CLU-IN Contaminated Site Clean-Up Information

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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)

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

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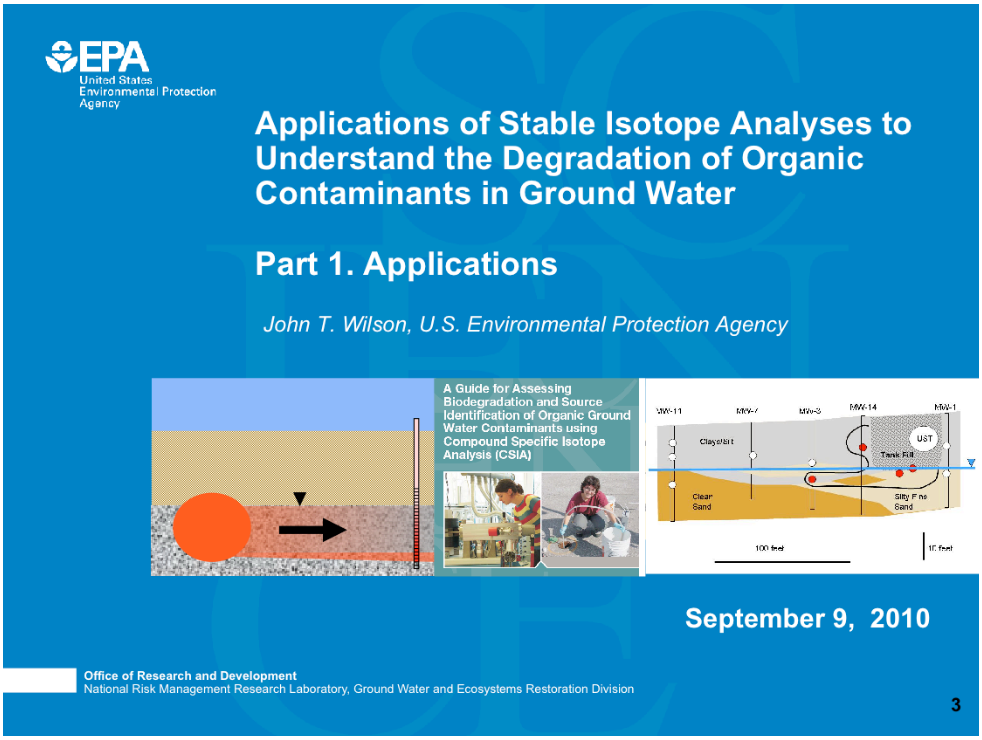


United States Environmental Protection Agency

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

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

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 the 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	^{1}H	0.99985
	^{2}H	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.

$\delta^{13}C$‰

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 $^{o}/_{oo}$ or permil or per mill.

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

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.

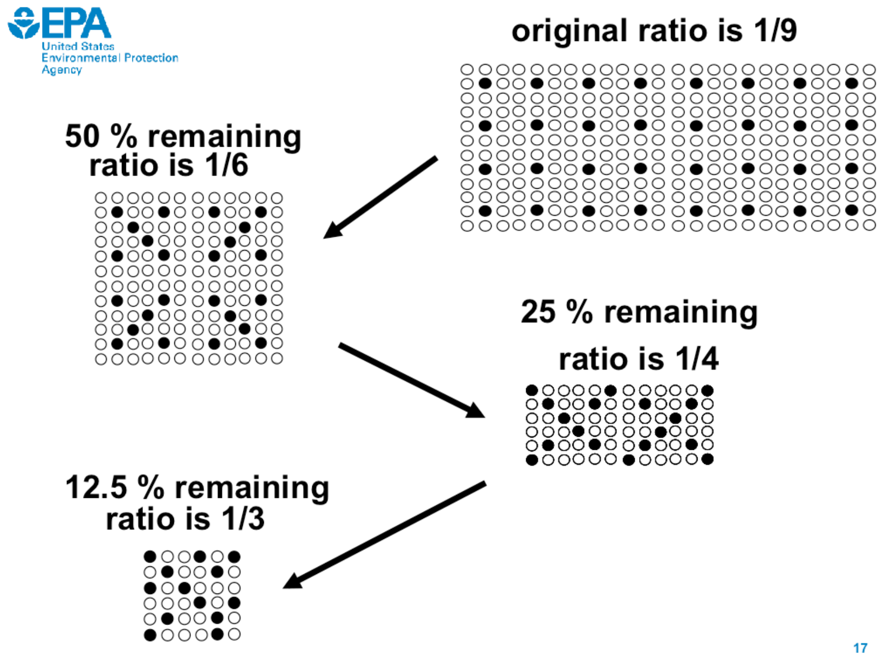
As the organic compound is biodegraded, the residual compound is enriched in ^{13}C.

CSIR has two main applications for understanding degradation or 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.

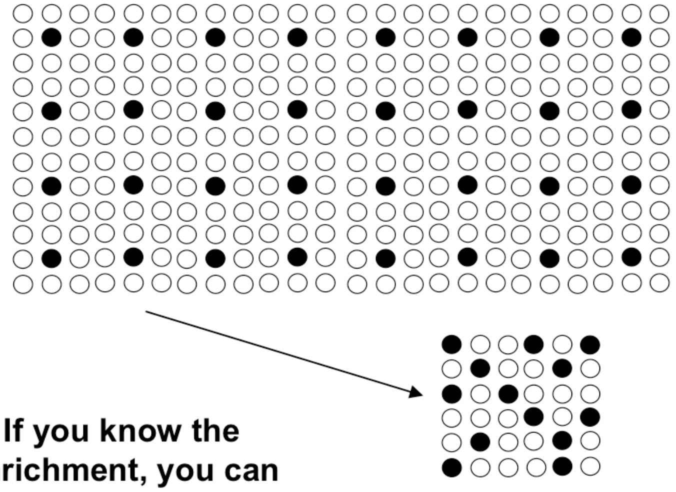


original ratio is 1/9

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?

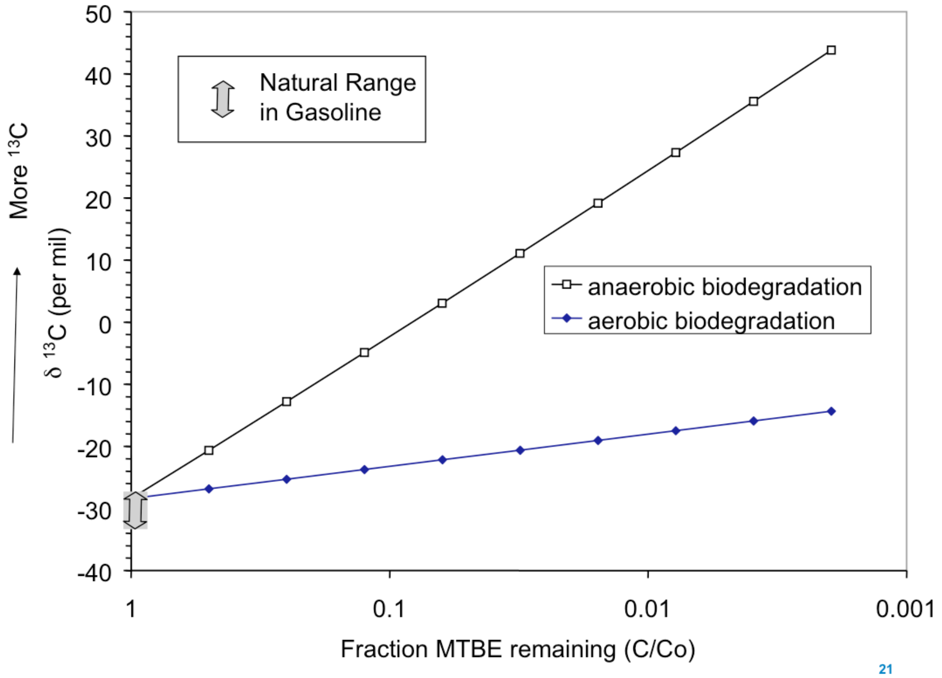
Example for MTBE

Stable Carbon Isotope Ratios of MTBE in Gasoline

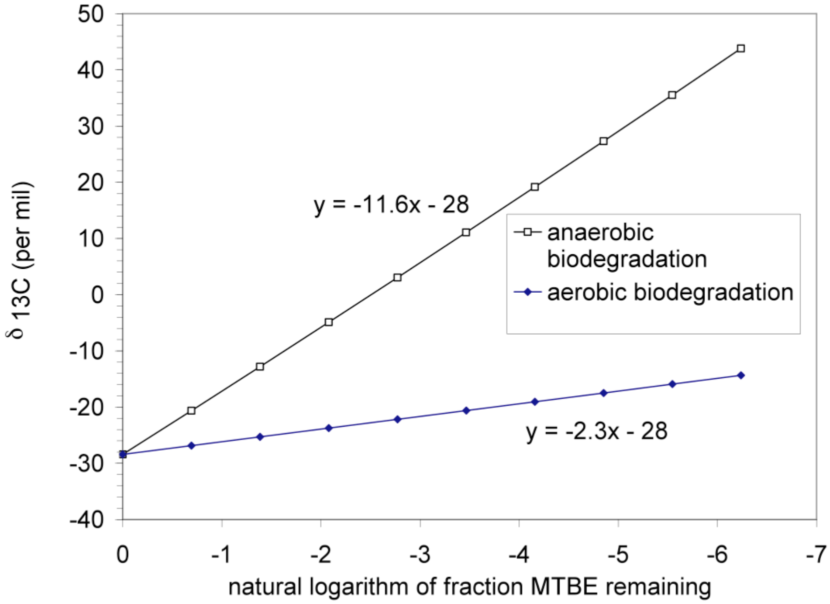
$$\delta^{13}C$$

Worldwide values range from
$-28\ ^{o}/_{oo}$ to $-33\ ^{o}/_{oo}$

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.


Natural Range in Gasoline
anaerobic biodegradation
aerobic biodegradation
More ^{13}C
δ ^{13}C (per mil)
50
40
30
20
10
0
-10
-20
-30
-40
1
0.1
0.01
0.001
Fraction MTBE remaining (C/Co)

◻

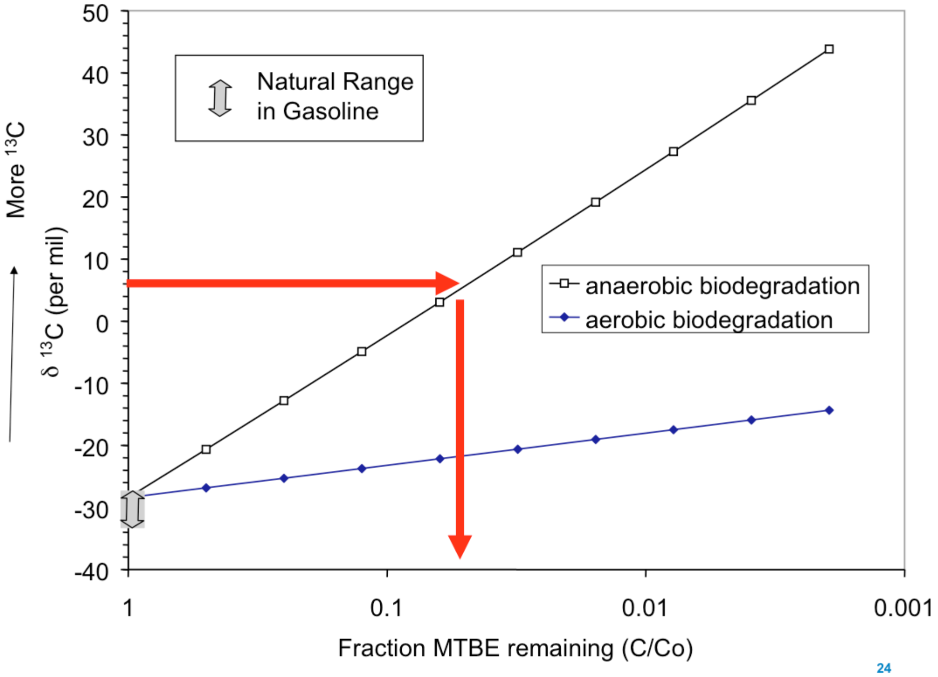


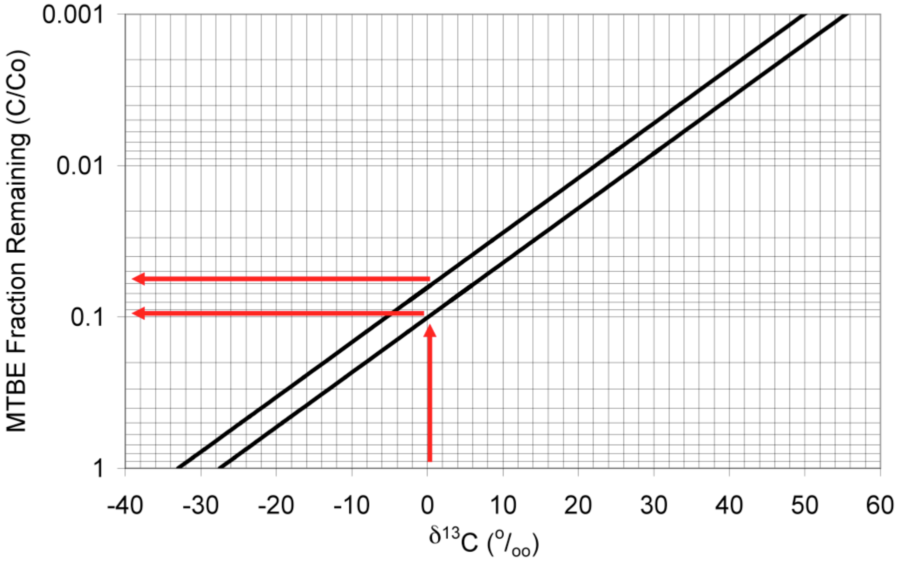
50
40
30
20
10
0
-10
-20
-30
-40
δ 13C (per mil)
0
-1
-2
-3
-4
-5
-6
-7
natural logarithm of fraction MTBE remaining
y = -11.6x - 28
y = -2.3x - 28
anaerobic biodegradation
aerobic biodegradation

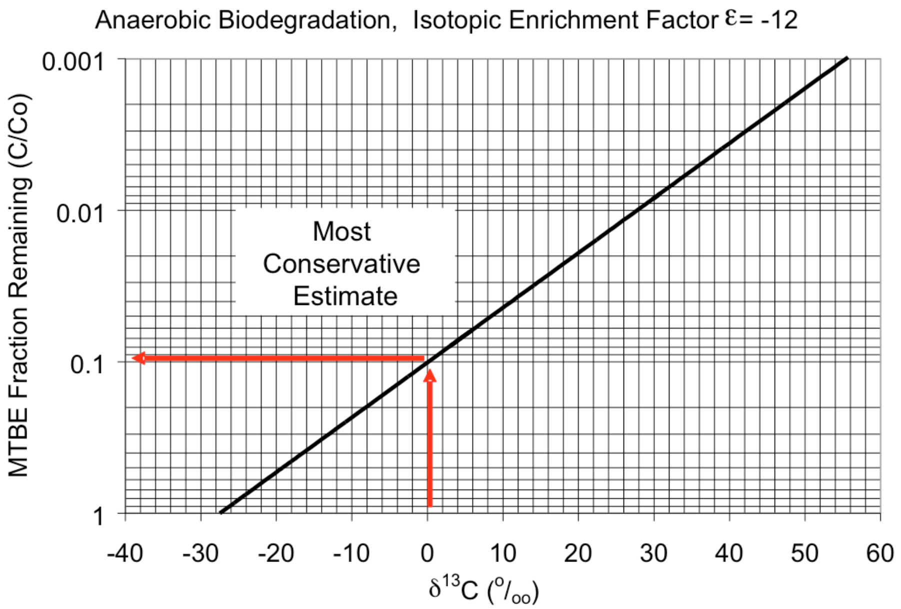
22

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

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/Co or F).


50
40
30
20
10
0
-10
-20
-30
-40
More ^{13}C
δ ^{13}C (per mil)
Natural Range in Gasoline
anaerobic biodegradation
aerobic biodegradation
1
0.1
0.01
0.001
Fraction MTBE remaining (C/Co)


Anaerobic Biodegradation, Isotopic Enrichment Factor ε= -12


Anaerobic Biodegradation, Isotopic Enrichment Factor ε= -12
MTBE Fraction Remaining (C/Co)
0.001
0.01
0.1
1
Most Conservative Estimate
-40
-30
-20
-10
0
10
20
30
40
50
60
$\delta^{13}C$ (°/oo)

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.
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Environmental Protection
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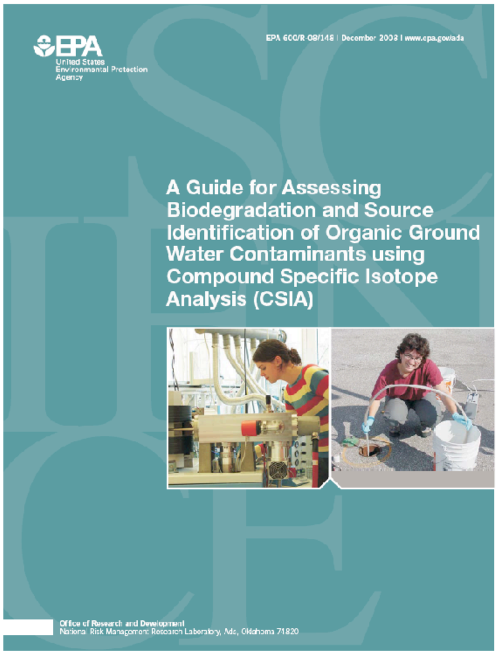
Section 4 in

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



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

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

Office of Research and Development
National Risk Management Research Laboratory, Ada, Oklahoma 74820

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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”

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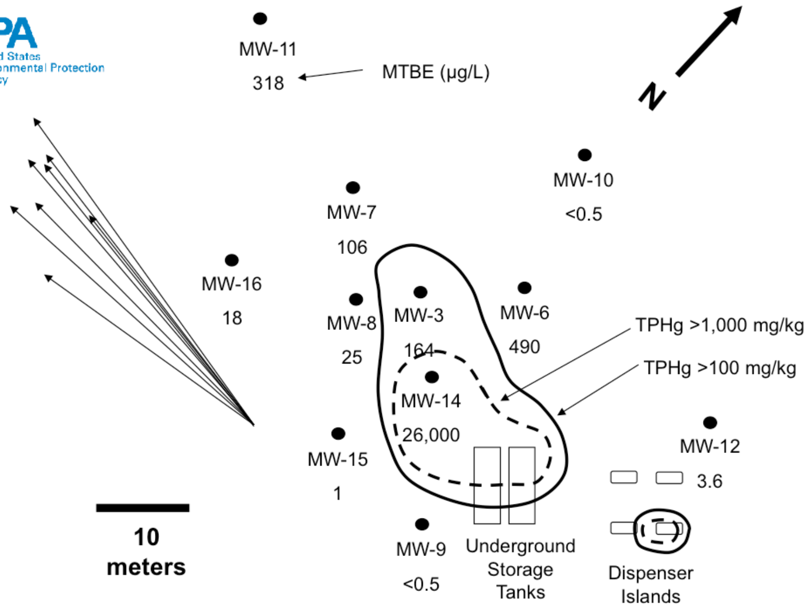
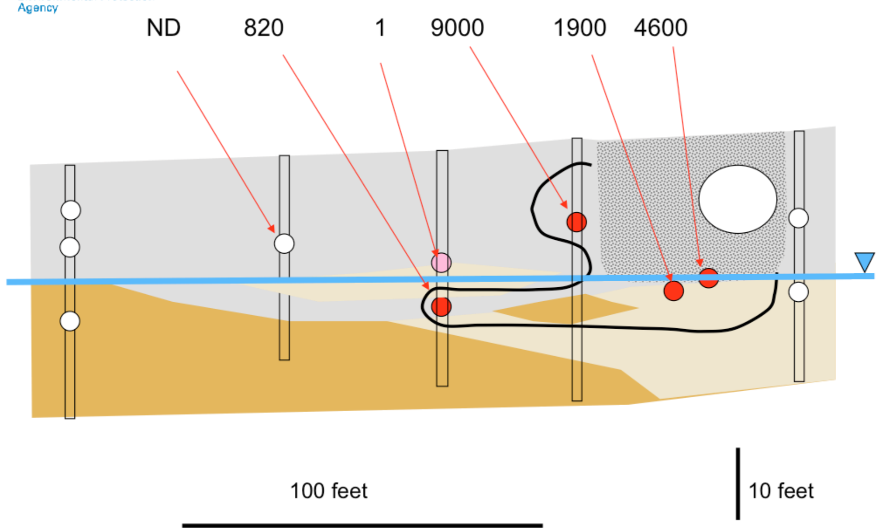
A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis

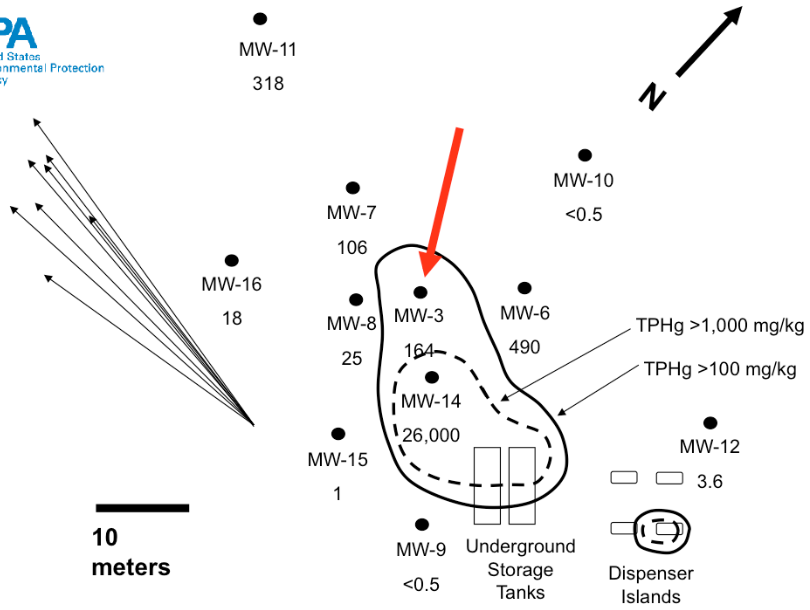


Samples collect 2004

TPHg mg/kg



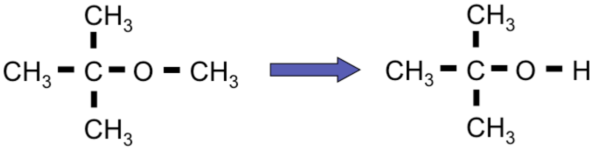
United States Environmental Protection Agency



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

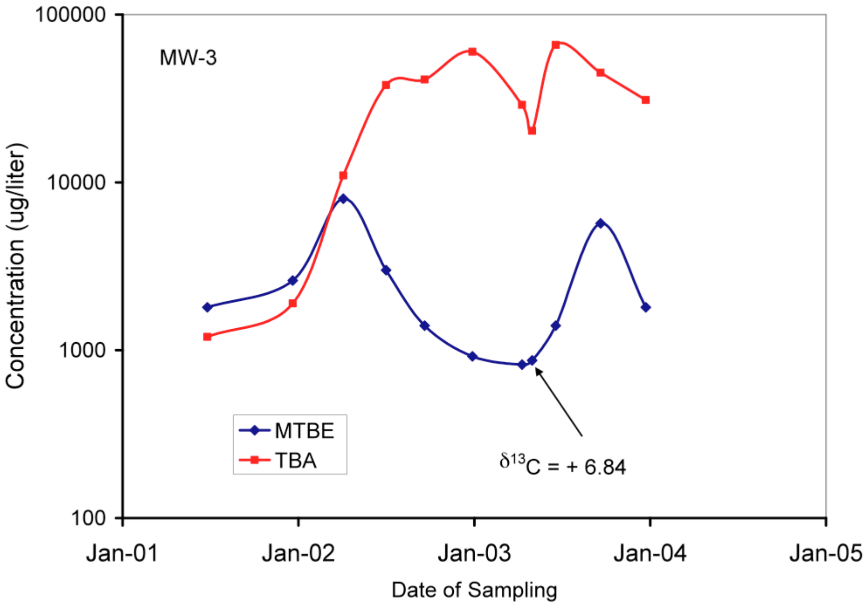
TBA is also a minor component of the technical grade of MTBE used in gasoline.

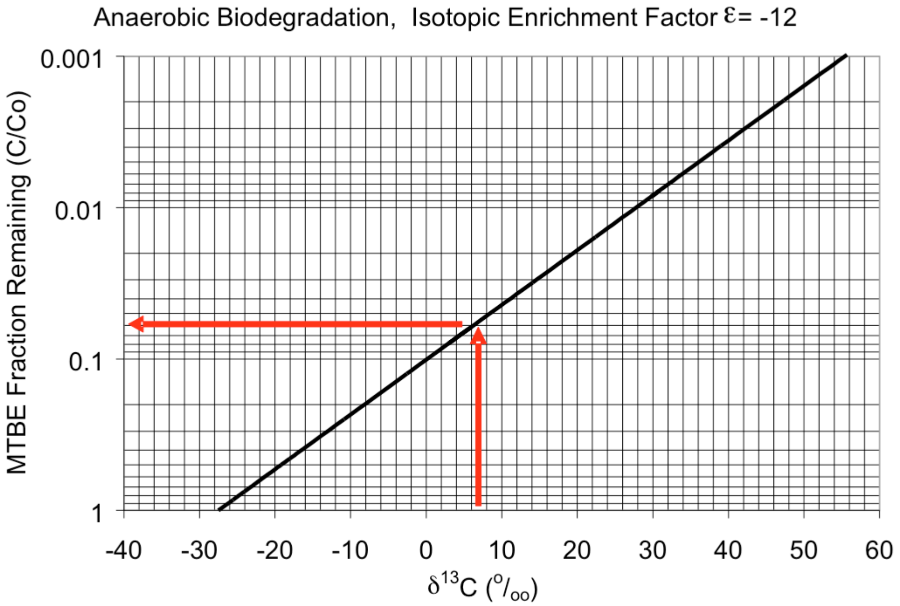
The accumulation of TBA over time is an indication of the biodegradation of MTBE.

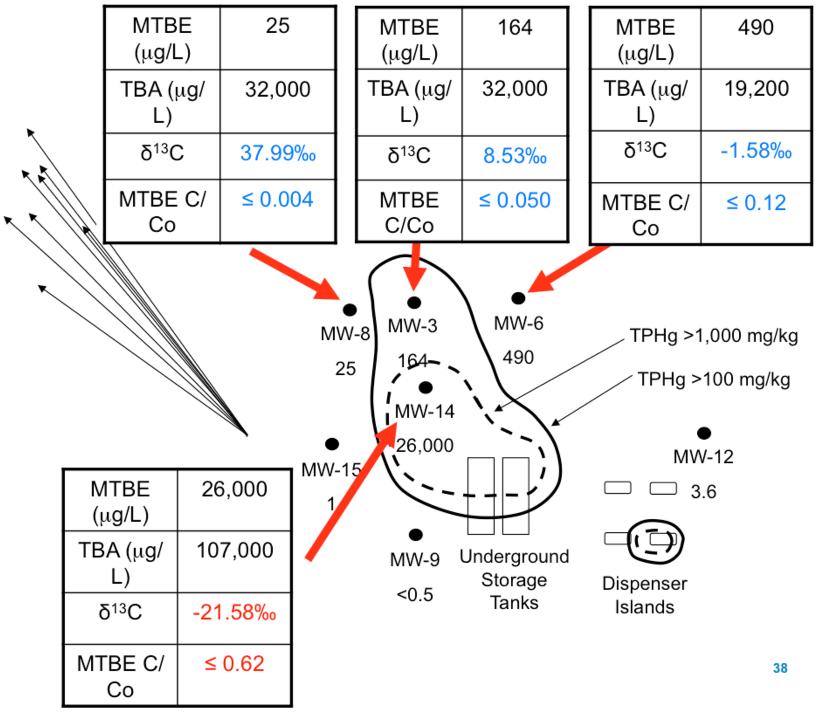


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_3 \rightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-H$$

▫


100000
10000
1000
100
Concentration (ug/liter)
MW-3
MTBE
TBA
$\delta^{13}C$ = + 6.84
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Date of Sampling


Anaerobic Biodegradation, Isotopic Enrichment Factor ε= -12
MTBE Fraction Remaining (C/Co)
0.001
0.01
0.1
1
-40
-30
-20
-10
0
10
20
30
40
50
60
δ13C (o/oo)



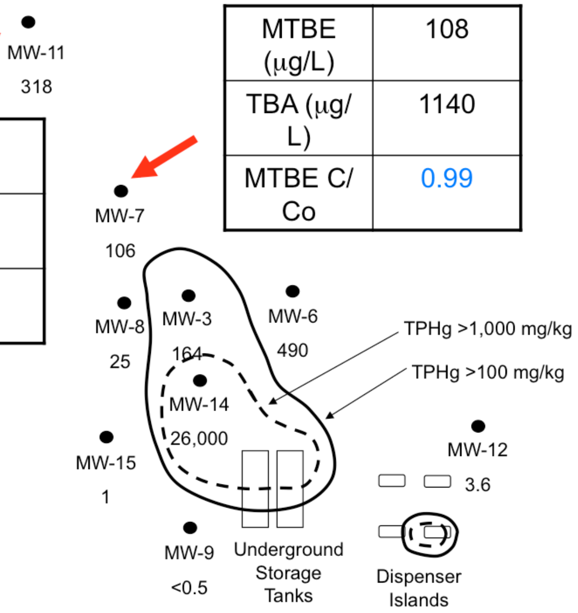
MTBE (μg/L)	25
TBA (μg/L)	32,000
$\delta^{13}C$	37.99‰
MTBE C/Co	≤ 0.004

MTBE (μg/L)	164
TBA (μg/L)	32,000
$\delta^{13}C$	8.53‰
MTBE C/Co	≤ 0.050

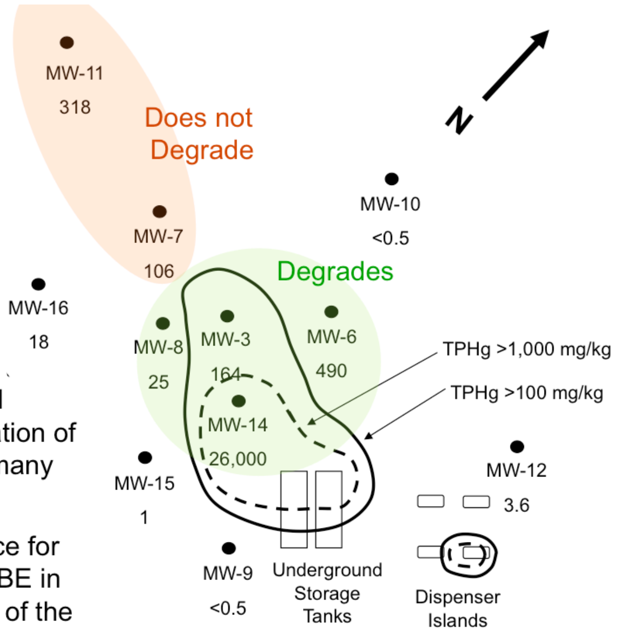
MTBE (μg/L)	490
TBA (μg/L)	19,200
$\delta^{13}C$	-1.58‰
MTBE C/Co	≤ 0.12

MTBE (μg/L)	26,000
TBA (μg/L)	107,000
$\delta^{13}C$	-21.58‰
MTBE C/Co	≤ 0.62

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!

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)	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

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.

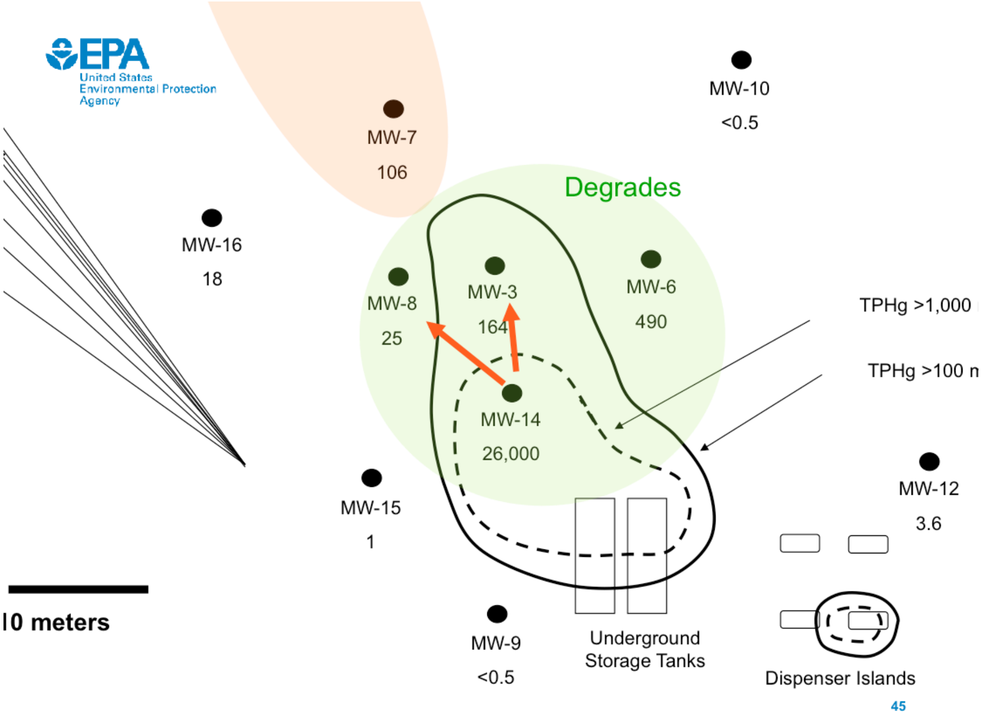
$$k_{\text{with distance}} = -\ln(F)/d$$

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

F is the fraction of MTBE remaining

d is the distance between the wells

v is the ground water seepage velocity


MW-10
<0.5
MW-7
106
Degrades
MW-16
18
MW-3
164
MW-6
490
MW-8
25
TPHg >1,000
TPHg >100 n
MW-14
26,000
MW-12
3.6
MW-15
1
10 meters
MW-9
<0.5
Underground
Storage Tanks
Dispenser Islands
45

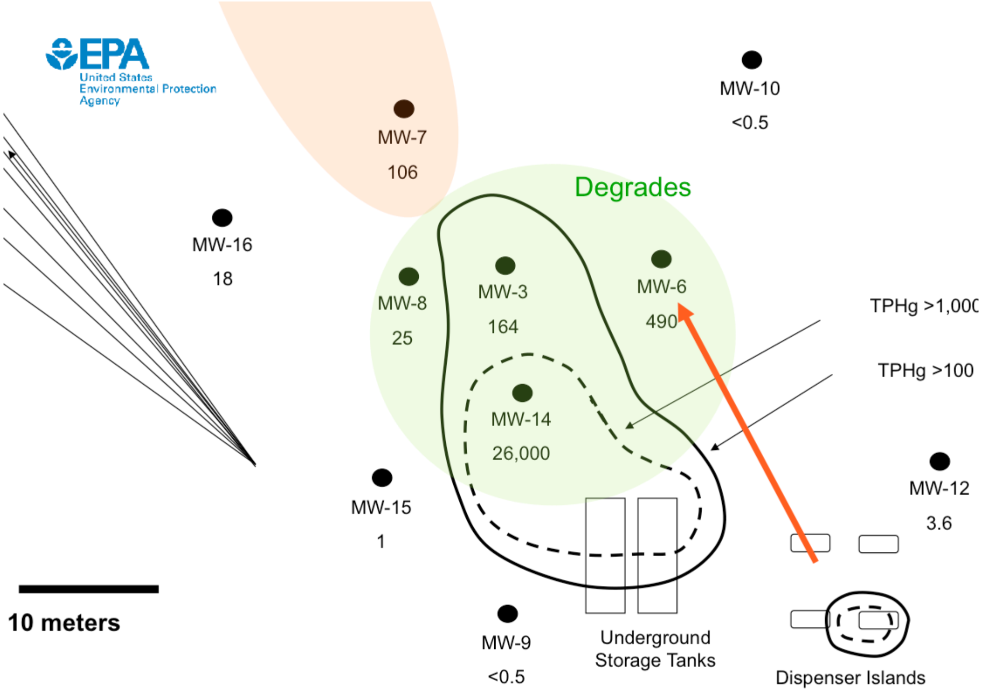
Well	Date	Fraction MTBE Remaining (C/C_o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Distance (per meter)
MW-3	5/20/03	0.058	9.6	0.30
MW-3	8/18/04	0.050	9.6	0.31
MW-8	5/20/03	0.023	11.7	0.32
MW-8	8/18/04	0.0043	11.7	0.46

=LN (0.0043)/11.7

seepage velocity is 37 meters per year

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

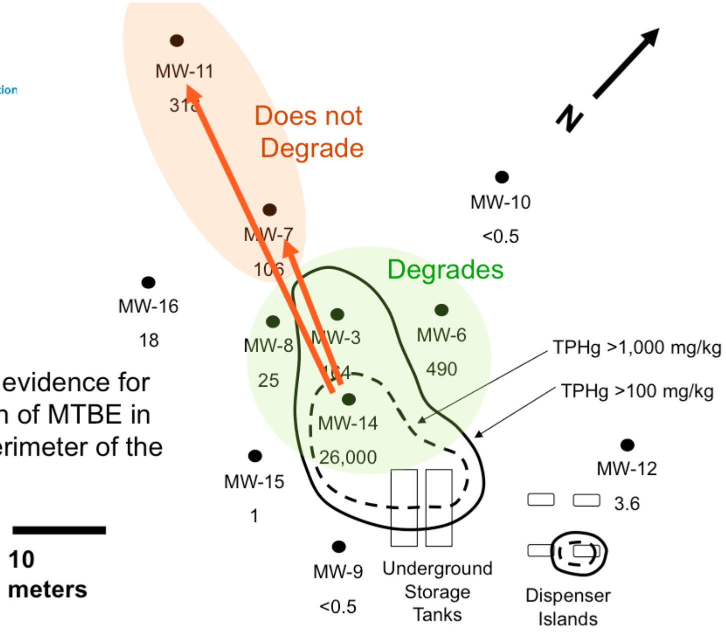
= 37 meters per year * 0.46 per meter



Degrades
MW-7
106
MW-10
<0.5
MW-16
18
MW-8
25
MW-3
164
MW-6
490
TPHg >1,00
TPHg >100
MW-14
26,000
MW-15
1
MW-12
3.6
MW-9
<0.5
Underground Storage Tanks
Dispenser Islands
10 meters

▫

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



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

Well	Date	TBA measured (µg/L)	MTBE measured (µg/L)	$\delta^{13}C$ 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 $\delta^{13}C$; the precision of the estimate of $\delta^{13}C$ was ±3 ‰ rather than ± 0.1 ‰.

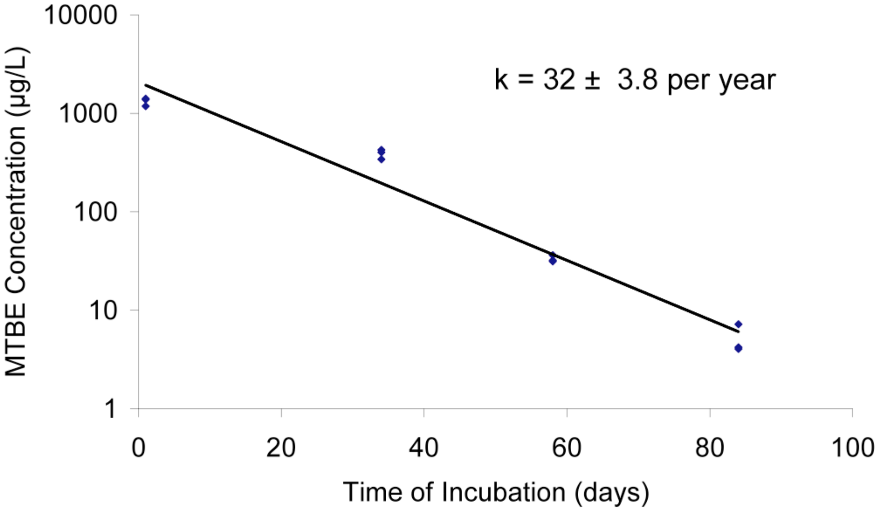
Well	Date	Fraction MTBE Remaining (C/C_o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Distance (per meter)
MW-7	8/18/04	0.994	23.0	0.00025
MW11	5/20/03	1.0	44.1	0
MW11	8/18/04	1.0	44.1	0

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


6
B-10
B-03C9-6
BTEX
60
2B9-60
UNITED STATES OF AMERICA
LIBERTY
QUARTER DOLLAR


FLAMMABLE
KEEP FIRE AWAY
Kimwipes

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

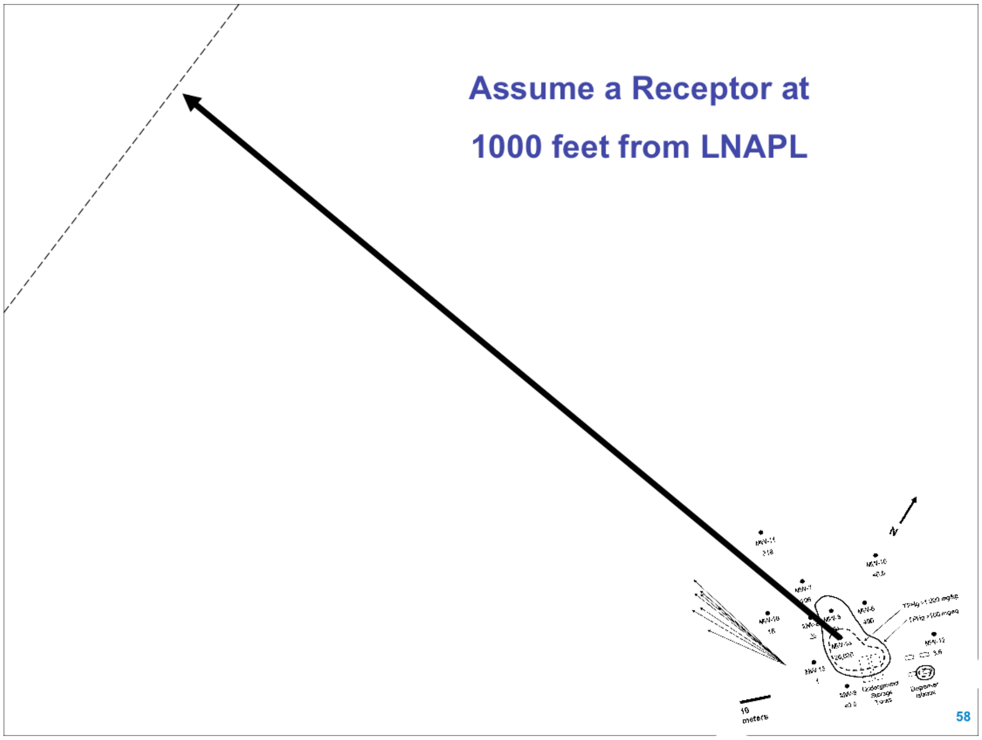


Huntington Beach, Orange County California

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.



Assume a Receptor at 1000 feet from LNAPL

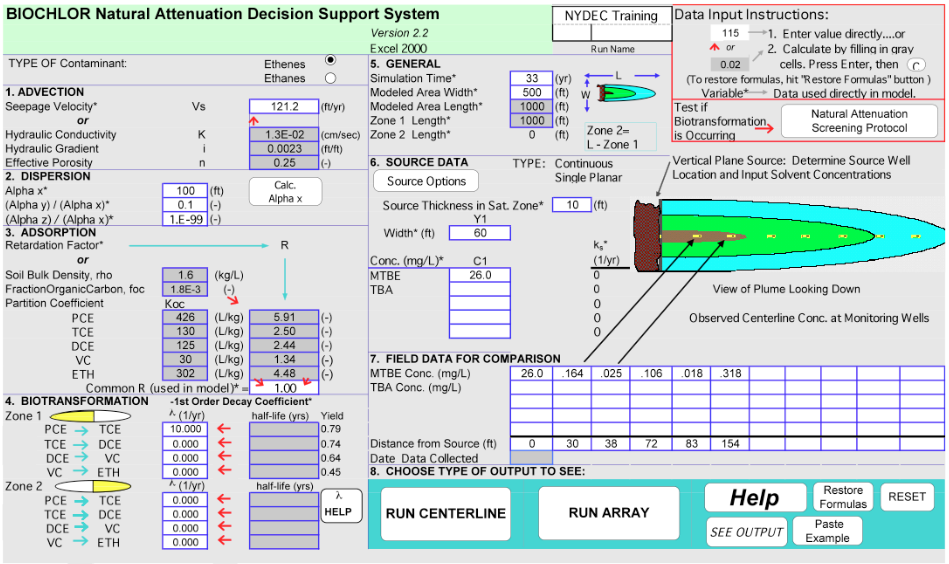
BIOCHLOR 2.2 will be used to evaluate the potential exposure to the receptor.

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

NYDEC Training
Run Name

TYPE OF Contaminant: Ethenes ● Ethanes ○

1. ADVECTION
Seepage Velocity* Vs 121.2 (ft/yr)
or
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
or
Soil Bulk Density, rho 1.6 (kg/L)
FractionOrganicCarbon, foc 1.8E-3 (-)

Partition Coefficient	Koc		R	
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	λ (1/yr)	half-life (yrs)	Yield
PCE → TCE	10.000		0.79
TCE → DCE	0.000		0.74
DCE → VC	0.000		0.64
VC → ETH	0.000		0.45

Zone 2	λ (1/yr)	half-life (yrs)
PCE → TCE	0.000	
TCE → DCE	0.000	
DCE → VC	0.000	
VC → ETH	0.000	

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)
Zone 2= L - Zone 1

6. SOURCE DATA TYPE: Continuous Single Planar
Source Thickness in Sat. Zone* 10 (ft)
Y1
Width* (ft) 60

Conc. (mg/L)*	C1	ks* (1/yr)
MTBE	26.0	0
TBA		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

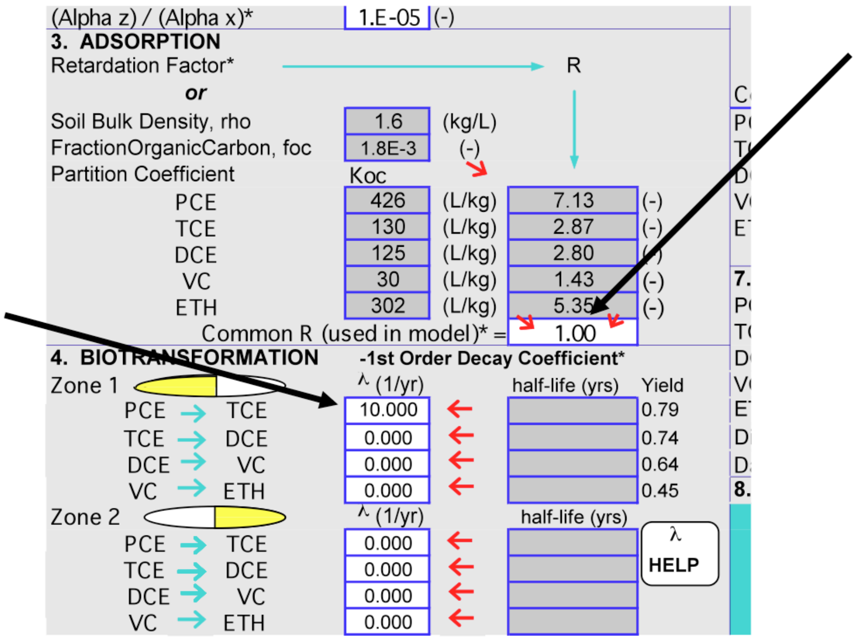
7. FIELD DATA FOR COMPARISON

MTBE Conc. (mg/L)	26.0	.164	.025	.106	.018	.318					
TBA Conc. (mg/L)											
Distance from Source (ft)	0	30	38	72	83	154					
Date Data Collected											

8. CHOOSE TYPE OF OUTPUT TO SEE:

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

Test if Biotransformation is Occurring



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

3. ADSORPTION

Retardation Factor* → R

or

Soil Bulk Density, rho	1.6	(kg/L)
FractionOrganicCarbon, foc	1.8E-3	(-)

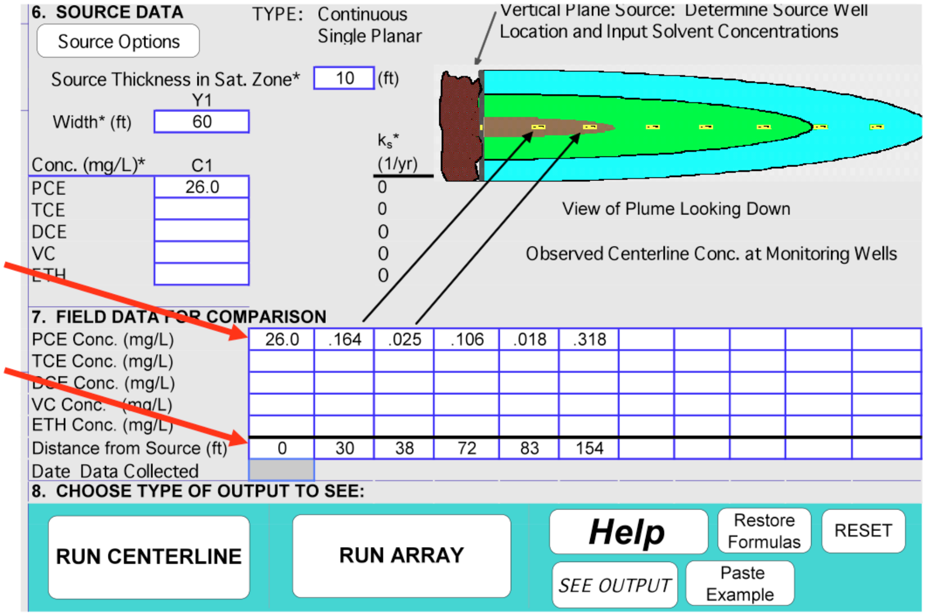
Partition Coefficient	Koc		R	
PCE	426	(L/kg)	7.13	(-)
TCE	130	(L/kg)	2.87	(-)
DCE	125	(L/kg)	2.80	(-)
VC	30	(L/kg)	1.43	(-)
ETH	302	(L/kg)	5.35	(-)

Common R (used in model)* = 1.00

4. BIOTRANSFORMATION **-1st Order Decay Coefficient***

Zone 1	λ (1/yr)	half-life (yrs)	Yield
PCE → TCE	10.000		0.79
TCE → DCE	0.000		0.74
DCE → VC	0.000		0.64
VC → ETH	0.000		0.45

Zone 2	λ (1/yr)	half-life (yrs)
PCE → TCE	0.000	
TCE → DCE	0.000	
DCE → VC	0.000	
VC → ETH	0.000	



6. SOURCE DATA

TYPE: Continuous
Single Planar

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

Source Thickness in Sat. Zone* 10 (ft)

Width* (ft) Y1 60

Conc. (mg/L)*	C1	k_s* (1/yr)
PCE	26.0	0
TCE		0
DCE		0
VC		0
ETH		0

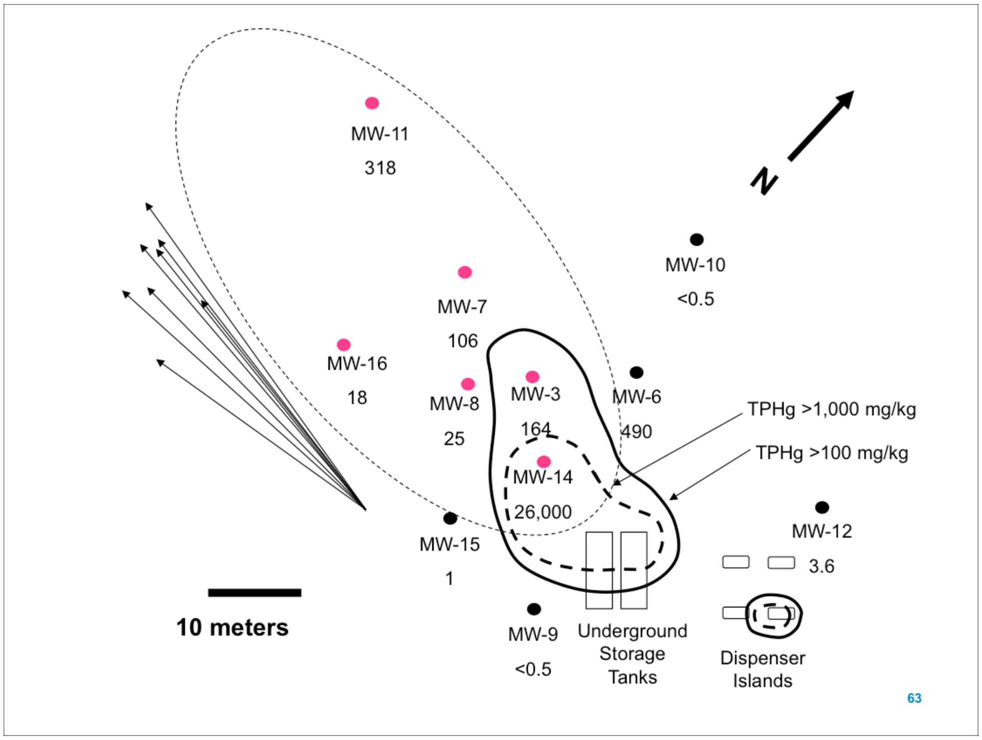
View of Plume Looking Down

Observed Centerline Conc. at Monitoring Wells

7. FIELD DATA FOR COMPARISON

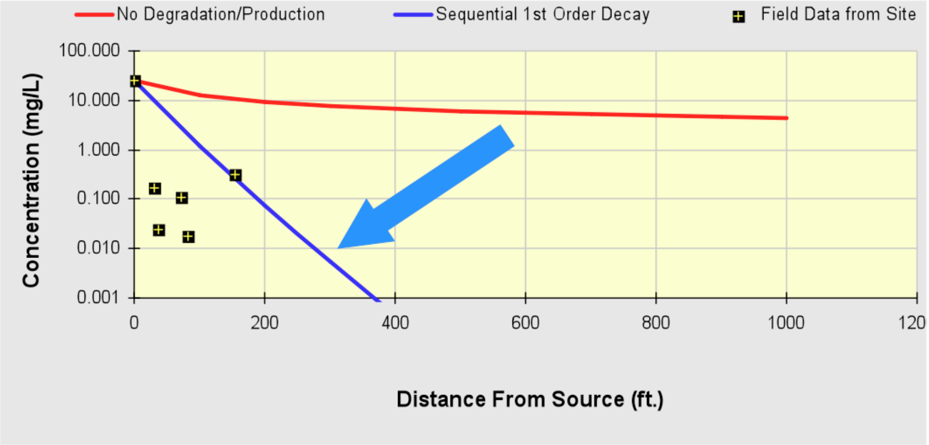
PCE Conc. (mg/L)	26.0	.164	.025	.106	.018	.318					
TCE Conc. (mg/L)											
DCE Conc. (mg/L)											
VC Conc. (mg/L)											
ETH Conc. (mg/L)											
Distance from Source (ft)	0	30	38	72	83	154					
Date Data Collected											

8. CHOOSE TYPE OF OUTPUT TO SEE:

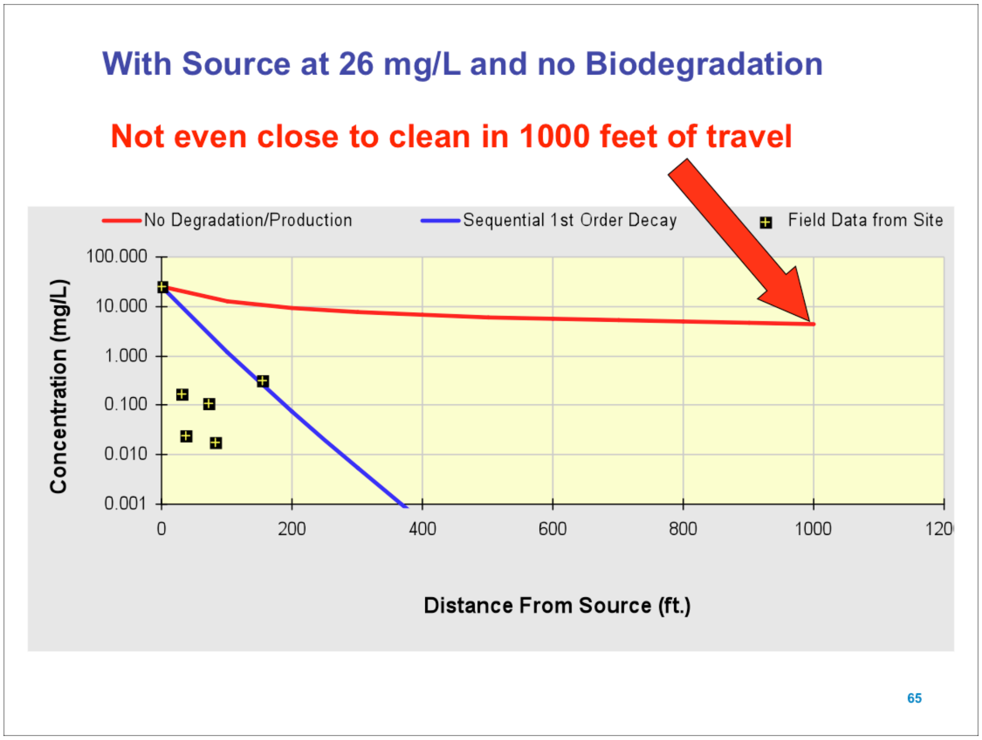

MW-11
318
N
MW-10
<0.5
MW-7
106
MW-16
18
MW-3
164
MW-6
490
MW-8
25
TPHg >1,000 mg/kg
TPHg >100 mg/kg
MW-14
26,000
MW-12
3.6
MW-15
1
10 meters
MW-9
<0.5
Underground Storage Tanks
Dispenser Islands
63

□

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

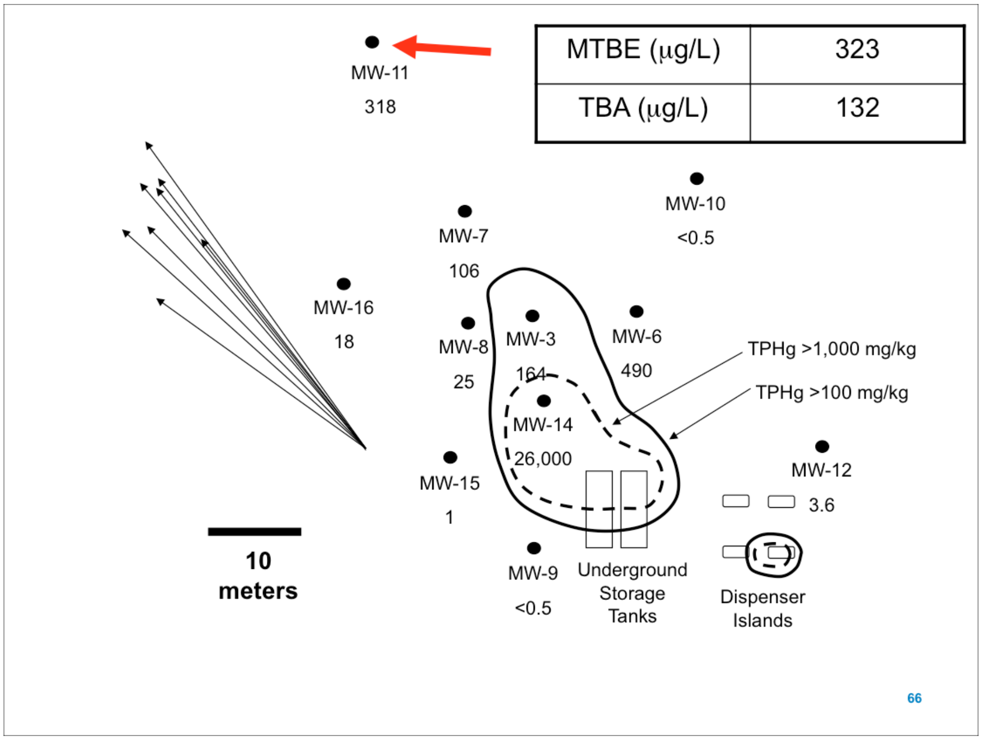


Clean in approximately 300 feet of travel



With Source at 26 mg/L and no Biodegradation

Not even close to clean in 1000 feet of travel

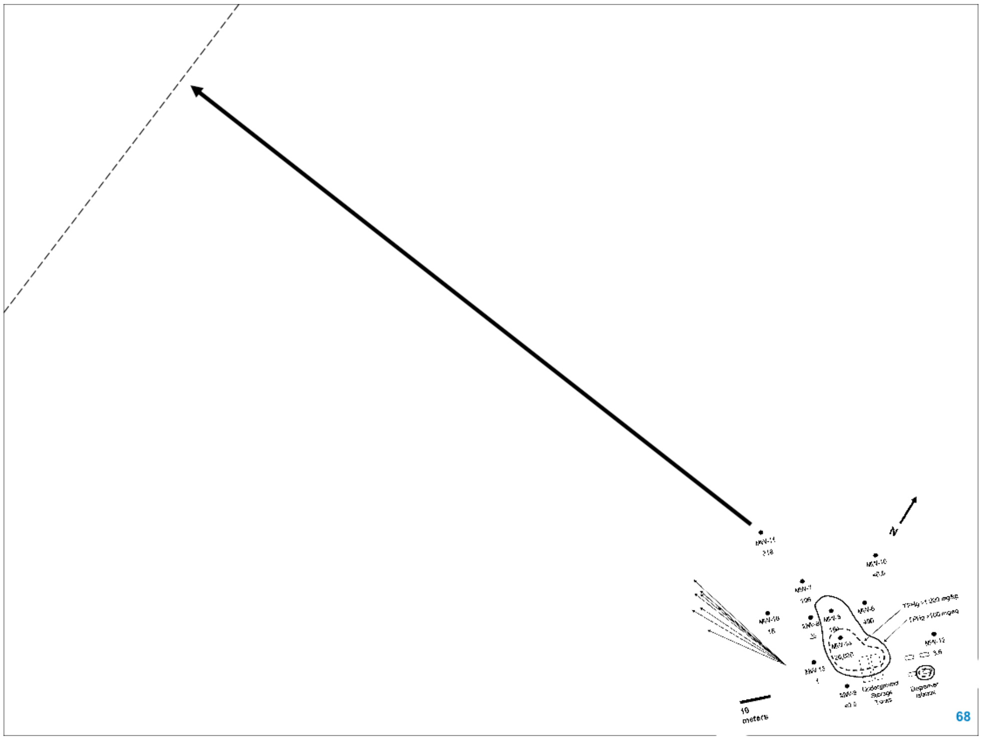


MTBE (μg/L)	323
TBA (μg/L)	132

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.

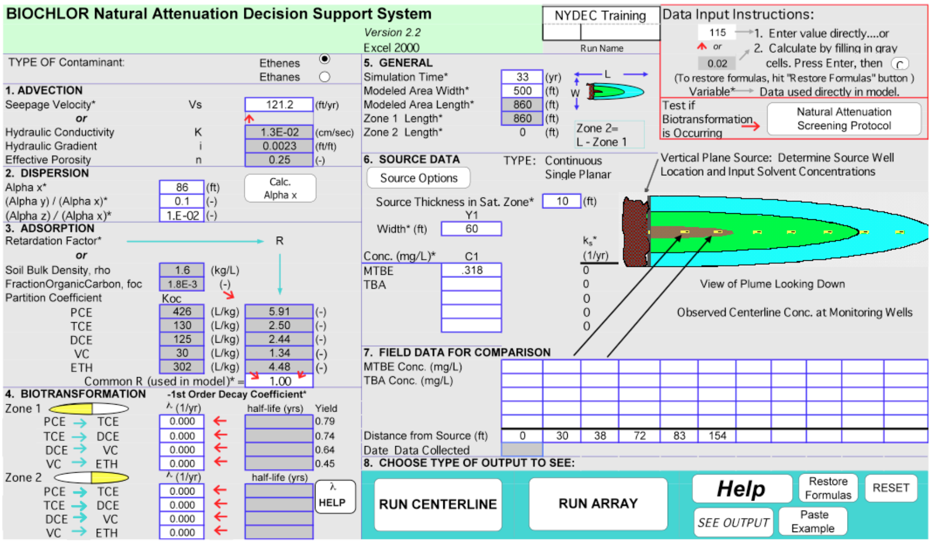
3) Determine the extent of the periphery of the plume there is no biodegradation.


N
MW-11
318
MW-10
<2.5
MW-7
106
MW-16
15
MW-8
MW-5
150
MW-6
490
MW-5a
26,000
TPHg >1,000 mg/kg
TPHg >100 mg/kg
MW-12
3.6
MW-15
1
MW-9
<2.5
Underground
Storage
Tanks
Dispenser
islands
10
meters

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:
115 → 1. Enter value directly....or
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.

Test if Biotransformation is Occurring → Natural Attenuation Screening Protocol

TYPE OF Contaminant: Ethenes ● Ethanes ○

1. ADVECTION

Seepage Velocity*	Vs	121.2	(ft/yr)
or			
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)
(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)
FractionOrganicCarbon, foc	1.8E-3	(-)

Partition Coefficient	Koc		R	
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	λ (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

Zone 2	λ (1/yr)	half-life (yrs)
PCE → TCE	0.000	
TCE → DCE	0.000	
DCE → VC	0.000	
VC → ETH	0.000	

5. GENERAL

Simulation Time*	33	(yr)
Modeled Area Width*	500	(ft)
Modeled Area Length*	860	(ft)
Zone 1 Length*	860	(ft)
Zone 2 Length*	0	(ft)

Zone 2= L - Zone 1

6. SOURCE DATA TYPE: Continuous Single Planar

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

Source Thickness in Sat. Zone* 10 (ft)

Width* (ft) Y1: 60

Conc. (mg/L)*	C1	k_s* (1/yr)
MTBE	.318	0
TBA		0
		0
		0
		0

View of Plume Looking Down

Observed Centerline Conc. at Monitoring Wells

7. FIELD DATA FOR COMPARISON

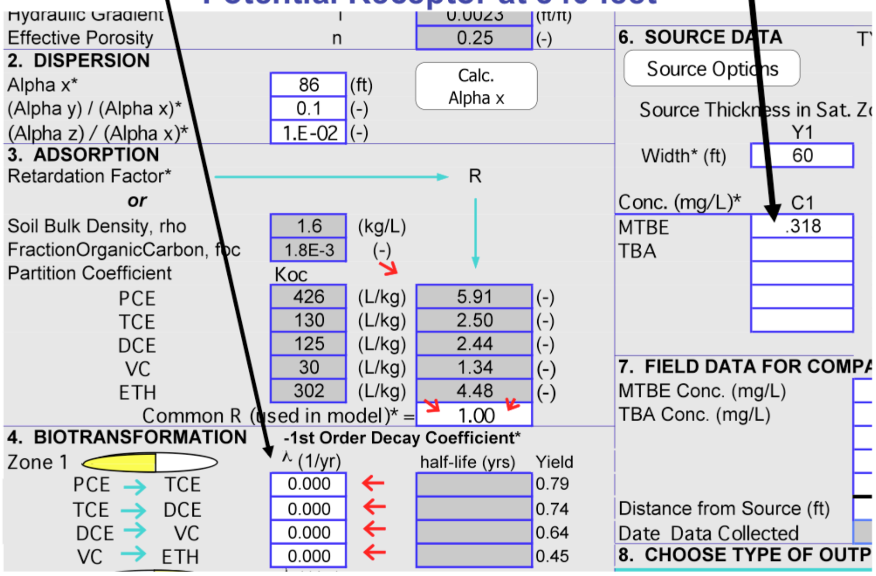
MTBE Conc. (mg/L)											
TBA Conc. (mg/L)											
Distance from Source (ft)	0	30	38	72	83	154					
Date Data Collected											

8. CHOOSE TYPE OF OUTPUT TO SEE:

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)		
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	(-)
Common R (used in model)* =				1.00	

4. BIOTRANSFORMATION	-1st Order Decay Coefficient*		
Zone 1	λ (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 T

Source Options

Source Thickness in Sat. Z

	Y1
Width* (ft)	60
Conc. (mg/L)*	C1
MTBE	.318
TBA	

7. FIELD DATA FOR COMPA

MTBE Conc. (mg/L)

TBA Conc. (mg/L)

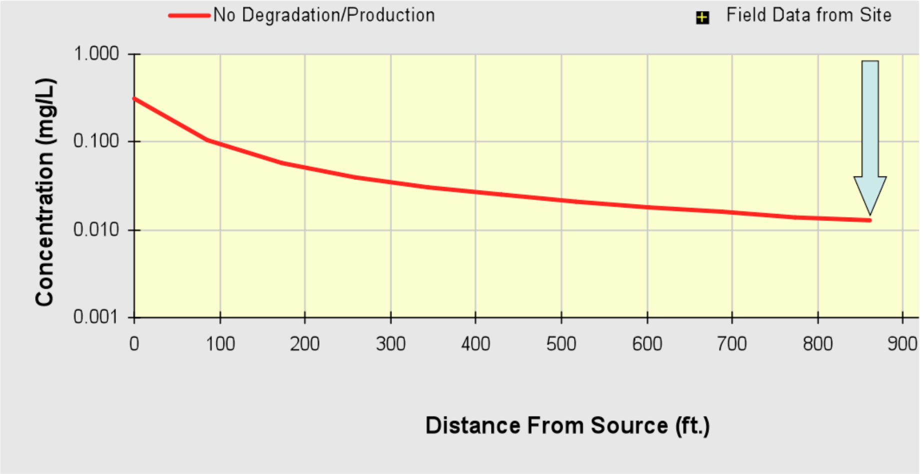
Distance from Source (ft)

Date Data Collected

8. CHOOSE TYPE OF OUTP

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/Co 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

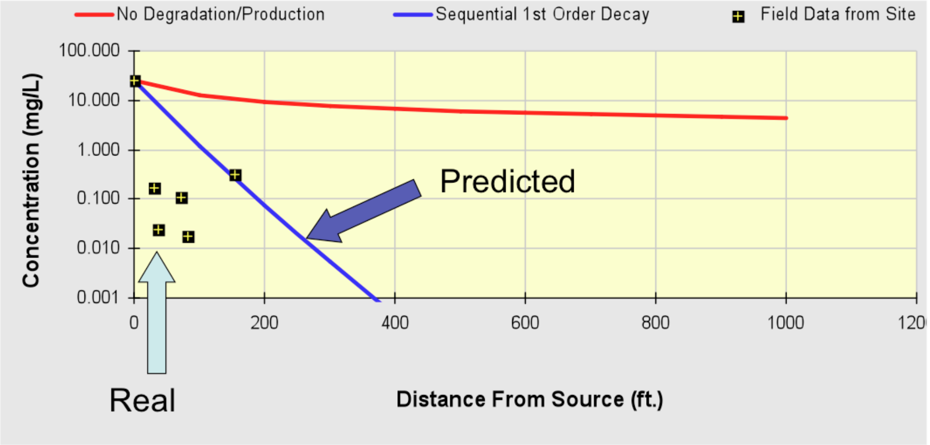
2) Proximity to NAPL or other source of contamination to ground water

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 well 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

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

Three types of site-specific information may be required:

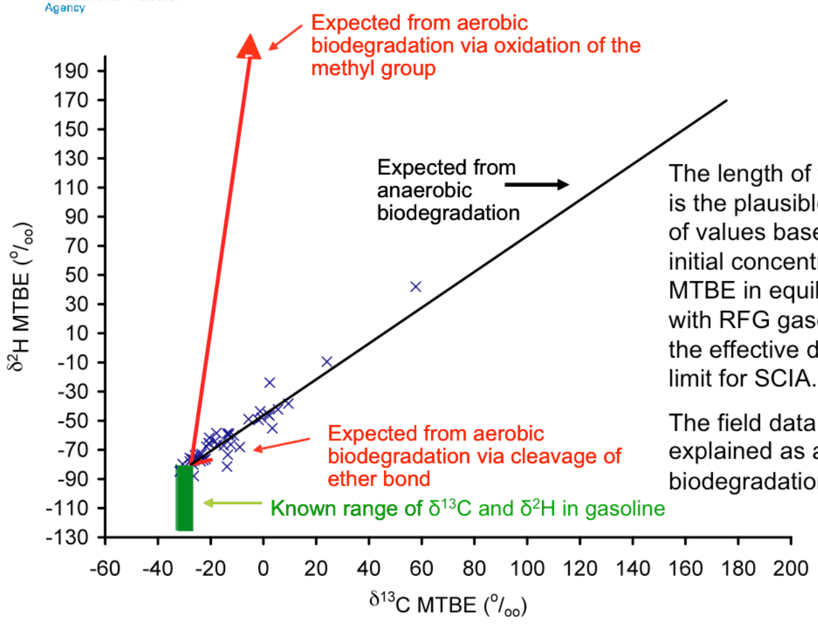
1. Historical ground water and/or soil chemistry data demonstrates a trend of declining contaminant concentration.
2. Hydrogeologic and geochemical data that demonstrate NA processes and rates.
3. Data from field or microcosm studies which directly demonstrate the occurrence of a particular attenuation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

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			
	ε_{carbon} (‰)	ε_{carbon} (‰)	Reference
Aerobic via oxygenase	-2.4	-30	Gray et al. 2002 *ES&T* 36:1931-1938
Aerobic via ether hydrolysis	-0.48	-0.2	Rosell et al. 2007 *ES&T* 41:2036-2043
Anaerobic	-13	-16	Kuder et al. 2005 *ES&T* 39:213-220

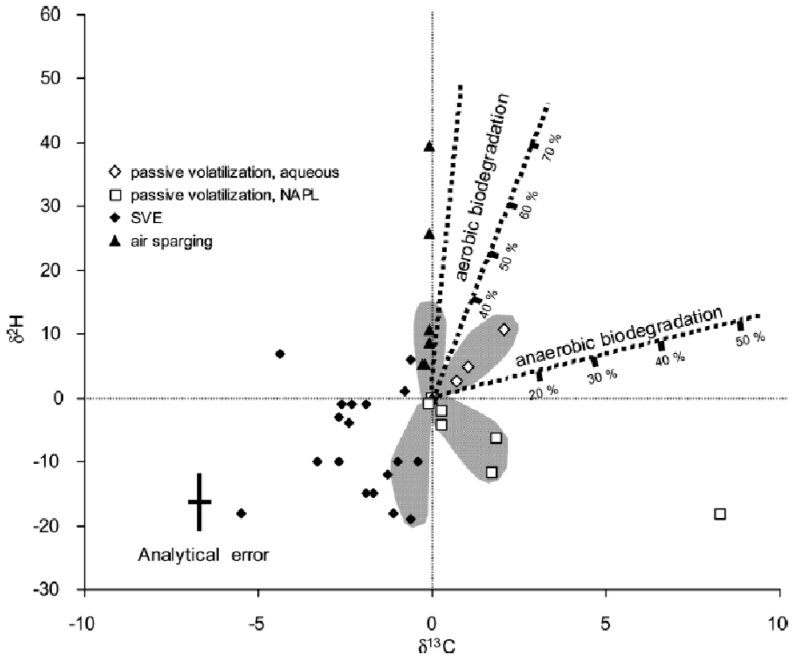


The length of the lines is the plausible range of values based on an initial concentration of MTBE in equilibrium with RFG gasoline and the effective detection limit for SCIA.

The field data are best explained as anaerobic biodegradation.

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


60
50
40
30
20
10
0
-10
-20
-30
δ²H
-10
-5
0
5
10
δ¹³C
◇ passive volatilization, aqueous
□ passive volatilization, NAPL
◆ SVE
▲ air sparging
aerobic biodegradation
40 %
50 %
60 %
70 %
anaerobic biodegradation
20 %
30 %
40 %
50 %
Analytical error

82

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

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 is 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.

United States
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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.

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United States
Environmental Protection
Agency

Commercial Source of Analytical Services

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United States
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Agency

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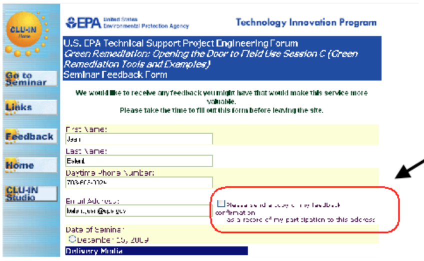
E-mail: bslollar@chem.utoronto.ca

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



U.S. EPA Technical Support Project Engineering Forum
Green Remediation: Opening the Door to Field Use Session C (Green Remediation Tools and Examples)
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Date of Seminar: ○ December 15, 2009
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