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: June 16, 2010, 2:00 PM - 4:00 PM, EDT (18:00-20:00 GMT)

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Moderator:
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Housekeeping

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  - press *6 to mute #6 to unmute your lines at anytime
- Q&A
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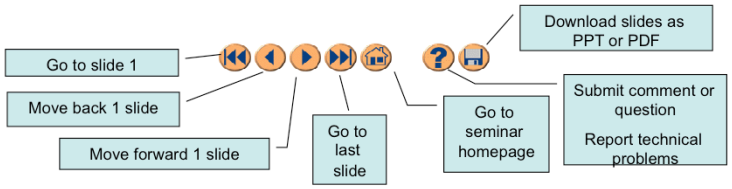

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Although I'm sure that some of you have these rules memorized from previous CLU-IN events, let's run through them quickly for our new participants.

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 interupt 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.

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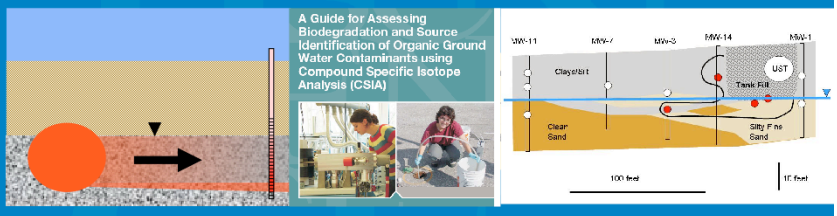
Applications of Stable Isotope Analyses to Understand the Degradation of Organic Contaminants in Ground Water

Part 1. Applications

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



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

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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.

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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.

The ratio in the reference sample

Rs = 0.0112372

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$$\delta^{13}C$$

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.

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$$\delta^{13}C = \left(\frac{R}{R_s} - 1 \right) \cdot 1000$$

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.

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A recent advance:

Compound specific stable isotope analyses can provide an unambiguous conservative boundary on the extent of biodegradation of MTBE in ground water.

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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.

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

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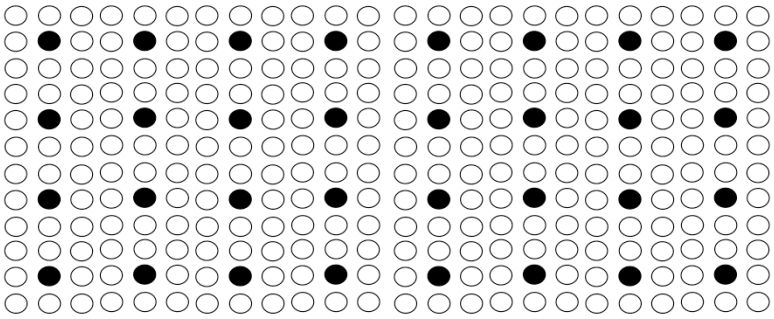
original ratio is 1/9



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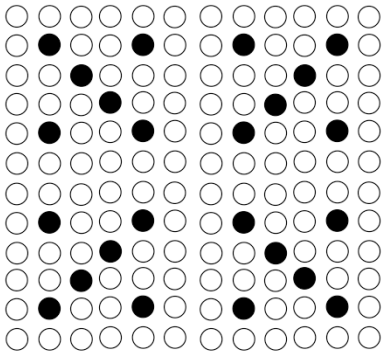
50 % remaining
ratio is 1/6



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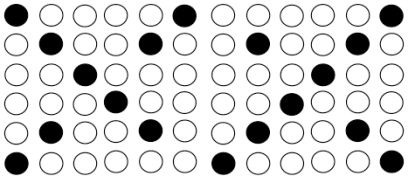
25 % remaining

ratio is 1/4



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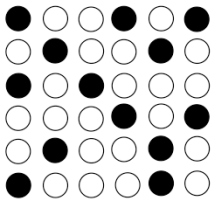
12.5 % remaining

ratio is 1/3



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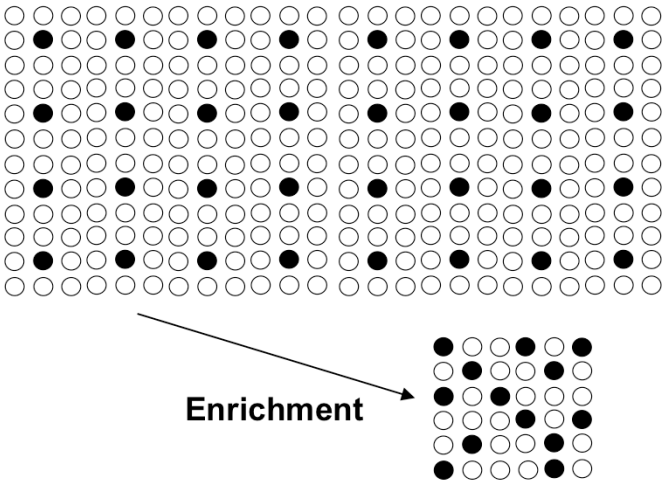

18

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

Example for MTBE

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

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).

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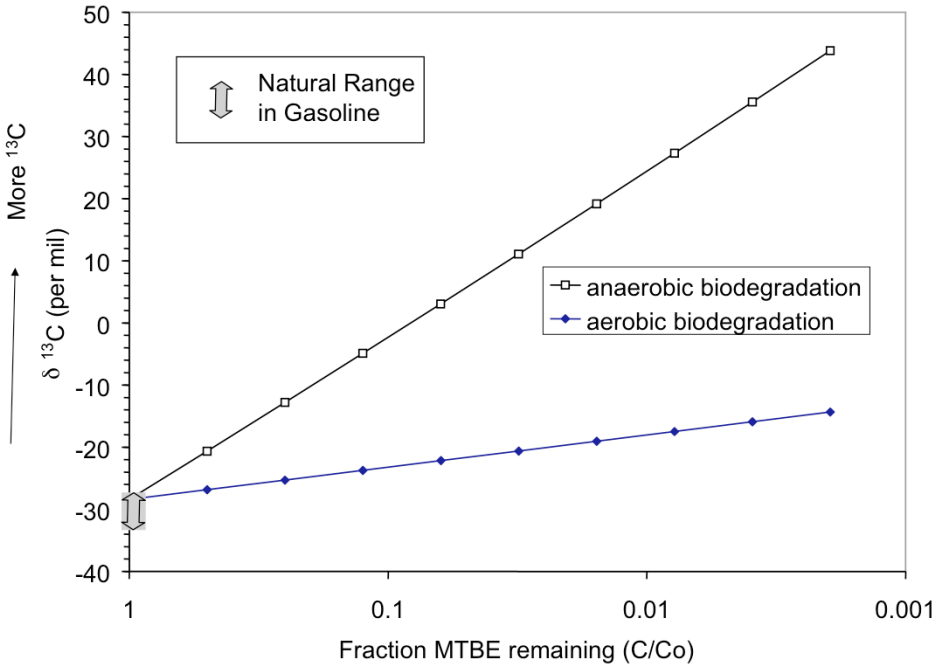
Stable Carbon Isotope Ratios of MTBE in Gasoline

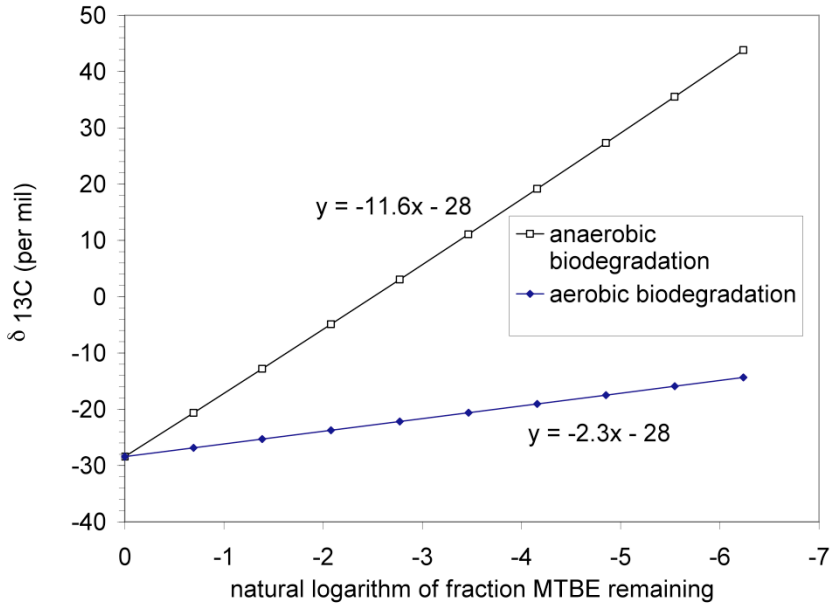
$$\delta^{13}C$$

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

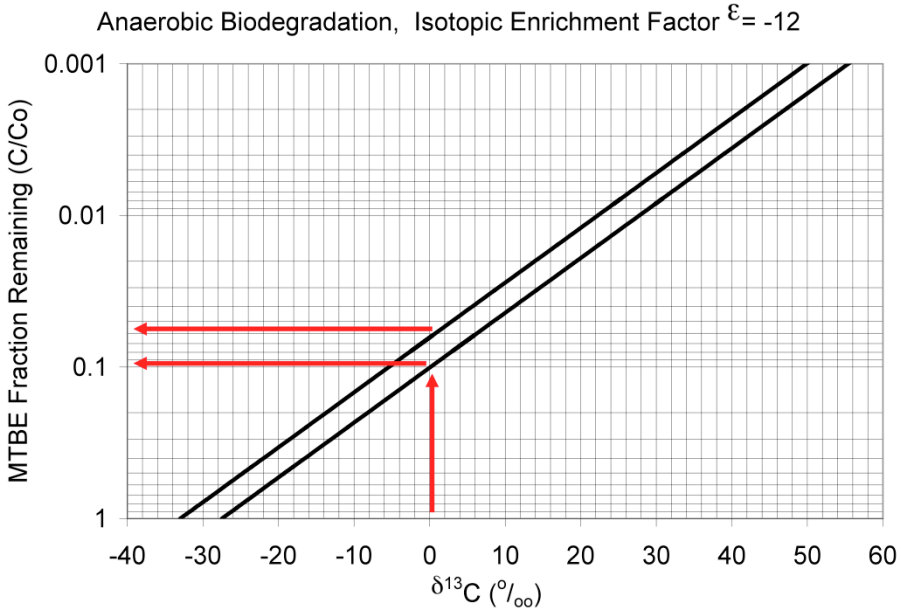
O'Sullivan, G., G. Boshoff, A. Downey, and R. M. Kalin. "Carbon isotope effect during the abiotic oxidation of methyl-tert-butyl ether (MTBE). In Proceedings of the Seventh International In Situ and On-Site Bioremediation Symposium, Orlando, FL, 2003.


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

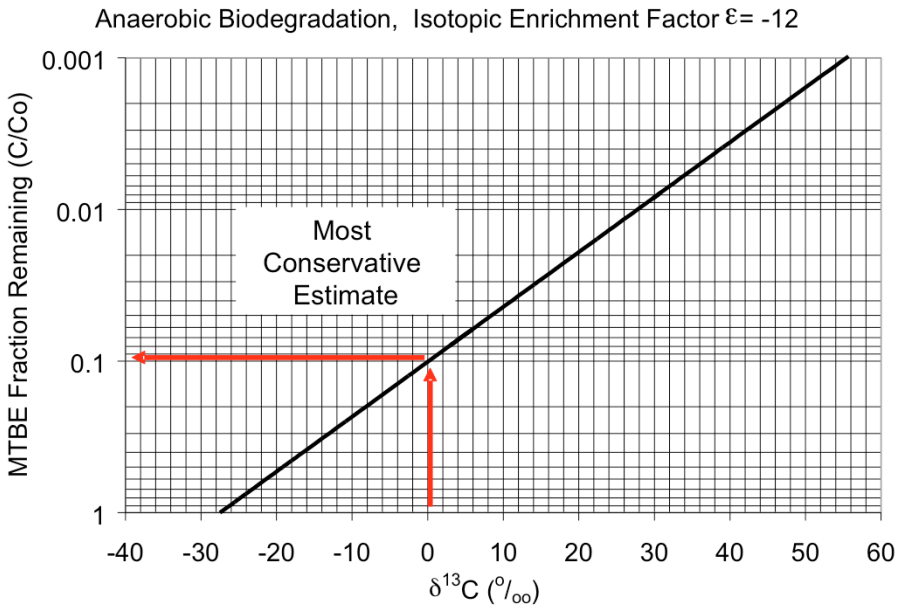
22


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

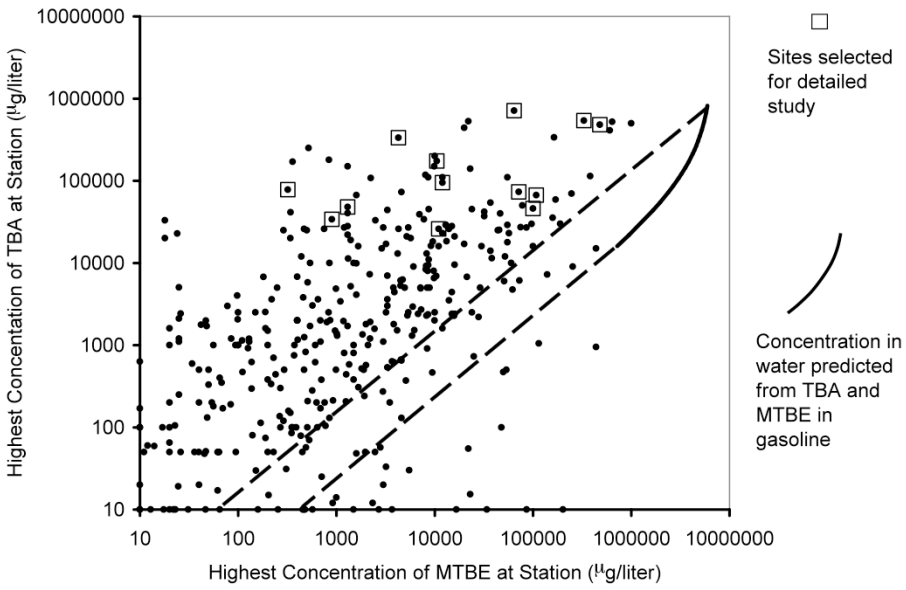
23


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)

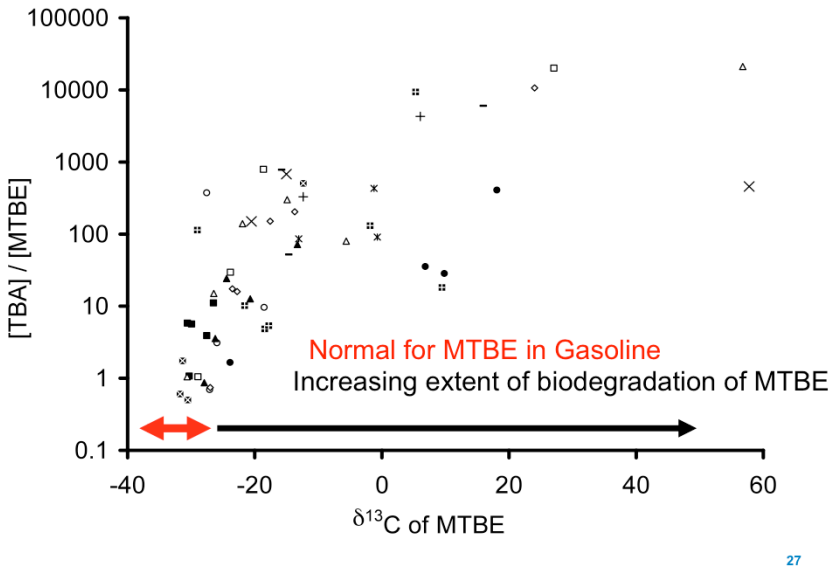
24


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
δ13C (o/oo)

25


Highest Concentation of TBA at Station (µg/liter)
10000000
1000000
100000
10000
1000
100
10
10
100
1000
10000
100000
1000000
10000000
Highest Concentration of MTBE at Station (µg/liter)
Sites selected for detailed study
Concentration in water predicted from TBA and MTBE in gasoline

26

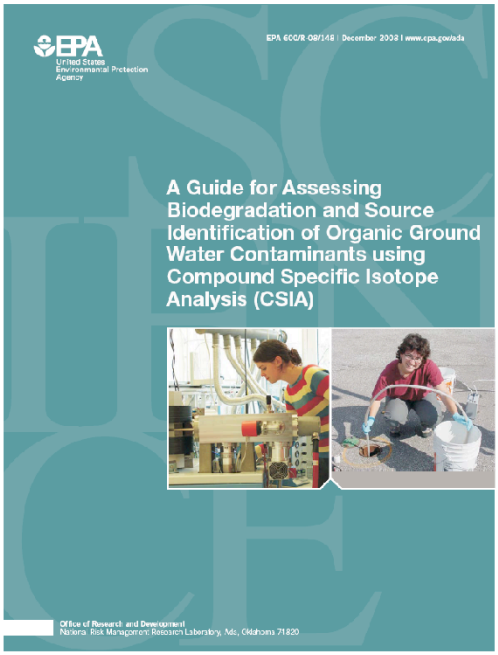

EPA
United States
Environmental Protection
Agency
100000
10000
1000
100
10
1
0.1
[TBA] / [MTBE]
-40
-20
0
20
40
60
δ13C of MTBE
Normal for MTBE in Gasoline
Increasing extent of biodegradation of MTBE
27

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

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



29

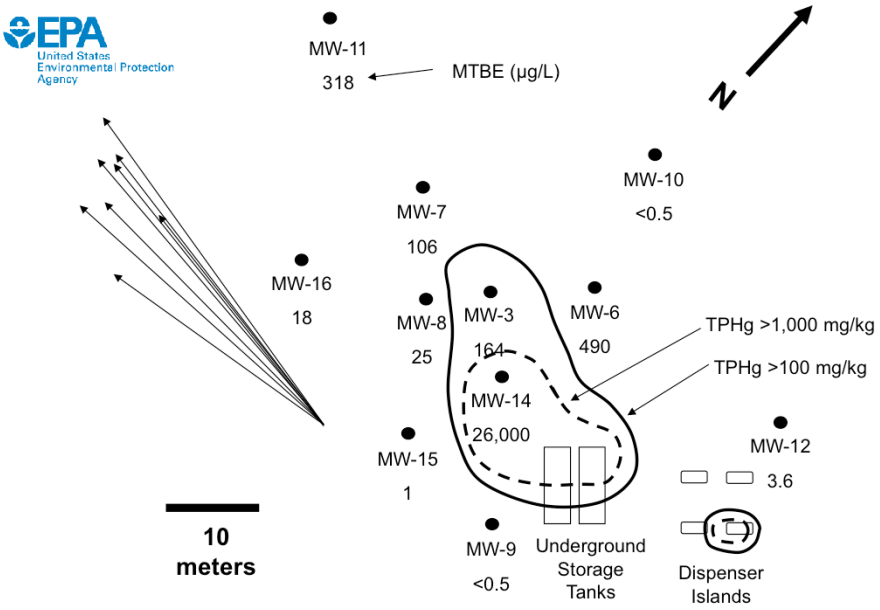
Google: EPA Ada Oklahoma

Select: Ground Water and Ecosystems Restoration Research

Go to publications in white menu bar on left.

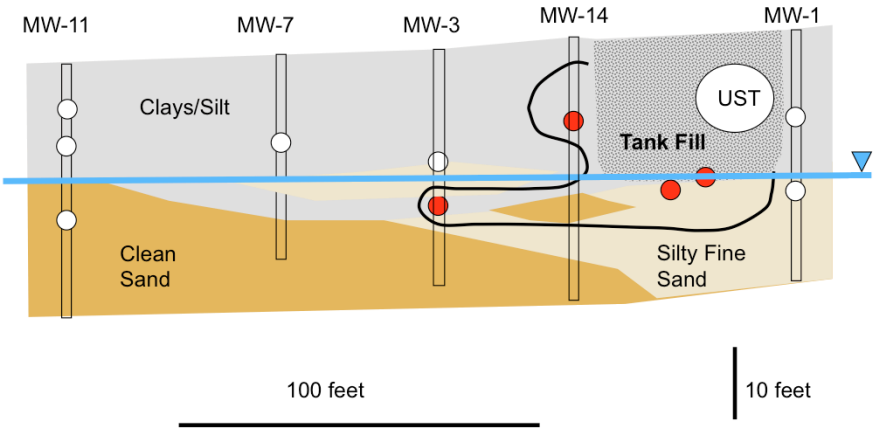
Open: Year

Select 2008

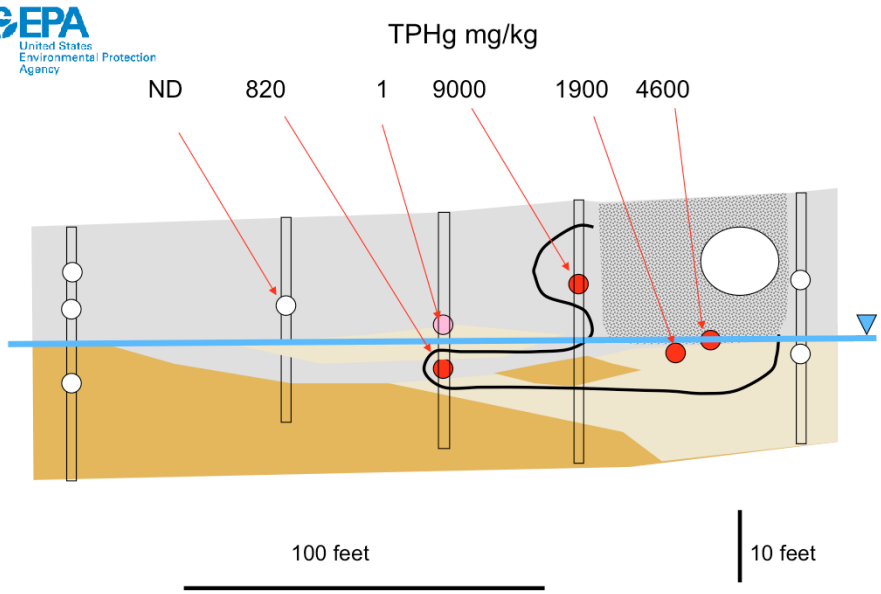


Samples collect 2004

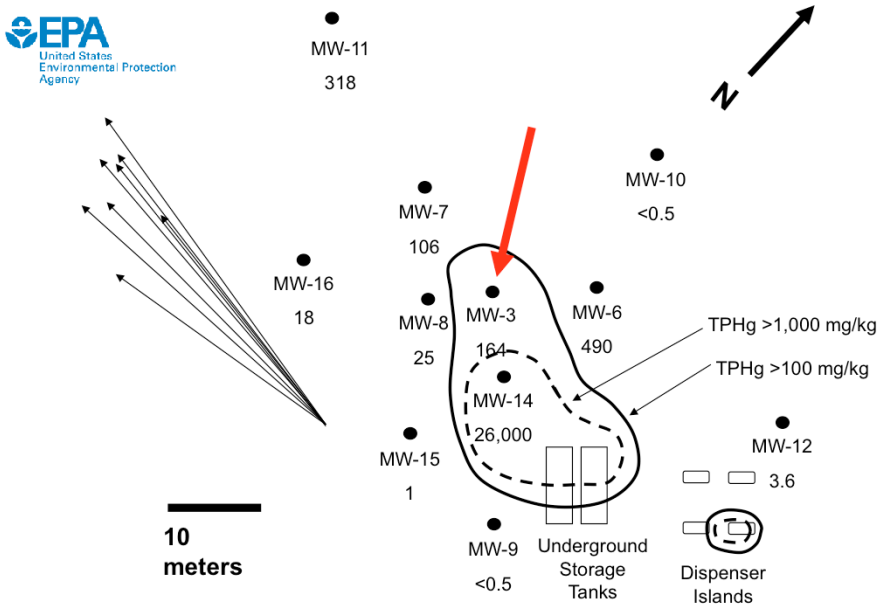
31


MW-11
MW-7
MW-3
MW-14
MW-1
Clays/Silt
UST
Tank Fill
Clean
Sand
Silty Fine
Sand
100 feet
10 feet

32


EPA
United States
Environmental Protection
Agency
TPHg mg/kg
ND
820
1
9000
1900
4600
100 feet
10 feet

33

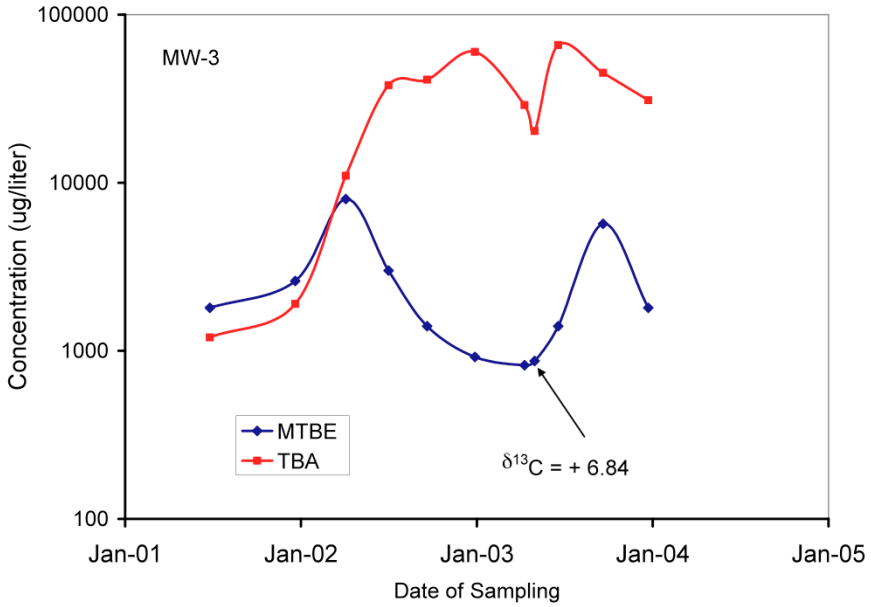

EPA
United States
Environmental Protection
Agency
MW-11
318
N
MW-10
<0.5
MW-7
106
MW-16
18
MW-8
25
MW-3
164
MW-6
490
TPHg >1,000 mg/kg
TPHg >100 mg/kg
MW-14
26,000
MW-15
1
MW-12
3.6
10
meters
MW-9
<0.5
Underground
Storage
Tanks
Dispenser
Islands

34

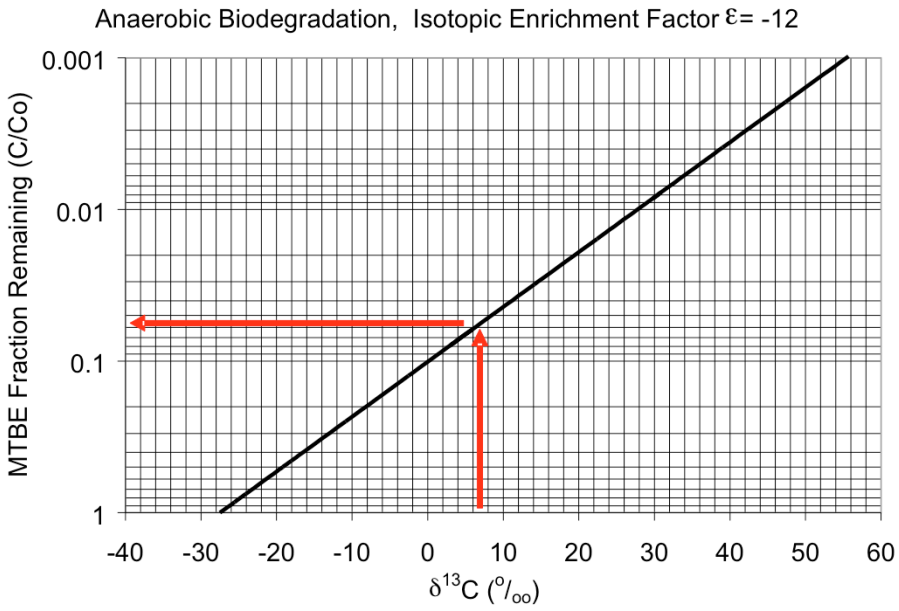
Tertiary Butyl Alcohol (TBA) is the first product of the biodegradation of MTBE.

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

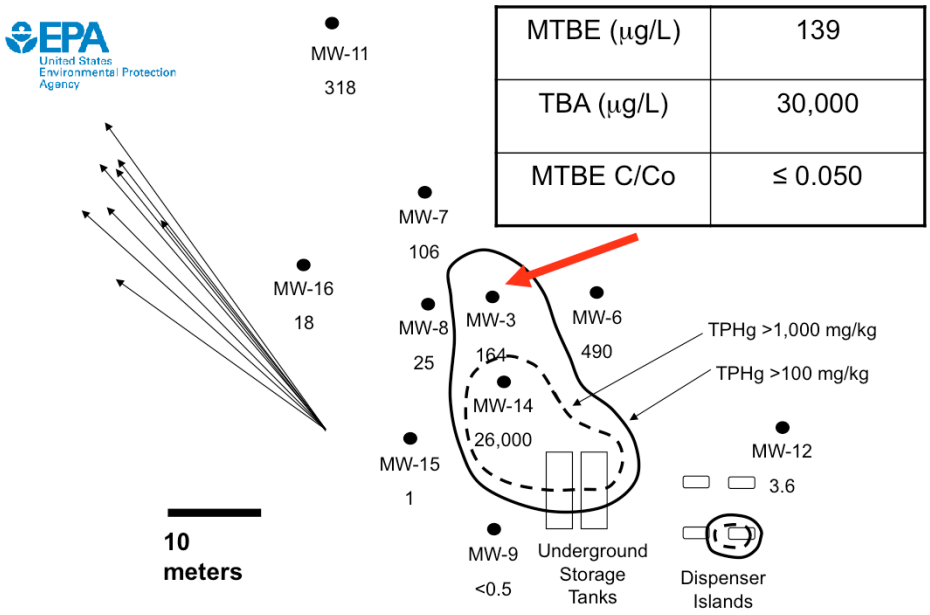
The accumulation of TBA over time is an indication of the biodegradation of MTBE.


MW-3
100000
10000
1000
100
Concentration (ug/liter)
MTBE
TBA
δ13C = + 6.84
Jan-01
Jan-02
Jan-03
Jan-04
Jan-05
Date of Sampling

36


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)

37


EPA
United States
Environmental Protection
Agency
MW-11
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MW-16
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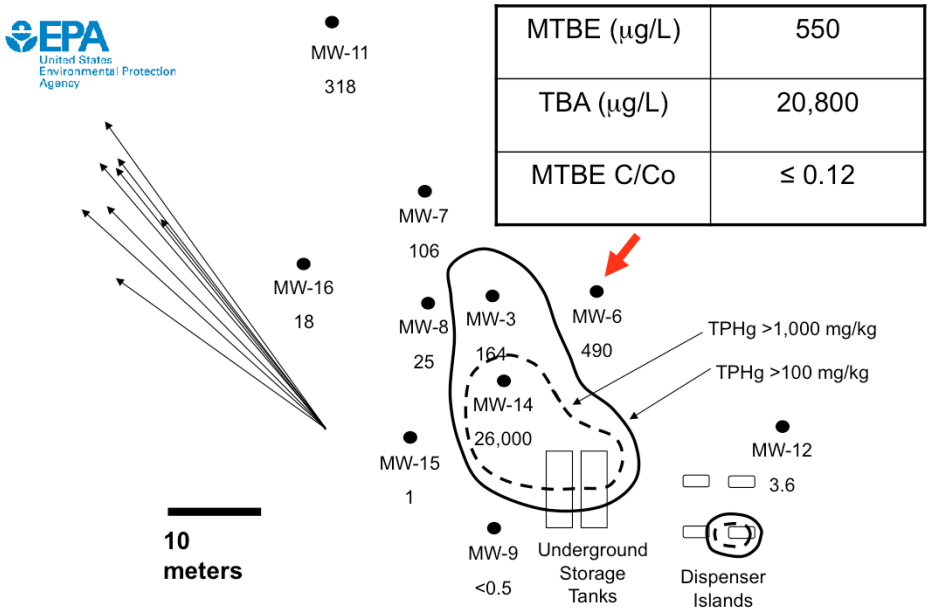
MW-7
106
MW-8
25
MW-3
164
MW-6
490
MW-14
26,000
MW-15
1
MW-9
<0.5
MW-12
3.6
TPHg >1,000 mg/kg
TPHg >100 mg/kg
10
meters
Underground
Storage
Tanks
Dispenser
Islands
MTBE (µg/L) 139
TBA (µg/L) 30,000
MTBE C/Co ≤ 0.050

38


EPA
United States
Environmental Protection
Agency
MW-11
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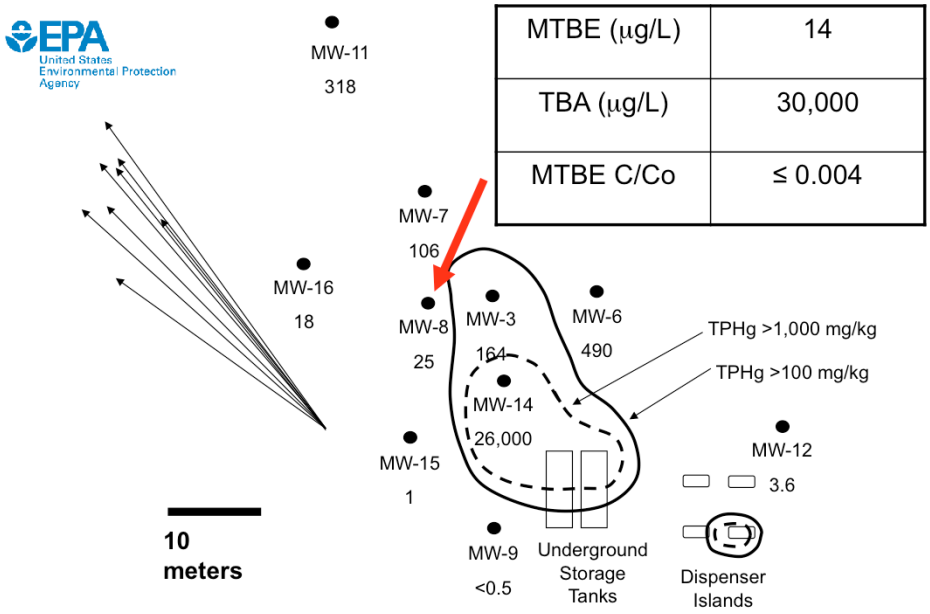
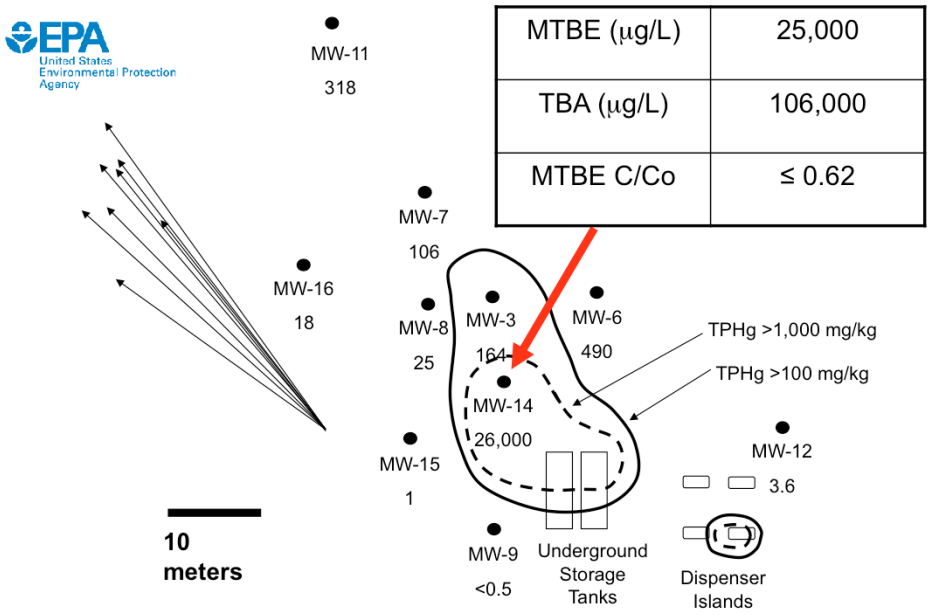
MW-7
106
MW-16
18
MW-8
25
MW-3
164
MW-6
490
MW-14
26,000
MW-15
1
MW-12
3.6
MW-9
<0.5
Underground
Storage
Tanks
Dispenser
Islands
10
meters
TPHg >1,000 mg/kg
TPHg >100 mg/kg
MTBE (µg/L) 550
TBA (µg/L) 20,800
MTBE C/Co ≤ 0.12

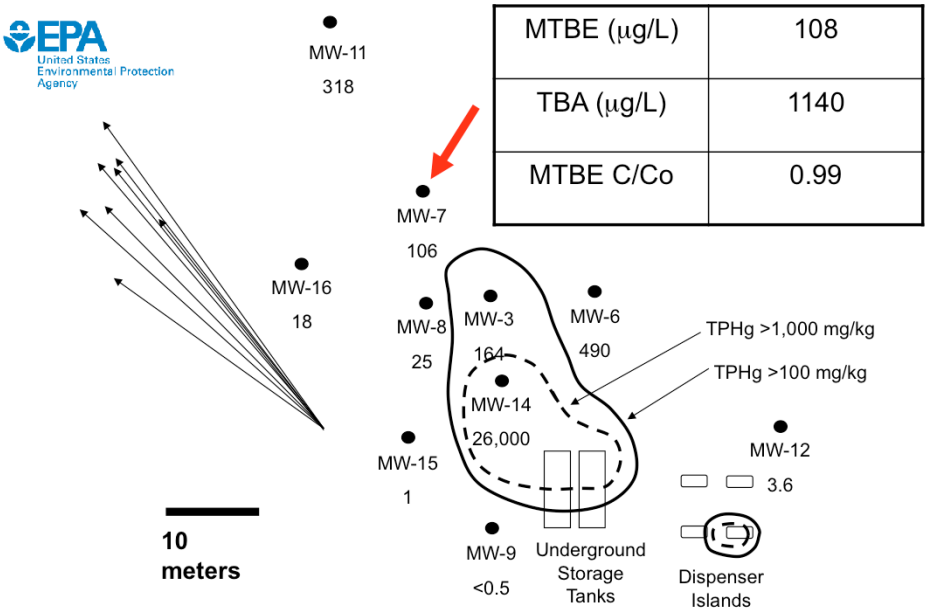
39


EPA
United States
Environmental Protection
Agency
MW-11
318
MW-16
18
MW-7
106
MW-8
25
MW-3
164
MW-6
490
MW-14
26,000
MW-15
1
MW-9
<0.5
MW-12
3.6
TPHg >1,000 mg/kg
TPHg >100 mg/kg
10
meters
Underground
Storage
Tanks
Dispenser
Islands
MTBE (µg/L) 14
TBA (µg/L) 30,000
MTBE C/Co ≤ 0.004

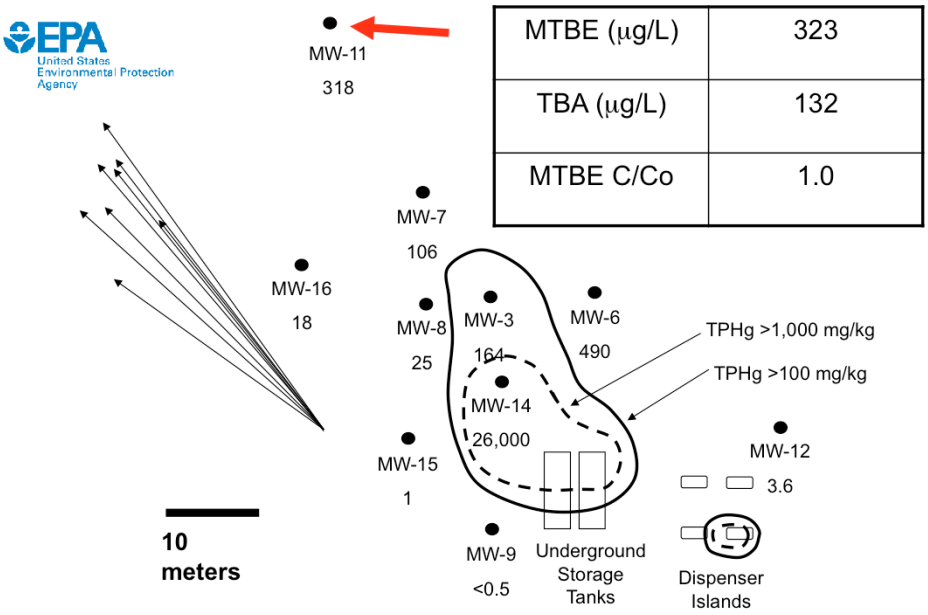
40


EPA
United States
Environmental Protection
Agency
MW-11
318
MW-7
106
MW-16
18
MW-8
25
MW-3
164
MW-6
490
MW-14
26,000
MW-15
1
MW-9
<0.5
MW-12
3.6
TPHg >1,000 mg/kg
TPHg >100 mg/kg
10
meters
Underground
Storage
Tanks
Dispenser
Islands
MTBE (µg/L) 25,000
TBA (µg/L) 106,000
MTBE C/Co ≤ 0.62

41


EPA
United States
Environmental Protection
Agency
MW-11
318
MW-7
106
MW-16
18
MW-8
25
MW-3
164
MW-6
490
MW-14
26,000
MW-15
1
MW-12
3.6
MW-9
<0.5
Underground
Storage
Tanks
Dispenser
Islands
TPHg >1,000 mg/kg
TPHg >100 mg/kg
10
meters
MTBE (µg/L) 108
TBA (µg/L) 1140
MTBE C/Co 0.99

42


EPA
United States
Environmental Protection
Agency
MW-11
318
MTBE (µg/L) 323
TBA (µg/L) 132
MTBE C/Co 1.0
MW-7
106
MW-16
18
MW-8
25
MW-3
164
MW-6
490
TPHg >1,000 mg/kg
TPHg >100 mg/kg
MW-14
26,000
MW-15
1
MW-12
3.6
10
meters
MW-9
<0.5
Underground
Storage
Tanks
Dispenser
Islands

43

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!

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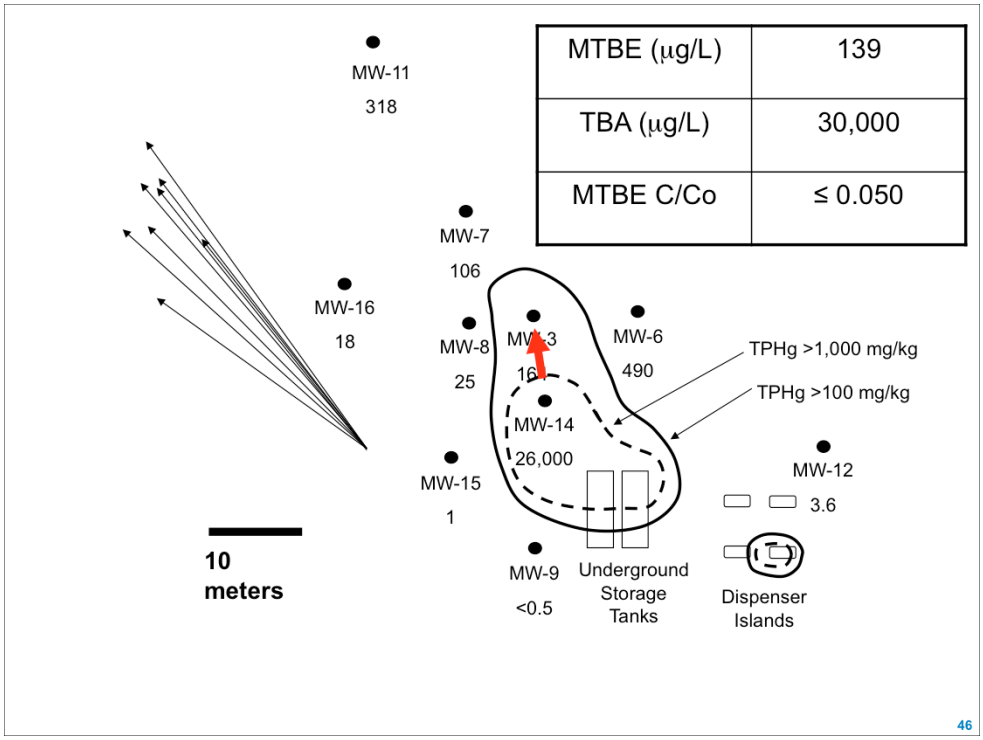
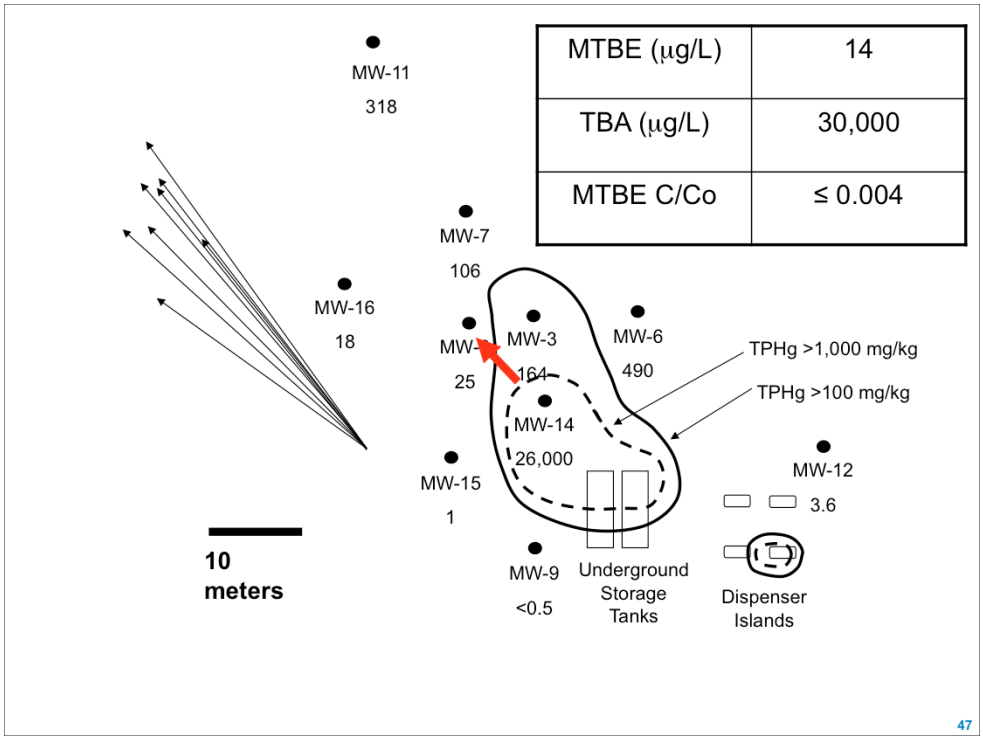
An approach to deal with heterogeneity in biodegradation

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.


MW-11
318
MW-7
106
MW-16
18
MW-8
25
MW-3
16
MW-6
490
MW-14
26,000
MW-15
1
MW-9
<0.5
MW-12
3.6
TPHg >1,000 mg/kg
TPHg >100 mg/kg
10
meters
Underground
Storage
Tanks
Dispenser
Islands
MTBE (µg/L) 139
TBA (µg/L) 30,000
MTBE C/Co ≤ 0.050
46


MW-11
318
MW-7
106
MW-16
18
MW-3
164
MW-6
490
MW-
25
MW-14
26,000
MW-15
1
MW-12
3.6
MW-9
<0.5
Underground
Storage
Tanks
Dispenser
Islands
TPHg >1,000 mg/kg
TPHg >100 mg/kg
10
meters
MTBE (µg/L) 14
TBA (µg/L) 30,000
MTBE C/Co ≤ 0.004
47

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

Well	Date	TBA measured (µg/L)	MTBE measured (µg/L)	$\delta^{13}C$ 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

48

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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.

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

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

F is the fraction of MTBE remaining

d is the distance between the wells

v is the ground water seepage velocity

50

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

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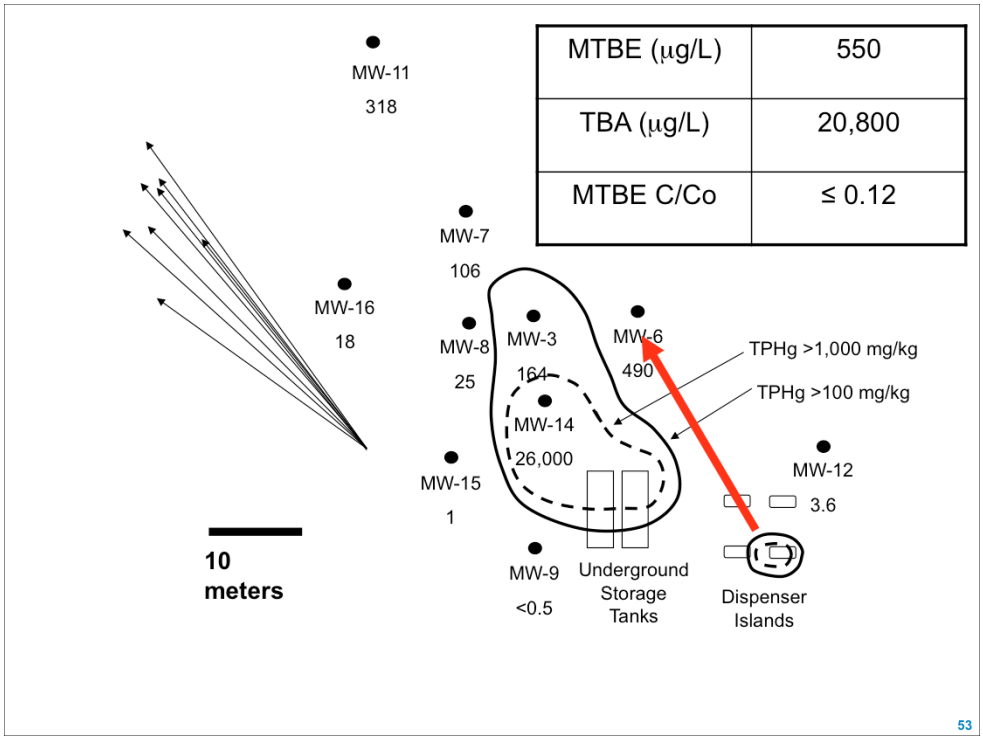
Well	Date	Fraction MTBE Remaining (C/C_o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Time (per year)
MW-3	5/20/03	0.058	9.6	10.9
MW-3	8/18/04	0.050	9.6	11.5
MW-8	5/20/03	0.023	11.7	11.9
MW-8	8/18/04	0.0043	11.7	17.1


MW-11
318
MW-7
106
MW-16
18
MW-8
25
MW-3
164
MW-6
490
MW-14
26,000
MW-15
1
MW-12
3.6
MW-9
<0.5
Underground
Storage
Tanks
Dispenser
Islands
TPHg >1,000 mg/kg
TPHg >100 mg/kg
10
meters
MTBE (µg/L) 550
TBA (µg/L) 20,800
MTBE C/Co ≤ 0.12
53

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Well	Date	TBA measured (µg/L)	MTBE measured (µg/L)	$\delta^{13}C$ 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

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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

55

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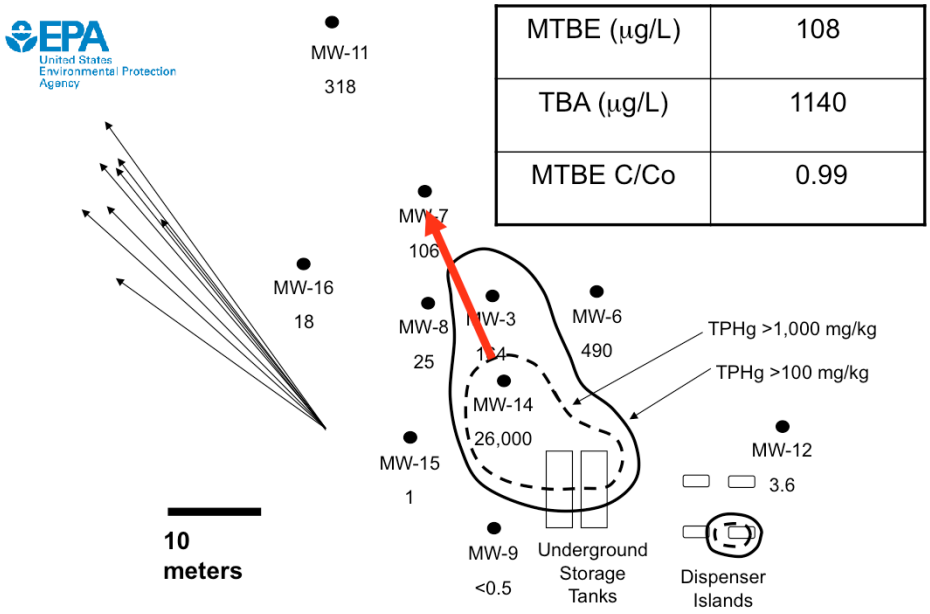
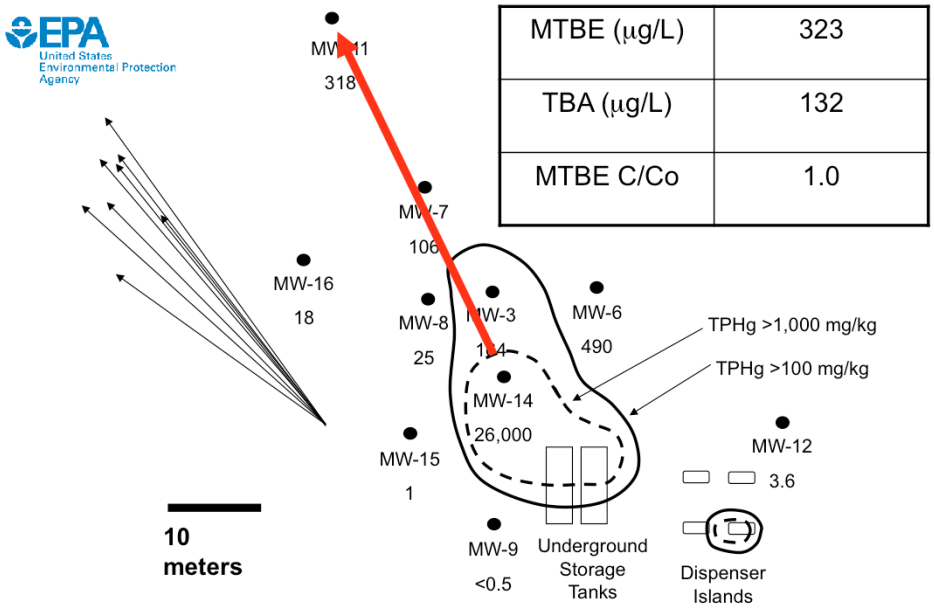
Well	Date	Fraction MTBE Remaining (C/C_o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Time (per year)
MW-6	5/20/03	0.045	31.1	3.7
MW-6	8/18/04	0.116	31.1	2.6



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

57


EPA
United States
Environmental Protection
Agency
MW-11
318
MW-7
106
MW-16
18
MW-8
25
MW-3
1.4
MW-6
490
MW-14
26,000
MW-15
1
MW-9
<0.5
MW-12
3.6
TPHg >1,000 mg/kg
TPHg >100 mg/kg
10
meters
Underground
Storage
Tanks
Dispenser
Islands
MTBE (µg/L) 323
TBA (µg/L) 132
MTBE C/Co 1.0
58

EPA United States Environmental Protection Agency

Well	Date	TBA measured (µg/L)	MTBE measured (µg/L)	$\delta^{13}C$ 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-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 ‰.

EPA United States Environmental Protection Agency

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

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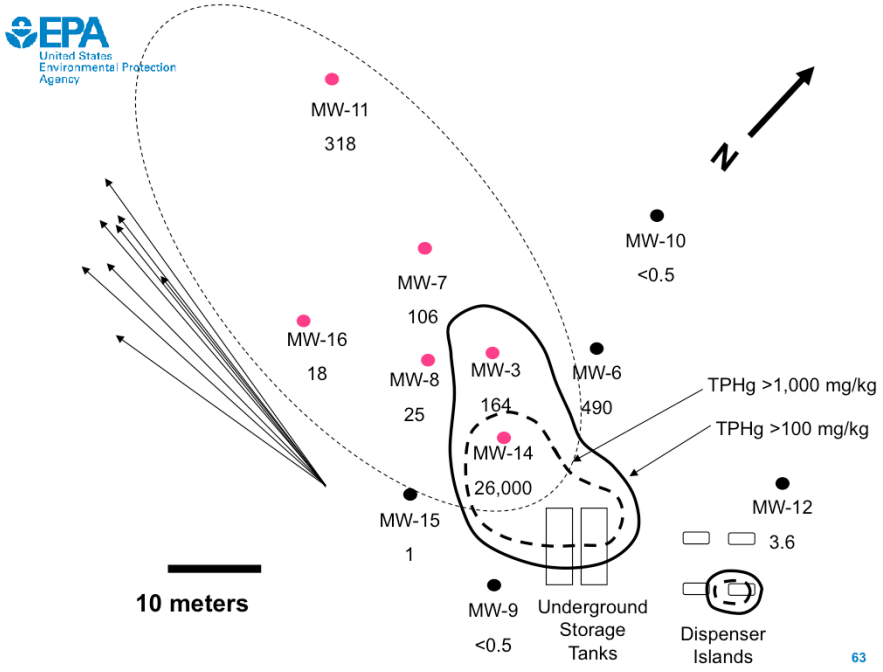
Well	Date	Fraction MTBE Remaining (C/C_o)	Distance from MW-14 (meters)	Projected Rate Biodegradation with Time (per year)
MW-7	8/18/04	0.994	23.0	0.0093
MW11	5/20/03	1.0	44.1	0
MW11	8/18/04	1.0	44.1	0

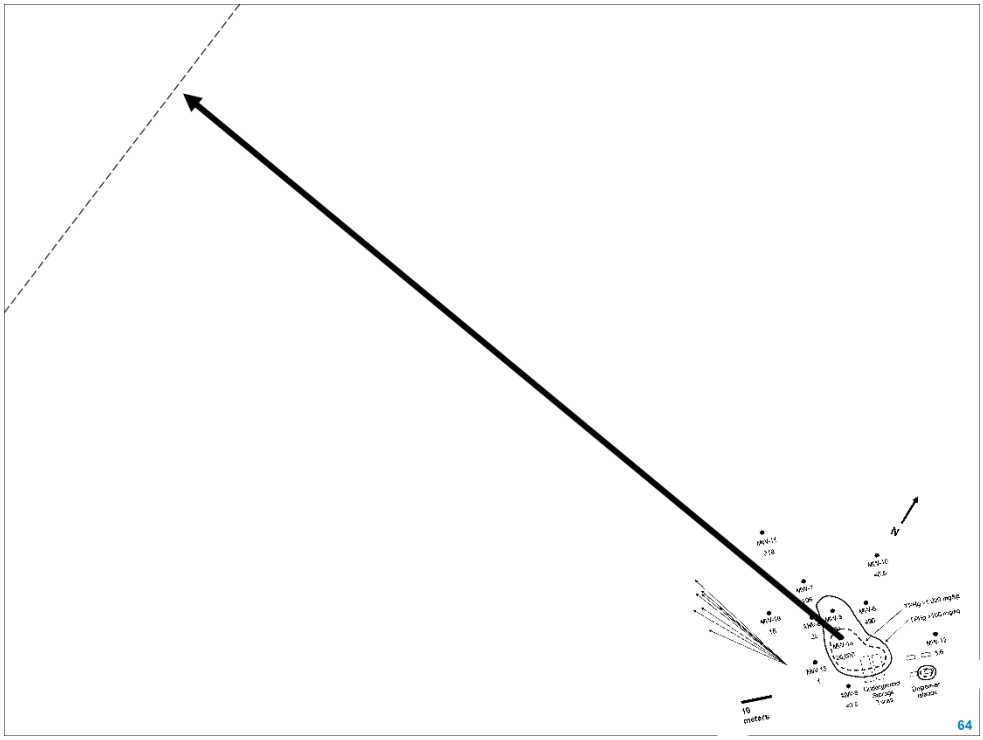
EPA United States Environmental Protection Agency

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.


EPA
United States
Environmental Protection
Agency
MW-11
318
N
MW-10
<0.5
MW-7
106
MW-16
18
MW-8
25
MW-3
164
MW-6
490
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


N
MW-11
MW-10
MW-7
MW-6
MW-9
MW-8
MW-12
MW-13
SMW-5
Underground Storage Tanks
Dispenser Island
10 meters
64

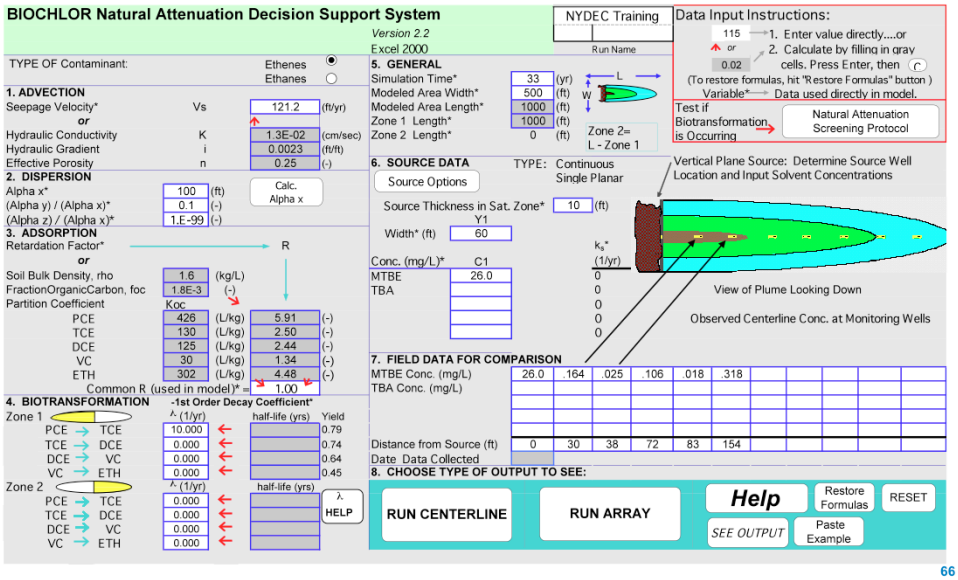
BIOCHLOR 2.2 will be used to evaluate the potential exposure to the receptor.

Available at

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

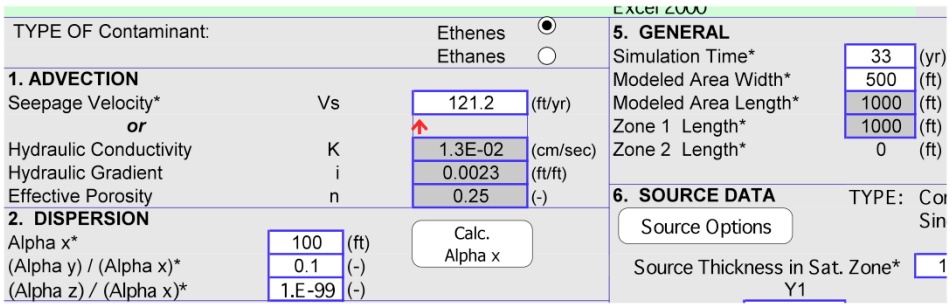
With Source at 26 mg/L and Biodegradation = 10 per year

Assume a Receptor at 1000 feet from LNAPL

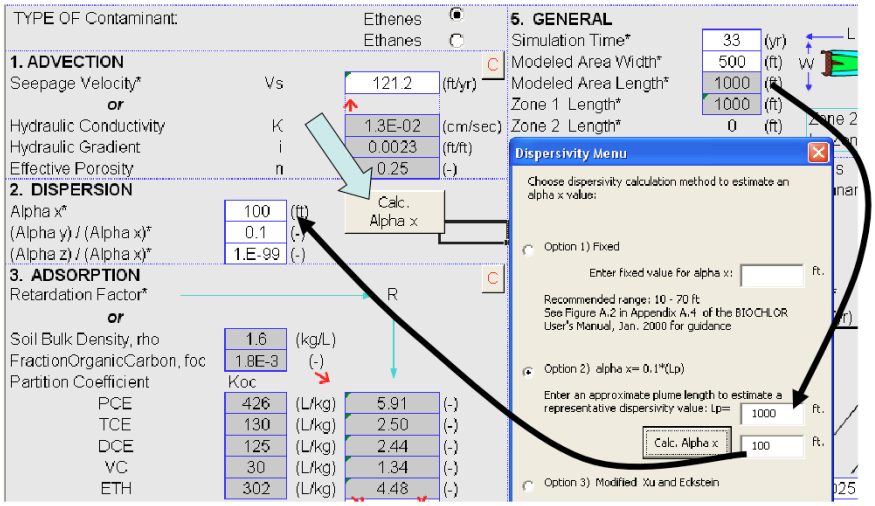


66

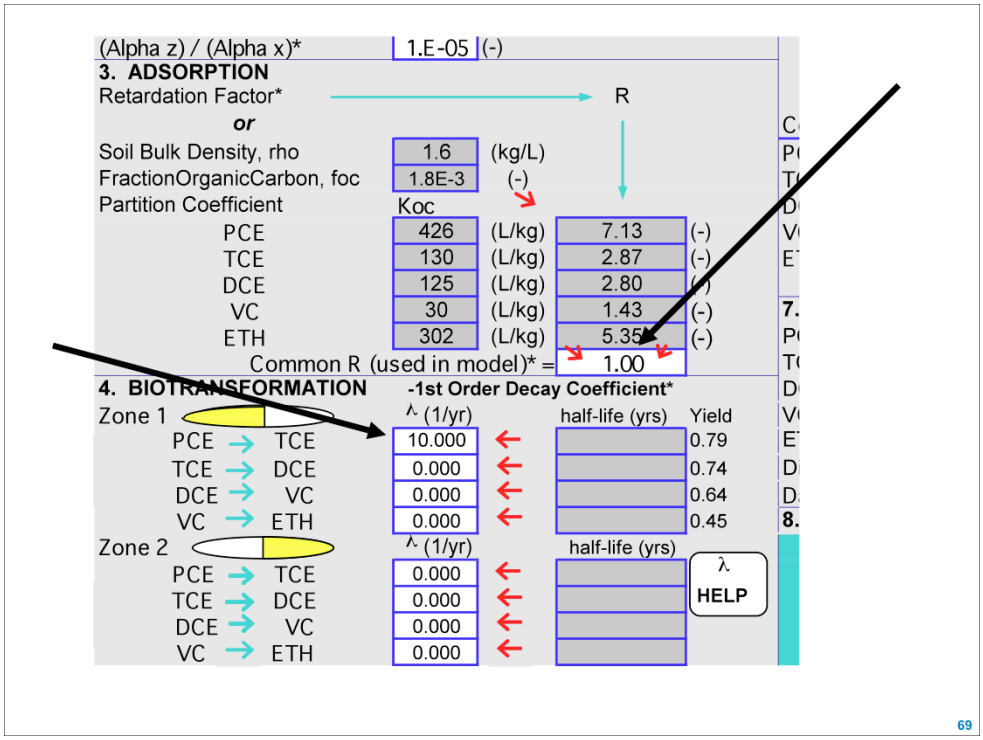
With Source at 26 mg/L and Biodegradation = 10 per year

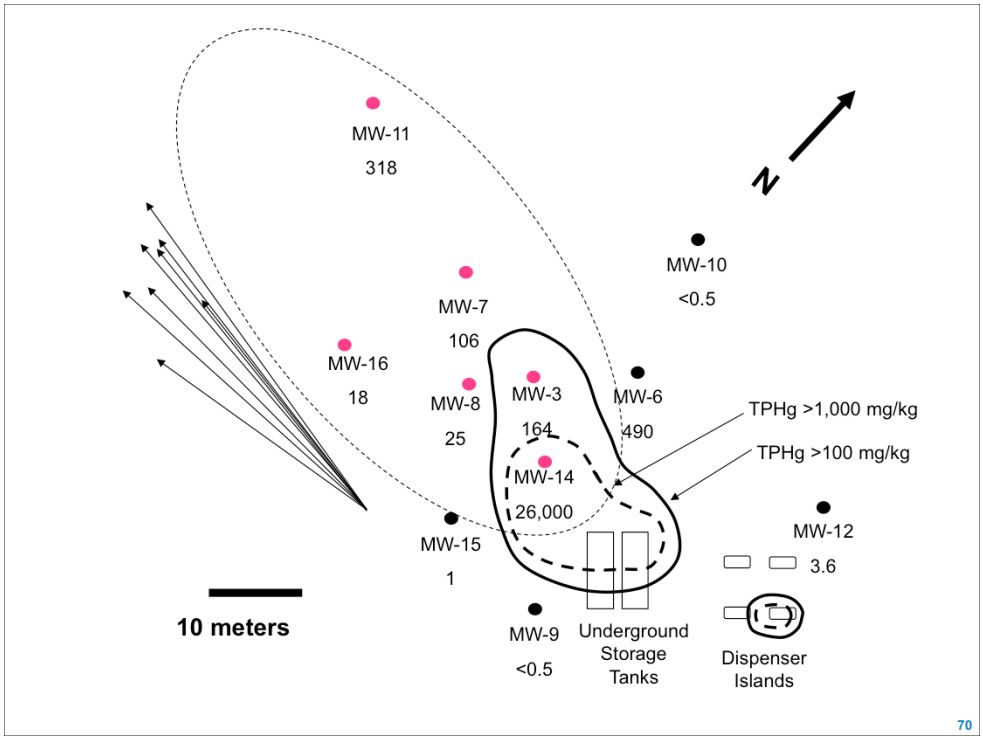


67


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
(-)
Calc. Alpha x
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
(-)
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
L
W
Zone 2

68


(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
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
λ
HELP
69


MW-11
318
N
MW-10
<0.5
MW-7
106
MW-16
18
MW-8
25
MW-3
164
MW-6
490
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
70

6. SOURCE DATA TYPE: Continuous Single Planar

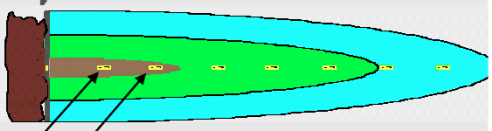
Source Options

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

Source Thickness in Sat. Zone* 10 (ft)

Y1

Width* (ft) 60



View of Plume Looking Down

Observed Centerline Conc. at Monitoring Wells

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

7. FIELD DATA FOR COMPARISON

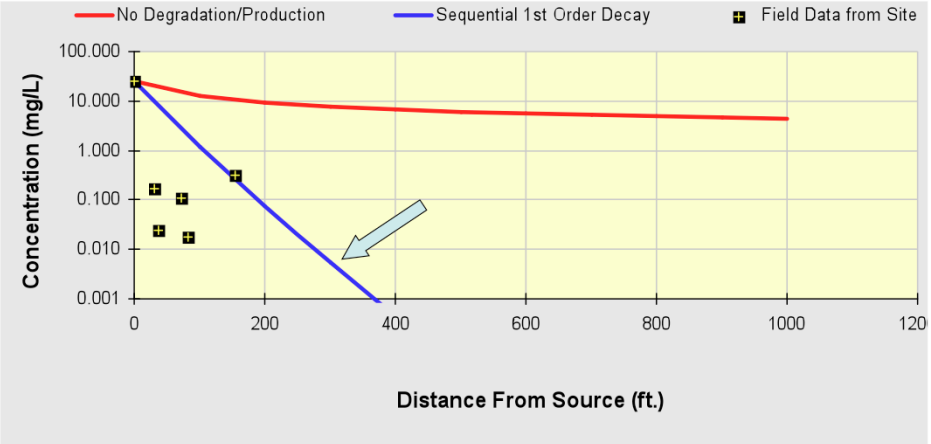
PCE Conc. (mg/L)	26.0	.164	.025	.106	.018	.318					
TCE Conc. (mg/L)											
DCE Conc. (mg/L)											
VC Conc. (mg/L)											
ETH Conc. (mg/L)											
Distance from Source (ft)	0	30	38	72	83	154					
Date Data Collected											

8. CHOOSE TYPE OF OUTPUT TO SEE:

RUN CENTERLINE | RUN ARRAY | Help | Restore Formulas | RESET | SEE OUTPUT | Paste Example

71

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

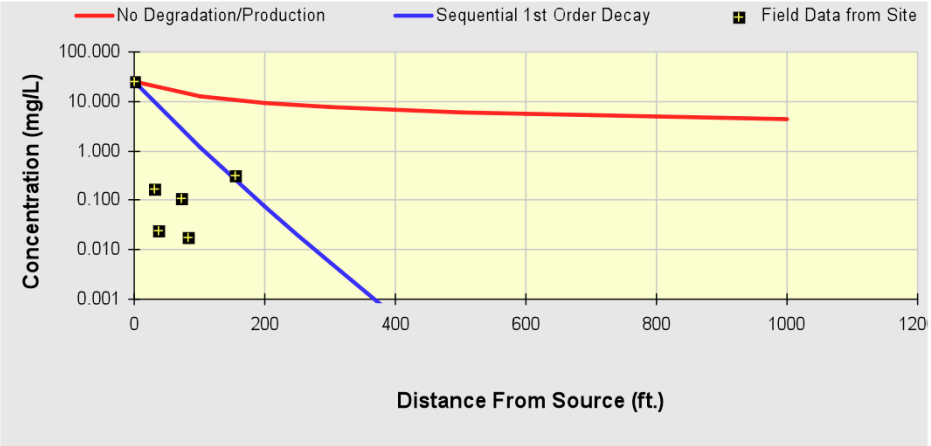


Clean in approximately 300 feet of travel

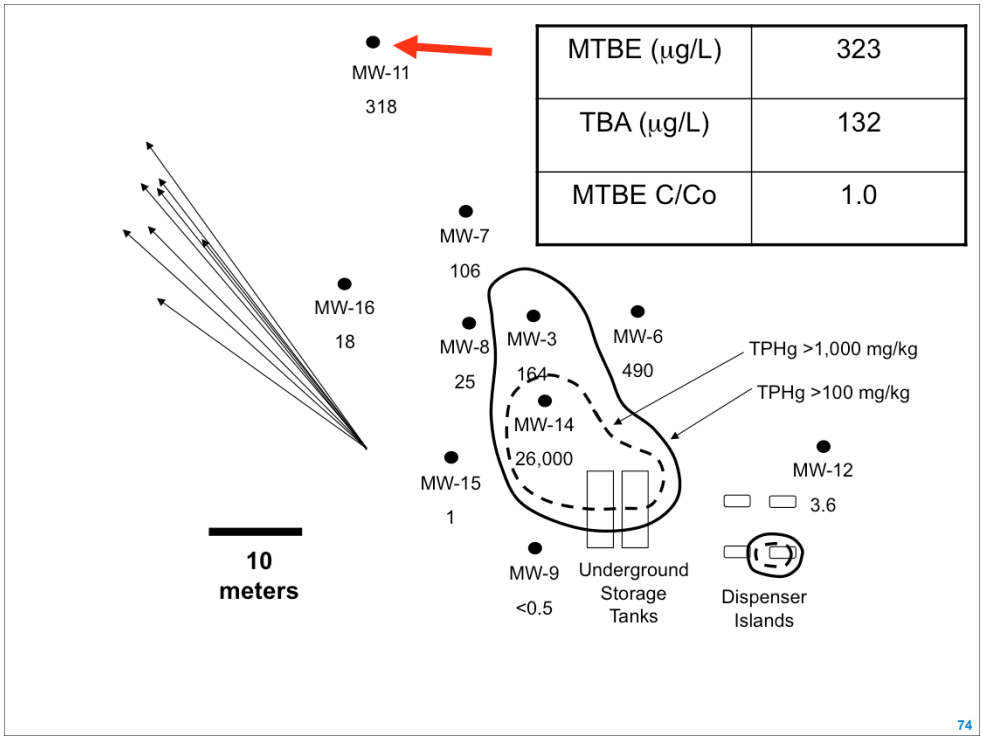
72

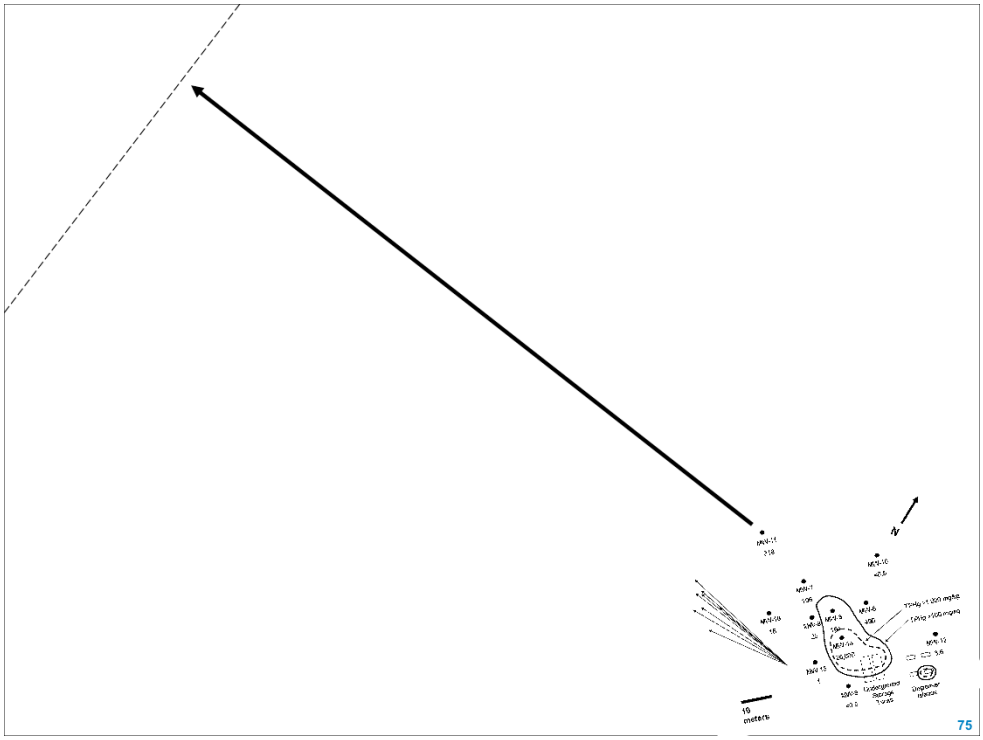
With Source at 26 mg/L and no Biodegradation

Not even close to clean in 1000 feet of travel



73


MW-11
318
MTBE (µg/L) 323
TBA (µg/L) 132
MTBE C/Co 1.0
MW-7
106
MW-16
18
MW-8
25
MW-3
164
MW-6
490
TPHg >1,000 mg/kg
TPHg >100 mg/kg
MW-14
26,000
MW-15
1
MW-12
3.6
10
meters
MW-9
<0.5
Underground
Storage
Tanks
Dispenser
Islands
74


N
MW-11
MW-10
MW-7
MW-9
MW-6
MW-8
MW-14
MW-13
MW-12
SMW-5
Underground Storage Tanks
Dispenser Island
10 meters
75

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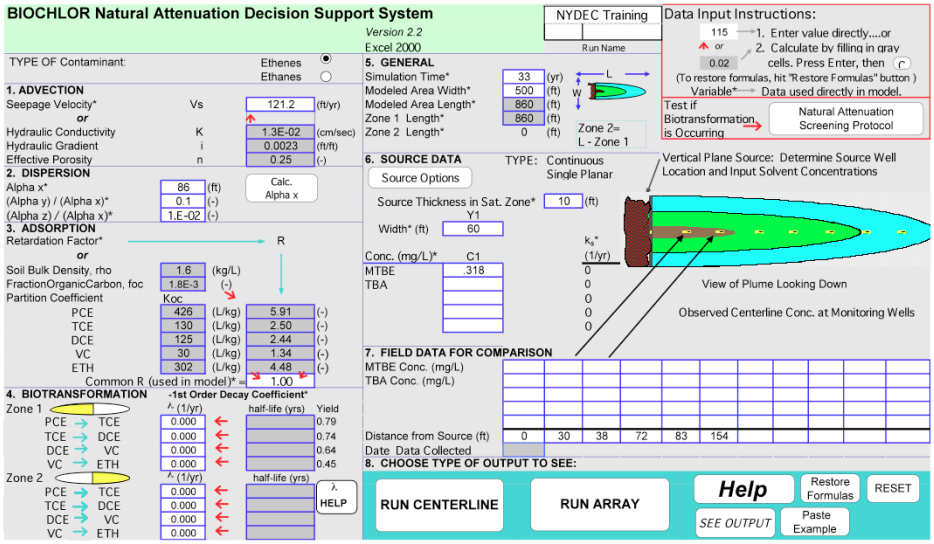
1) Determine if biodegradation (when it occurs) is stable over time.
2) Determine the extent of the core of the plume if controlled by biodegradation.
3) **Determine the extent of the periphery of the plume there is no biodegradation.**

With Source at MW-11 at 0.318 mg/L

Biodegradation = 0.0004 per year

Potential Receptor at 860 feet from MW-11

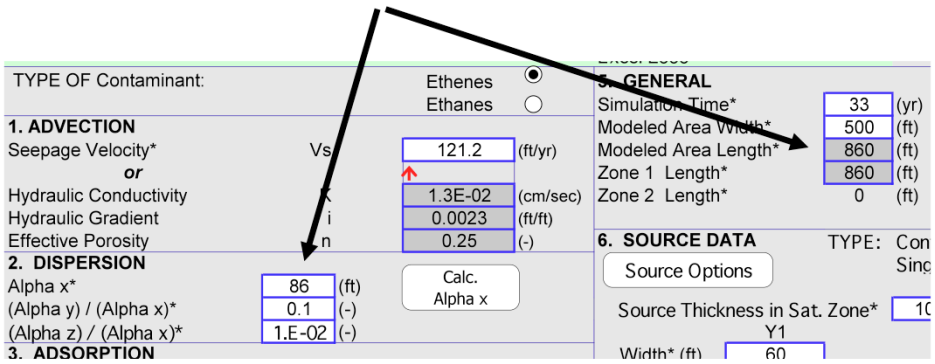


77

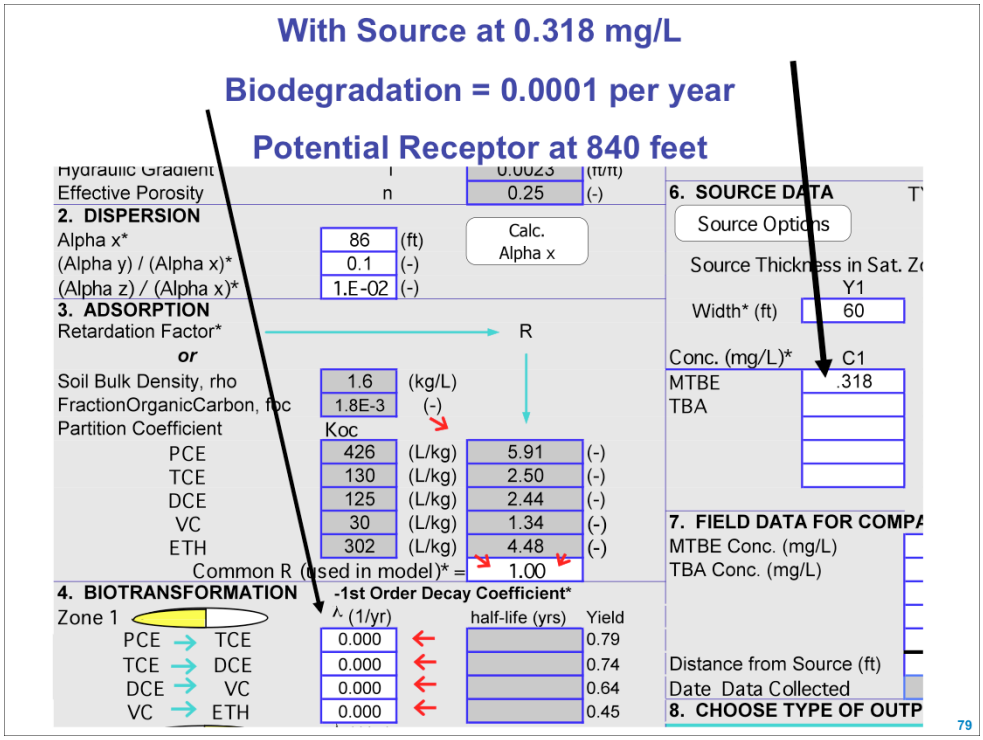
With Source at 0.318 mg/L

Biodegradation = 0.0004 per year

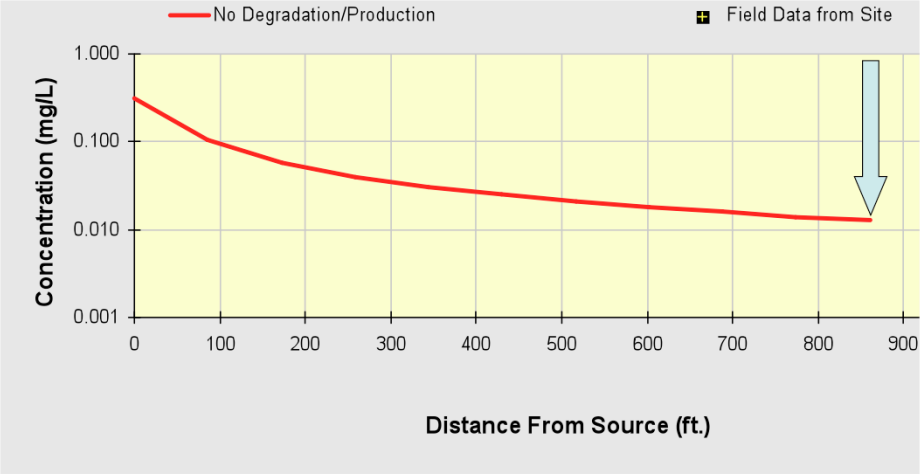
Potential Receptor at 860 feet



78


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)
(Alpha y) / (Alpha x)* 0.1 (-)
(Alpha z) / (Alpha x)* 1.E-02 (-)
Calc. Alpha x
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
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
79

With Source at 0.318 mg/L and No Biodegradation



80

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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.

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.

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

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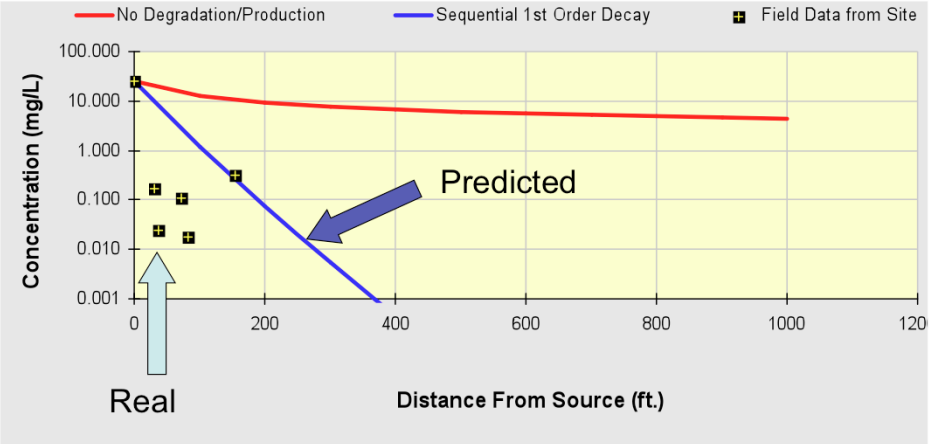
Note that the real attenuation in concentrations were substantially greater than would be expected from the prediction of C/Co based on the analysis of stable carbon isotopes.

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

85

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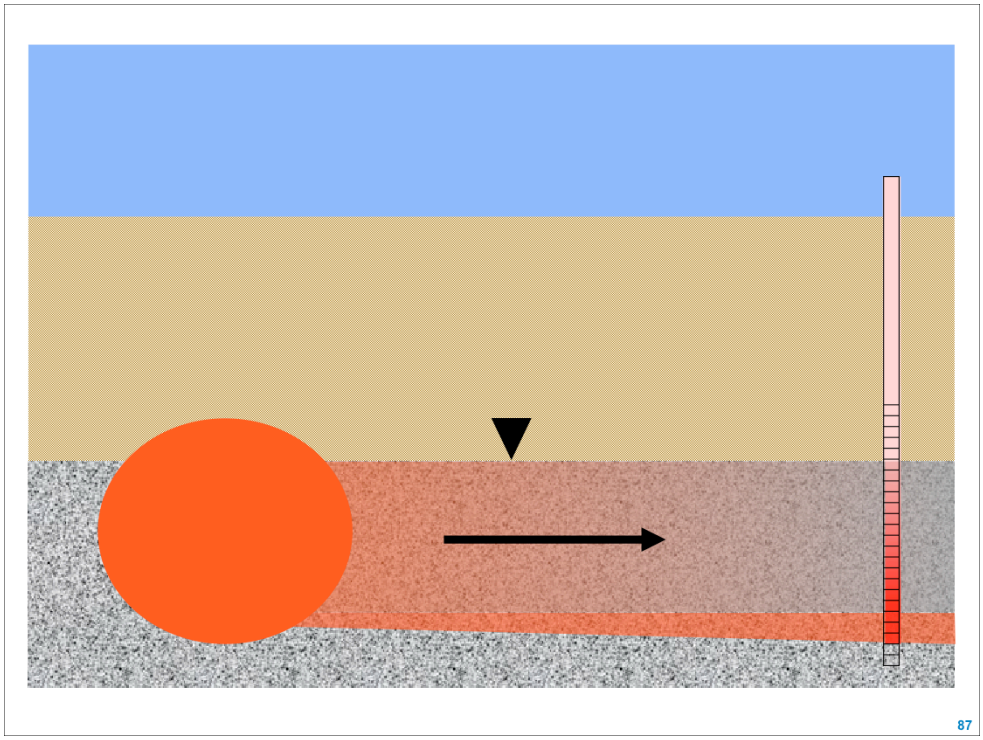
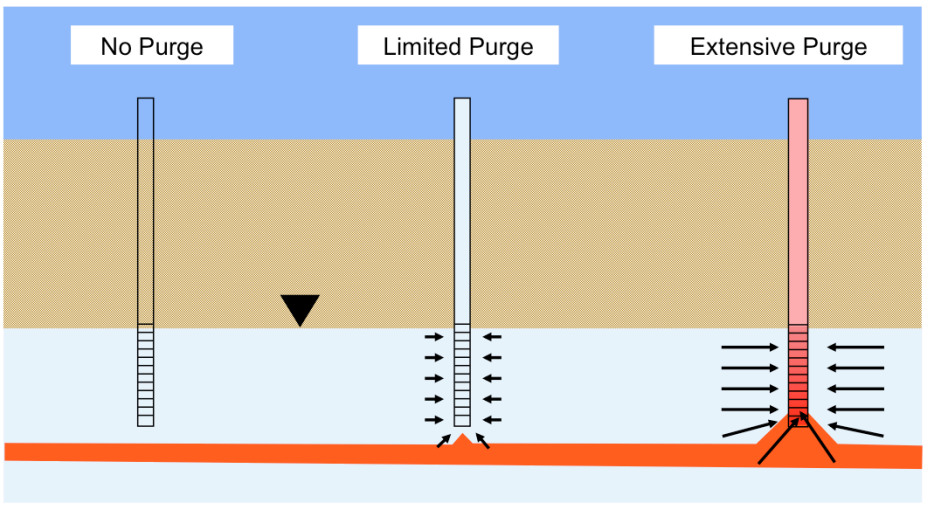
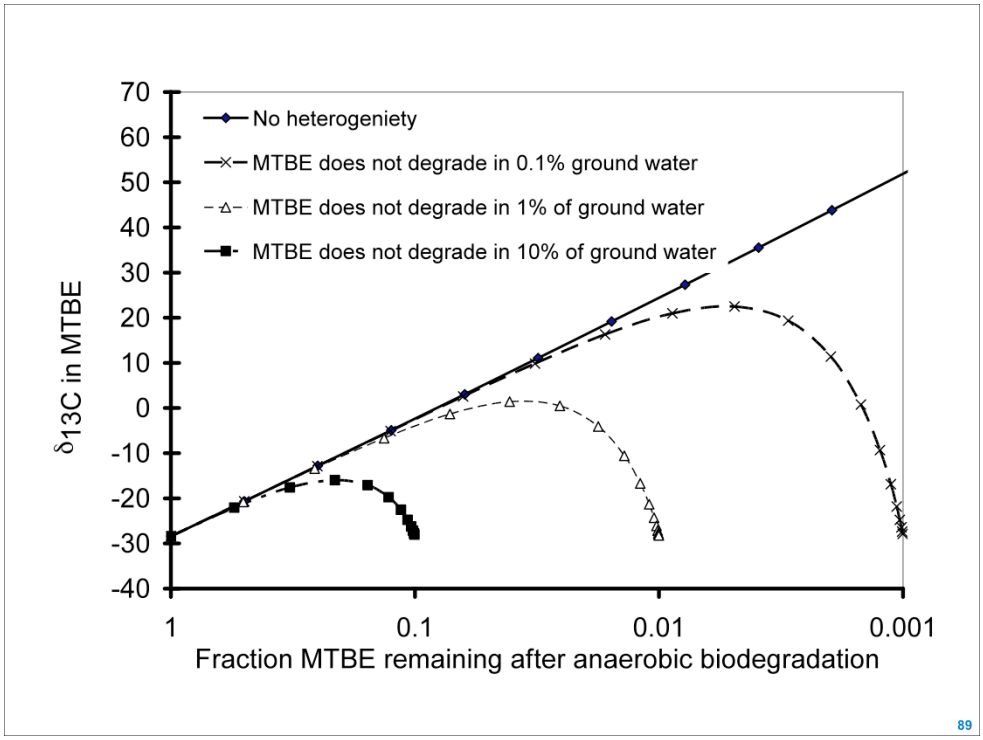
1) Heterogeneity produces blended samples.
2) The extent of fractionation well be less than expected from the true extent of biodegradation.
3) Heterogeneity causes CSIR to underestimate biodegradation.


87



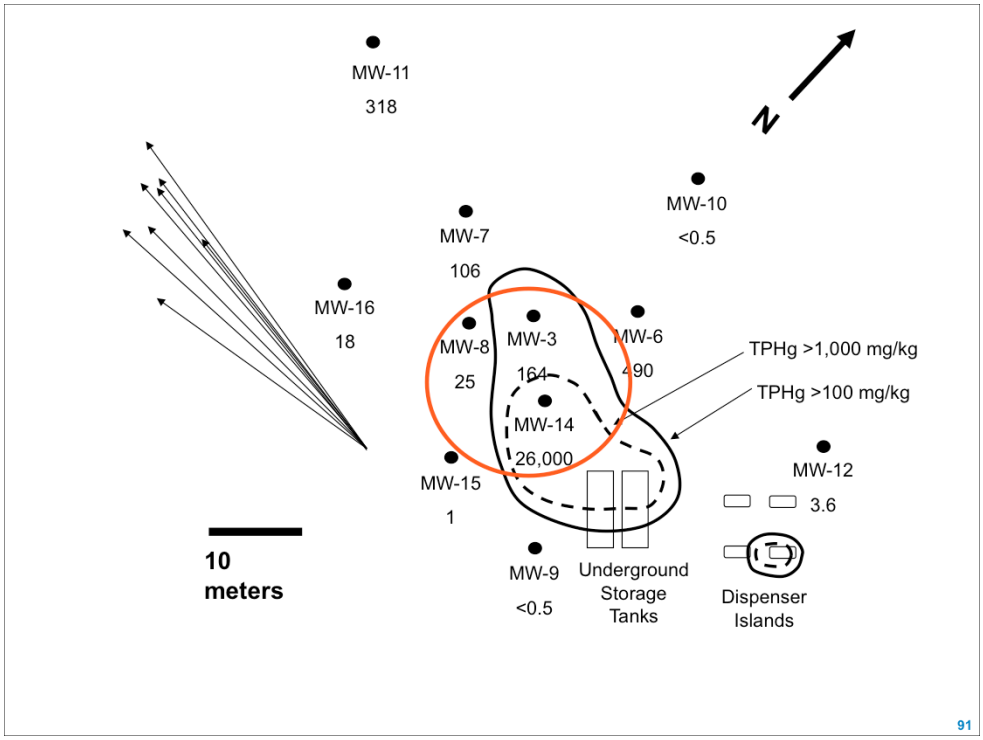
88


70
60
50
40
30
20
10
0
-10
-20
-30
-40
δ13C in MTBE
No heterogeniety
MTBE does not degrade in 0.1% ground water
MTBE does not degrade in 1% of ground water
MTBE does not degrade in 10% of ground water
1
0.1
0.01
0.001
Fraction MTBE remaining after anaerobic biodegradation
89

Proximity to NAPL or other source of new contamination to ground water allows fresh (unfractionated) material to dissolve into water to replace the material that was removed by degradation.

This dilutes the fractionated material, and reduces the overall value of $\delta^{13}C$.

CSIR will underestimate the true extent of degradation.


MW-11
318
N
MW-10
<0.5
MW-7
106
MW-16
18
MW-8
25
MW-3
164
MW-6
490
TPHg >1,000 mg/kg
TPHg >100 mg/kg
MW-14
26,000
MW-15
1
MW-12
3.6
10
meters
MW-9
<0.5
Underground
Storage
Tanks
Dispenser
Islands
91

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Assume all the TBA formed from degradation of MTBE, and that none of the TBA was further degraded.

Effect of Proximity to NAPL on Prediction of Fraction Remaining from $\delta^{13}C$

Well	Date	TBA (µg/L)	MTBE (µg/L)	MTBE C/Co	$\delta^{13}C$ of MTBE (‰)	Predicted MTBE C/C0
MW-14	5/20/03	13,000	11,000	0.42	-23.88	0.75
	8/18/04	107,000	26,000	0.17	-21.58	0.62
MW-3	5/20/03	20,000	870	0.035	6.84	0.058
	8/18/04	32,000	164	0.0043	8.53	0.050
MW-8	5/20/03	10,000	19	0.0016	18.11	0.023
	8/18/04	32,000	25	0.00065	37.99	0.0043

93

Variations in expression of carbon isotope fractionation of chlorinated ethenes during biologically enhanced PCE dissolution close to a source zone

P.L. Morrill, B.E. Sleep, D.J. Seepersad, M.L. McMaster, E.D. Hood, C. LeBron, D.W. Major, E.A. Edwards and B. Sherwood Lollar

Journal of Contaminant Hydrology, Volume 110, Issues 1-2, 3 November 2009, Pages 60-71

Despite extensive degradation of PCE that could be recognized by the accumulation of products, isotopic fractionation of PCE was not detectable above the uncertainty in the measurement in ground water in contact with NAPL PCE.

These two interactions have important consequences for design of a sampling strategy for CSIA.

Samples should be evenly balanced between high concentrations, intermediate concentrations, and low concentrations. Putting an heavy emphasis on wells with low concentrations of organic contaminants may seriously underestimate the true contribution of degradation processes at a site.

These two interactions have important consequences for design of a sampling strategy for CSIA.

The absence of fractionation in particular wells, particularly in wells with low concentrations of contaminant, should not be taken as evidence for there is no degradation in the plume.

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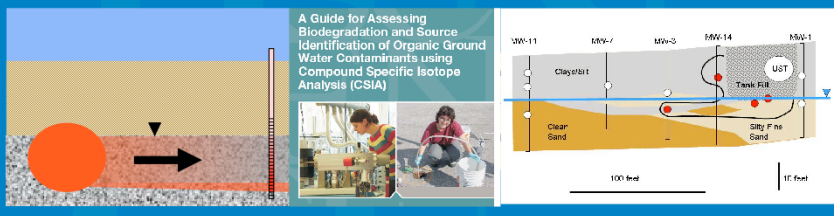
Applications of Stable Isotope Analyses to Understand the Degradation of Organic Contaminants in Ground Water

Part 2. Data Quality Issues

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



Documenting Quality for CSIR analyses

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

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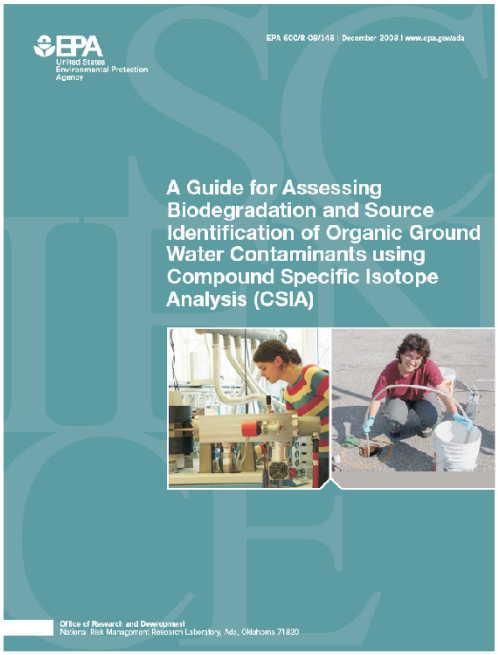
A *Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA)*

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



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Recommendations for sample collection, sample preservation, and sample analysis.

Recommendations on QA/QC issues

Details on calculations.

Catalogue of values for $\delta^{13}C$, $\delta^{2}H$, and ε.

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Sensitive QA/QC issues

1) Use of Standards to document accuracy and precision.
2) Recommendation for baseline separation of compounds during gas chromatography.

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The following comments apply to analysis of stable isotopes of carbon.

They can be typically extrapolated as needed to analysis of stable isotopes of hydrogen and chlorine.

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Standards for carbon isotope analyses

The isotope ratio mass spectrometer measures the isotope ratios of carbon dioxide produced from the combustion of the compound of interest. There are three standards:

The International Atomic Energy Agency standard (primary standard)

The laboratory's CO_2 working standard (secondary standard)

The laboratory's compound specific working standard for a particular VOA.

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The International Atomic Energy Agency Standard

Samples provided by the IAEA that have a known ratio of carbon stable isotopes. In the United States the standard is provided by the National Bureau of Standards.

The IAEA Standard allows comparability of data from one lab to the other. Used for primary calibration of instruments.

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The laboratory's CO_2 working standard

Calibrated against the IAEA international standard.

Used for tuning the instrument and day to day calibration checks of the instrument.

Provides the value against which all target peaks in a given run are standardized.

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The laboratory's compound specific working standard

A sample of the compound being analyzed that has a known value for $\delta^{13}C$.

The standard is analyzed periodically in a sample set to document that the instrument is properly calibrated.

The compound specific working standard is also used to document the effective detection limit as discussed later.

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At a minimum, the CO_2 working standard is analyzed twice at the beginning of each sample run. The automatic software routine uses one of these CO_2 peaks as the reference to calculate isotope ratios for the other peaks, including those of the second (or multiple) CO_2 peaks.

At least every fifth sample should be a sample replicate. At least every tenth sample should be the compound specific working standard.

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Require the vendor to provide the true value of $\delta^{13}C$ for each compound working standard.

Ask the vendor to report the values determined for their compound specific working standard during analysis of the samples.

The scope of work or the QAPP should specify an acceptable range of determined values from the true value for the compound working standard.

The determined values of the compound specific working standard should fall within the acceptable range from the true value.

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How to determine the acceptable range of values to specify in the scope of work or the QAPP?

Ask the vendors to provide the acceptable range of values in their bid or quote.

Review and determine if the range in acceptable values meets the requirements of your project based on the comparisons you are going to make.

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How much degradation can you detect at the proposed resolution?

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

Select a conservative value for the enrichment factor from the literature (a value with a low absolute value), and solve the equation for the fraction remaining (*F*), based on the difference in $\delta^{13}C$ that you can resolve based on the acceptable range of the compound specific working standard proposed by the vendor.

As a rule of thumb, you can resolve samples with good confidence when they differ by twice the acceptable range.

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Values of ε are tabulated in Table 8.1 of the U.S. EPA Guide. Suppose you were interested anaerobic biodegradation of TCE.

The value of ε with the lowest absolute value is -2.56‰.

If the quoted acceptable range was 0.5‰, you can distinguish samples that differ by 1.0‰.

$$F = e^{(1/(-2.5))} = 0.67$$

The extent of degradation that can be detected is-

$$1 - F = 1 - 0.67 = 0.33 \text{ or } 33\%$$

113

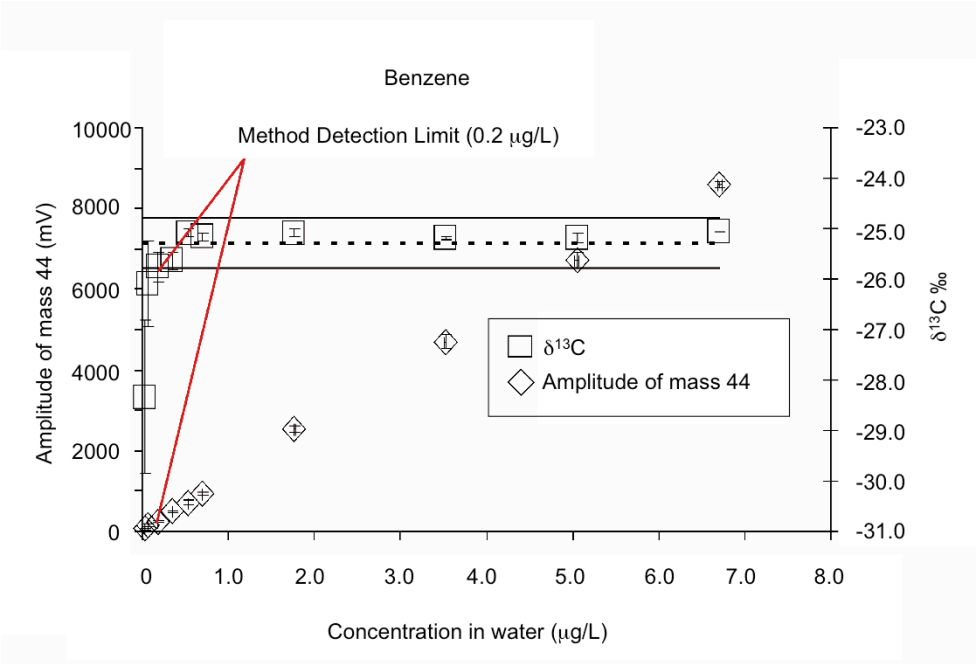
How to establish the effective detection limit for determination of $\delta^{13}C$ for a particular compound?

Customers tend to think of the detection limit as a concentration of the chemical being analyzed.

The concentration is related to the amplitude of the mass 44 peak, expressed as a voltage, or the area of the peak, expressed as volt-seconds.

The next slide is Figure 2.5 in A *Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA).* The following is the figure legend.

Example of the evaluation of method detection limits (MDLs) in CSIA. The squares represent the $\delta^{13}C$ values in ‰ and the diamonds show the amplitude of mass 44 in mV. Error bars indicate the standard deviation of triplicate measurements. The horizontal broken line represents the iteratively calculated mean value after the methods of Jochmann et al. (2006) and Sherwood Lollar et al. (2007). The solid lines around the mean value represent the standard deviation on the mean of triplicate measurements. Figure modified after Jochmann et al. (2006).


Benzene
Method Detection Limit (0.2 μg/L)
Amplitude of mass 44 (mV)
10000
8000
6000
4000
2000
0
-23.0
-24.0
-25.0
-26.0
-27.0
-28.0
-29.0
-30.0
-31.0
δ13C ‰
δ13C
Amplitude of mass 44
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Concentration in water (μg/L)

116

Citations:

Jochmann, et al. A new approach to determine method detection limits for compound specific isotope analysis of volatile organic carbons. *Rapid Communications in Mass Spectrometry* 20: 3639-3648 (2006).

Sherwood Lollar,et al. An approach for assessing total instrumental uncertainty in compound-specific carbon isotope analysis: implications for environmental remediation studies. *Analytical Chemistry* 79: 3469-3475 (2007).

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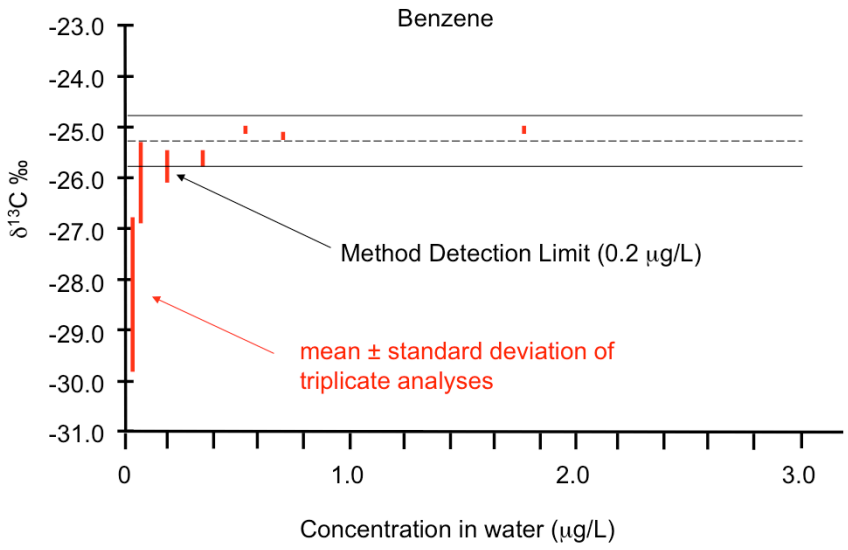
Jochmann et al. 2006 suggested an appropriate method detection limit (MDL) could be defined as *the signal size below which the standard deviation of the mean exceeds 0.5‰ and the $\delta^{13}C$ values are outside the 0.5‰ interval around the running* mean.

Sherwood Lollar et al. 2007 suggest that a more conservative approach might be to *define the method detection limit as the point at which the variance around the mean significantly increases (typically at signal size < 0.5 V).*


Benzene
-23.0
-24.0
-25.0
-26.0
-27.0
-28.0
-29.0
-30.0
-31.0
δ13C ‰
Method Detection Limit (0.2 μg/L)
mean ± standard deviation of
triplicate analyses
0
1.0
2.0
3.0
Concentration in water (μg/L)

119

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One vendor specifies a practical quantitation limit that is round number that is slightly larger than the method detection limit (MDL). This PQL allows for minor variations in the sensitivity of the instrument.

If the area of the mass 44 peak is less than the MDL, the vendor does not report an isotope ratio and flags the analysis as “U”.

If the peak area is between the MDL and PQL, the vendor reports the peak area and the isotope ratio and flags the isotope ratio with a “J”.

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Provide guidance on QA in the scope of work or QA Project Plan.

Determine the difference in $\delta^{13}C$ or $\delta^{2}H$ that you need to resolve.

If you really don't know what difference you need to resolve, as a default, require that the standard deviation of the samples of triplicate samples of the compound working standard be equal to or less than +/-0.5‰ for $\delta^{13}C$ and equal to or less than +/-5‰ for $\delta^{2}H$.

At this level of uncertainty, you can resolve a difference between samples when the difference in $\delta^{13}C$ >1‰ or the difference in $\delta^{2}H$ >15‰.

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Detection limits should always be determined using the same chromatographic column and working conditions as the samples.

The compound working standards should be subjected to the entire analytical procedure including any extraction and concentration steps.

The compound working standards should be spiked into water, then extracted and prepared for gas chromatography following the same procedures as the samples.

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Based on the requirements of your project, identify the lowest concentration of the VOA that you are interested in analyzing for isotope ratios.

The method detection limit, or practical quantitation limit, should correspond to a concentration that is lower than this lowest concentration you have identified for the project.

Ask the vendor to provide the MDLs or PQLs in their bid. Compare their capability to your requirement.

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Require the vendor to report the values of replicate analyses (n=3) of the compound specific working standard at this lowest concentration.

As an estimate of precision in the determination of isotope ratio for the compound specific standard at this lowest concentration, calculate the mean and standard deviation on the samples.

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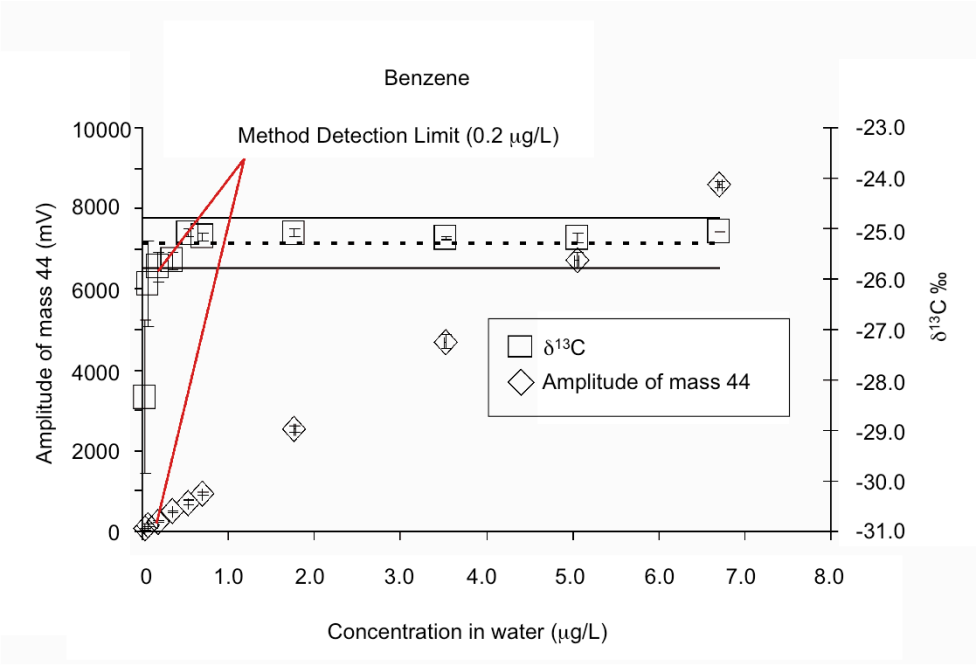
The mean should not differ from the true value by more than the acceptable range. The sample standard deviation should not be greater than the acceptable range.

As an alternative, one vendor prefers to calculate the sample standard deviation of the range of the samples as the best indication of system performance.


Benzene
Method Detection Limit (0.2 μg/L)
Amplitude of mass 44 (mV)
10000
8000
6000
4000
2000
0
-23.0
-24.0
-25.0
-26.0
-27.0
-28.0
-29.0
-30.0
-31.0
δ13C ‰
δ13C
Amplitude of mass 44
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Concentration in water (μg/L)

126

Notice that the amplitude of the mass 44 ion is roughly proportional to concentration of compound of interest.

There will be an amplitude of the mass 44 ions that is associated with the lowest concentration of compound that you are interested in.

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An Alternative:

After you see the data, you may be very interested in certain samples that had low concentrations of the VOA. Those samples may have experienced the most biodegradation.

Require the vendor to flag $\delta^{13}C$ values that were performed on any samples where the amplitude of the mass 44 ion corresponded to concentrations that were below that lowest concentration of compound you identified to the vendor.

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An Alternative:

Require the vendor to report the values of $\delta^{13}C$ of replicate analyses (n=3) of the compound specific working standard at a concentration that corresponds to the amplitude of the mass 44 ion in the flagged samples.

A replicate of the original sample should be included in the same sample run as the replicates of the diluted compound specific working standard.

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An Alternative:

This is a very open-ended approach. It is impossible to determine before hand how much labor would be involved.

Expect to pay the vendor for the additional work necessary to determine the precision of the isotope ratio analysis on the flagged samples.

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Detection limits should always be determined using the same chromatographic column and working conditions (including split ratios) as the samples.

The compound working standards should be subjected to the entire analytical procedure.

The compound working standards should be spiked into water, then extracted and prepared for gas chromatography following the same procedures as the samples.

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An isotope ratio mass spectrometer can analyze samples over a fairly narrow range concentrations.

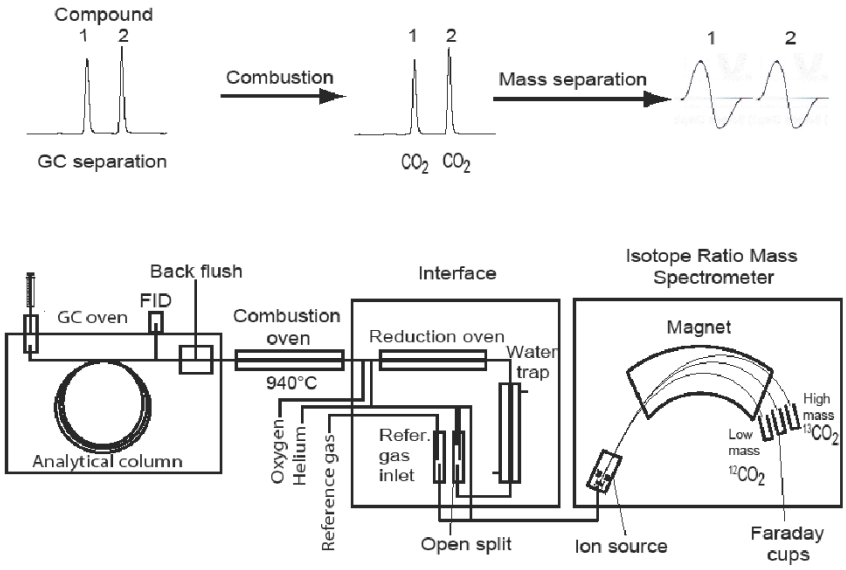
All samples should stay within the acceptable range and above the established threshold limit.

If a sample falls outside the acceptable range, the concentrations of the analytes should be adjusted, if possible, to bring the sample within the acceptable range, and the sample analyzed a second time.

This is one reason the vendors want so many replicate water samples. There may be several repeat analyses.

Figure 2.1 of U.S. EPA Guide.

GC IRMS requires clean separation of peaks of individual compounds.



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In most plumes of chlorinated solvents, there are usually few VOA compounds in the water, and peaks of individual compound are clearly separated from each other.

In plumes that originate from spills of petroleum, conventional GC columns may not separate peaks for the compounds of interest from co-eluting compounds.

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In many states, the concentrations of MTBE and benzene in ground water at UST sites are determined by Gas Chromatography with a Mass Spectrometer Detector (EPA Method 8260) instead of Gas Chromatography with a Flame Ionization Detector (EPA Method 8015).

The more expensive method (8260) is required because the GC column often can not separate the MTBE or benzene from other components of the fuel.

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For some compounds baseline resolution is impossible:

1. isomers of chlorobenzene

2. higher molecular hydrocarbons in the gasoline or diesel range that elute on top of a rising baseline.

3. MTBE and 1,1-dichloroethane co-elute on some columns.

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Determination of concentrations using GC Mass Spectrometry is fairly forgiving of overlapping peaks in the chromatograph. The ions characteristic to a specific compound can be used to recognize and quantify the compound of interest.

The Flame Ionization Detector works by burning the compounds. It can not distinguish between compounds in overlapping peaks.

Like a Flame Ionization Detector, the Isotope Ratio Mass Spectrometer is not forgiving. All of the compounds are oxidized to CO_2, and the mass ratio of the CO_2 that is derived from each compound is determined separately.

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It is impossible to determine beforehand whether there will be overlap of peaks in the chromatograph from a particular sample.

As a result, it is difficult to protect against this source of error in a scope of work or QAPP.

However, there are things that can be done to recognize overlap of peaks and alternatives to improve the separation of peaks.

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One way to detect problems with co-elution is to examine the chromatogram for shoulders on the front or back of each target peak, or more generally, any differences in peak shape as compared to the standard.

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You might task the vendor to provide in the report one or a few of the most complex chromatographs. There are the chromatographs where there is a greater chance that peaks of other compounds will overlap the peaks for the compounds of interest.

You might require that “analyses only be performed when peaks for the compound of interest are clearly resolved from co-eluting peaks.” However, without some quantitative description of “clearly resolved”, the requirement is ambiguous.

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Often, the Project Plan will require data on concentrations was well as isotopic ratios.

To minimize operator time on the IRMS, some vendors require that an analyses of concentrations of VOCs to be provided by the client.

Frequently, the samples will be analyzed for concentrations using Method 8260 or equivalent.

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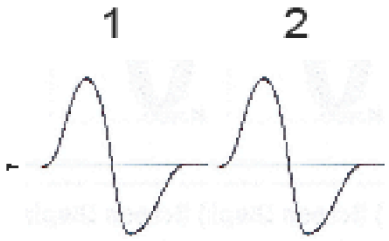
If the same chromatographic column and conditions are being used for Method 8260 and the CSIA, examine the full-scan mass spectra of the peak compared to the mass spectrum of a standard, and look for the presence of mass fragments in the sample spectrum that are unaccounted for in the spectrum of the standard.

Look at the non-background-subtracted spectra, to avoid subtracting out the contribution from a compound in the shoulder of the main peak. Anything that has an abundance greater than 10% of the base peak is suspect, and requires further consideration and evaluation.

Part of Figure 2.1 of U.S. EPA Guide.



The ratio of mass 45 to mass 44 (^{13}C-CO_2 to ^{12}C-CO_2) is called the ratio trace of the peak. If there are co-eluting peaks, the shape of the trace will depart from a trace of the pure compound.

The error caused by co-eluting peaks will be the greatest when concentrations of the VOA are low, and the difference in isotopic ratios between samples is small.

When these circumstances apply, you might require the vendor to compare the ratio trace for each analysis against the trace of the compound specific standard. For particularly crucial analyses, you might require the vendor to provide copies of the ratio traces in the report.

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Other factors can influence the shape of the ion trace, including the extent of isotopic fractionation of the sample compared to the compound specific standard.

Interpreting the trace is best left to an analytical chemist that is familiar with the instrument and the analytical protocol that was used to acquire the data.

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As mentioned previously, the amplitude of area of the ion 44 peak is roughly proportional to the concentration of the VOA. Linear extrapolation can provide an estimate of the concentration of the VOA from the amplitude or area of the ion 44 peak.

If there is a concern with the symmetry of the ion ratio trace, you may task the analyst to compare the estimate of concentration from the IRMS to the concentration reported using GS/MS such as Method 8260. Extreme differences between the two estimates may indicate problems with co-elution or other matrix effects.

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To perform CSIR of EDB in gasoline spills, Paul Philp's lab at the University of Oklahoma had to use two dimensional chromatography to get good peak separation. In this case, "two dimensional" means they used two different GC columns in sequence to achieve adequate separation.

Natural Attenuation of the Lead Scavengers 1,2-Dibromoethane (EDB) and 1,2-Dichloroethane (1,2-DCA) at Motor Fuel Release Sites and Implications for Risk Management. EPA 600/R-08/107 | September 2008 | www.epa.gov/ada.

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Analysis $\delta^{13}C$ or $\delta^{2}H$ of aromatic hydrocarbons or chlorinated VOCs should be performed on a conventional water sample in a 40 ml VOA vial preserved with HCl to pH <2.

Preserve samples of ethers such as MTBE with trisodium phosphate to pH>10.5.

As of this date, appropriate preservation of chlorinated VOCs for $\delta^{37}Cl$ has not been specifically evaluated but similar approaches to the above are likely to be required.

Require the vendor to specify the appropriate technique to preserve samples.

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Under some circumstances, analyses for CSIA must wait for analyses on concentrations of VOAs in the samples. The clock is running on holding time while the vendor for the CSIA is waiting for the concentration data.

Data in the EPA Guide (Section 3.4) documents the capacity of hydrochloric acid and trisodium phosphate (as appropriate) to preserve samples for 28 days.

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It is best to collect samples for analysis of concentrations and for CSIA at the same time.

The analyses can be performed on the same sample set, and the results are directly comparable.

Avoid collecting samples for concentrations and CSIA on different days.

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Vendors may require as many as nine replicate samples from each well.

The vendor should specify the number of replicates in the bid.

You really can't sample the same ground water twice. The cost of the vials is a tiny part of the cost of sampling. Collect more samples than you think you will need, and discard them if they are not needed.

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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

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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.

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

•Usually much less expensive.

•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.

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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 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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Commercial Source of Analytical Services

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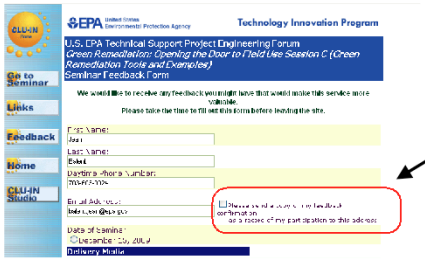
Resources & Feedback

- 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



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