MTBE = 16

K_{NAPL} for TBA = 0.24





Predicting the Ratio of TBA to MTBE
using equilibrium partitioning theory:

If MTBE was the primary oxygenate,
should never expect more than three
times as much TBA as MTBE.

At realistic concentrations of TPH in
aquifer sediment, the concentration of
TBA should be less than the
concentration of MTBE. However, there
are high ratios of TBA to MTBE at many
spill sites.

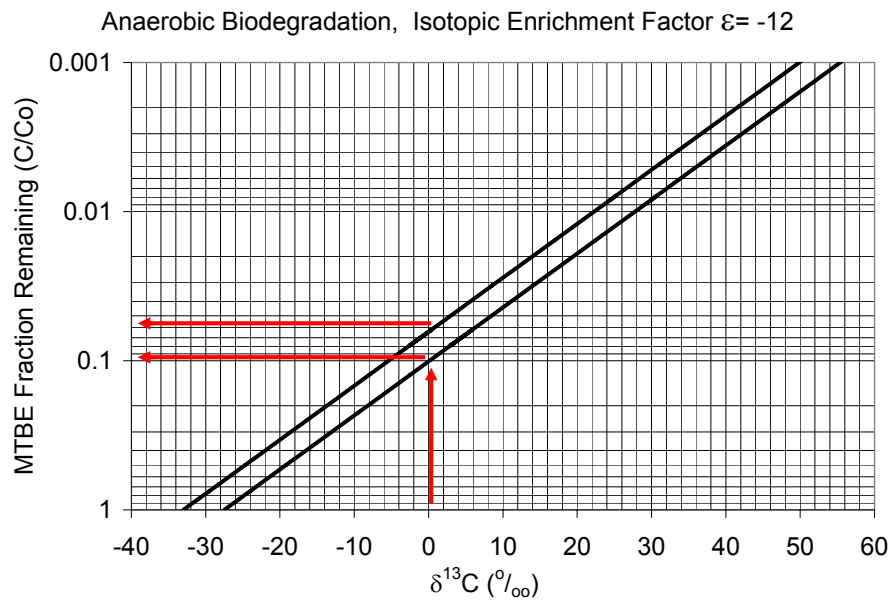
How much TBA is coming from
biodegradation of MTBE?

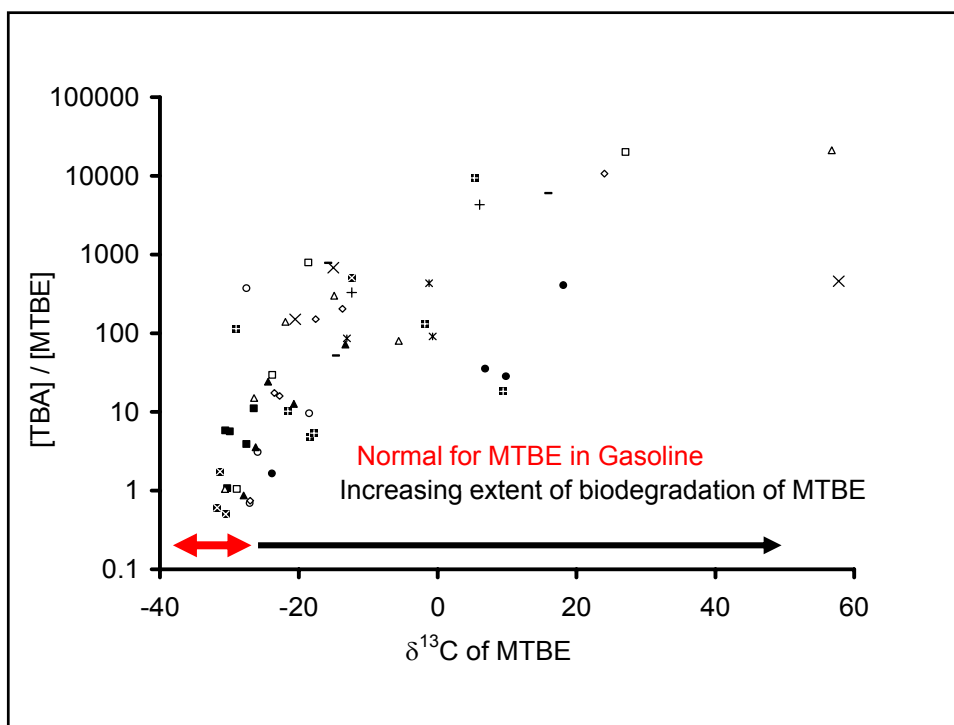
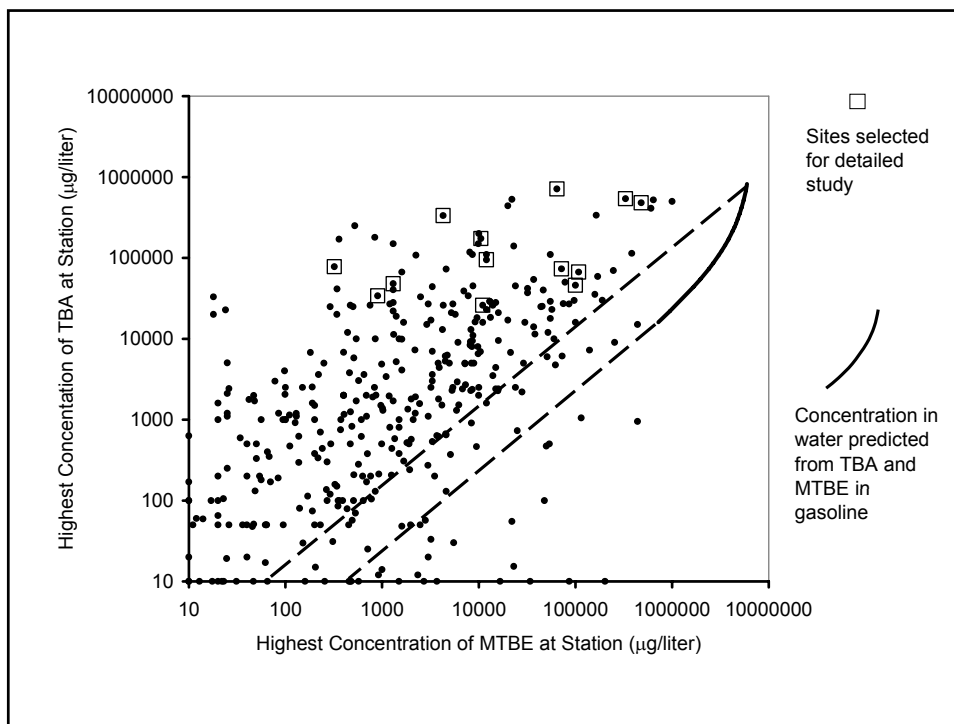
How can we recognize MTBE
biodegradation
at field scale?

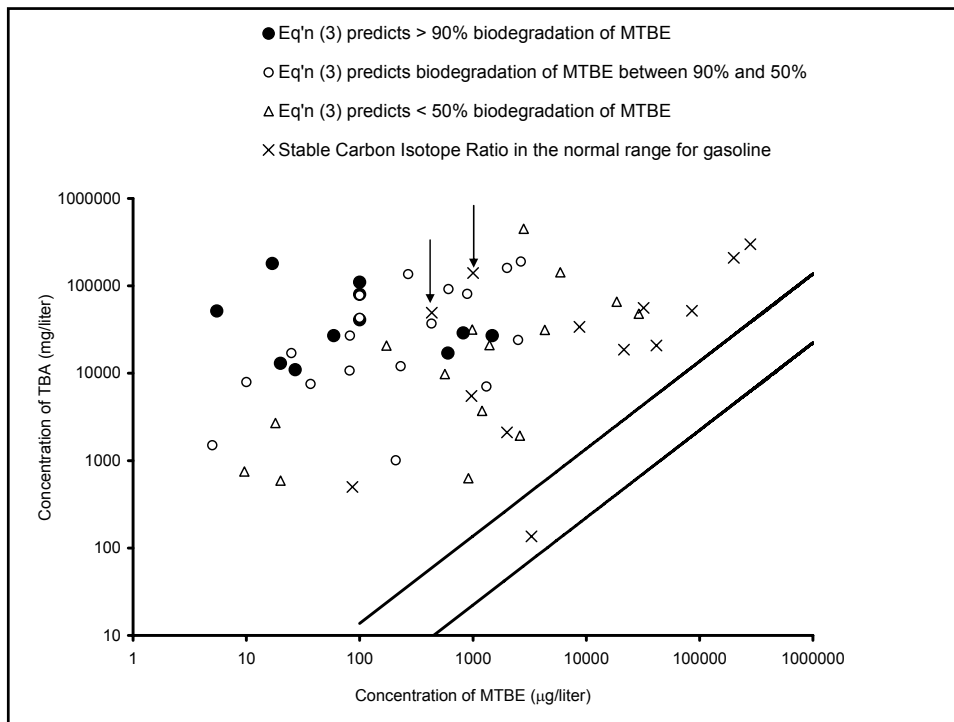
We Need Some New Approaches

Compound specific stable
isotope analyses can provide
an unambiguous conservative
boundary on the extent of
biodegradation

What is the Relationship between SCIR and extent of Biodegradation?





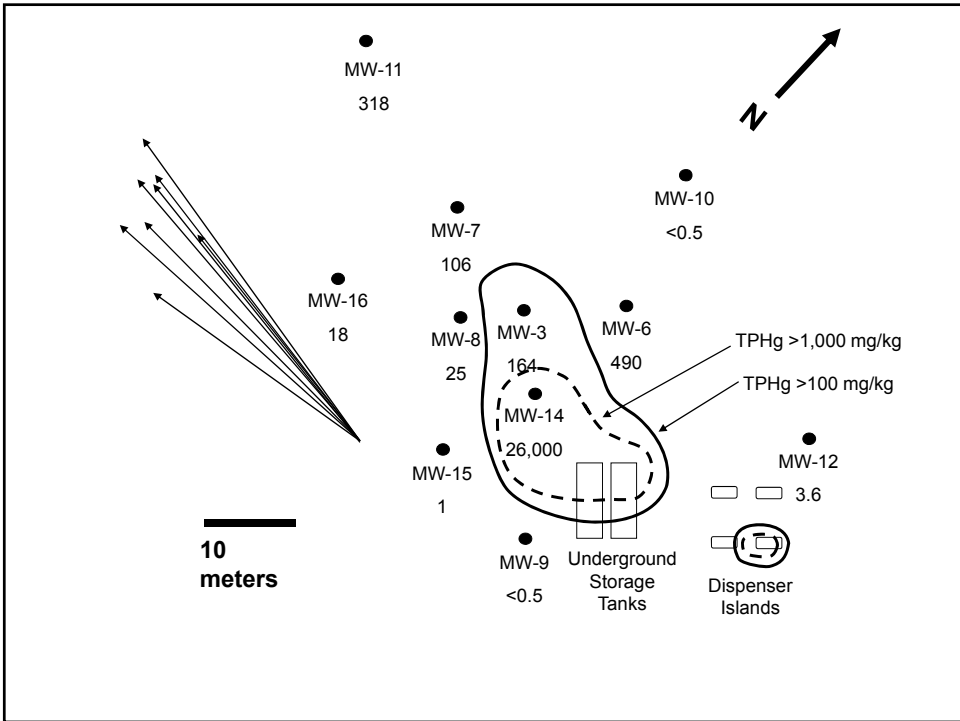
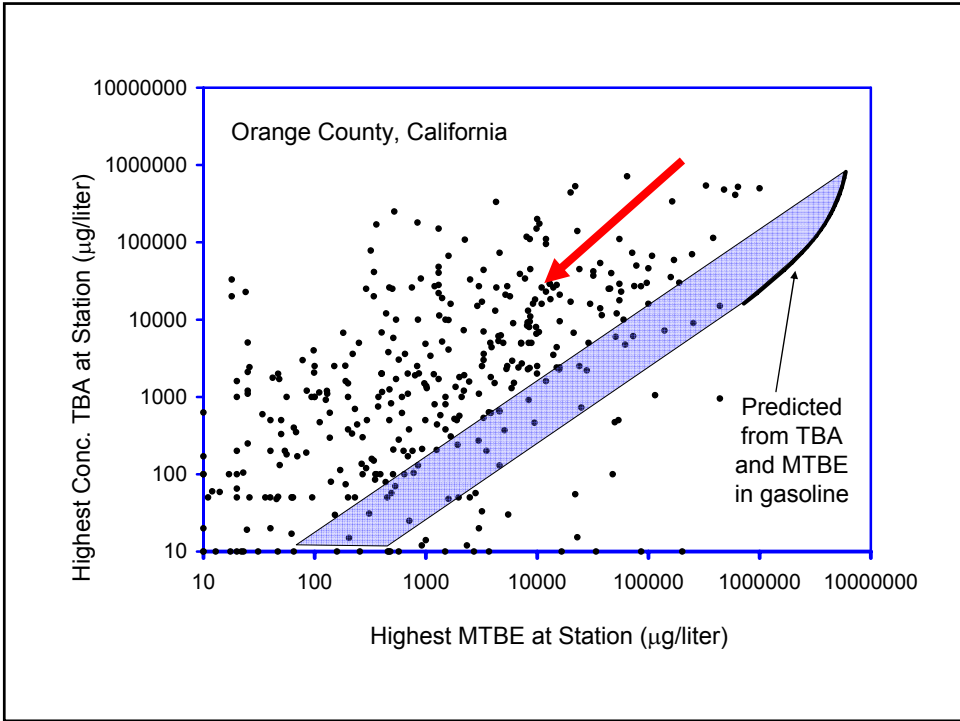


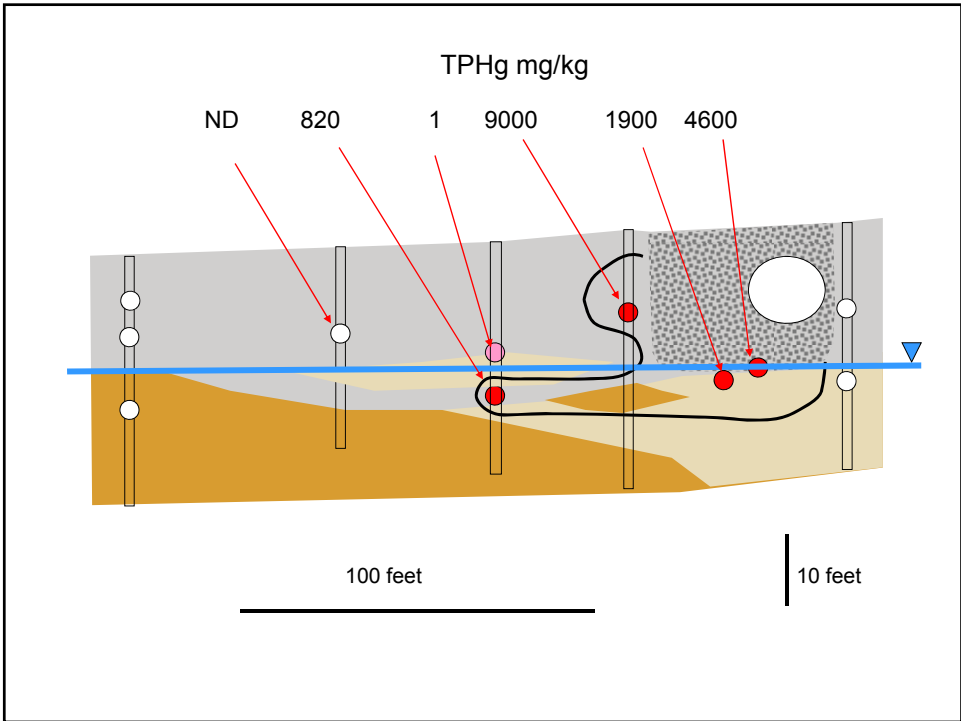
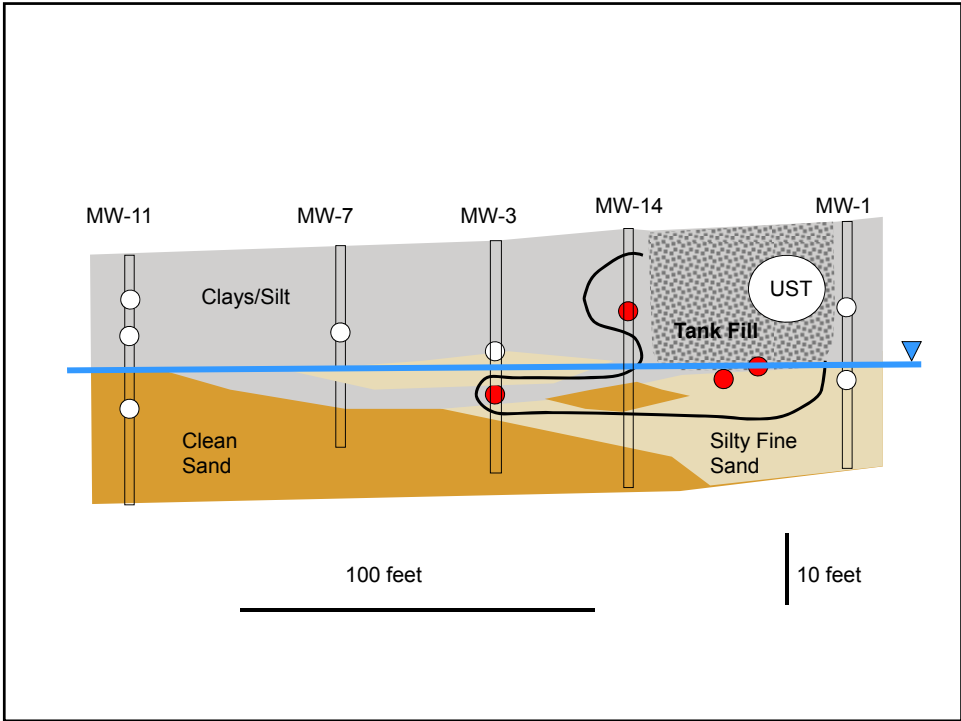
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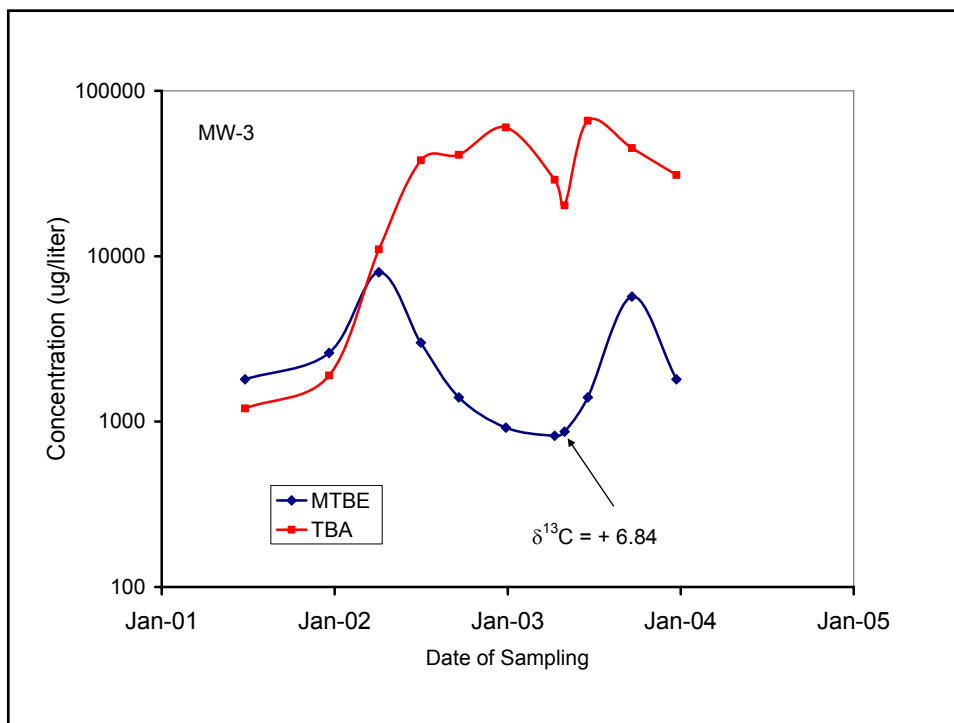
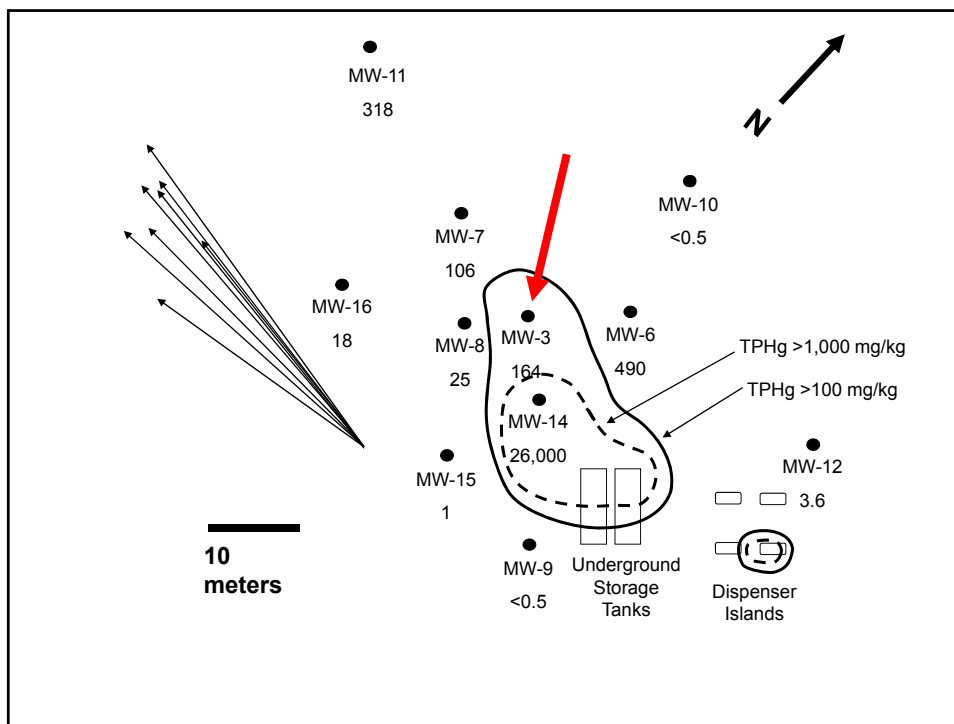
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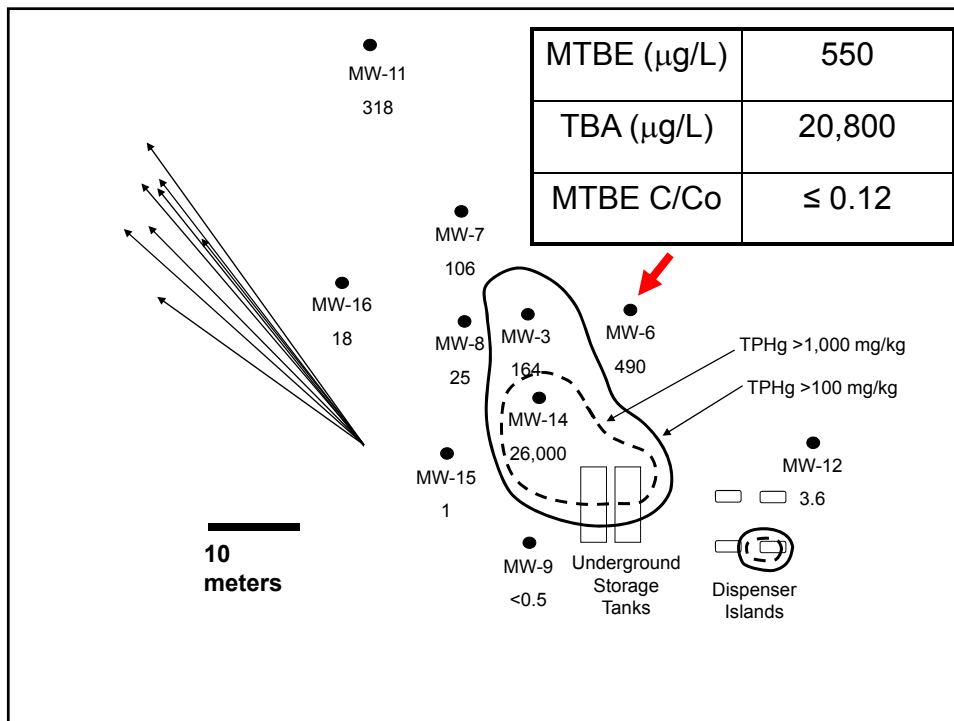
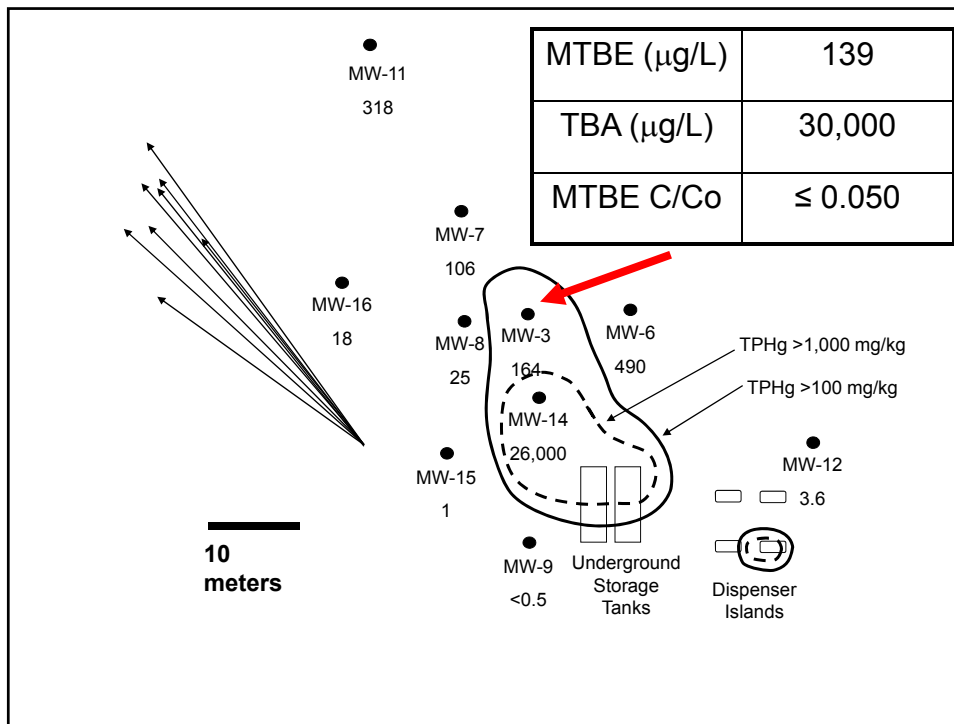
Evidence of Natural MTBE Biodegradation

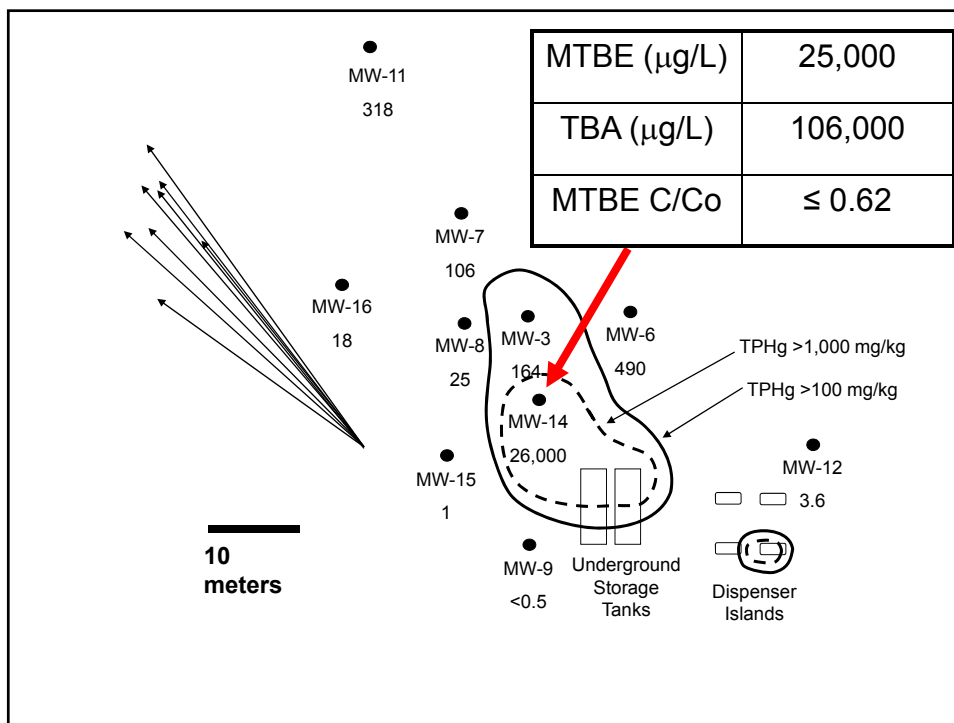
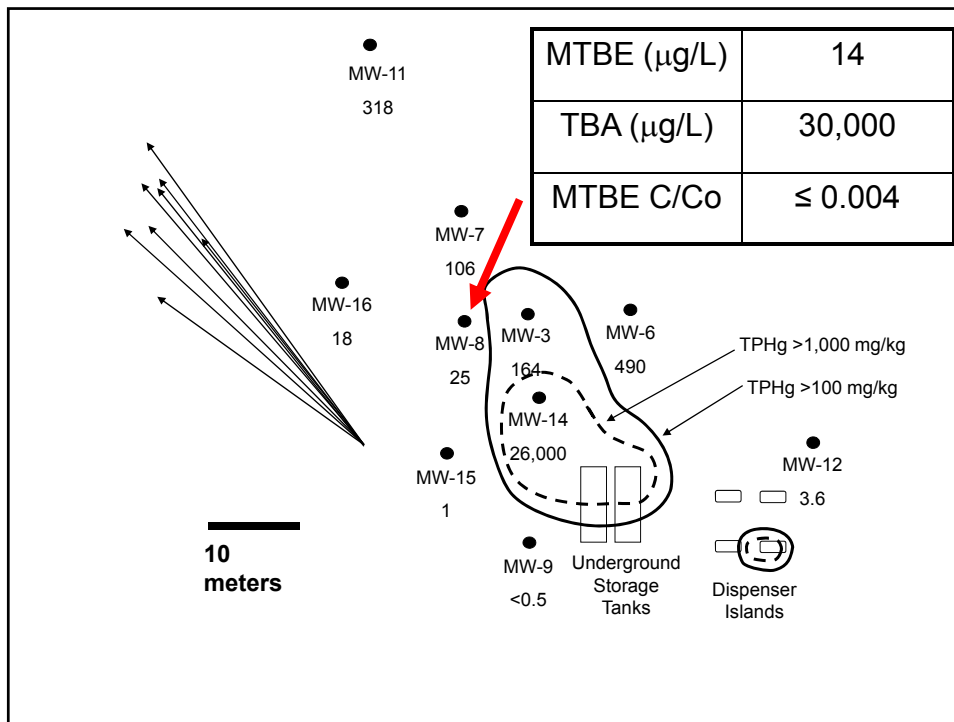
The red arrow in the next figure is the datum for the gasoline spill site used for a case study.

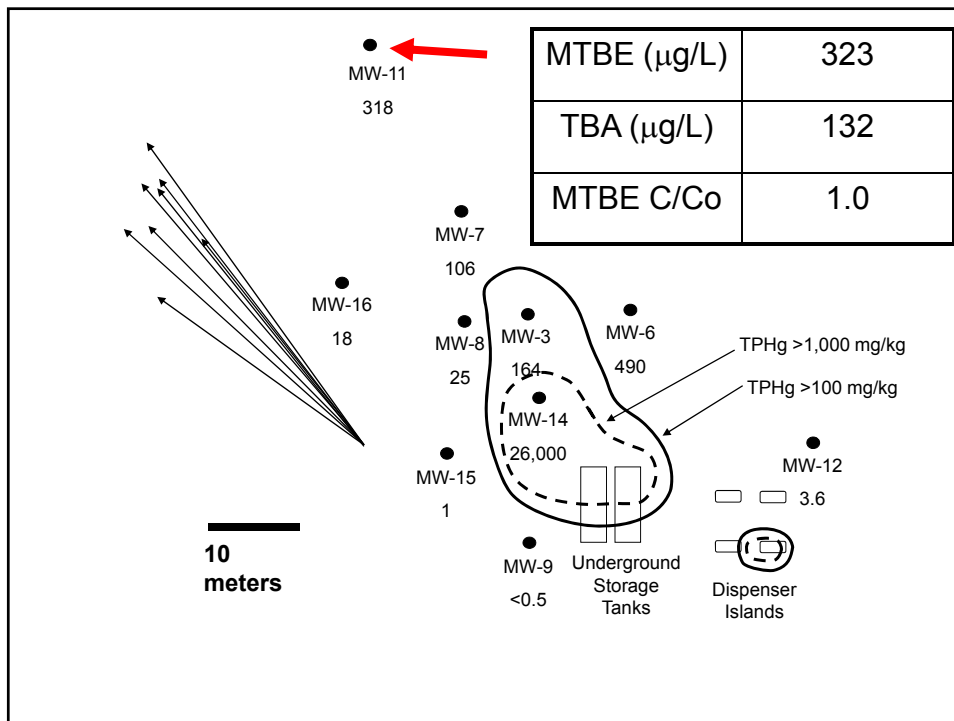
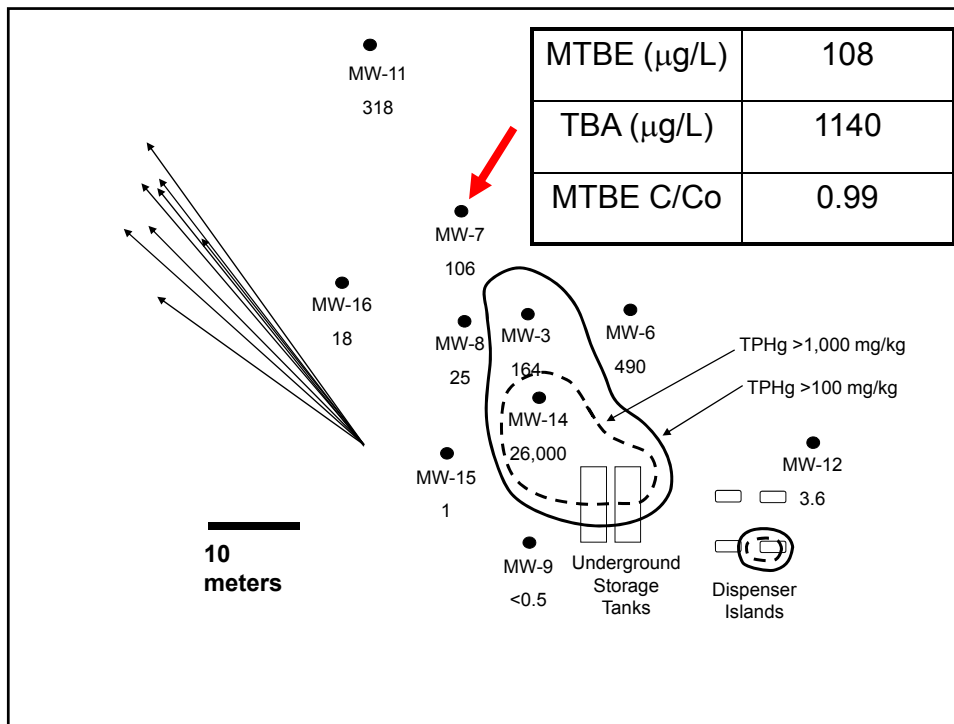












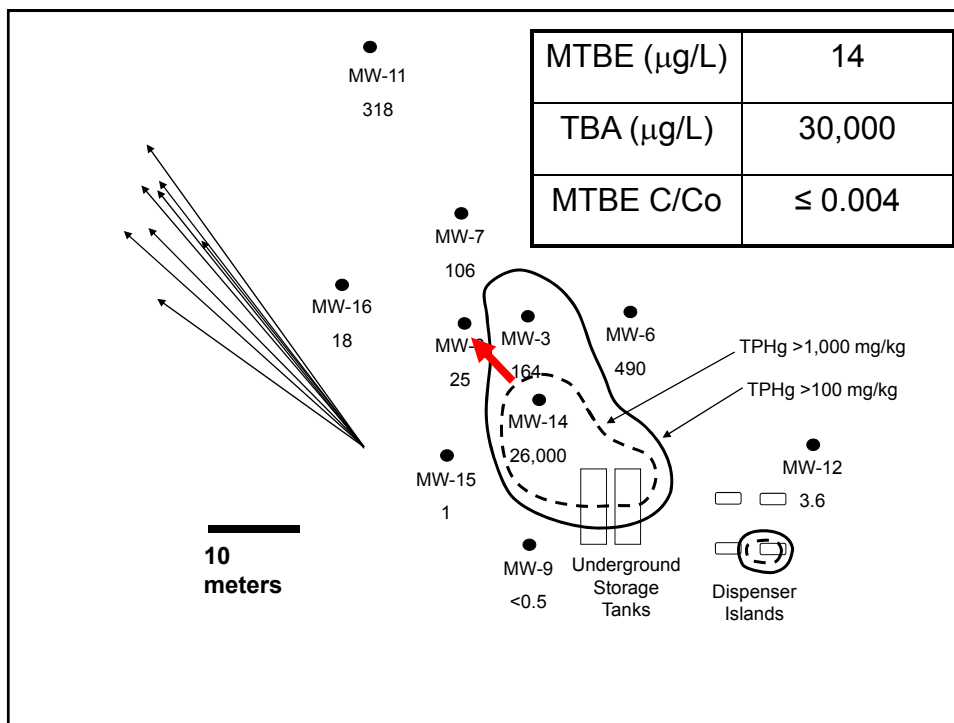
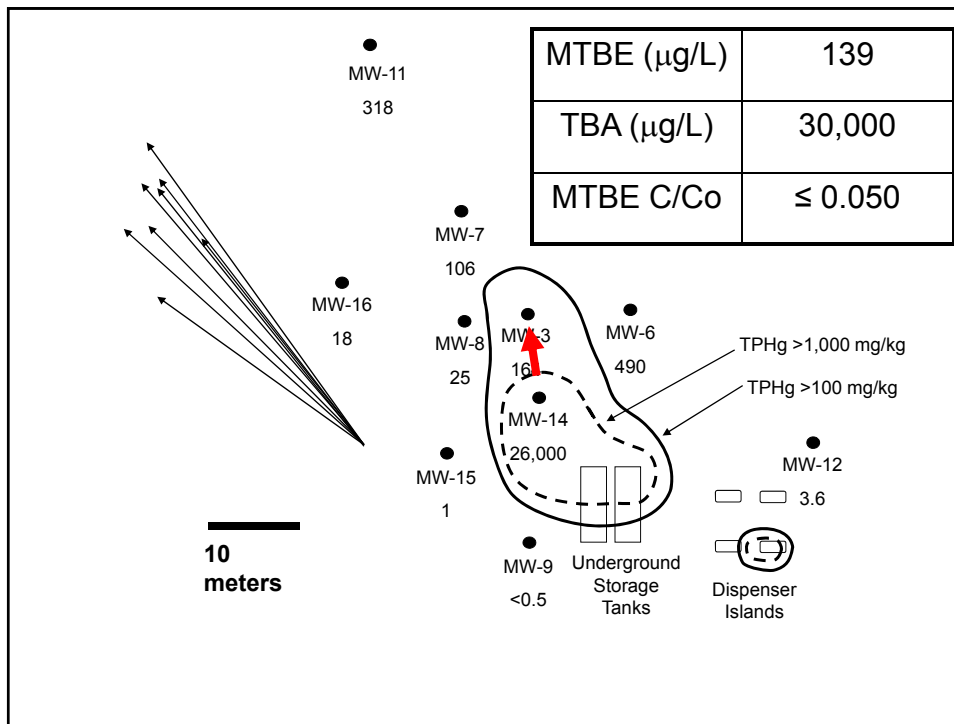
Evidence of Natural MTBE Biodegradation

There was substantial anaerobic biodegradation of MTBE in water from many wells.

There was no biodegradation of MTBE in wells at the perimeter of the plume!

Approach to deal with heterogeneity in biodegradation

- 1) Determine if biodegradation (when it occurs) is stable over time.**
- 2) Determine the extent of the core of the plume if controlled by biodegradation.**
- 3) Determine the extent of the periphery of the plume if there is not biodegradation.**



Reproducibility of Stable Carbon Isotope Ratios over time at field scale.

Well	Date	TBA measured (µg/L)	MTBE measured (µg/L)	δ ¹³ C of MTBE (‰)	Faction MTBE remaining
MW-14	5/20/03	13,000	11,000	-23.88	0.75
	8/18/04	107,000	26,000	-21.58	0.62
MW-3	5/20/03	20,000	870	6.84	0.058
	8/18/04	32,000	164	8.53	0.050
MW-8	5/20/03	10,000	19	18.11	0.023
	8/18/04	32,000	25	37.99	0.0043

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The average hydraulic conductivity based on slug tests of monitoring wells was 11 meters per day.

The average hydraulic gradient was 0.0023 meter/meter based on thirteen rounds of water table elevations.

Assuming an effective porosity of 0.25, the average seepage velocity is 37 meters per year.

$$k_{\text{with distance}} = -\ln(F) / d$$

$$k_{\text{with time}} = -\ln(F) * v / d$$

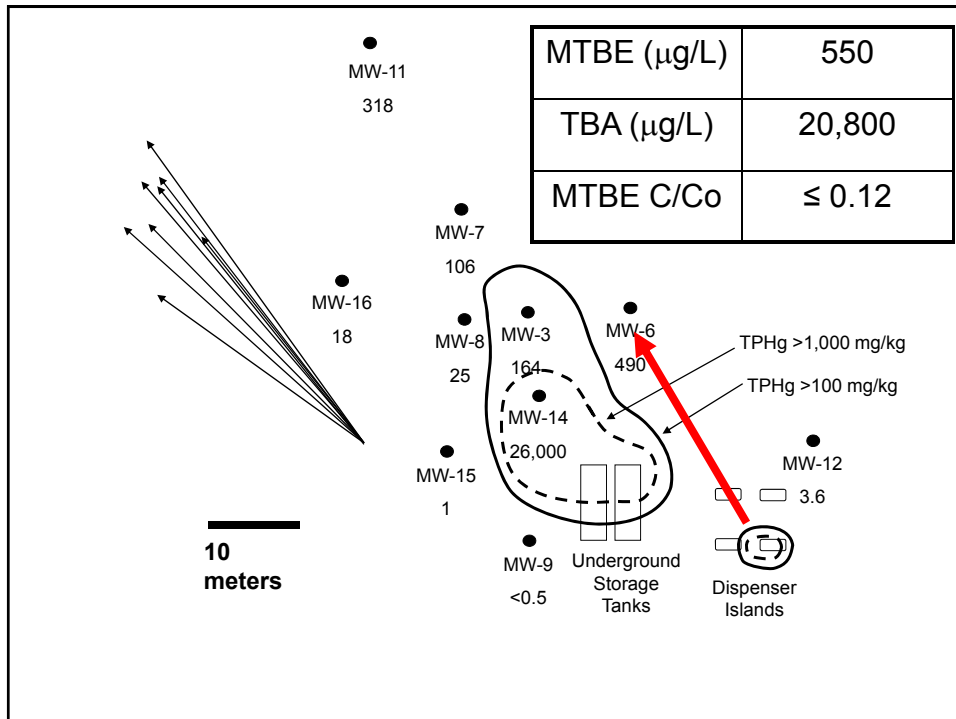
F is the fraction of MTBE remaining

d is the distance between the wells

v is the ground water seepage velocity

Well	Date	Fraction MTBE Remaining (C/C _o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Distance (per meter)
MW-3	5/20/03	0.058	9.6	0.30
MW-3	8/18/04	0.050	9.6	0.31
MW-8	5/20/03	0.023	11.7	0.32
MW-8	8/18/04	0.0043	11.7	0.46

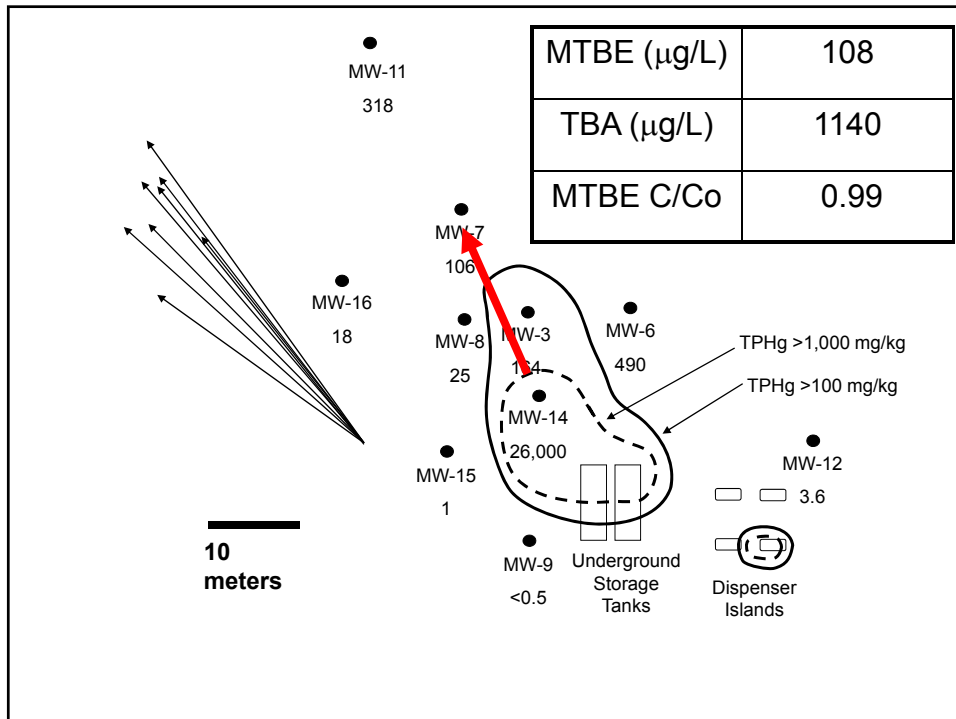
Well	Date	Fraction MTBE Remaining (C/C _o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Time (per year)
MW-3	5/20/03	0.058	9.6	10.9
MW-3	8/18/04	0.050	9.6	11.5
MW-8	5/20/03	0.023	11.7	11.9
MW-8	8/18/04	0.0043	11.7	17.1

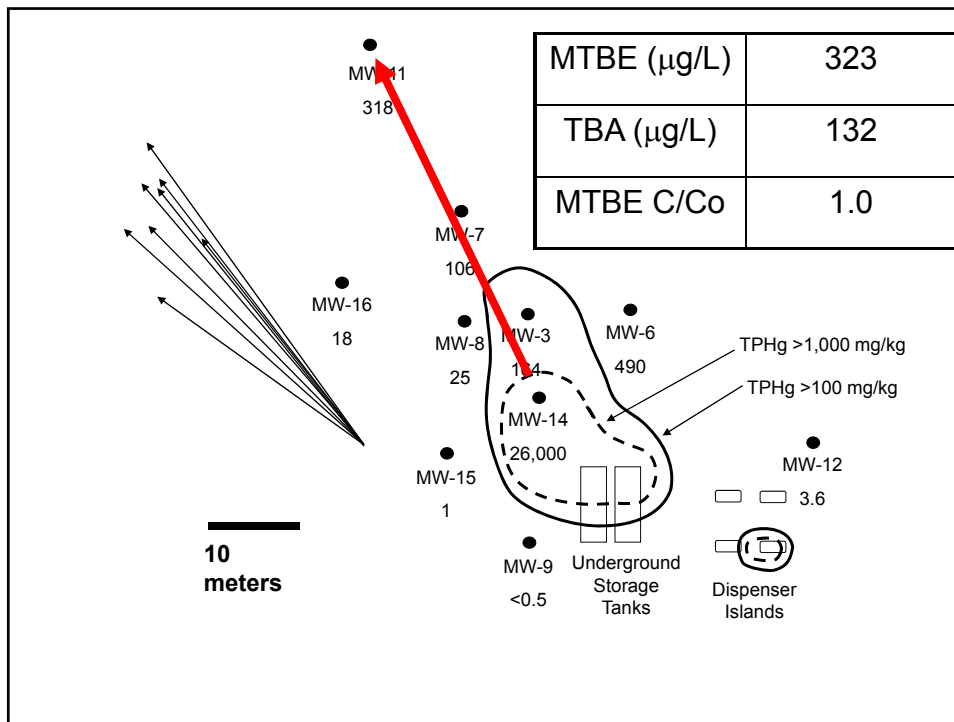


Well	Date	TBA measured (µg/L)	MTBE measured (µg/L)	$\delta^{13}\text{C}$ of MTBE (‰)	Faction MTBE remaining
MW-6	5/20/03	3,600	47	9.83	0.045
	8/18/04	19,200	490	-1.58	0.116

Well	Date	Fraction MTBE Remaining (C/C _o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Distance (per meter)
MW-6	5/20/03	0.045	31.1	0.10
MW-6	8/18/04	0.116	31.1	0.069

Well	Date	Fraction MTBE Remaining (C/C _o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Time (per year)
MW-6	5/20/03	0.045	31.1	3.7
MW-6	8/18/04	0.116	31.1	2.6





Well	Date	TBA measured (µg/L)	MTBE measured (µg/L)	$\delta^{13}\text{C}$ of MTBE (‰)	Faction MTBE remaining
MW-14	5/20/03	13,000	11,000	-23.88	0.75
	8/18/04	107,000	26,000	-21.58	0.62
MW-7	8/18/04	1,220	106	-27.33	0.994
MW-11	5/20/03	<10	1	-31.5*	1.41
	8/18/04	135	318	-28.92	1.14

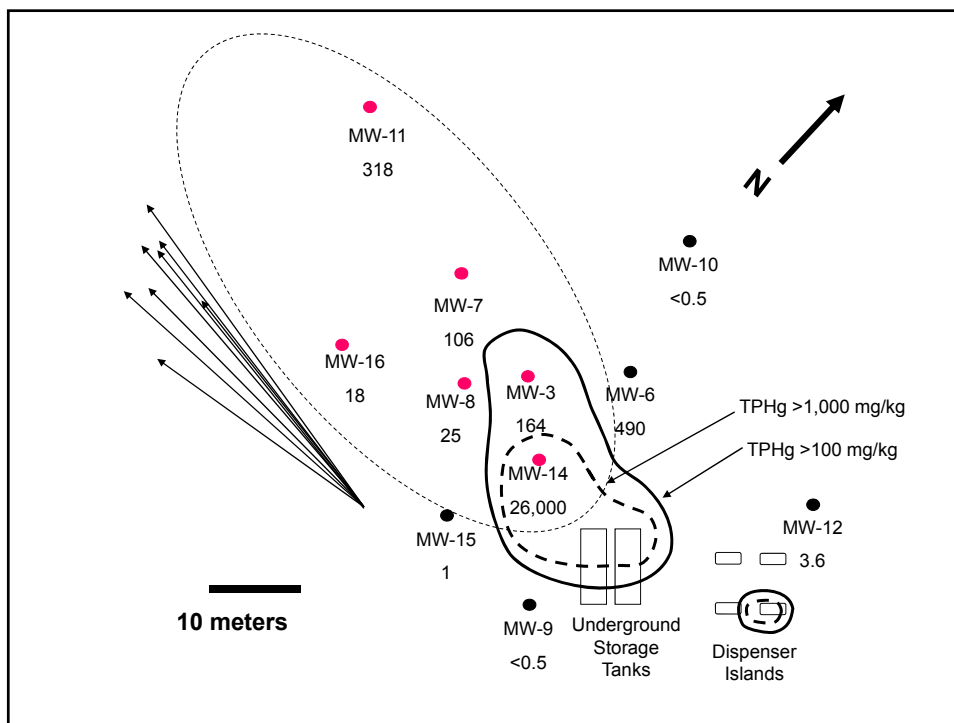
*The concentration MTBE was below the limit for the accurate determination of $\delta^{13}\text{C}$; the precision of the estimate of $\delta^{13}\text{C}$ was ± 3 ‰ rather than ± 0.1 ‰.

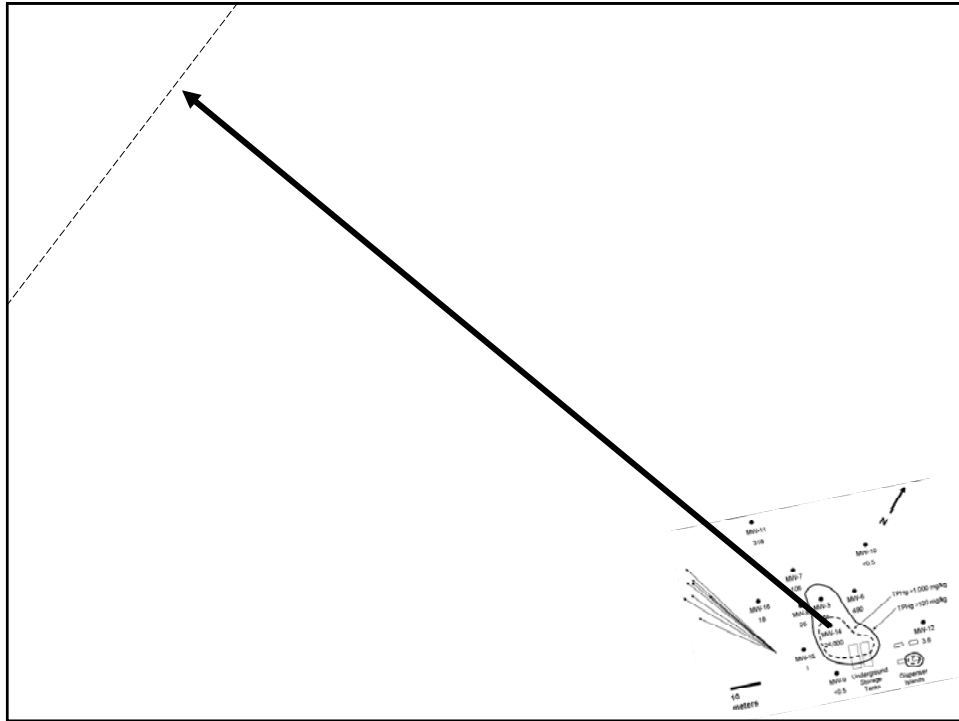
Well	Date	Fraction MTBE Remaining (C/C _o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Distance (per meter)
MW-7	8/18/04	0.994	23.0	0.00025
MW11	5/20/03	1.0	44.1	0
MW11	8/18/04	1.0	44.1	0

Well	Date	Fraction MTBE Remaining (C/C _o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Time (per year)
MW-7	8/18/04	0.994	23.0	0.0093
MW11	5/20/03	1.0	44.1	0
MW11	8/18/04	1.0	44.1	0

Approach to deal with heterogeneity in biodegradation

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- 2) Determine the extent of the core of the plume if controlled by biodegradation.
- 3) Determine the extent of the periphery of the plume if there is not biodegradation.





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BIOCHLOR 2.2 will be used to evaluate the potential exposure to the receptor.

Available at

<http://www.epa.gov/ada/csamos/models/biochlor.html>

TYPE OF Contaminant: Ethenes Ethanes

1. ADVECTION
 Seepage Velocity* Vs 121.2 (ft/yr)
 Hydraulic Conductivity K 1.3E-02 (cm/sec)
 Hydraulic Gradient i 0.0023 (ft/ft)
 Effective Porosity n 0.25 (-)

2. DISPERSION
 Alpha x* 100 (ft)
 (Alpha y) / (Alpha x)* 0.1 (-)
 (Alpha z) / (Alpha x)* 1.E-99 (-)

3. ADSORPTION
 Retardation Factor* R
 Soil Bulk Density, rho 1.6 (kg/L)
 FractionOrganicCarbon, foc 1.8E-3 (-)
 Partition Coefficient Koc

PCE	426 (L/kg)	5.91 (-)
TCE	130 (L/kg)	2.50 (-)
DCE	125 (L/kg)	2.44 (-)
VC	30 (L/kg)	1.34 (-)
ETH	302 (L/kg)	4.48 (-)

5. GENERAL
 Simulation Time* 33 (yr)
 Modeled Area Width* 500 (ft)
 Modeled Area Length* 1000 (ft)
 Zone 1 Length* 1000 (ft)
 Zone 2 Length* 0 (ft)

Dispersivity Menu
 Choose dispersivity calculation method to estimate an alpha x value:
 Option 1) Fixed
 Enter fixed value for alpha x: _____ ft.
 Recommended range: 10 - 70 ft
 See Figure A.2 in Appendix A.4 of the BIOCHLOR User's Manual, Jan. 2000 for guidance
 Option 2) alpha x = 0.1*(Lp)
 Enter an approximate plume length to estimate a representative dispersivity value: Lp = 1000 ft.
 Calc. Alpha x 100 ft.
 Option 3) Modified Xu and Eckstein

(Alpha z) / (Alpha x)* 1.E-05 (-)

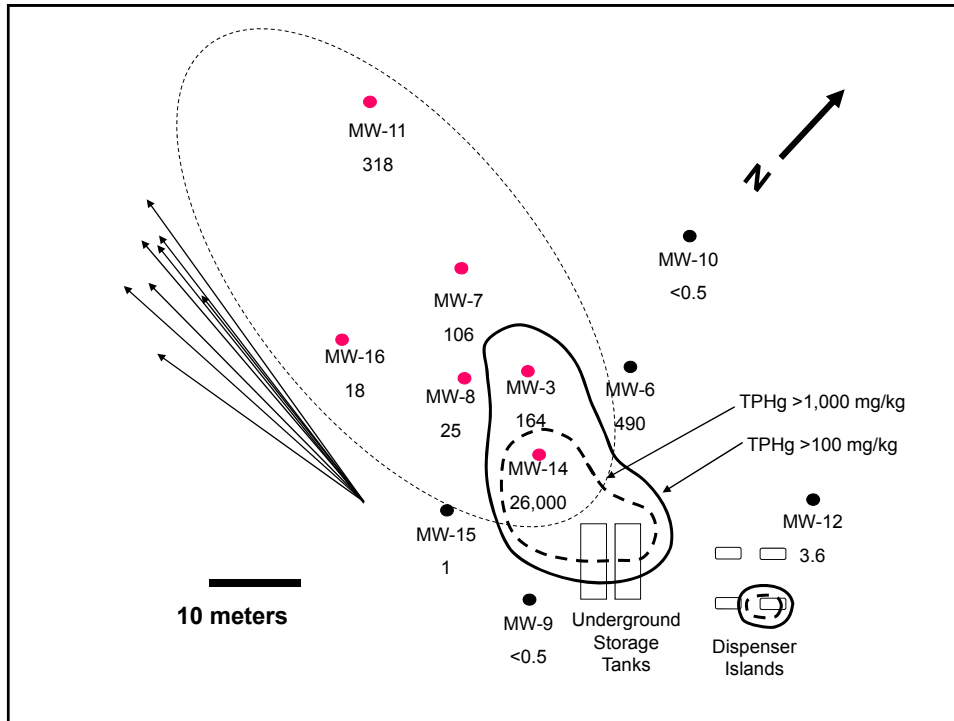
3. ADSORPTION
 Retardation Factor* R
 Soil Bulk Density, rho 1.6 (kg/L)
 FractionOrganicCarbon, foc 1.8E-3 (-)
 Partition Coefficient Koc

PCE	426 (L/kg)	7.13 (-)
TCE	130 (L/kg)	2.87 (-)
DCE	125 (L/kg)	2.80 (-)
VC	30 (L/kg)	1.43 (-)
ETH	302 (L/kg)	5.35 (-)

Common R (used in model)* = 1.00

4. BIOTRANSFORMATION
 -1st Order Decay Coefficient*
 Zone 1
 PCE → TCE λ (1/yr) 10.000 half-life (yrs) Yield 0.79
 TCE → DCE 0.000 ← 0.74
 DCE → VC 0.000 ← 0.64
 VC → ETH 0.000 ← 0.45
 Zone 2
 PCE → TCE 0.000 ←
 TCE → DCE 0.000 ←
 DCE → VC 0.000 ←
 VC → ETH 0.000 ←

λ HELP



6. SOURCE DATA TYPE: Continuous Single Planar

Source Options

Source Thickness in Sat. Zone* (ft)

Width* (ft)

Conc. (mg/L)* C1

PCE	26.0
TCE	
DCE	
VC	
ETH	

k_s^* (1/yr)

0
0
0
0
0
0

Vertical Plane Source: Determine Source Well Location and Input Solvent Concentrations

View of Plume Looking Down

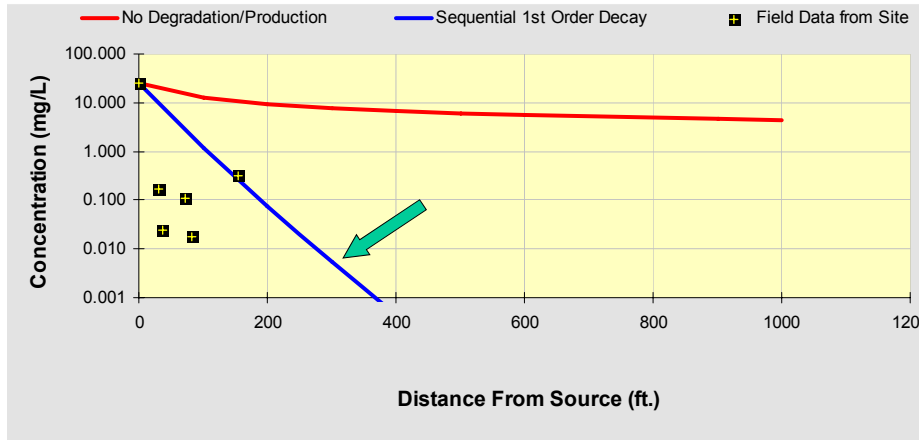
Observed Centerline Conc. at Monitoring Wells

7. FIELD DATA FOR COMPARISON

PCE Conc. (mg/L)	26.0	.164	.025	.106	.018	.318				
TCE Conc. (mg/L)										
DCE Conc. (mg/L)										
VC Conc. (mg/L)										
ETH Conc. (mg/L)										
Distance from Source (ft)	0	30	38	72	83	154				
Date Data Collected										

8. CHOOSE TYPE OF OUTPUT TO SEE:

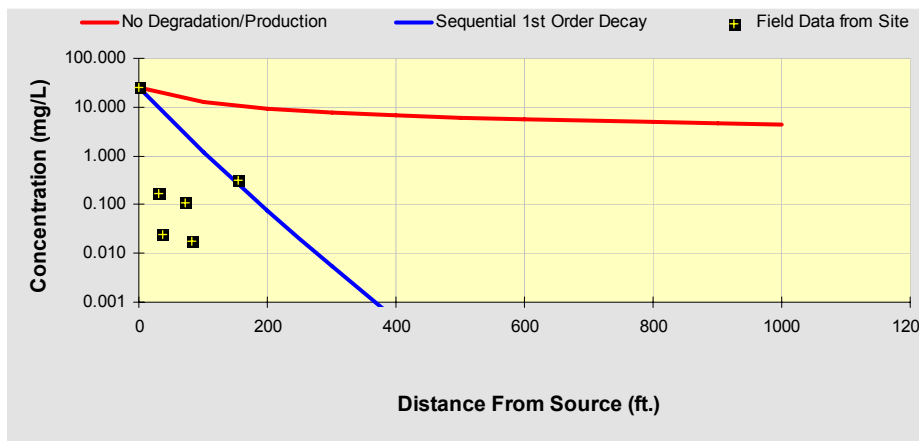
With Source at 26 mg/L and Biodegradation = 10 per year

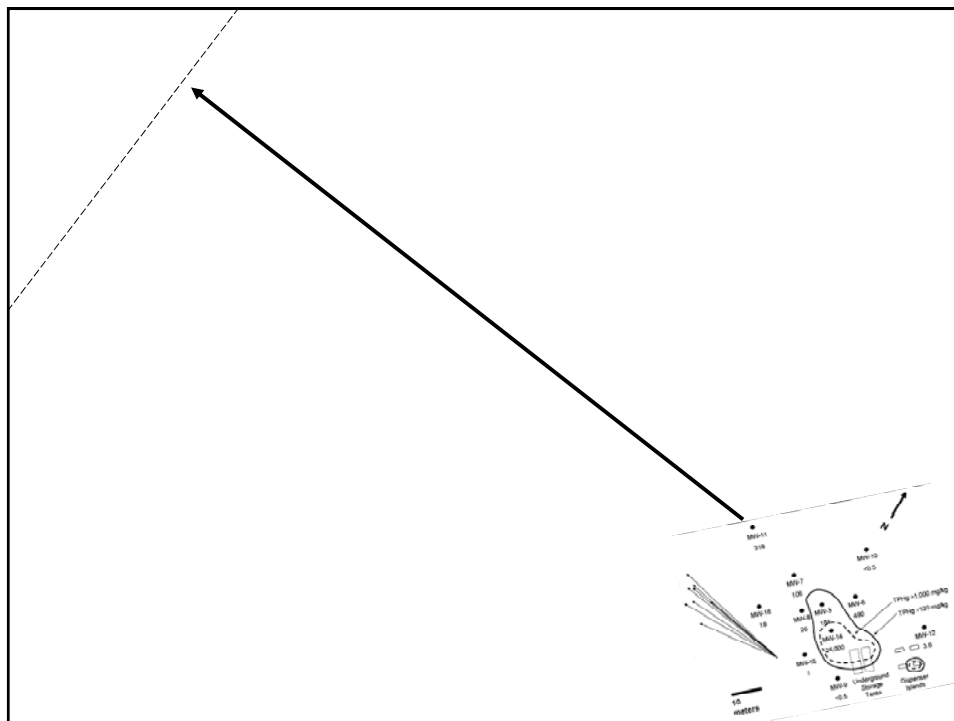
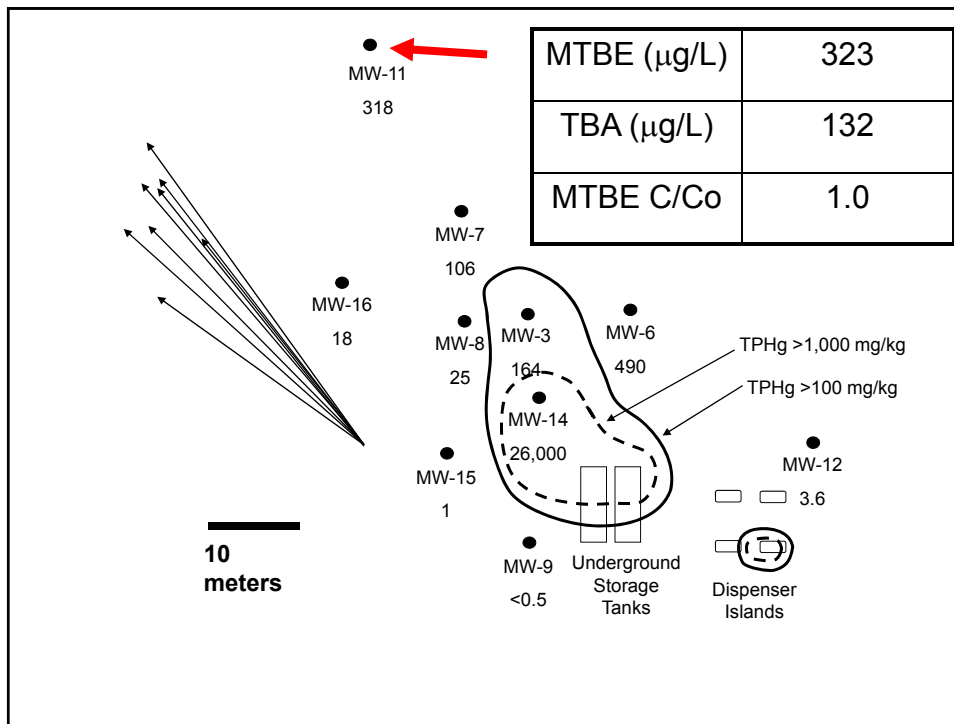


Clean in approximately 300 feet of travel

With Source at 26 mg/L and no Biodegradation

Not even close to clean in 1000 feet of travel





Approach to deal with heterogeneity in biodegradation

- 1) Determine if biodegradation (when it occurs) is stable over time.
- 2) Determine the extent of the core of the plume if controlled by biodegradation.
- 3) Determine the extent of the periphery of the plume if there is not biodegradation.

With Source at MW-11 at 0.318 mg/L

Biodegradation = 0.0004 per year

Potential Receptor at 860 feet from MW-11

BIOCHLOR Natural Attenuation Decision Support System Version 2.2 Excel 2000

NYDEC Training Run Name

Data Input Instructions:
 115 → 1. Enter value directly... or
 0.02 → 2. Calculate by filling in gray cells. Press Enter, then (C)
 (To restore formulas, hit "Restore Formulas" button)
 Variable* → Data used directly in model.

1. ADVECTION
 Seepage Velocity* Vs 121.2 (ft/yr)
 Hydraulic Conductivity K 1.3E-02 (cm/sec)
 Hydraulic Gradient i 0.0023 (ft/ft)
 Effective Porosity n 0.25 (-)

2. DISPERSION
 Alpha x* 86 (ft) Calc. Alpha x
 (Alpha y) / (Alpha x)* 0.1 (-)
 (Alpha z) / (Alpha x)* 1.E-02 (-)

3. ADSORPTION
 Retardation Factor* R
 Soil Bulk Density, rho 1.6 (kg/L)
 Fraction Organic Carbon, foc 1.8E-3 (-)
 Partition Coefficient Koc
 PCE 426 (L/kg) 5.91 (-)
 TCE 130 (L/kg) 2.50 (-)
 DCE 125 (L/kg) 2.44 (-)
 VC 30 (L/kg) 1.34 (-)
 ETH 302 (L/kg) 4.48 (-)
 Common R (used in model)* = 1.00

4. BIOTRANSFORMATION
 -1st Order Decay Coefficient*
 Zone 1
 PCE → TCE 0.000 λ (1/yr) half-life (yrs) Yield 0.79
 TCE → DCE 0.000 0.74
 DCE → VC 0.000 0.64
 VC → ETH 0.000 0.45
 Zone 2
 PCE → TCE 0.000 λ (1/yr) half-life (yrs) Yield
 TCE → DCE 0.000 0.74
 DCE → VC 0.000 0.64
 VC → ETH 0.000 0.45

5. GENERAL
 Simulation Time* 33 (yr) L
 Modeled Area Width* 500 (ft) W
 Zone 1 Length* 860 (ft) Zone 2 Length* 0 (ft) Zone 2= L - Zone 1

6. SOURCE DATA
 TYPE: Continuous Single Planar
 Source Options
 Source Thickness in Sat. Zone* 10 (ft)
 Width* (ft) Y1 60
 Conc. (mg/L)* C1
 MTBE 0.318
 TBA 0
 0
 0
 0
 0
 k₁* (1/yr)
 Vertical Plane Source: Determine Source Well Location and Input Solvent Concentrations
 View of Plume Looking Down
 Observed Centerline Conc. at Monitoring Wells

7. FIELD DATA FOR COMPARISON
 MTBE Conc. (mg/L)
 TBA Conc. (mg/L)

Distance from Source (ft) 0 30 38 72 83 154
 Date Data Collected

8. CHOOSE TYPE OF OUTPUT TO SEE:
 RUN CENTERLINE RUN ARRAY
 Help Restore Formulas RESET
 SEE OUTPUT Paste Example

With Source at 0.318 mg/L

Biodegradation = 0.001 per year

Potential Receptor at 860 feet

TYPE OF Contaminant:		Ethenes <input checked="" type="radio"/>	5. GENERAL	
		Ethanes <input type="radio"/>	Simulation Time*	33 (yr)
1. ADVECTION			Modeled Area Width*	500 (ft)
Seepage Velocity*	Vs	121.2 (ft/yr)	Modeled Area Length*	860 (ft)
or			Zone 1 Length*	860 (ft)
Hydraulic Conductivity	K	1.3E-02 (cm/sec)	Zone 2 Length*	0 (ft)
Hydraulic Gradient	i	0.0023 (ft/ft)	6. SOURCE DATA TYPE: Con Sing	
Effective Porosity	n	0.25 (-)	Source Options	
2. DISPERSION		Calc. Alpha x	Source Thickness in Sat. Zone*	10
Alpha x*			Y1	
(Alpha y) / (Alpha x)*			Width* (ft)	60
(Alpha z) / (Alpha x)*				
3. ADSORPTION				

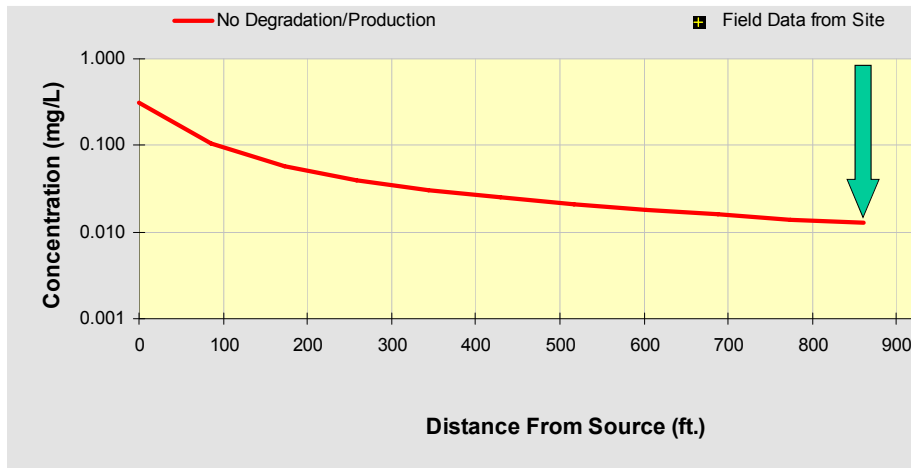
With Source at 0.318 mg/L

Biodegradation = 0.001 per year

Potential Receptor at 840 feet

Hydraulic Gradient	i	0.0023 (ft/ft)	6. SOURCE DATA TYPE: Con Sing	
Effective Porosity	n	0.25 (-)	Source Options	
2. DISPERSION		Calc. Alpha x	Source Thickness in Sat. Zone*	10
Alpha x*			Y1	
(Alpha y) / (Alpha x)*			Width* (ft)	60
(Alpha z) / (Alpha x)*			Conc. (mg/L)*	C1
3. ADSORPTION			MTBE	.318
Retardation Factor*	R		TBA	
or			7. FIELD DATA FOR COMPA	
Soil Bulk Density, rho		1.6 (kg/L)	MTBE Conc. (mg/L)	
Fraction Organic Carbon, f _{oc}		1.8E-3 (-)	TBA Conc. (mg/L)	
Partition Coefficient	K _{oc}		8. CHOOSE TYPE OF OUTP	
PCE		426 (L/kg)		
TCE		130 (L/kg)		
DCE		125 (L/kg)		
VC		30 (L/kg)		
ETH		302 (L/kg)		
Common R (used in model)* =		1.00		
4. BIOTRANSFORMATION		-1st Order Decay Coefficient*		
Zone 1				
PCE → TCE	λ (1/yr)	0.000	half-life (yrs)	0.79
TCE → DCE		0.000		0.74
DCE → VC		0.000		0.64
VC → ETH		0.000		0.45

**With Source at 0.318 mg/L
and No Biodegradation**



**RESEARCH &
DEVELOPMENT**

*Building a
scientific
foundation
for sound
environmental
decisions*

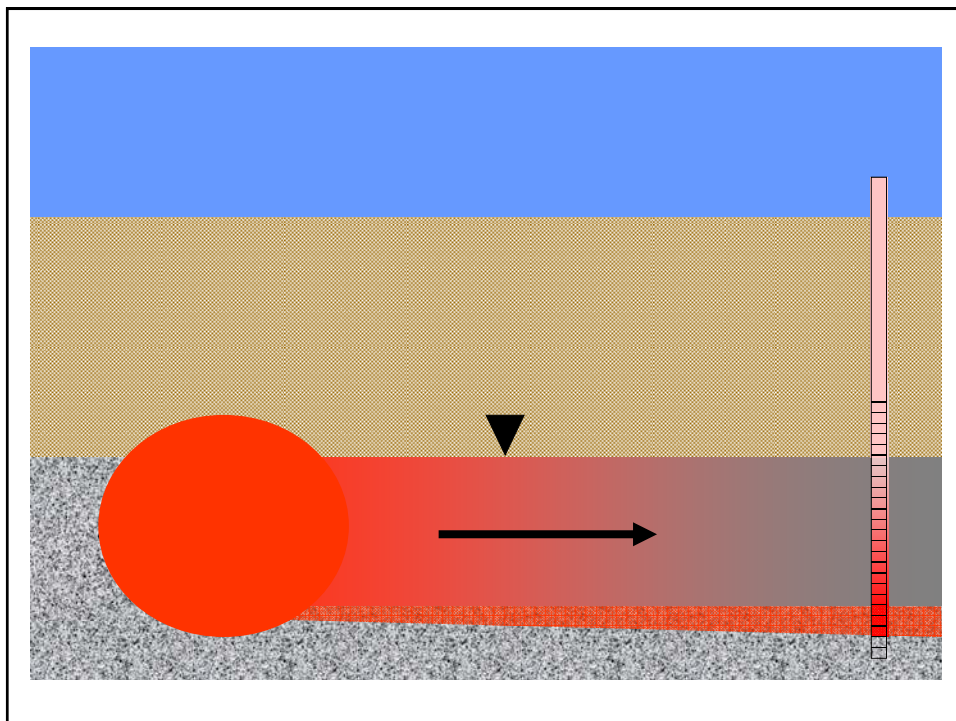
Given the uncertainty in modeling, there is substantial possibility that MTBE will impact the hypothetical receptor at unacceptable concentrations.

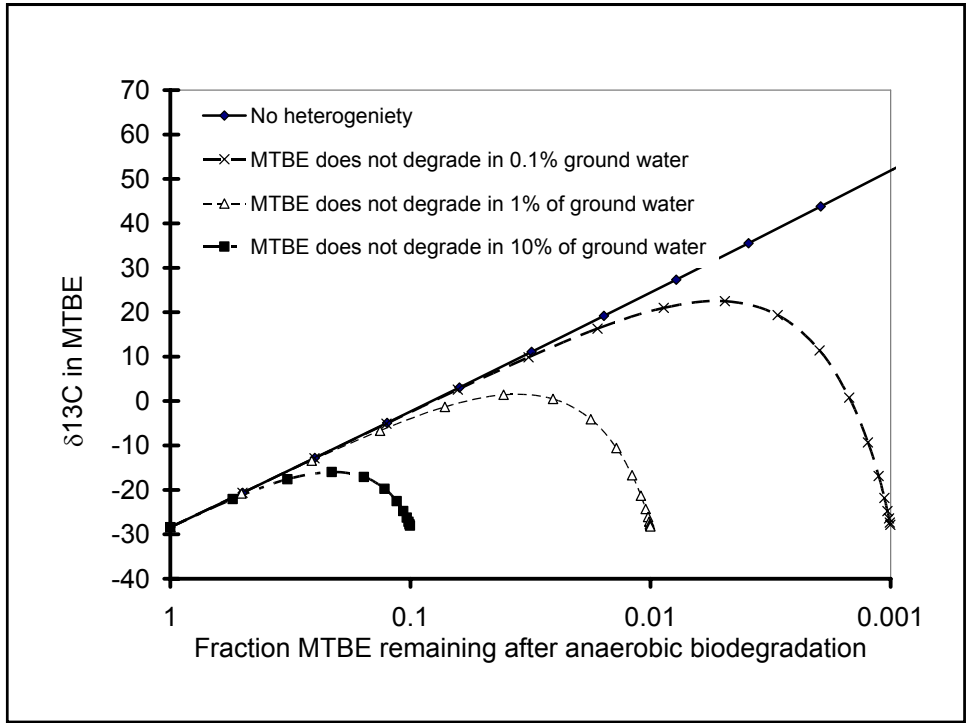
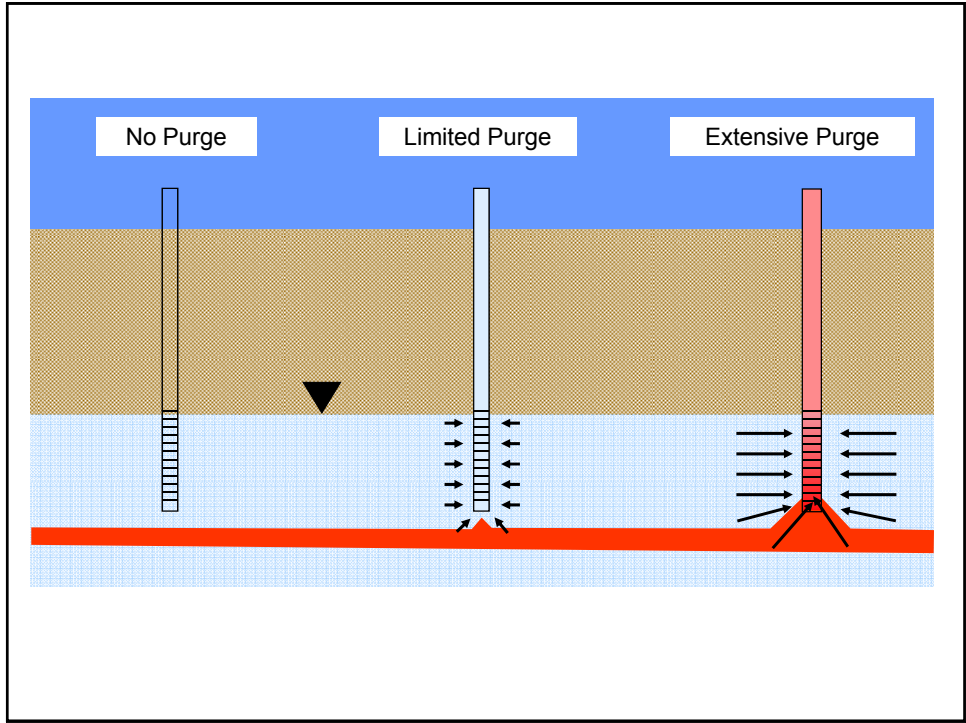
The hypothetical receptor at 1000 feet from the source was intentionally chosen to illustrate the dominant role of biodegradation on the attenuation of concentrations of contaminants in ground water.

The exposure assessment at most real sites will be much less ambiguous.

Effect of spatial heterogeneity on isotopic fractionation

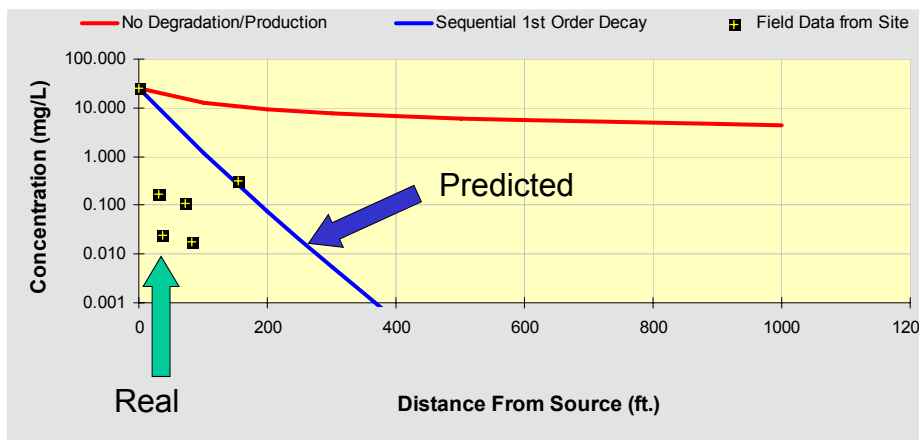
- 1) Heterogeneity produces blended samples.
- 2) The extent of fractionation will be less than expected from the true extent of biodegradation.
- 3) Heterogeneity causes SCIR to underestimate biodegradation.





Note that the real attenuation in concentrations were substantially greater than would be expected from the prediction of C/Co based on the analysis of stable carbon isotopes.

With Source at 26 mg/L and Biodegradation = 10 per year



Field scale reductions in concentration are greater than predicted from C/Co estimated from CSIA