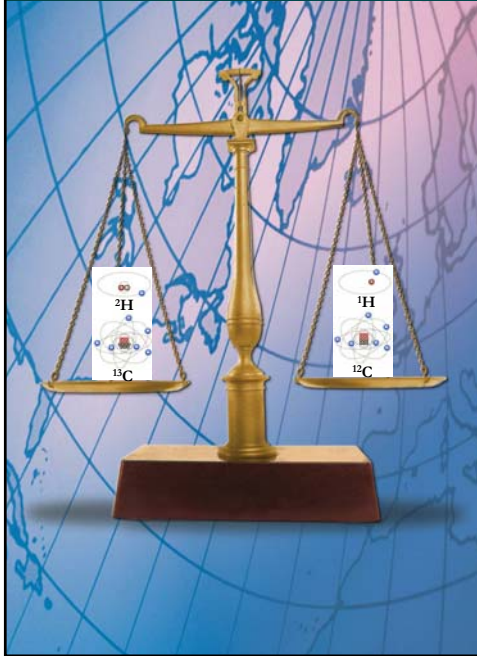


Use of CSIA in Site Management:

A Regulatory Perspective



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Talk Format and Intent

- **Format:** Case study application of Compound Specific Isotope Analysis to a large dissolved MTBE plume
- **Intent:**
 - To provide an example application of CSIA including:
 - Why / how CSIA was applied at fuel spill site in NYS
 - How the data was used to calculate a first order rate constant for MTBE degradation
 - How the information influenced regulatory decision-making and remedial design
 - The cost of acquiring the CSIA data
 - To suggest ways of assessing the cost effectiveness of such information from the point of view of a project manager / regulator
 - Highlight issues of data and analysis defensibility

Disclaimer

The analysis and conclusions presented are those of the presenter and do not represent those of the New York State Attorney General

Outline

- Compound Specific Isotope Analysis (CSIA) Applications to MTBE
- CSIA - Basic Concepts
- Long Island MTBE Mega-Plume:
 - Nature and Extent of the MTBE and TBA Plumes
 - Importance of the biodegradation component of the Conceptual Site Model
- 3 Rounds CSIA Sampling and Analysis
 - 2 Rounds of MTBE $\delta^{13}\text{C}$ data
 - 1 Round of combined MTBE $\delta^{13}\text{C}$ & MTBE $\delta^2\text{H}$ Data
 - Calculation of a first order rate constants for MTBE degradation:
 - based upon CSIA data
 - Based upon changes in total dissolved MTBE mass with time
- Conclusions
 - Comparison of first order rate constants based upon CSIA and changes in total dissolved mass
 - The value of the combined MTBE $\delta^{13}\text{C}$ & MTBE $\delta^2\text{H}$ data for support of remedial treatment alternatives and designs
 - Note on data defensibility
- Questions

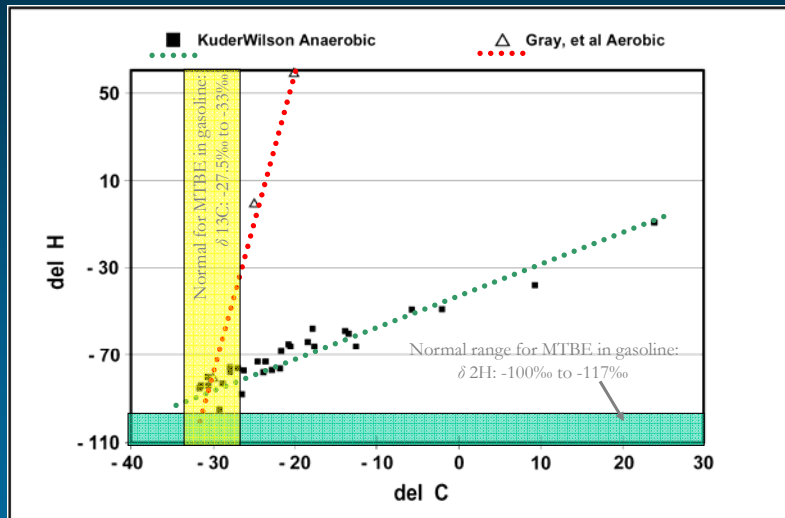
Compound Specific Isotope Analysis Applications to MTBE

- 2001: Early Compound Specific Stable Isotope Analysis (CSIA) applications to fuel oxygenate degradation
 - Finneran, Lovely. 2001. Anaerobic degradation of MTBE and TBA
 - Hunkeler, Butler, Aravena, Barker. 2001. Monitoring biodegradation of MTBE using compound specific carbon isotope analysis.
- 2004: CSIA applications to fuel oxygenate degradation numerous and fairly well understood
 - Schmidt, Zwank, Elsner, Berg, Meckenstock, Haderlein. 2004. Compound Specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects, and future challenges
- 2005-2007: CSIA integrated into MNA guidance (EPA/API)
 - Wilson, Kaiser, Adair. 2005. Monitored Natural Attenuation of MTBE as a Risk Management Option at Leaking Underground Storage Tank Sites
 - API PUBLICATION 4761. 2007 Technical Protocol for Evaluating the Natural Attenuation of MtBE

CSIA - Basic Concepts

- Measuring ratios of $^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$ within a specific compound such as MTBE
- Enrichment of ^{13}C and or ^2H in the remaining target contaminant can be indicative of, and is believed to be proportional to, the biodegradation pathway and the fraction of contaminant mass degraded, respectively
 - Enrichment in excess of the normal range for the target contaminant
 - Enrichment increasing along a contaminant flow path
- The ratio of either $^{13}\text{C}/^{12}\text{C}$ and/or $^2\text{H}/^1\text{H}$ measured in sample of residual target contaminant and is expressed relative to the $^{13}\text{C}/^{12}\text{C}$ and/or $^2\text{H}/^1\text{H}$ in a standard for that compound as an enrichment factor $\delta^2\text{H}$ and/or $\delta^{13}\text{C}$ as parts per thousand or per mil (‰)
- Normal range for MTBE in gasoline:
 - $\delta^{13}\text{C}$: -27.5‰ to -33‰
 - $\delta^2\text{H}$: -100‰ to -117‰

MTBE CSIA - Basic Concepts Cont. Aerobic vs. Anaerobic



Modified from Compound Specific Isotope Analysis: The Science, Technology and Selected Examples from the Literature with Application to Fuel Oxygenates and Chlorinated Solvents, Dr. Robert Pirkle, Microseps, July 2006

Nature and Extent of the MTBE and TBA Plumes

- 1,372 meter long, 244 meter wide and 41 meter thick (i.e. 5,938,307 cubic meter) plume of contaminated ground water containing 5,164 kg of dissolved MTBE (MTBE concentrations exceeding 1,000 mg/L)
- TBA concentrations exceeding 63,000 $\mu\text{g/L}$ found within a narrow region of the MTBE plume
- Multiple contaminant sources
- Two primary sources remediated to varying degrees by varying combinations of:
 - pump & treat
 - air sparging and vapor extraction
 - oxygen releasing compound

Site Background

Winter 2006 Monitoring Network Sampling
MTBE detected up to 1,330,000 ug/L



Site Background Cont.

Winter 2006 Monitoring Network Sampling
TBA – Detected up to 63,700 ug/L



Importance of the biodegradation component of the Conceptual Site Model

- Presence of high concentrations of MTBE and TBA seem to exclude natural biodegradation (NA) as a primary component of any remedial alternative
- The high concentrations of TBA potentially problematic for active remedial system designs
 - May require additional treatment technology from MTBE
 - Potential additional capital costs for TBA treatment in excess of \$500,000 (e.g. BIO-GAC)
- How much NA and is it the source of the TBA?
 - Co-contaminant in gasoline vs. MTBE biodegradation
 - Down-gradient MTBE / TBA ratio approx 10 / 1 (co-contaminant?)
 - Near source MTBE / TBA ratio approx 1/1 (biodegradation?)
- What is the fate of TBA?
 - Will it persist and drive remedial designs, or is it biodegrading away?

Finding Solutions/Answers

- Application of CSIA to residual MTBE to assess biodegradation of MTBE to TBA
- Expand monitoring network and collected additional sampling rounds in part to facilitate estimates of first order rate constants:
 - based upon changes in total dissolved mass with time
 - based upon ground water flow and contaminant transport model calibration
- Collect field readings for dissolved oxygen, ORP and other process relevant parameters

Initial CSIA (Summer 2006)

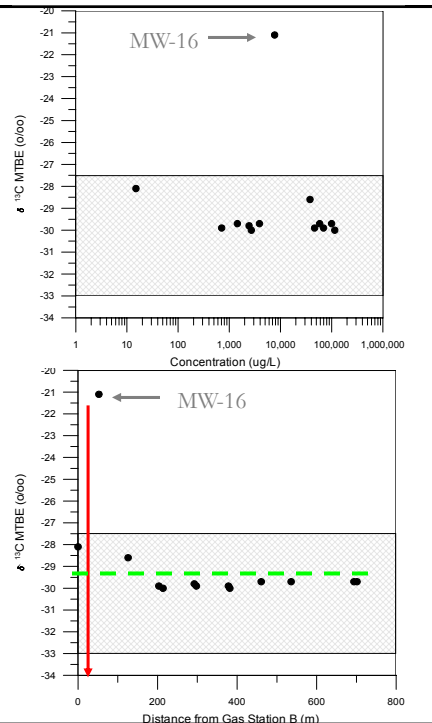
- 13 groundwater samples collected for $^{13}\text{C}/^{12}\text{C}$ analysis
- Samples selected to span both high concentrations of MTBE and TBA along GW flow lines



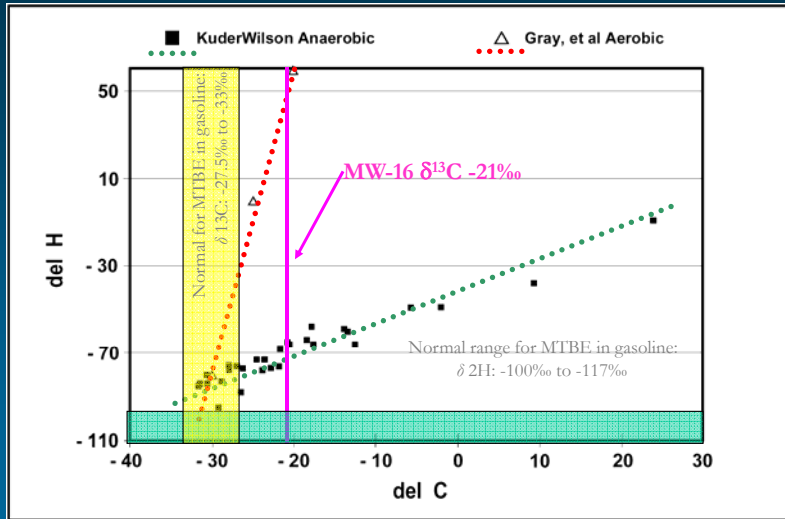
Initial CSIA Results

- 1 of 13 samples (MW-16) indicated $\delta^{13}\text{C}$ values indicating enrichment in excess of the normal range of MTBE in gasoline
- Enriched sample $\delta^{13}\text{C}$ was -21‰ and was located within 50 meters downgradient of station B (i.e. in the near source plume)
- Overall evidence of biodegradation was weak as there was no trend of enrichment along flow lines
- Enrichment in MW-16 was in conclusive as to pathway (anaerobic or aerobic?)

Highlighted area represents the reported range of ^{13}C MTBE in gasoline (Sullivan et al., 2003).



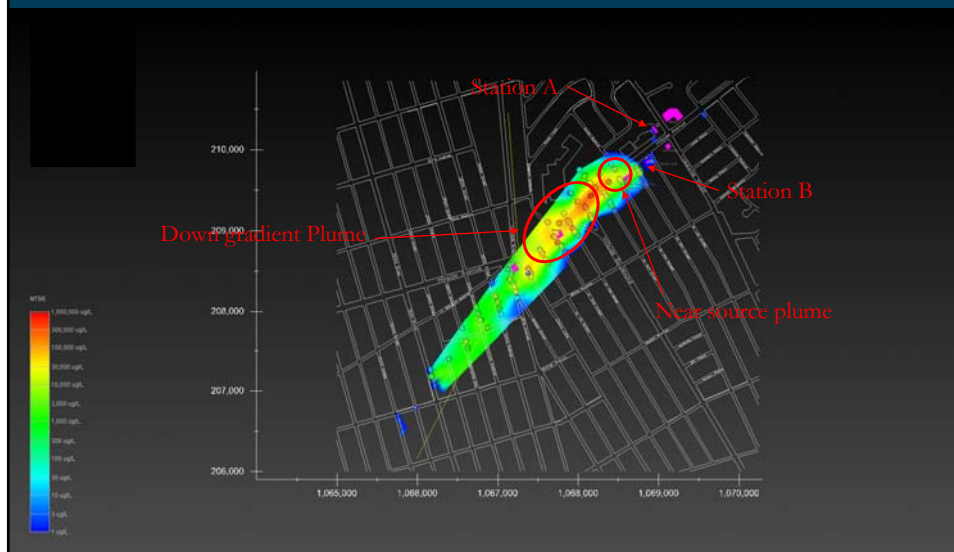
Initial CSIA Results Discussion



Modified from Compound Specific Isotope Analysis: The Science, Technology and Selected Examples from the Literature with Application to Fuel Oxygenates and Chlorinated Solvents, Dr. Robert Pirkle, Microseps, July 2006

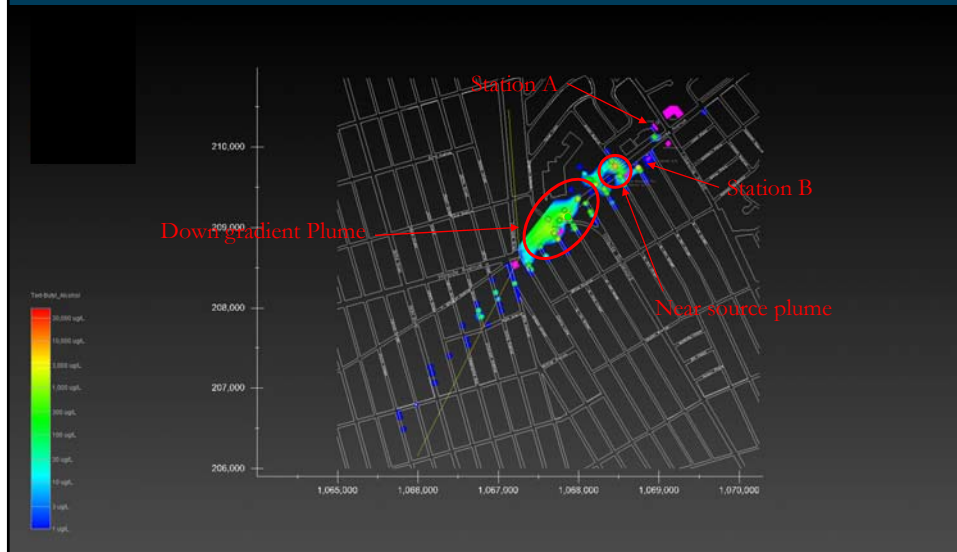
Expansion of Monitoring Network

Spring 2007 Understanding Dissolved Contamination
 MTBE detected up to 434,000 ug/L

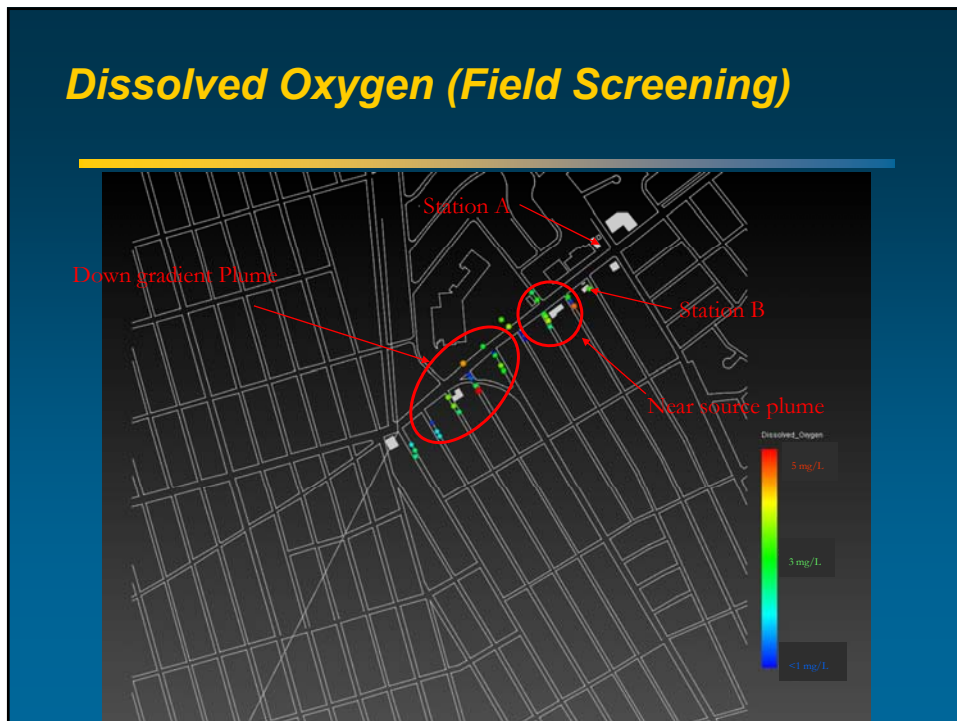


Expansion of Monitoring Network

Spring 2007 Understanding Dissolved Contamination
TBA detected up to 5,960 ug/L

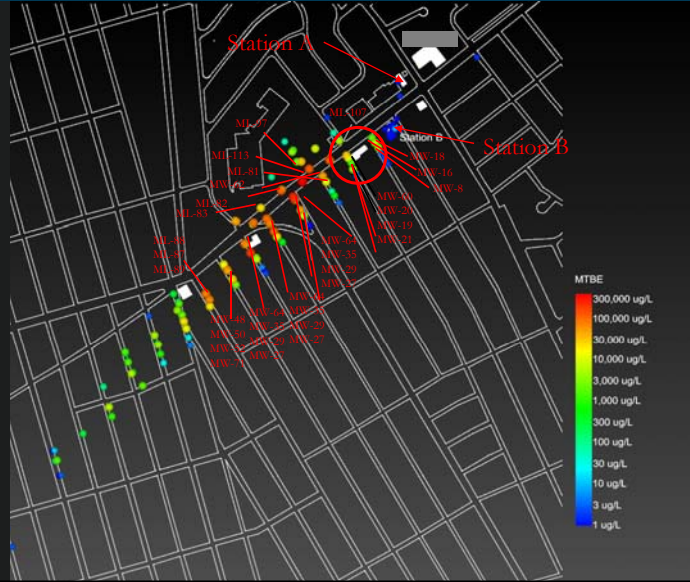


Dissolved Oxygen (Field Screening)



2nd Round CSIA (Spring 2007)

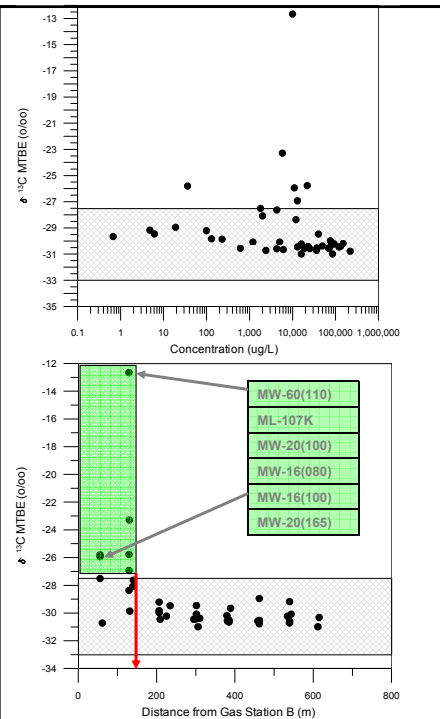
- 48 ground water samples collected
¹³C/¹²C and ²H/¹H analysis
- Samples selected to span both high concentrations of MTBE and TBA and in flow path line
- Re-evaluate previous CSIA data collected



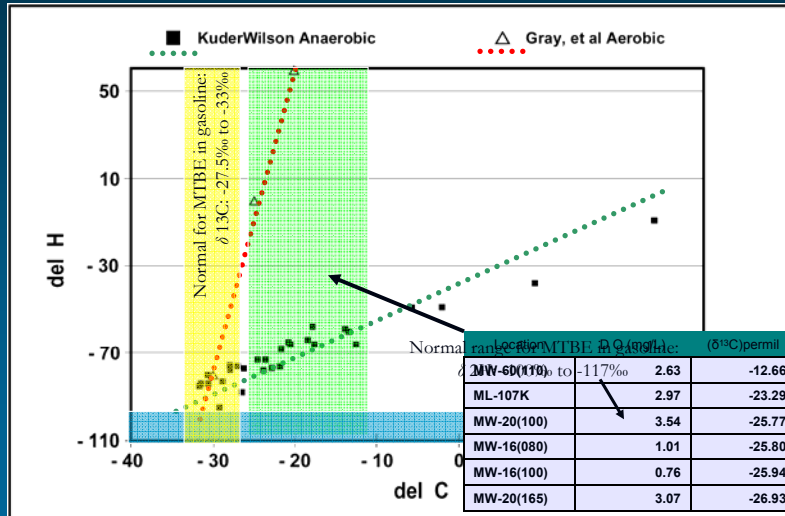
2nd Round CSIA

- Contracted laboratory was unable to report $\delta^{2}H$
- 6 of 48 samples indicated $\delta^{13}C$ values indicating enrichment in excess of the normal range of MTBE in gasoline
- All ¹³C enriches samples locations were within 130 meters downgradient of station B (i.e. near source)

Highlighted area represents the reported range of ¹³C MTBE in gasoline (Sullivan et al., 2003).



2nd Round CSIA



Initial conclusions based upon MTBE $\delta^{13}C$

- Nature of the $\delta^{13}C$ values of the MTBE in down gradient plume vs. the near source plume differed
- DO in the downgradient plume was lower than in the near source plume
- Differences in the ratio of MTBE/TBA in the downgradient plume vs. the near source plume persisted through time
 - Down-gradient MTBE / TBA ratio approx 10 / 1
 - Near source MTBE / TBA ratio approx 1/1
- Reported $\delta^{13}C$ values in conjunction with distribution of TBA (i.e. MTBE/TBA ratios) and the distribution of the DO, suggest that biological transformations of MTBE to TBA likely took place under near source aerobic conditions
 - Aerobic conditions likely resulted from source zone remediation (i.e. air sparging and oxygen releasing compound injection)

Combined MTBE $\delta^{13}\text{C}$ & MTBE $\delta^2\text{H}$ Data (Summer 2008)

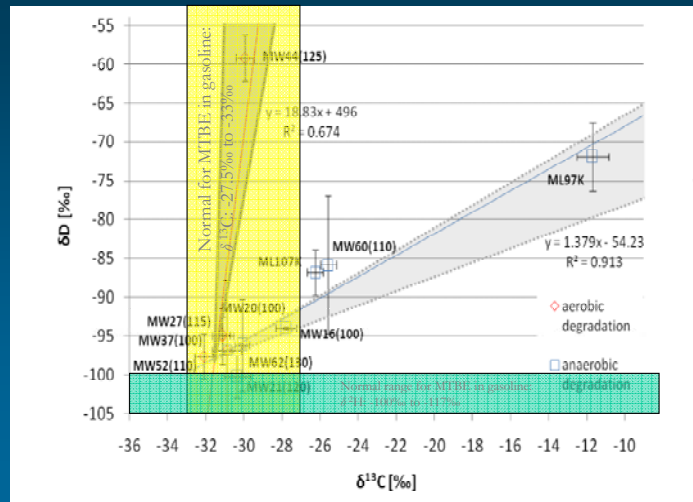
- 14 groundwater samples collected for $^{13}\text{C}/^{12}\text{C}$ and D/H analysis
- Samples selected to span both high concentrations of MTBE and TBA along GW flow lines
- Samples collected from both suspected Anaerobic and Aerobic portions of the plume(s)



Combined MTBE $\delta^{13}\text{C}$ & MTBE $\delta^2\text{H}$ Data

MTBE Specific Isotope Analysis					
Sample	Concentration [μgL^{-1}]	Dissolved O ₂ [mgL^{-1}]	Distance from source [m]	$\delta^{13}\text{C}$ [‰]	δD [‰]
MW16(100)	4600	-	56.00	-27.78±0.53	-94±1
MW60(110)	7900	0.68	129.00	-25.57±0.43	-86±9
MW20(165)	1000	2.06	130.00	-27.87±0.47	n.d.
ML107K	2200	0.31	130.00	-26.25±0.41	-87 ±3
MW20(100)	4800	0.88	130.00	-30.09±0.38	-96±6
ML97K	130	0.28	139.00	-11.68±0.86	-72±4
MW21(120)	2400	0.29	141.00	-30.36±0.70	-100±3
MW62(130)	37000	0.57	206.00	-30.9±0.78	-97±9
MW27(115)	13000	1.07	306.00	-31.12±0.56	-95±4
MW44(125)	74	4.82	385.00	-29.93±0.47	-60±3
MW37(100)	7700	5.24	459.00	-31.13±0.41	-95±2
MW52(110)	1000	1.29	540.00	-32.11±0.47	-98±3
ML87H	64000	0.6	615.00	-31.05±0.41	n.d.

Combined MTBE $\delta^{13}\text{C}$ & MTBE $\delta^2\text{H}$ Data



Calculations

- **Known:**
 - Anaerobic carbon enrichment factor = -11.6
 - Anaerobic hydrogen enrichment factor = -16
 - $\delta^{13}\text{C}$ in gasoline = -28 (more conservative)
 - $\delta\text{D}/\text{H}$ in gasoline = -100 (more conservative)
 - Seepage Velocity = 0.75 ft/day ($n=0.3$, $i=0.001$, $K=230$)
- **Estimate:**
 - Projected rate of biodegradation with distance and/or time
 - Time required to reach half initial concentration
 - Distance traveled before concentration reaches goal (i.e. 10 ug/L)

Anaerobic Degradation Calculations Utilizing Carbon Enrichment Factor of -11.6

Station	Distance from source	MTBE conc.	TBA Conc.	Stable Isotope Ratio (δ13C) per mil	MTBE Fraction Remaining After Biodegradation	Projected rate of biodegradation with distance from Source(per ft)	Projected rate of biodegradation with time from Source(per yr)	Time Required to Reach Half Initial Conc. (Yr.)	Time to Travel Before Concentration Reaches 10ug/L (yrs)
MW-16(080)	182.25	7	400	-	-	-	-	-	-
MW-16(100)	182.25	4,600	500	-27.78	0.981	0.00011	0.029	24	213
MW-60(110)	424.64	7,900	3,300	-25.57	0.811	0.00049	0.135	5	49
MW-20(100)	425.16	4,800	480	-30.09	1.000	0.00000	0.000	-	-
MW-20(165)	425.16	1,000	6	-27.87	0.989	0.00003	0.007	96	638
ML-107K*	705.84	2,200	3,600	-26.25	0.860	0.000213	0.058	12	92
ML-97K*	705.84	130	6,100	-11.68	0.245	0.001993	0.546	1	5
MW-21(120)	461.66	2,400	180	-30.36	1.000	0.00000	0.000	-	-
MW-62(130)	677.38	37,000	230	-30.90	1.000	0.00000	0.000	-	-
MW-27(115)	1,003.15	13,000	95	-31.12	1.000	0.00000	0.000	-	-
MW-44(125)	1,262.33	74	<2.5	-29.93	1.000	0.00000	0.000	-	-
MW-37(100)	1,504.92	7,700	29	-31.13	1.000	0.00000	0.000	-	-
MW-52(110)	1,770.37	1,000	<2.5	-32.11	1.000	0.00000	0.000	-	-
ML-87H	2,017.93	64,000	300	-31.05	1.000	0.00000	0.000	-	-

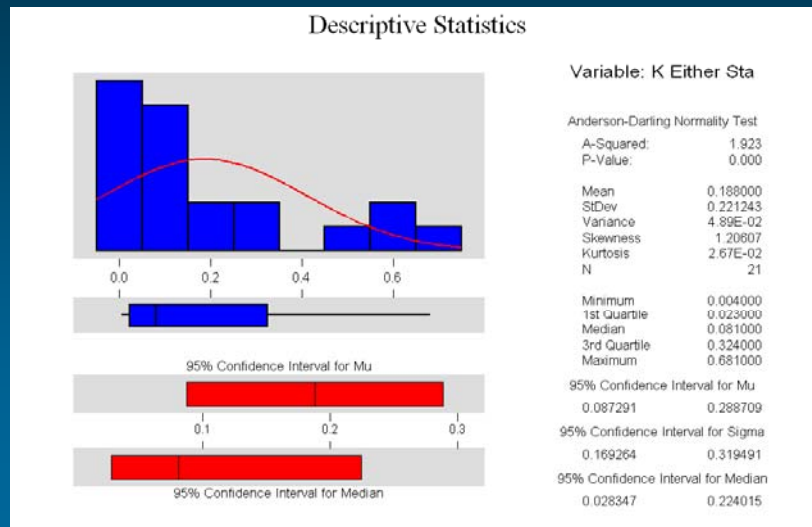
Projected maximum rate of biodegradation
ML-97K approximately 76% of MTBE degraded to TBA

Anaerobic Degradation Calculations Utilizing Hydrogen Enrichment Factor of -16

Station	Distance from source	MTBE conc.	TBA Conc.	Stable Isotope Ratio (δD/H) per mil	MTBE Fraction Remaining After Biodegradation	Projected rate of biodegradation with distance from Source(per ft)	Projected rate of biodegradation with time from Source(per yr)	Time Required to Reach Half Initial Conc. (Yr.)	Time to Travel Before Concentration Reaches 10ug/L (yrs)
MW-16(080)	182.25	7	400	-	-	-	-	-	-
MW-16(100)	182.25	4,600	500	-93.96	0.685	0.00207	0.567	1	11
MW-60(110)	424.64	7900	3,300	-85.85	0.413	0.00208	0.570	1	12
MW-20(100)	425.16	4,800	480	-96.13	0.785	0.00057	0.156	4	40
MW-20(165)	425.16	1000	6	-	-	-	-	-	-
ML-107K*	705.84	2,200	3,600	-86.76	0.437	0.00117	0.321	2	17
ML-97K*	705.84	130	6,100	-71.90	0.173	0.00249	0.681	1	4
MW-62(130)	677.38	37000	230	-96.80	0.819	0.00030	0.081	9	102
MW-27(115)	1,003.15	13,000	95	-95.00	0.732	0.00031	0.085	8	84
MW-44(125)	1,262.33	74	<2.5	-59.16	0.078	0.00202	0.554	1	4
MW-37(100)	1,504.92	7,700	29	-94.90	0.727	0.00021	0.058	12	115
MW-52(110)	1,770.37	1000	<2.5	-97.66	0.864	0.00008	0.023	31	203
ML-87H	2,017.93	64,000	300	-	-	-	-	-	-

Projected maximum rate of biodegradation
ML-97K approximately 83% of MTBE degraded to TBA

Average MTBE degradation rate Constant based upon combined (per year)

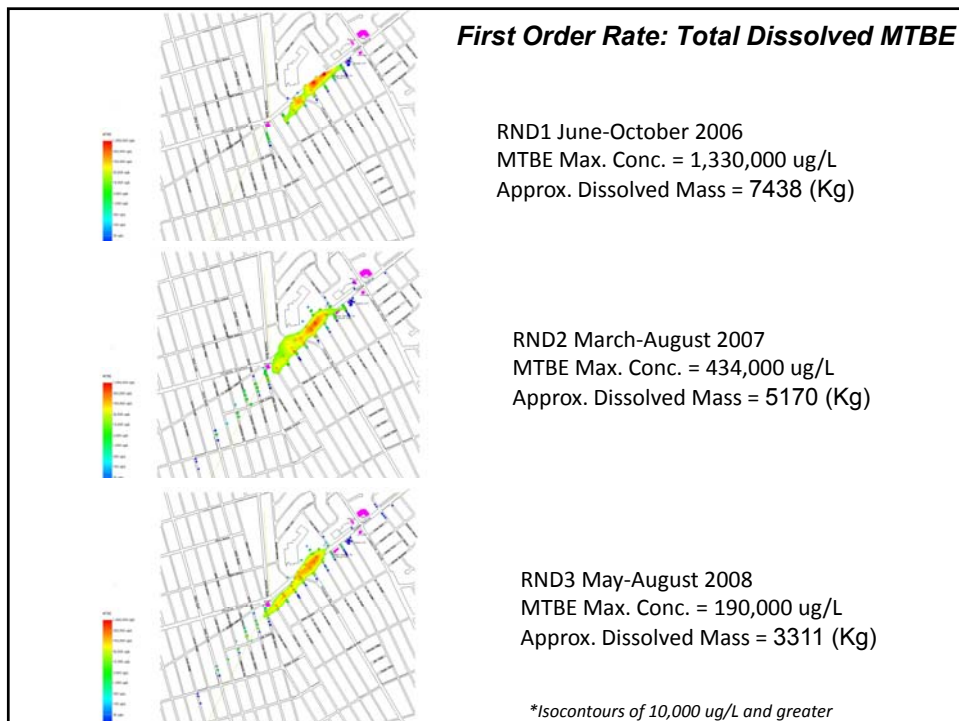


CSIA: MTBE Deg. Rate Constant

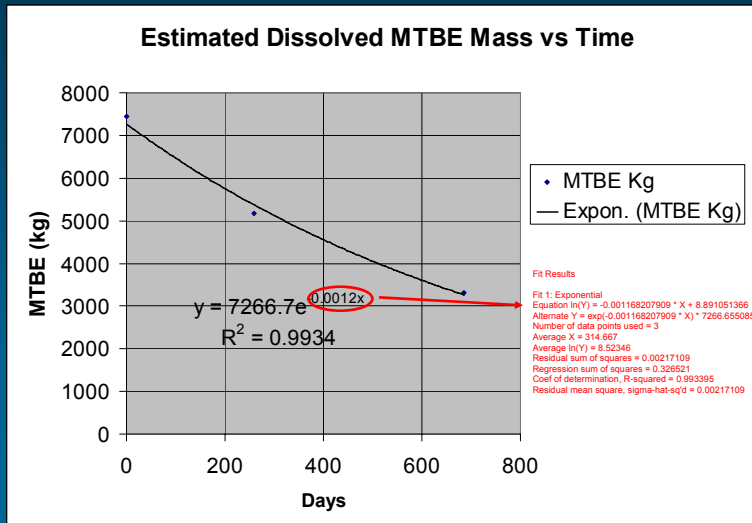
MTBE Deg. Rate Constant	year ⁻¹	day ⁻¹	t ^{1/2} (years)
Maximum CSIA	0.681	0.00186	1.02
Average CSIA	0.188	0.000512	3.69

CSIA Conclusions

- The combined MTBE $\delta^{2}\text{H}$ and MTBE $\delta^{13}\text{C}$ data confirmed that transformation of MTBE to TBA like took place under both anaerobic and aerobic conditions prevailing within different portions of the plume.
- The data also helped explained the 1:1 MTBE to TBA concentration ratio observed in the anaerobic portion of the plume
- The data also helped explained the 1:1 MTBE to TBA concentration ratio observed in the anaerobic portion of the plume
- Provided an independent basis for new site specific estimates of the MTBE anaerobic and aerobic degradation rates



First Order Rate: Based upon total dissolved mass of MTBE



CSIA: MTBE Deg. Rate Constant

MTBE Deg. Rate Constant	year ⁻¹	day ⁻¹	t ^{1/2} (years)
Maximum CSIA	0.681	0.00186	1.02
Average CSIA	0.188	0.000512	3.69
Dissolved MTBE Mass	0.438	0.0012	1.58

Value of the combined MTBE $\delta^{13}\text{C}$ & MTBE $\delta^2\text{H}$ data

- The value of the CSIA data can be assessed by comparison with the data costs (approximately \$33,000) with the:
 - the costs of the additional rounds of sampling / analysis required to obtain estimates of dissolved MTBE mass
 - the cost reduction envisaged based upon revised remedial scenarios stemming from quantification of MTBE degradation

Value of CSIA rate constant relative that derived by changes dissolved MTBE mass

- 2 additional full sampling rounds of the of 1617 point monitoring network
 - ~Cost \$265,000 / per round (including estimated analytical) = ~\$530,000
 - Potential value of CSIA = ~\$500,000

CSIA value relative to alternative remedial design



Potential value of CSIA = ~\$1,000,000

Remedial alternative prior to first order rate constant based upon CSIA

gpm through treatment	400
LPAST (4)	\$400,000
Carbon (4)	\$400,000
RW installation (subcontract)	\$90,000
building/foundation	\$300,000
PVC pipe	\$105,000
Misc. materials (i.e. wire, pumps etc.)	\$150,000
Horizontal Drilling (subcontract)	\$80,000
trenching and piping (EAR) ~8,400'	\$420,000
Stop and Shop Property Rental*	\$200,000
Restoration (asphalt only)	\$45,000
Discharge rate/year (NCDPW)	\$674,520
total	\$2,864,520

Remedial alternative post to first order rate constant based upon CSIA

gpm through treatment	200
LPAST (3)	\$300,000
Carbon (2)	\$200,000
RW installation (subcontract)	\$90,000
building/foundation	\$300,000
PVC pipe	\$70,000
Misc. materials (i.e. wire, pumps etc.)	\$100,000
trenching and piping (EAR) ~7,500'	\$375,000
Restoration (asphalt only)	\$40,000
Discharge rate/year	\$337,435
total	\$1,812,435

Conclusions

- The CSIA data provided the basis of new independent site specific estimates of the MTBE anaerobic and aerobic degradation rates
- The value of 2D CSIA was greater than the 1D CSIA data and overall value (estimated reduced project management costs) CSIA data greatly exceeded the cost associated with its generation
- The combined MTBE δ 2H and MTBE δ 13C data indicated that bio-transformation of MTBE to TBA likely took place under both anaerobic and aerobic conditions prevailing within different portions of the plume

Conclusions *continued*



- **Data defensibility criterion/ considerations**
 - General acceptance in the relevant scientific community
 - Does not require absolute "unanimity of views within the scientific community"
 - Both the underlying theory and the general procedures used to produce results
 - The proponent of the evidence must demonstrate that correct scientific procedures were done in the particular case
- No examples of CSIA data being admitted but it is likely that it would be admitted
- Possible argument to exclude or diminish the weight of CSIA data & analysis
 - Diffusion should not be neglected as an isotope enrichment process such as:
 - LaBolle, E. M., G. E. Fogg, J. B. Eweis, J. Gravner, and D. G. Leaist (2008), Isotopic fractionation by diffusion in groundwater, *Water Resour. Res.*, 44, W07405, doi:10.1029/2006WR005264.
 - Eweis, J.B., E. M. LaBolle, D.A. Benson, and G.E. Fogg, The role of volatilization in apparent TBA enrichment at MTBE contaminated sites, *Environ Sci Technol.* 2007 Oct 1;41 (19):6822-7 17969701.
- Limiting arguments in opposition to CSIA data and related analysis
 - CSIA samples best taken prior to remedial action or beyond remedial influence
 - The influence of remedial activity upon the areas from which CSIA samples are obtained should be understood
 - The role of diffusion in transport / remedial processes should be considered during data collection and analysis

Contact Information



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