



Welcome to the CLU-IN Internet Seminar

Stable Isotope Analyses to Understand the Degradation of
Organic Contaminants in Ground Water

Sponsored by: U.S. EPA Technology Innovation and Field
Services Division

Delivered: September 9, 2010, 2:00 PM - 4:00 PM, EDT (18:00-20:00
GMT)

Instructor:

John T. Wilson, U.S. EPA, R.S. Kerr Environmental Research Center (wilson.johnt@epa.gov)

Moderator:

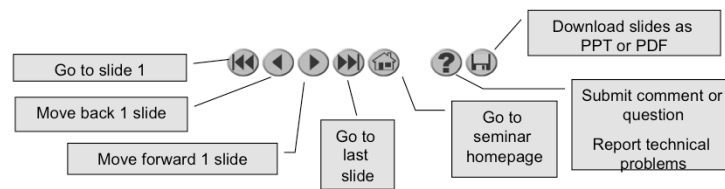
Jean Balent, U.S. EPA, Technology Innovation and Field Services Division (balent.jean@epa.gov)

Visit the Clean Up Information Network online at www.cluin.org

1

Housekeeping

- Please mute your phone lines, Do NOT put this call on hold
 - press *6 to mute #6 to unmute your lines at anytime
- Q&A
- Turn off any pop-up blockers
- Move through slides using # links on left or buttons



- This event is being recorded
- Archives accessed for free <http://clu.in.org/live/archive/>

2

Although I'm sure that some of you have these rules memorized from previous CLU-IN events, let's run through them quickly for our new participants.

Please mute your phone lines during the seminar to minimize disruption and background noise. If you do not have a mute button, press *6 to mute #6 to unmute your lines at anytime. Also, please do NOT put this call on hold as this may bring delightful, but unwanted background music over the lines and interrupt the seminar.

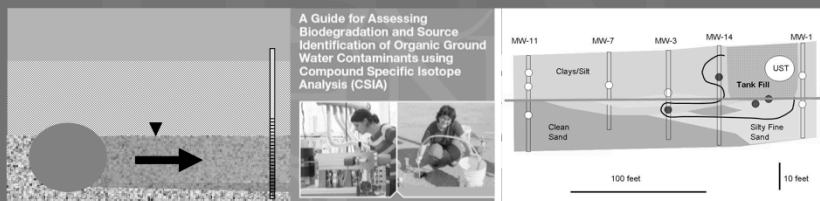
You should note that throughout the seminar, we will ask for your feedback. You do not need to wait for Q&A breaks to ask questions or provide comments. To submit comments/questions and report technical problems, please use the ? Icon at the top of your screen. You can move forward/backward in the slides by using the single arrow buttons (left moves back 1 slide, right moves advances 1 slide). The double arrowed buttons will take you to 1st and last slides respectively. You may also advance to any slide using the numbered links that appear on the left side of your screen. The button with a house icon will take you back to main seminar page which displays our agenda, speaker information, links to the slides and additional resources. Lastly, the button with a computer disc can be used to download and save today's presentation materials.

With that, please move to slide 3.

Applications of Stable Isotope Analyses to Understand the Degradation of Organic Contaminants in Ground Water

Part 1. Applications

John T. Wilson, U.S. Environmental Protection Agency



September 9, 2010

Office of Research and Development
National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division



If you have questions, or want to request a copy
of the Powerpoint file, send e-mail to
wilson.johnt@epa.gov.



Volatile organic contaminants in ground water are usually composed of carbon, hydrogen and chloride.

Each of these elements have more than one stable isotope. These stable isotopes are not radioactive. The stable isotopes differ from each other in the number of neutrons in the nucleus of the atom.

As organic compounds degrade, the ratio of stable isotopes in the fraction remaining after degradation may change in a predictable way.

Compound specific stable isotope analyses (CSIA) can provide an unambiguous conservative boundary on the extent of degradation of organic compounds in ground water.



**OSWER Directive 9200.4-17P
in regard to-
Sites Where MNA May Be Appropriate**

- MNA is appropriate as remedial approach only where it:
 - Can be demonstrated to achieve remedial objectives within a reasonable time frame, and
- Meets the applicable remedy selection criteria for the particular regulatory program.

*To make the evaluation, must know the
rate of natural attenuation.*



OSWER Directive 9200.4-17P
in regard to-
Demonstrating the Performance of MNA

Three types of site-specific information may be required:

1. Historical ground water and/or soil chemistry data demonstrates a trend of declining contaminant concentration.
2. Hydrogeologic and geochemical data that demonstrate NA processes and rates.
3. Data from field or microcosm studies which directly demonstrate the occurrence of a particular attenuation process and its ability to degrade the contaminants of concern.



By documenting degradation, CSIA can provide the third line of evidence.

In appropriate circumstances, CSIA be used to identify the mechanisms and provide an estimate of the rate of degradation.

Element	Stable Isotopes	Relative Abundance
Hydrogen	^1H	0.99985
	^2H	0.00015
Carbon		
	^{12}C	0.9889
	^{13}C	0.0111
Chlorine	^{35}Cl	0.7577
	^{37}Cl	0.2423

Analysis of Stable Carbon Isotope Ratios

The ratio of stable isotopes is determined with an Isotope Ratio Mass Spectrometer (IRMS).

The IRMS compares the ratio of ^{13}C to ^{12}C in the sample against the ratio of ^{13}C to ^{12}C in a reference standard.

$$\delta^{13}\text{C}\text{‰}$$

Delta C thirteen is the conventional unit for the stable carbon isotope ratio in the sample. It is a measure of how much it varies from the standard.

Notice that delta C thirteen is expressed in parts per thousand.

You will see this expressed as
 ‰ or permil or per mill.

$$\delta^{13}\text{C}\text{‰} = \left[\frac{R}{R_s} - 1 \right] \cdot 1000$$

Where R is the ratio of ^{13}C
to ^{12}C in the sample and
 R_s is the ratio in the
standard.

molecules containing ^{12}C are metabolized
more rapidly than molecules containing ^{13}C .

As the organic compound is biodegraded,
the residual compound is enriched in ^{13}C .

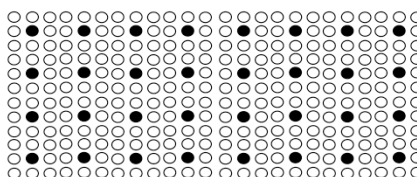
CSIR has two main applications for understanding degradation of organic contaminants.

- 1) to establish that degradation is happening.
- 2) To estimate rate constants for degradation that can be used to forecast future behavior of contamination.

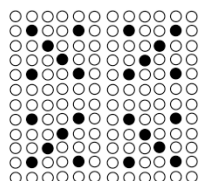


**Enrichment in black dots
when the rate of removal of
black dots is 75% of the
rate of removal of white
dots.**

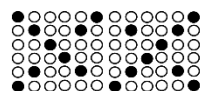
original ratio is 1/9



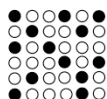
**50 % remaining
ratio is 1/6**

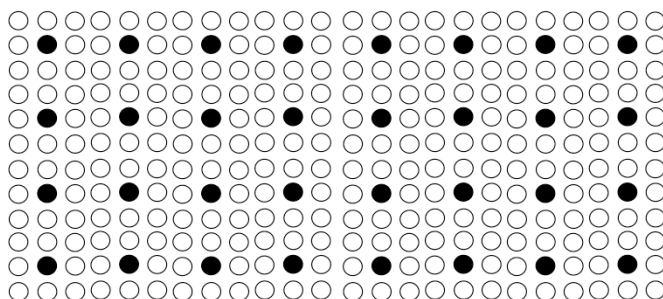


**25 % remaining
ratio is 1/4**

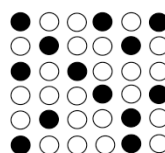


**12.5 % remaining
ratio is 1/3**





**If you know the
enrichment, you can
estimate the extent of
degradation**



What is the relationship between changes in
the ratio of stable carbon isotopes and the
extent of Biodegradation?

Example for MTBE



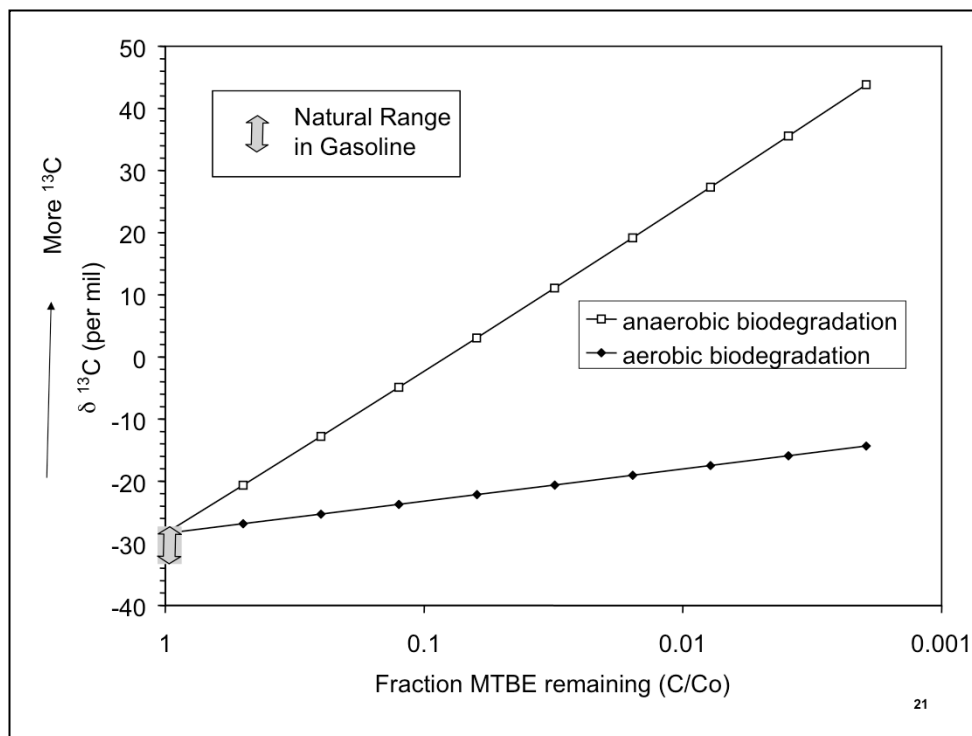
Stable Carbon Isotope Ratios of MTBE in Gasoline

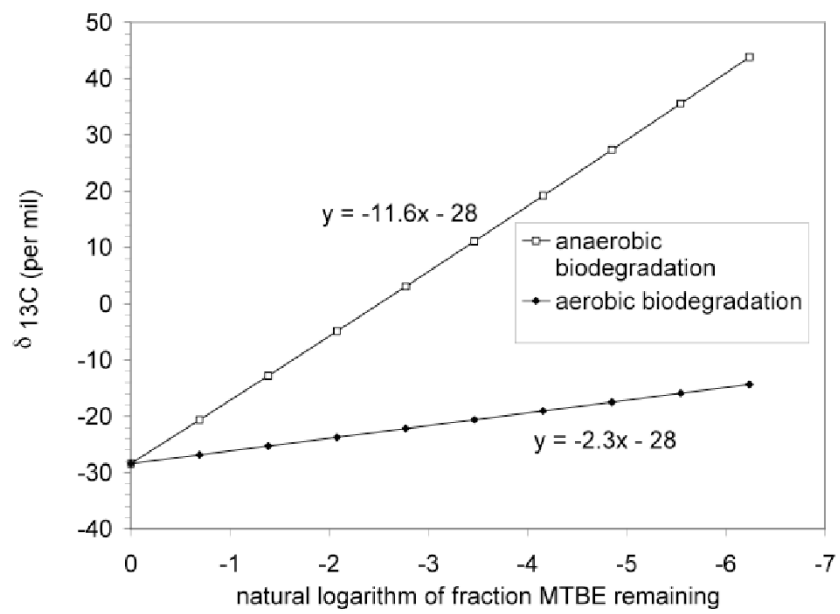


Worldwide values range from
–28 ‰ to –33 ‰

O'Sullivan, G., G. Boshoff, A. Downey, and R. M. Kalin.
"Carbon isotope effect during the abiotic oxidation of
methyl-tert-butyl ether (MTBE). In Proceedings of the
Seventh International In Situ and On-Site Bioremediation
Symposium, Orlando, FL, 2003.

20

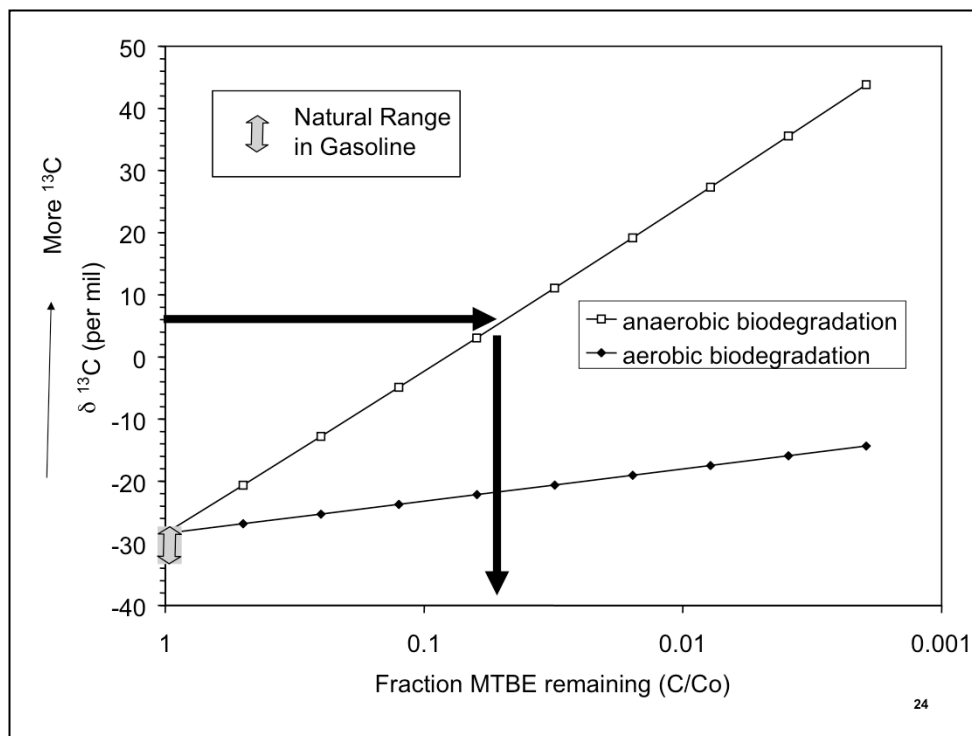


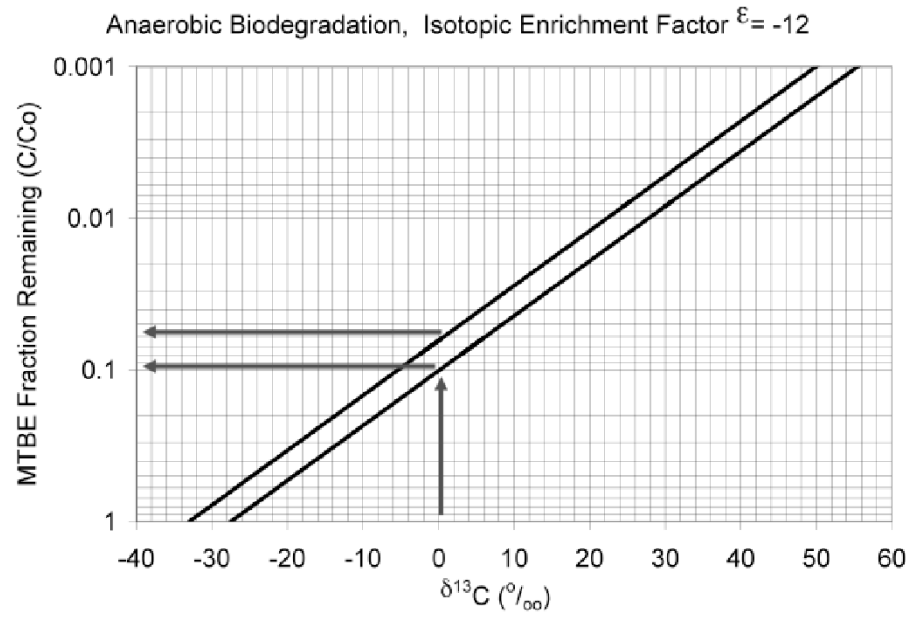


22

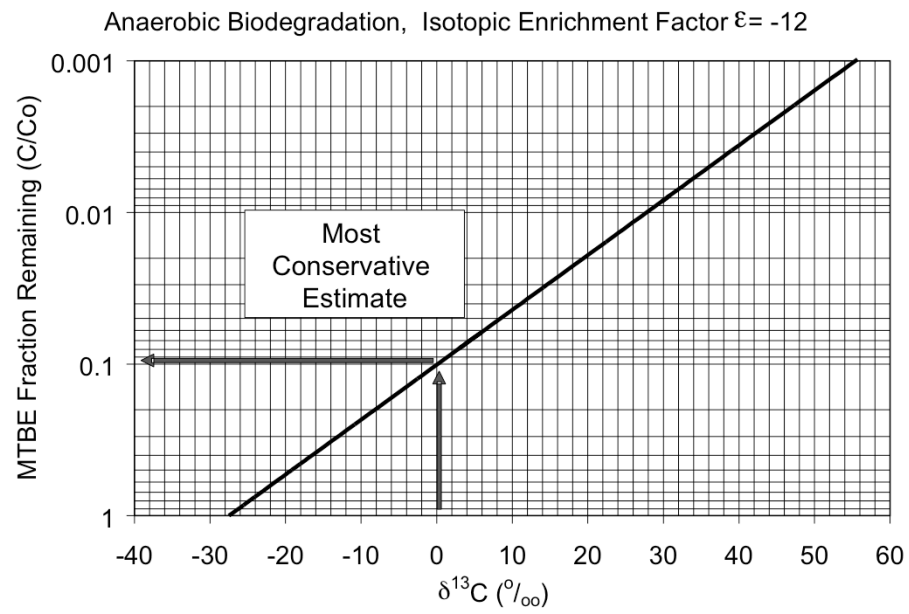
$$F = C / C_o = e^{((\delta^{13}C_{MTBE\ in\ ground\ water} - \delta^{13}C_{MTBE\ in\ gasoline}) / \epsilon)}$$

ϵ is the “enrichment factor”, calculated as the slope of a linear regression of $\delta^{13}C$ on the natural logarithm of the fraction remaining of MTBE (C/C_o or F).





25





Application for an plume of MTBE
from a spill of motor fuel from an
underground storage tank



OSWER Directive 9200.4-17P
in regard to-
Demonstrating the Performance of MNA

Three types of site-specific information may be required:

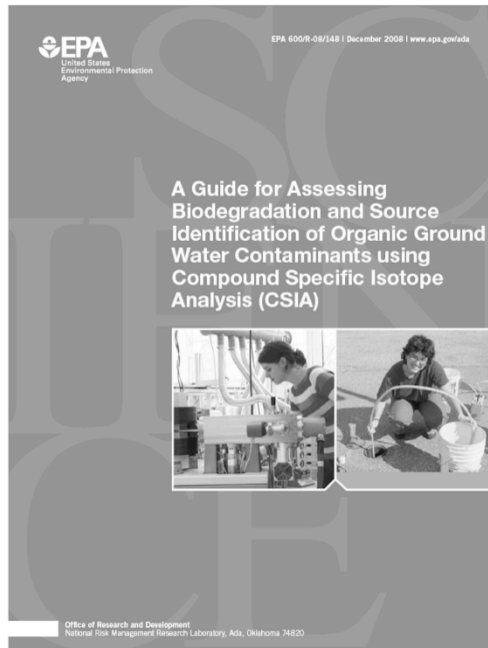
1. Historical ground water and/or soil chemistry data demonstrates a trend of declining contaminant concentration.
2. Hydrogeologic and geochemical data that demonstrate NA processes and rates.
3. Data from field or microcosm studies which directly demonstrate the occurrence of a particular attenuation process and its ability to degrade the contaminants of concern.



Section 4 in

A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA)

EPA 600/R-08/148 |
December 2008 |
www.epa.gov/ada





Google: EPA Ada Oklahoma

Select: Ground Water and Ecosystems
Restoration Research

Go to publications in white menu bar on
left.

Open: Year

Select 2008

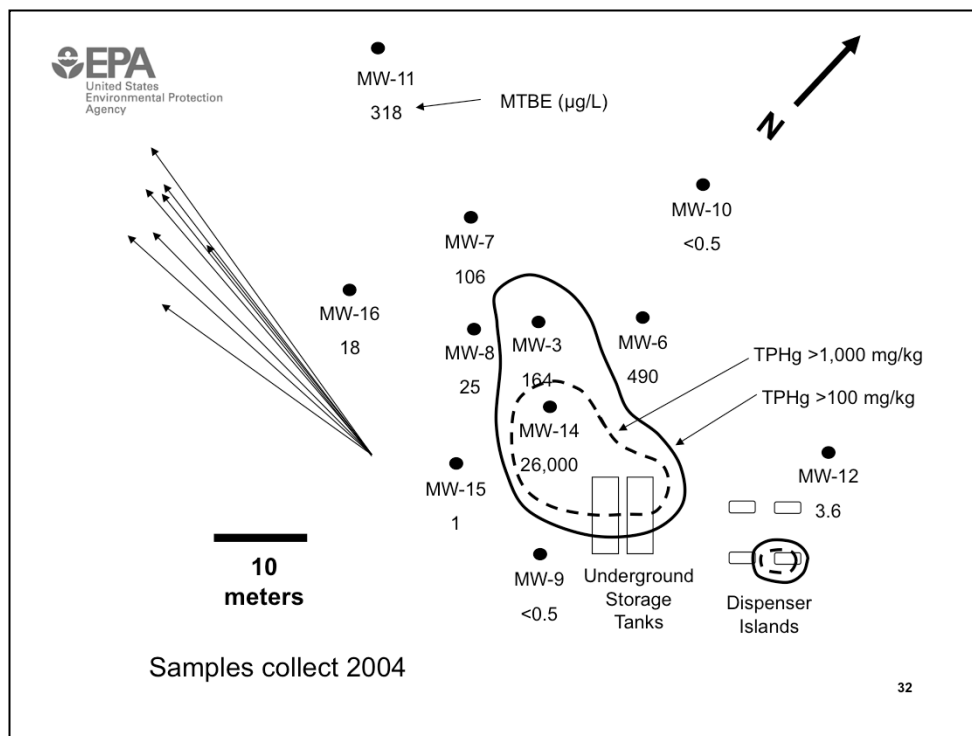
Select "A Guide for Assessing
Biodegradation and Source Identification
of Organic Ground Water Contaminants
using Compound Specific Isotope
Analysis"

30



Google:

A Guide for Assessing Biodegradation and
Source Identification of Organic Ground
Water Contaminants using Compound
Specific Isotope Analysis



TPHg mg/kg

ND

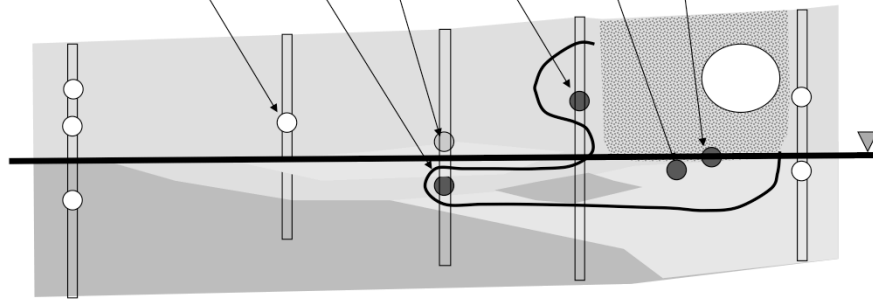
820

1

9000

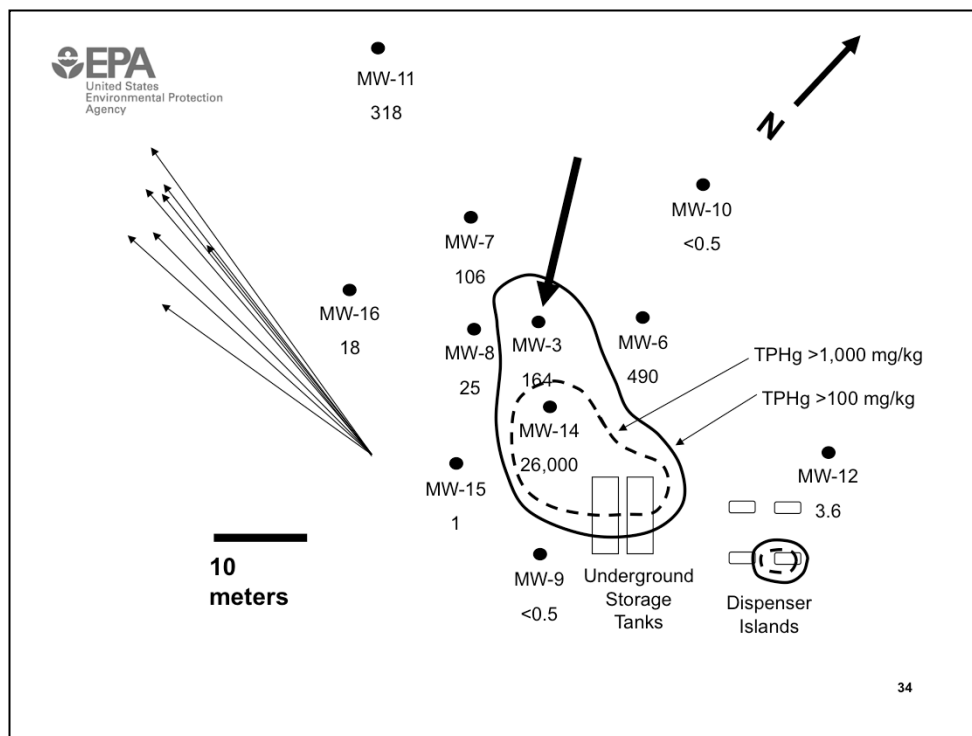
1900

4600



100 feet

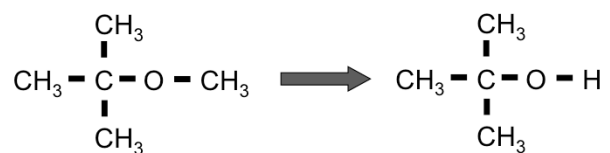
10 feet

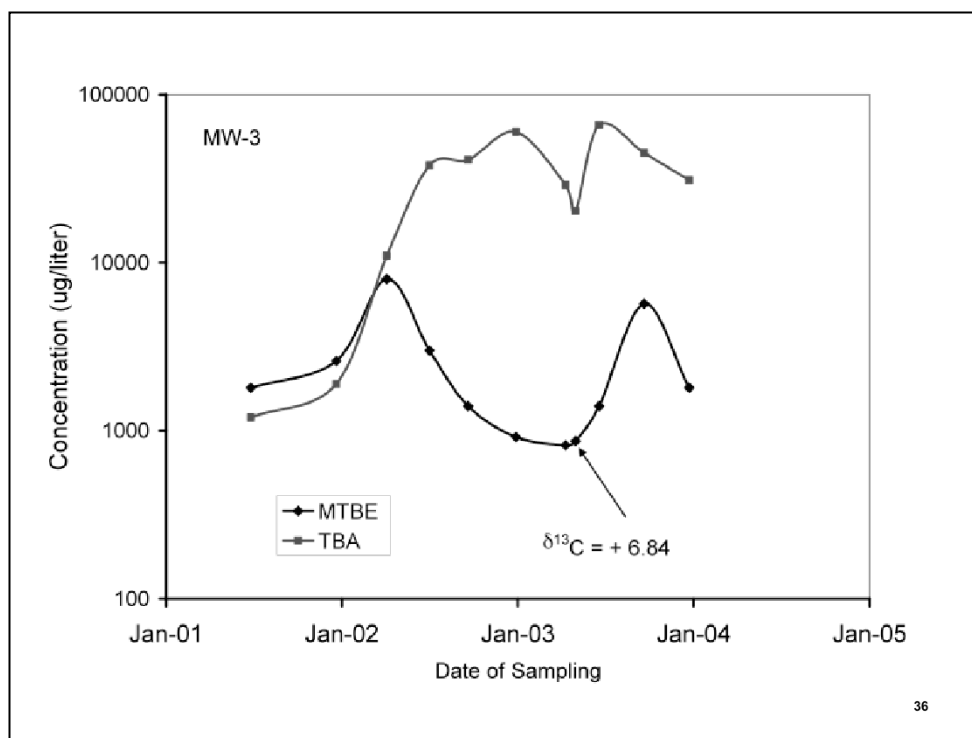


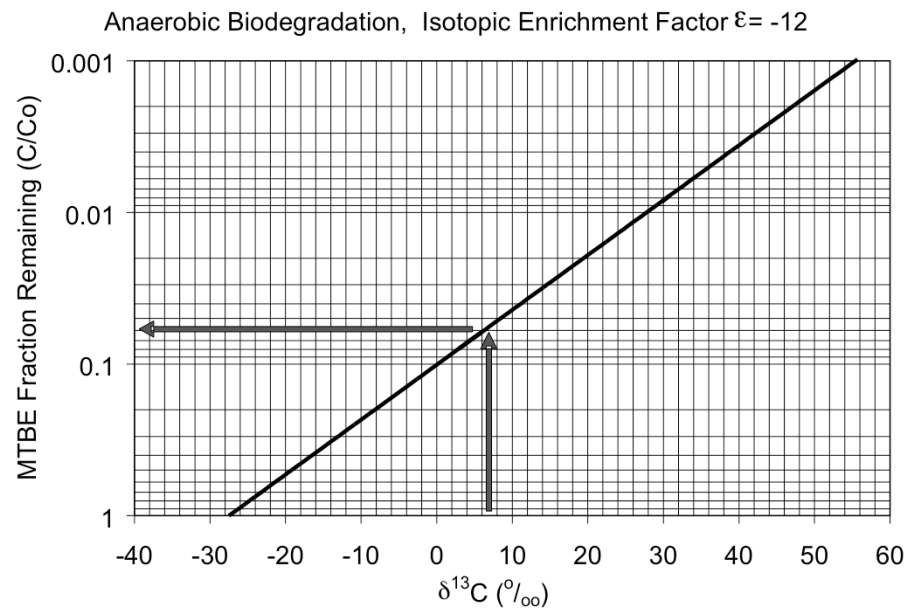
Tertiary Butyl Alcohol (TBA) is the first product of the biodegradation of MTBE.

TBA is also a minor component of the technical grade of MTBE used in gasoline.

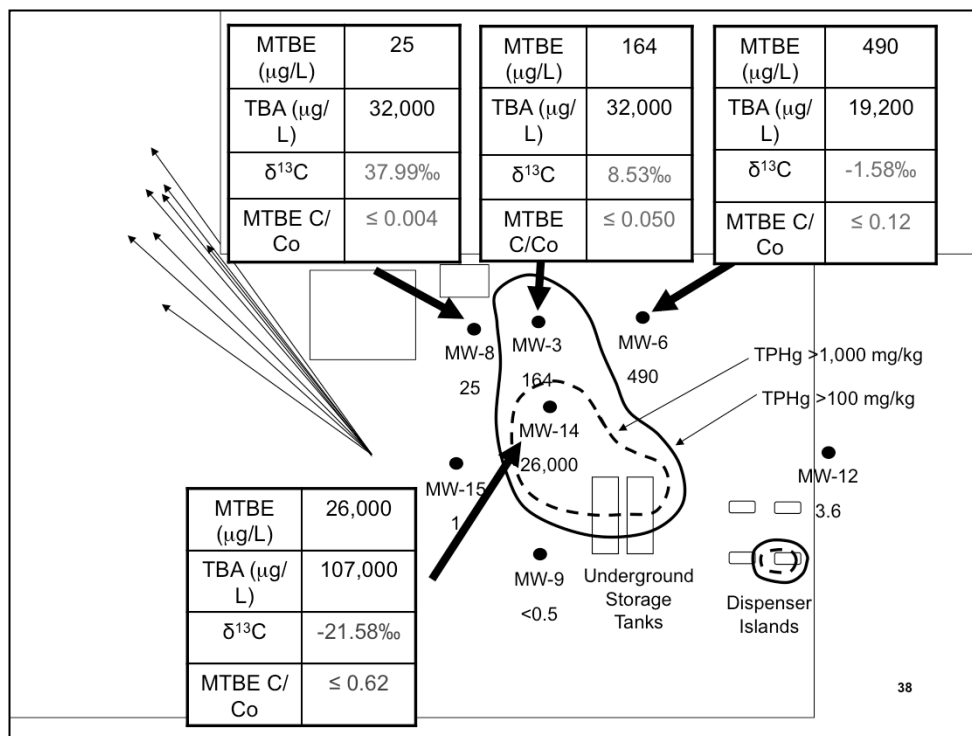
The accumulation of TBA over time is an indication of the biodegradation of MTBE.







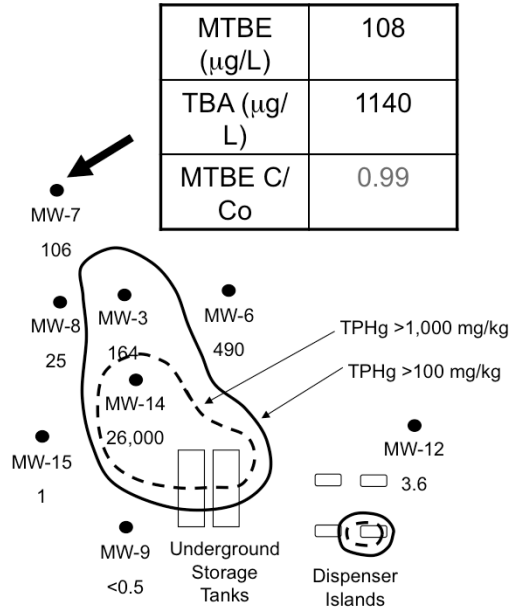
37





MTBE (µg/L)	323
TBA (µg/L)	132
MTBE C/Co	1.0

MTBE (µg/L)	108
TBA (µg/L)	1140
MTBE C/Co	0.99



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

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

MW-11
318

Does not
Degrade

MW-10
<0.5

MW-7
106

Degrades

MW-16
18

MW-8
25

MW-3
164

MW-6
490

TPHg >1,000 mg/kg

TPHg >100 mg/kg

MW-15
1

MW-14
26,000

MW-12

MW-9
<0.5

Underground
Storage
Tanks

3.6
Dispenser
Islands



An 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 there is no biodegradation.

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

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-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

42



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.

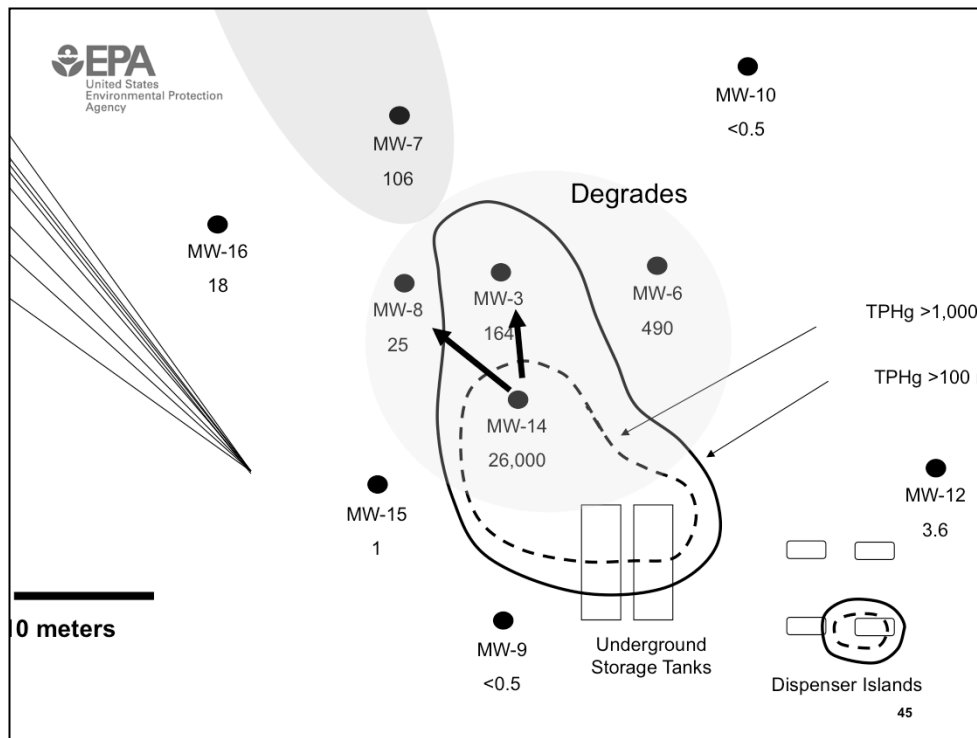
$$k_{\text{with distance}} = -\ln(F) / d$$

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

F is the fraction of MTBE remaining

d is the distance between the wells

v is the ground water seepage velocity



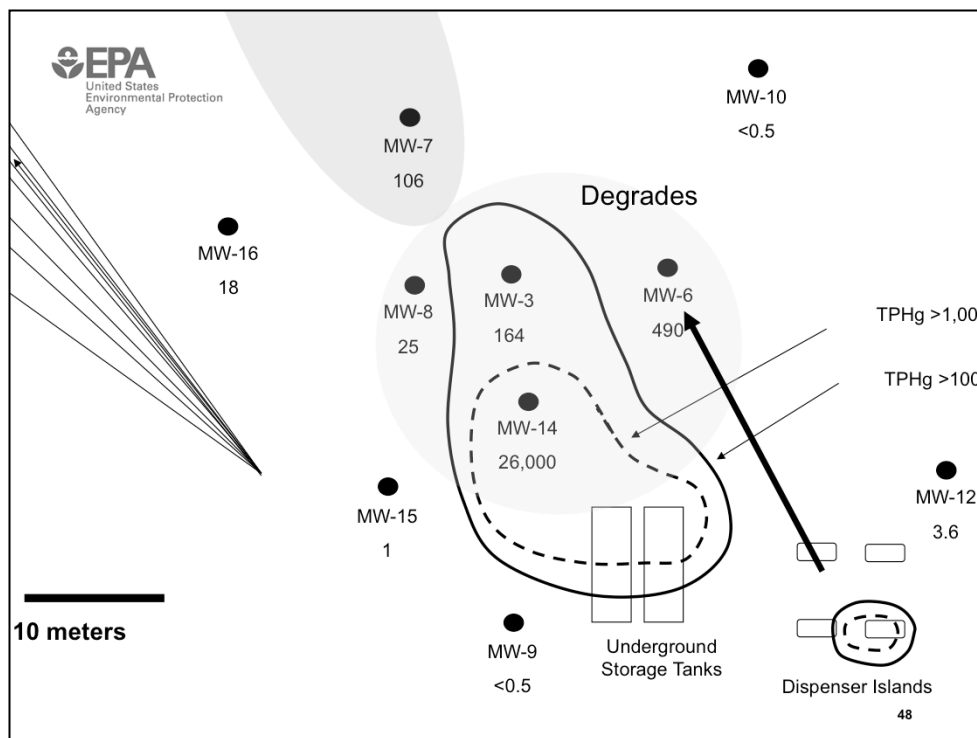
Well	Date	Fraction MTBE Remaining (C/C _o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Distance (per meter)
MW-3	5/20/03	0.058	9.6	0.30
MW-3	8/18/04	0.050	9.6	0.31
MW-8	5/20/03	0.023	11.7	0.32
MW-8	8/18/04	0.0043	11.7	0.46

$= \text{LN} (0.0043)/11.7$

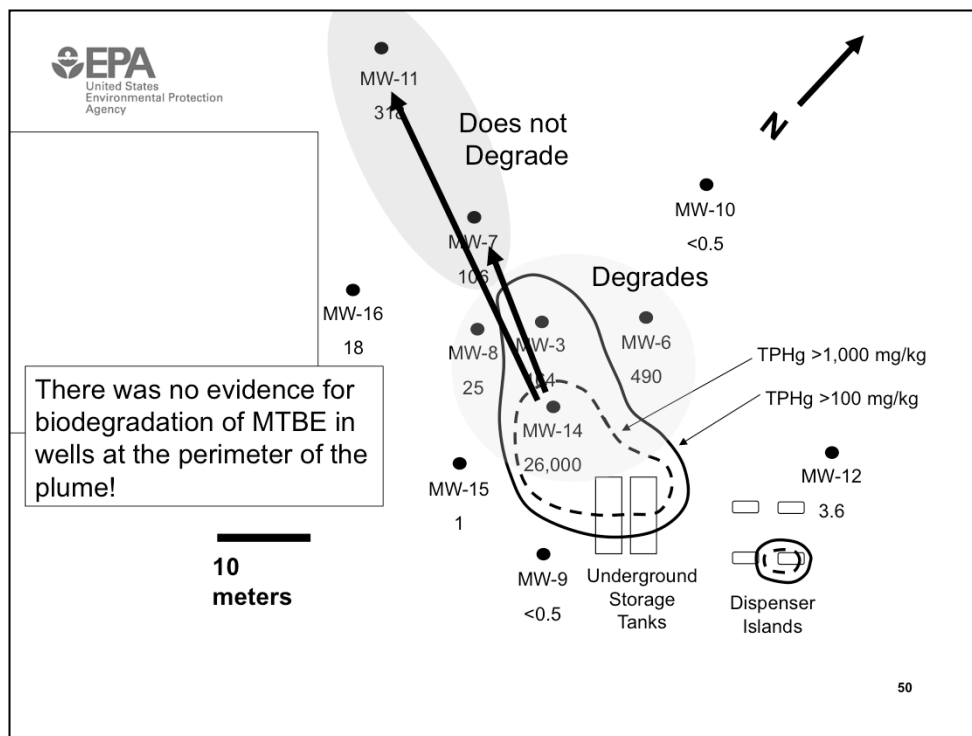
seepage velocity is 37 meters per year

Well	Date	Fraction MTBE Remaining (C/C ₀)	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

= 37 meters per year * 0.46 per meter



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)	δ ¹³ C of MTBE (‰)	Faction MTBE remaining
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

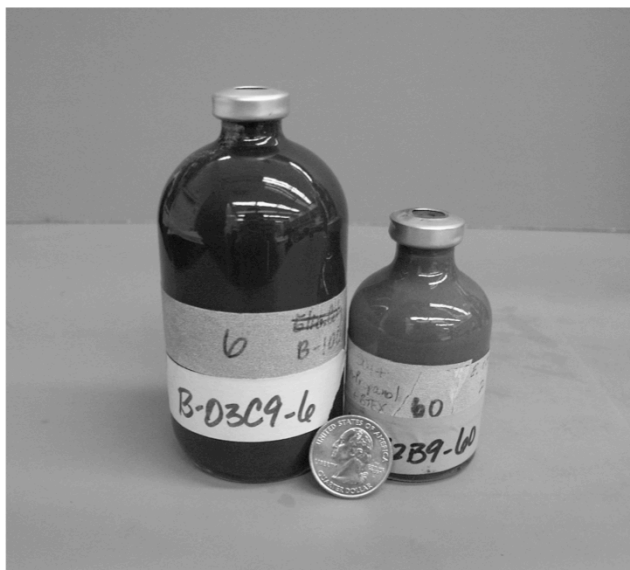
*The concentration MTBE was below the limit for the accurate determination of δ¹³C; the precision of the estimate of δ¹³C was ±3 ‰ rather than ± 0.1 ‰.

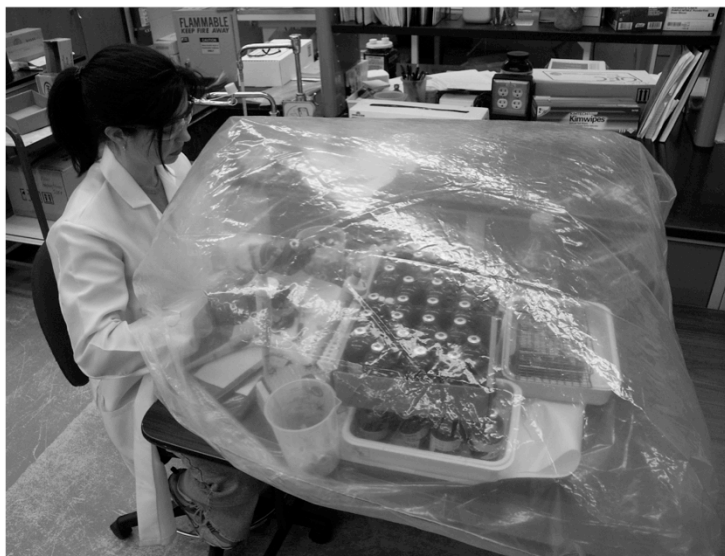


Well	Date	Fraction MTBE Remaining (C/C _o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Distance (per meter)
MW-7	8/18/04	0.994	23.0	0.00025
MW11	5/20/03	1.0	44.1	0
MW11	8/18/04	1.0	44.1	0



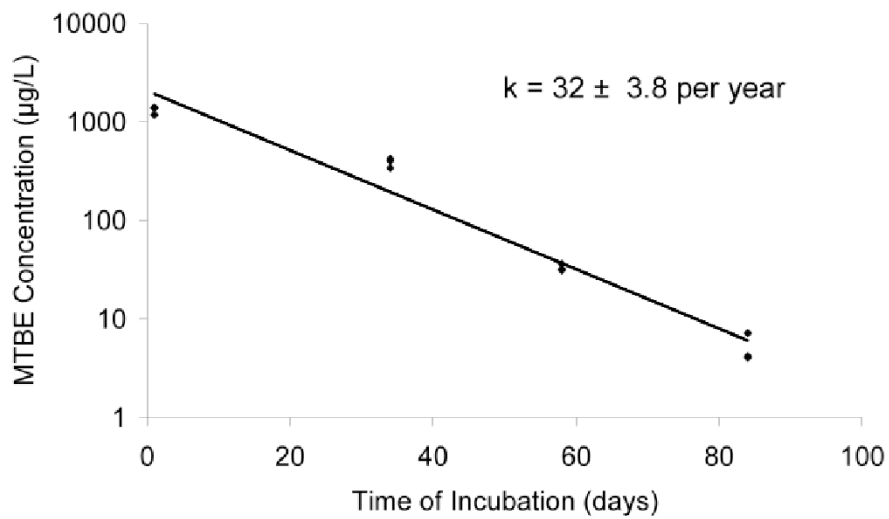
Well	Date	Fraction MTBE Remaining (C/C _o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Time (per year)
MW-7	8/18/04	0.994	23.0	0.0093
MW11	5/20/03	1.0	44.1	0
MW11	8/18/04	1.0	44.1	0



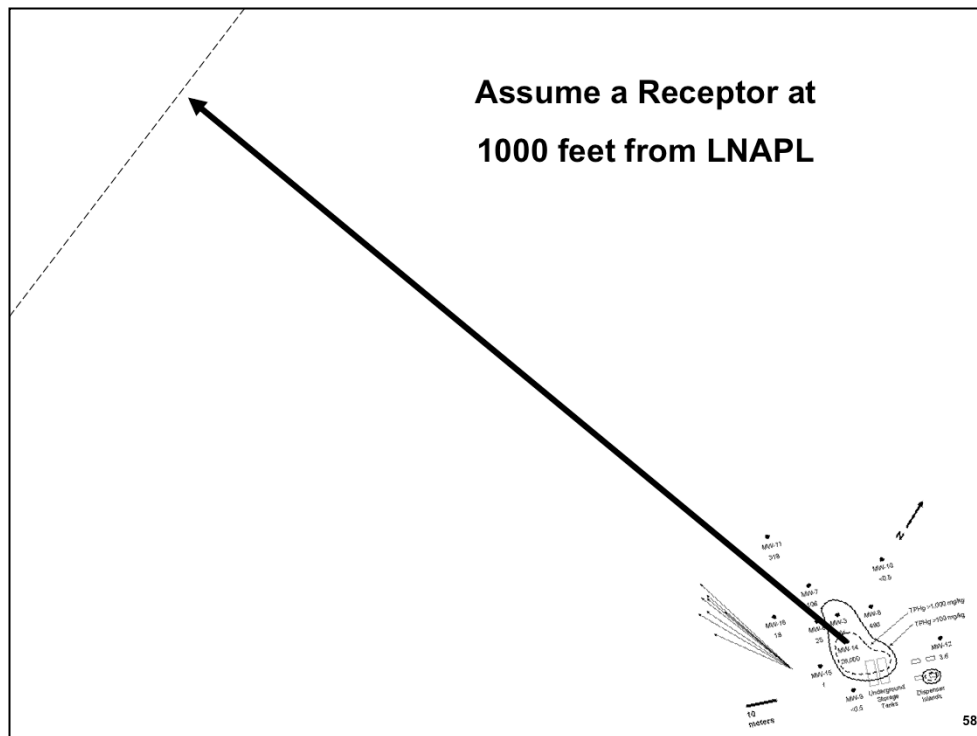


*Laboratory microcosm study with sediment
from UST site in Southern California.*

Huntington Beach, Orange County California



- 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 there is no biodegradation.





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

Available at

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

With Source at 26 mg/L and Biodegradation = 10 per year
Assume a Receptor at 1000 feet from LNAPL

BIOCHLOR Natural Attenuation Decision Support System

Version 2.2
Excel 2000

TYPE OF Contaminant:

1. **ADVECTION**
Seepage Velocity* V_s (ft/yr)

Hydraulic Conductivity K (cm/sec)
 Hydraulic Gradient (ft/ft)
 Effective Porosity n (-)

2. **DISPERSION**
 Alpha x* (ft)
 (Alpha y) / (Alpha x)* (-)
 (Alpha z) / (Alpha x)* (-)

3. **ADSORPTION**
 Retardation Factor* (-)

Soil Bulk Density, rho (kg/L)
 Fraction Organic Carbon, f_{oc} (-)
 Partition Coefficient K_{oc}

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

Common R (used in model)* (-)

4. **BIOTRANSFORMATION**
 Zone 1 k_d (1/yr) \leftarrow half-life (yrs) Yield
 TCE \rightarrow DCE \leftarrow half-life (yrs)
 DCE \rightarrow VC \leftarrow half-life (yrs)
 VC \rightarrow ETH \leftarrow half-life (yrs)

Zone 2 k_d (1/yr) \leftarrow half-life (yrs)
 PCE \rightarrow TCE \leftarrow half-life (yrs)
 TCE \rightarrow DCE \leftarrow half-life (yrs)
 DCE \rightarrow VC \leftarrow half-life (yrs)
 VC \rightarrow ETH \leftarrow half-life (yrs)

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

6. SOURCE DATA
 TYPE: Continuous Single Planar
 Source Options
 Source Thickness in Sat. Zone* (ft)
 Width* (ft) (ft)
 Conc. (mg/L)* (mg/L)
 MTBE (mg/L)
 TBA (mg/L)
 (mg/L)
 (mg/L)
 (mg/L)
 (mg/L)

7. FIELD DATA FOR COMPARISON
 MTBE Conc. (mg/L)
 TBA Conc. (mg/L)
 Distance from Source (ft)
 Date Data Collected

8. CHOOSE TYPE OF OUTPUT TO SEE:

DATA INPUT INSTRUCTIONS:

- Enter value directly....or
- Calculate by filling in gray cells. Press Enter, then (To restore formulas, hit "Restore Formulas" button) Variable* Data used directly in model.

Test if Biotransformation is Occurring

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

View of Plume Looking Down

Observed Centerline Conc. at Monitoring Wells

(Alpha z) / (Alpha x)*

1.E-05

(-)

3. ADSORPTION

Retardation Factor*

→ R

or

Soil Bulk Density, rho

1.6

(kg/L)

Fraction Organic Carbon, 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

10.000

(1/yr)

half-life (yrs)

Yield

0.79

TCE → DCE

0.000

(1/yr)

half-life (yrs)

0.74

DCE → VC

0.000

(1/yr)

half-life (yrs)

0.64

VC → ETH

0.000

(1/yr)

half-life (yrs)

0.45

Zone 2

PCE → TCE

0.000

(1/yr)

half-life (yrs)

TCE → DCE

0.000

(1/yr)

half-life (yrs)

DCE → VC

0.000

(1/yr)

half-life (yrs)

VC → ETH

0.000

(1/yr)

half-life (yrs)

λ

HELP

6. SOURCE DATA TYPE: Continuous Single Planar

Source Options

Source Thickness in Sat. Zone* 10 (ft)

Width* (ft) 60

Conc. (mg/L)* C1

PCE 26.0

TCE

DCE

VC

ETH

k_s^* (1/yr)

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:

RUN CENTERLINE

RUN ARRAY

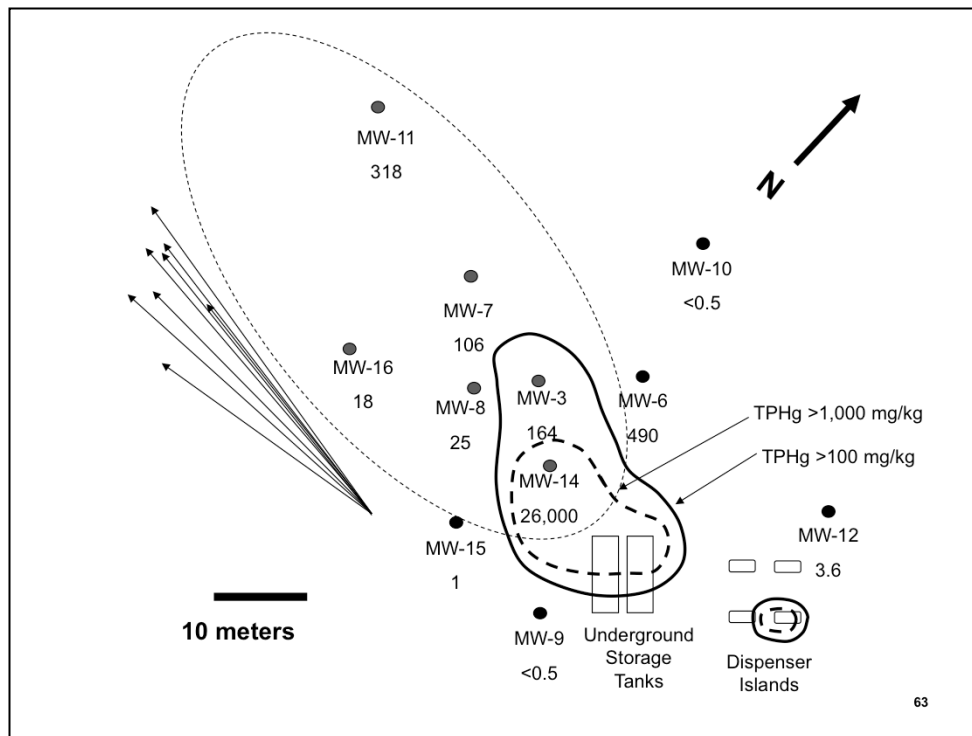
Help

Restore Formulas

RESET

SEE OUTPUT

Paste Example



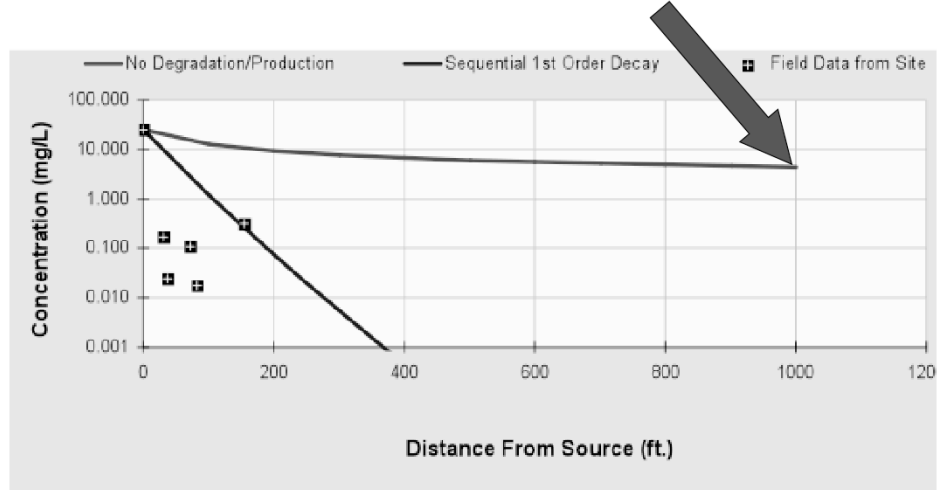
With Source at 26 mg/L and Biodegradation = 10 per year

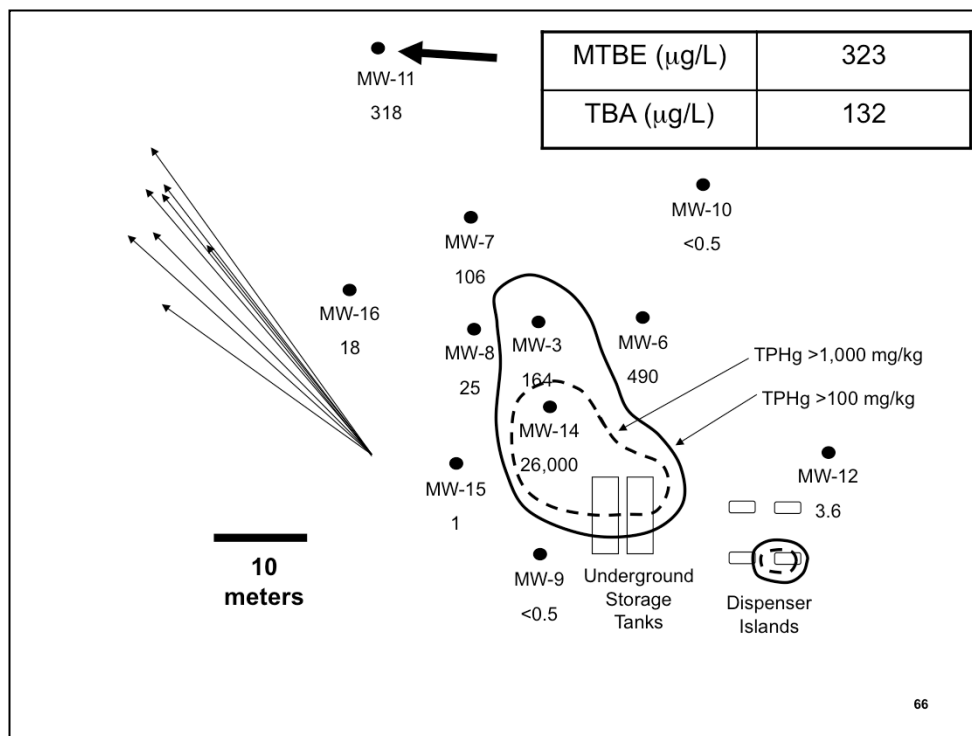


Clean in approximately 300 feet of travel

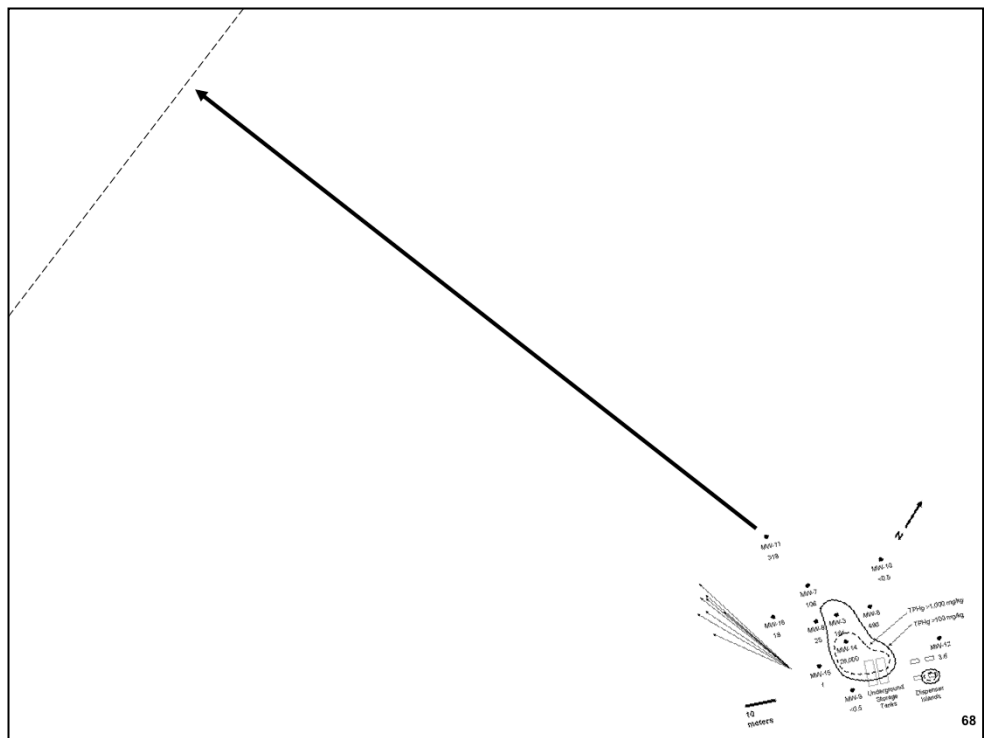
With Source at 26 mg/L and no Biodegradation

Not even close to clean in 1000 feet of travel





- 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 there is no biodegradation.**



With Source at MW-11 at 0.318 mg/L

Biodegradation = 0.0001 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:
1. Enter value directly...or
2. Calculate by filling in gray cells. Press Enter, then
Variable → Data used directly in model.
(To restore formulas, hit "Restore Formulas" button)
Test if Biodegradation is Occurring → Natural Attenuation Screening Protocol

TYPE OF Contaminant: Ethenes ☒ Ethanes

1. **ADVECTION**
Seepage Velocity* V_s 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, f_{oc} 1.8E-3 (-)
Partition Coefficient K_{oc} 428 (L/kg)
PCE 5.91 (-)
TCE 2.50 (-)
DCE 2.44 (-)
VC 1.34 (-)
ETH 4.48 (-)
Common R (used in model)* 1.00
4. **BIOTRANSFORMATION**
-1st Order Decay Coefficient* A_i (1/yr)
Zone 1
PCE → TCE 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
Zone 2
PCE → TCE 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

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

6. **SOURCE DATA**
Source Options
TYPE: Continuous Single Planar
Source Thickness in Sat. Zone* 10 (ft)
Width* (ft) 60
Conc. (mg/L)* C1
MTBE 0
TBA 0
k_d* (1/yr) 0
View of Plume Looking Down
Observed Centerline Conc. at Monitoring Wells

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

8. **CHOOSE TYPE OF OUTPUT TO SEE:**
Distance from Source (ft) 0 30 38 72 83 154
Date Data Collected
RUN CENTERLINE RUN ARRAY
Help Restore Formulas RESET
SEE OUTPUT Paste Example

69

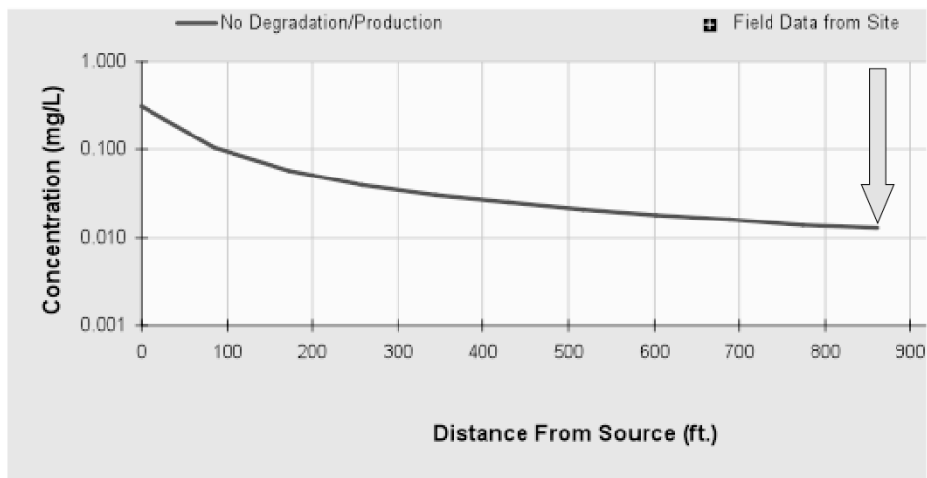
With Source at 0.318 mg/L

Biodegradation = 0.0001 per year

Potential Receptor at 840 feet

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		
or			
Soil Bulk Density, rho	1.6	(kg/L)	
Fraction Organic Carbon, f _{oc}	1.8E-3	(-)	
Partition Coefficient	K _{oc}		
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			
Zone 1	-1st Order Decay Coefficient*		
	lambda (1/yr)	half-life (yrs)	Yield
PCE → TCE	0.000	←	0.79
TCE → DCE	0.000	←	0.74
DCE → VC	0.000	←	0.64
VC → ETH	0.000	←	0.45
6. SOURCE DATA			
Source Options			
Source Thickness in Sat. Zone			
Y1			
Width* (ft)			
60			
Conc. (mg/L)*			
C1			
MTBE			
.318			
TBA			
7. FIELD DATA FOR COMPARISON			
MTBE Conc. (mg/L)			
TBA Conc. (mg/L)			
Distance from Source (ft)			
Date Data Collected			
8. CHOOSE TYPE OF OUTPUT			

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





The projected concentration at the hypothetical receptor is right at the acceptance level in California.

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

The exposure assessment for most real receptors will be much less ambiguous.

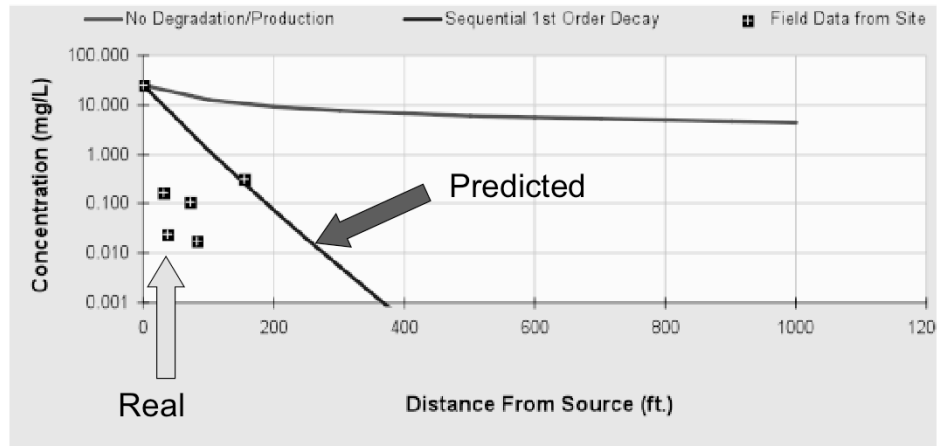
Note that the real attenuation in concentrations were substantially greater than would be expected from the prediction of C/C_o based on the analysis of stable carbon isotopes.

There are two interactions that can substantially confuse the interpretation of CSIR data.

- 1) Heterogeneity in flow paths
- 2) Proximity to NAPL or other source of contamination to ground water

- 1) Heterogeneity and proximity to the NAPL produces blended samples or samples that are diluted with un-fractionated material.
- 2) The overall extent of isotopic fractionation will be less than expected from the true extent of biodegradation.
- 3) Heterogeneity or proximity to the NAPL causes CSIR to underestimate biodegradation.

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

76



**OSWER Directive 9200.4-17P
in regard to-
Demonstrating the Performance of MNA**

Three types of site-specific information may be required:

1. Historical ground water and/or soil chemistry data demonstrates a trend of declining contaminant concentration.
2. Hydrogeologic and geochemical data that demonstrate NA processes and rates.
3. Data from field or microcosm studies which directly demonstrate the occurrence of a particular attenuation process and its ability to degrade the contaminants of concern.

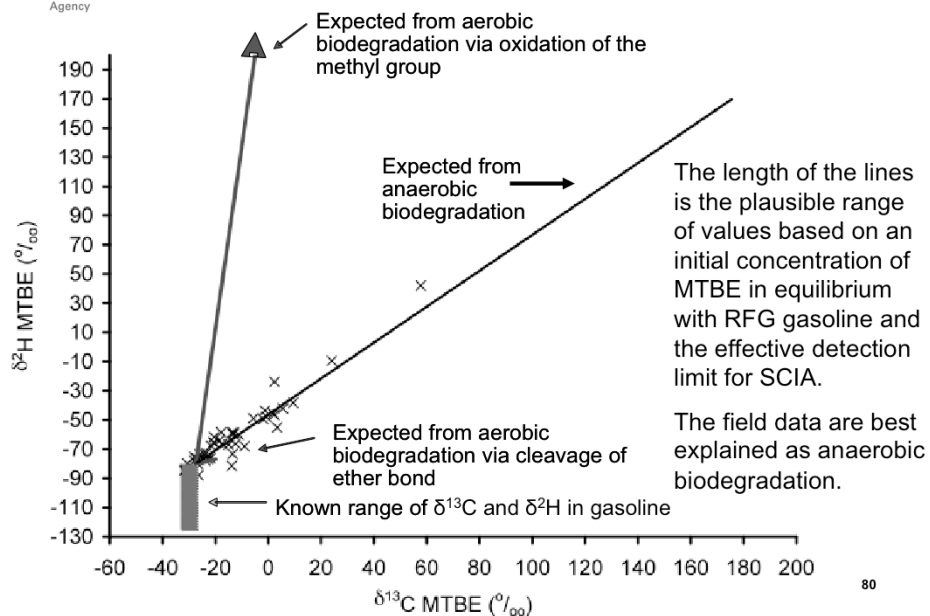
77

Application of CSIA to two elements in the same compound at the same time is often called two dimensional CSIR. With the recent advent of SCIR for chlorine, three dimensional CSIR is feasible.

In many applications two dimensional CSIR can resolve mechanisms and biodegradation pathways.

Application to Identify the Mechanism of Biodegradation

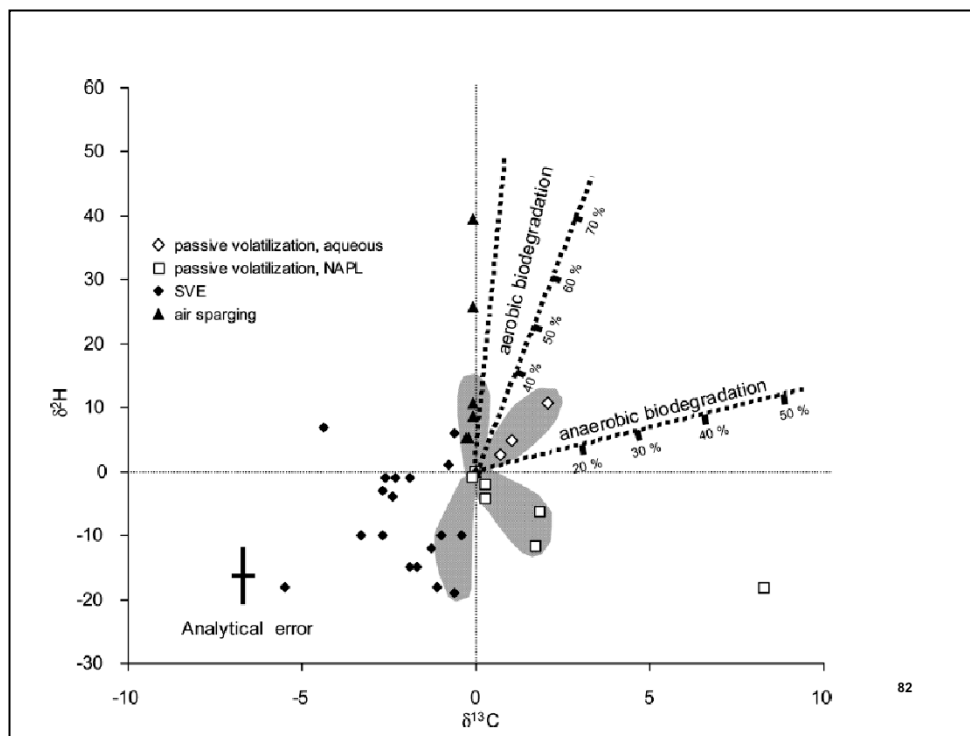
Fractionation of C and H during biodegradation of MTBE by different metabolic pathways			
	$\epsilon_{\text{carbon}} (\text{‰})$	$\epsilon_{\text{carbon}} (\text{‰})$	Reference
Aerobic via oxygenase	-2.4	-30	Gray et al. 2002 <i>ES&T</i> 36:1931-1938
Aerobic via ether hydrolysis	-0.48	-0.2	Rosell et al. 2007 <i>ES&T</i> 41:2036-2043
Anaerobic	-13	-16	Kuder et al. 2005 <i>ES&T</i> 39:213-220





The following slide shows an application of two dimensional SCIA to evaluate the relative importance of fractionation due to biodegradation of MTBE and fractionation due to phase transfer phenomena.

Kuder et al. 2009. *ES&T* 43: 1763–1768



Resources necessary to conduct a CSIA study



From Section 5 of U.S. EPA Guide

Preliminary Survey to Justify Comprehensive Study	4 to 6 Wells
Comprehensive Survey MNA on one plume	13 to 24 wells
Up gradient of source	1 to 2 wells
Source zone	3 to 5 wells
Center flow line	4 to 5 wells
Boundary of plume	4 to 8 wells
Vertical extent	1 to 4 wells
Plume stability, resample one to three years later	6 to 15 wells

84



Approximate Cost is \$200 to \$400 for one sample for one compound for one isotope ratio.

Additional compounds determined for the same isotope ratio can cost \$50 to \$100 per sample.

Circumstances can reduce this cost.

Don't compare the costs of CSIA to the cost to analyze samples for concentrations. They are different analyzes conducted for different purposes.



A CSIA survey answers the same question as a microcosm study, except it does a better job.

- Usually much less expensive. A simple microcosm study can cost \$50,000.
- Quicker. Takes two months or less compared to six months to two years.
- More direct. Detects degradation that has already happened, instead of simply documenting a capability to degrade the contaminants.
- Not subject to disturbance artifacts associated with microcosm studies.

86



At many hazardous waste sites, we are content to collect data on concentrations four times a year for five or ten years, and then try to make inferences about biodegradation that are not satisfying or compelling.

Twenty to forty analyses using Method 8260 at a cost of \$100 each don't answer the question about biodegradation because they provide the wrong information.

When conditions are favorable, one CSIA analysis on water from one well can document the extent of biodegradation. CSIA analyses on water from two wells can provide an estimate of the rate of degradation.

87



Commercial Source of Analytical Services

Patrick McLoughlin
pmcloughlin@microseeps.com
Microseeps
University of Pittsburgh Applied Research Center
220 William Pitt Way,
Pittsburgh, PA 15238
412 826 5245
fax 3433



Commercial Source of Analytical Services

Paul Philp
Department of Geology and Geophysics
100 East Boyd Avenue
University of Oklahoma
Norman, Oklahoma 73019
405 325 4469
fax (405)-325-3140
pphilp@ou.edu



Commercial Source of Analytical Services

Zymax Forensics
Yi Wang
Director, Zymax Forensics Isotope
600 South Andreasen Drive
Suite B,
Escondido, California
92029
yi.wang@zymaxUSA.com



Commercial Source of Analytical Services

Barbara Sherwood Lollar
Department of Geology
University of Toronto
22 Russell Street, Toronto, Ontario
M5S 3B1

Phone: (416) 978-0770
Fax: (416) 978-3938
E-mail: bslollar@chem.utoronto.ca

Resources & Feedback

- To view a complete list of resources for this seminar, please visit the **Additional Resources**
- Please complete the **Feedback Form** to help ensure events like this are offered in the future

The screenshot shows a web form titled "U.S. EPA Technical Support Project Engineering Forum Green Remediation: Opening the Door to Field Use Session C (Green Remediation: Tools and Examples) Seminar Feedback Form". The form is part of the "Technology Innovation Program" and is hosted by the "U.S. EPA Environmental Protection Agency". It includes a sidebar with links to "Go to Seminar", "Links", "Feedback", "Home", and "CLU-IN Studio". The main form area contains the following fields: "First Name:" (with "Jean" entered), "Last Name:" (with "Bent" entered), "Daytime Phone Number:" (with "703-603-9924" entered), "Email Address:" (with "jeant@epa.gov" entered), and "Date of Seminar:" (with "December 15, 2009" selected). There is a checkbox labeled "Please send a copy of my feedback confirmation as a record of my participation to this address." which is currently unchecked. A "Delivery Media" dropdown menu is visible at the bottom left of the form.

Need confirmation of your participation today?

Fill out the feedback form and check box for confirmation email.