Emerging Tools for Fuel Oxygenate Characterization and Remediation

Eric Nichols, LFR Inc.

Contamination des Sols et des Nappes Aquifères par le MTBE et l'ETBE: Où en est-on en France, en Europe et aux États-Unis?

Lyons, France
30 Mars 2006

LFR

Presentation Overview

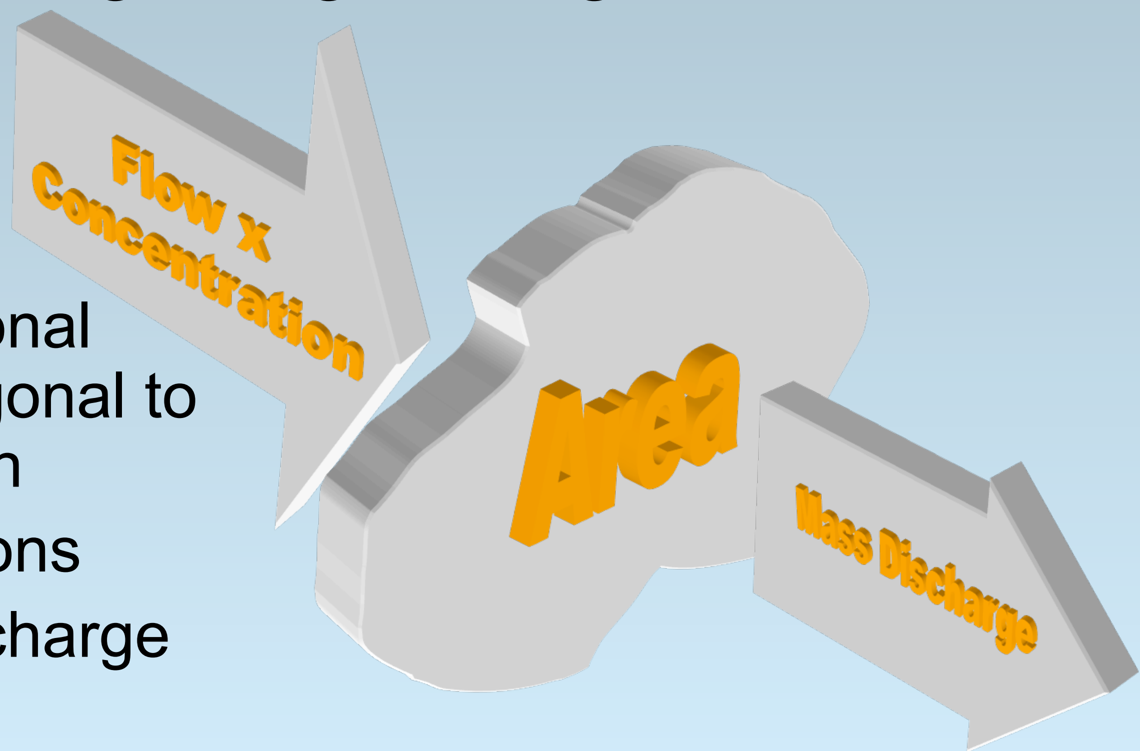
- Tools for Dissolved Mass Flux
- Tools for Diving Plumes
- New MTBE/TBA Remediation Guidance Documents

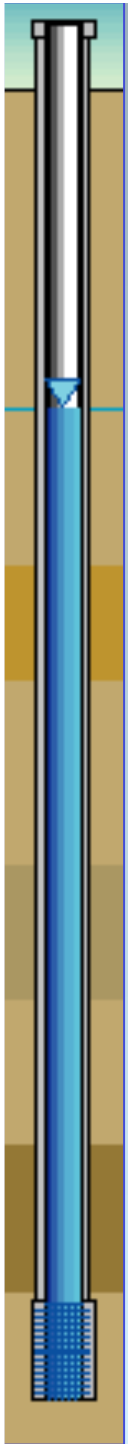
Tools for
Dissolved Mass Flux

Outils pour
le flux de masse dissous

Mass Flux or Mass Discharge

- Total mass of dissolved-phase constituent migrating through the subsurface over time
  - Cross-sectional plane orthogonal to flow direction
  - Concentrations
  - Specific discharge





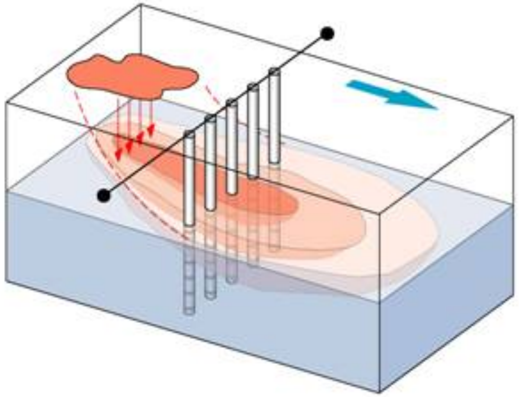
Mass Flux Estimates

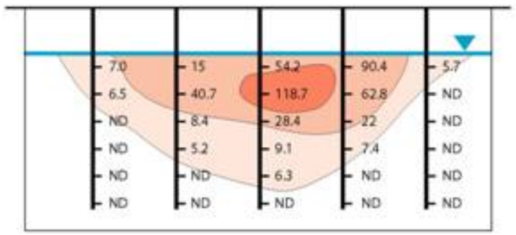
- Mass flux estimates can be used to evaluate:
  - Potential water quality impacts on downgradient water supply wells
  - Natural attenuation of contaminant mass with distance downgradient of source
  - Relative benefits of various remedial actions based on anticipated reductions in mass flux from source to receptor

Transect Method

$$M_f = \sum_{i=1}^{i=n} C_i * A_i * q_i$$

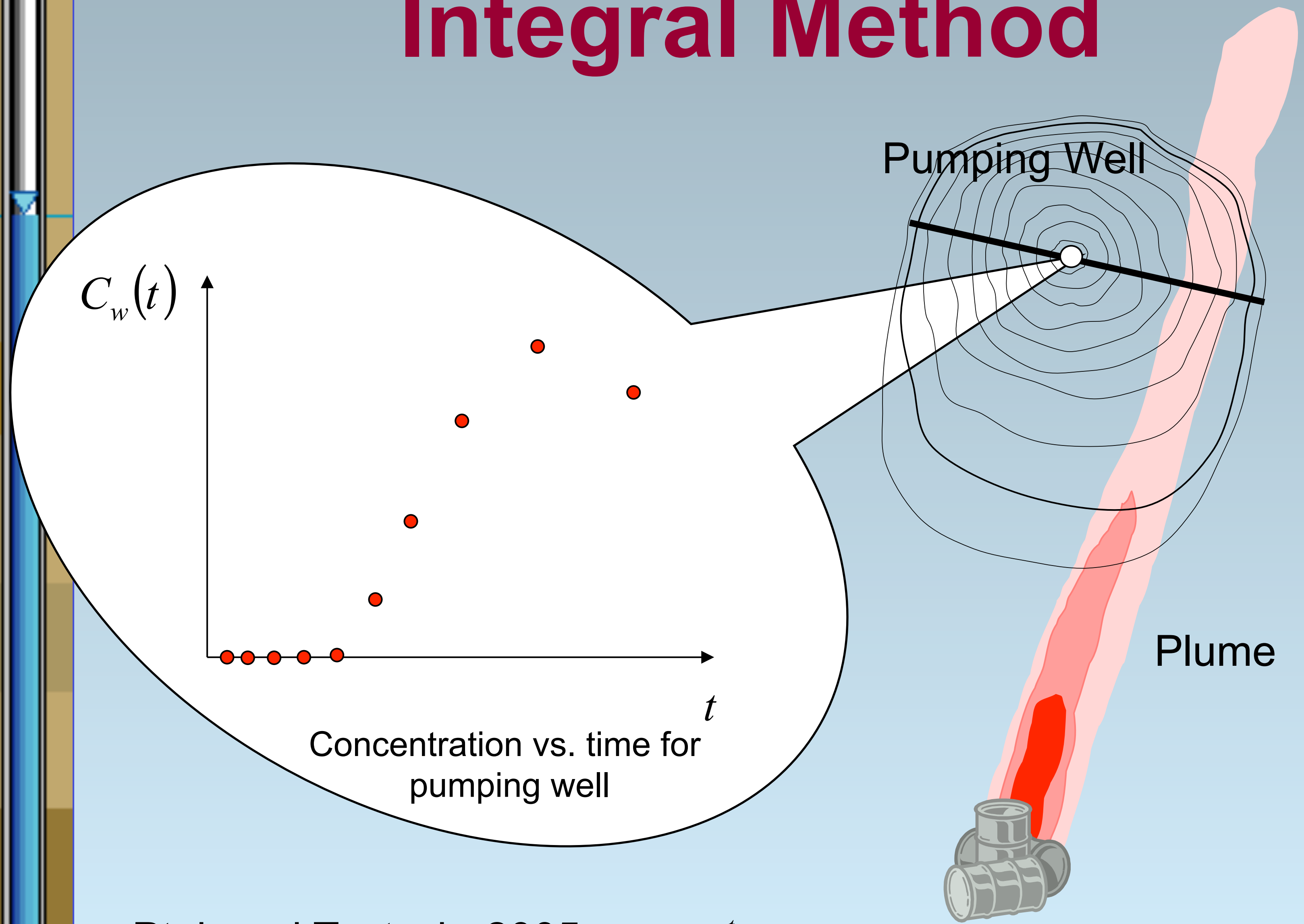
- 2D or 3D Network
- Discretize Subareas $i \dots n$
- Concentrations, hydraulic conductivity
- Sum the subarea fluxes for total mass discharge





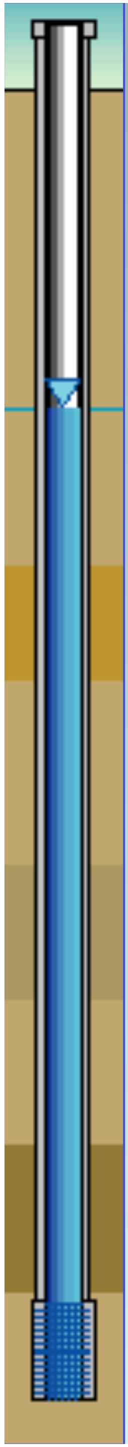
7.0	15	54.2	90.4	5.7
6.5	40.7	118.7	62.8	0
0	8.4	28.4	22	0
0	5.2	9.1	7.4	0
0	0	6.3	0	0
0	0	0	0	0

Integral Method



Ptak and Teutsch, 2005

$$Q\int_0^t C_w(\tau)\,d\tau = \int_{V_I(t)} C_0(x,y,z)\,n_e(x,y,z)\,dV$$



Supply Well Impacts

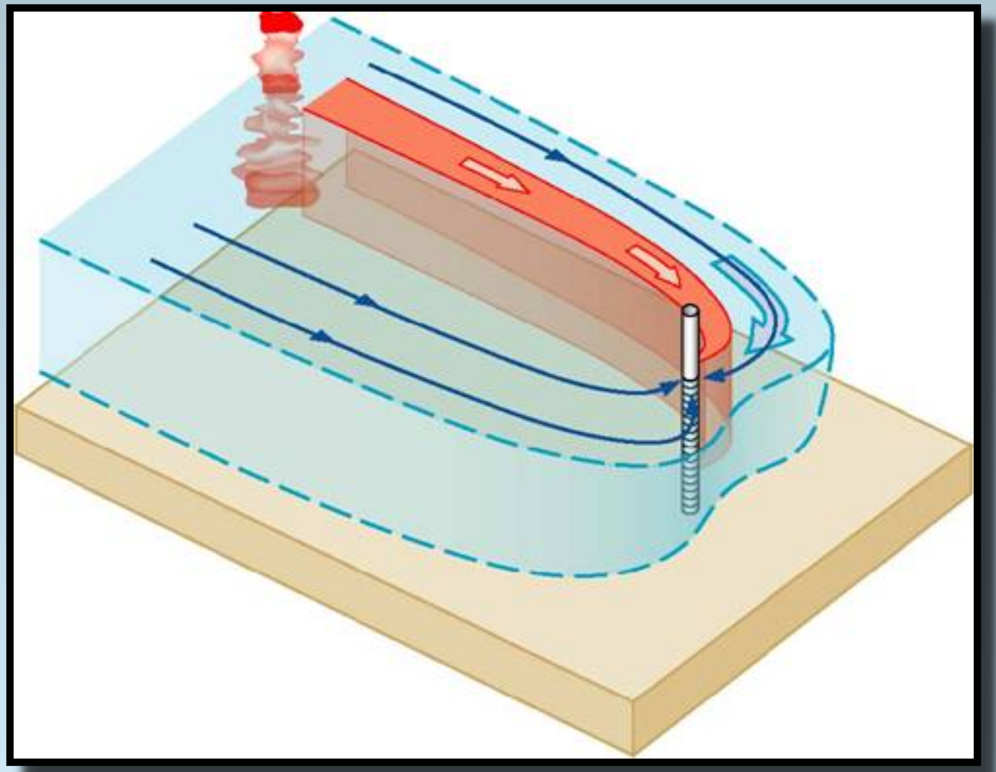
Supply Well Capture of a Plume:

$C_{sw} = M_f / Q_{sw}$

- estimate concentrations in a hypothetical supply well

$M_f = C_{sw} * Q_{sw}$

- calculate mass discharge targets protective of water quality criteria



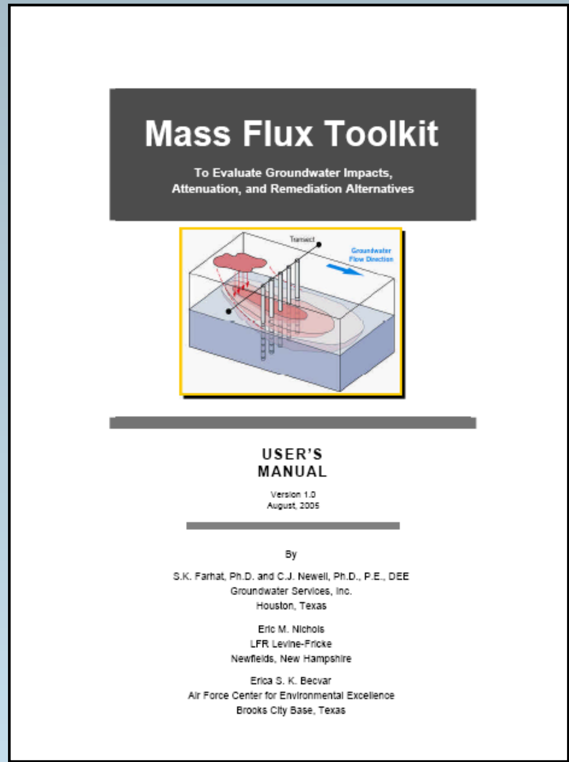
Einarson and Mackay, 2001

Oxygenates and Mass Flux

- Ether oxygenates and TBA may attenuate more slowly than other fuel constituents
- Plumes may be longer and have increased potential to impact water supply wells
- Therefore, methods that consider mass flux are particularly relevant to ether oxygenates and TBA

Mass Flux ToolKit

Provides tools to calculate mass flux of contaminants in groundwater



Mass Flux Toolkit

To Evaluate Groundwater Impacts, Attenuation, and Remediation Alternatives

USER'S MANUAL

Version 1.0
August, 2005

By

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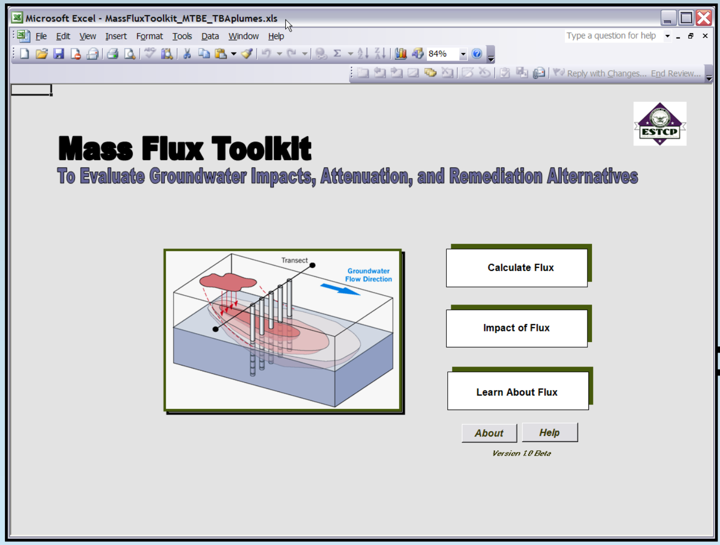
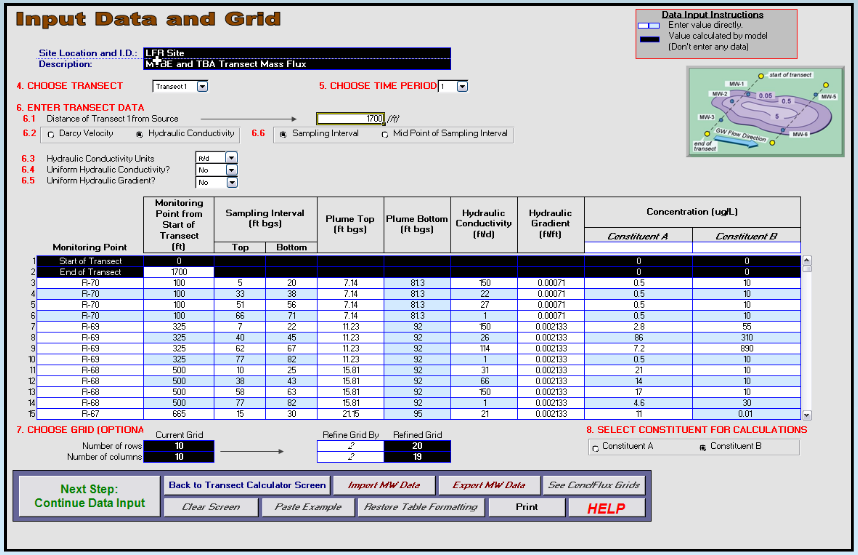


Free software application in Microsoft Excel

Developed for the Environmental Security Technology Certification Program by Groundwater Services, Inc., Houston, Texas with assistance from LFR.

ToolKit Features

- Calculation of total mass flux across one or more transects of a plume
- Flexible grid spacing
- Four choices for interpolating concentration, hydraulic conductivity, hydraulic gradient:
  - User Defined
  - Nearest Neighbor
  - Linear Interpolation
  - Log Transformation

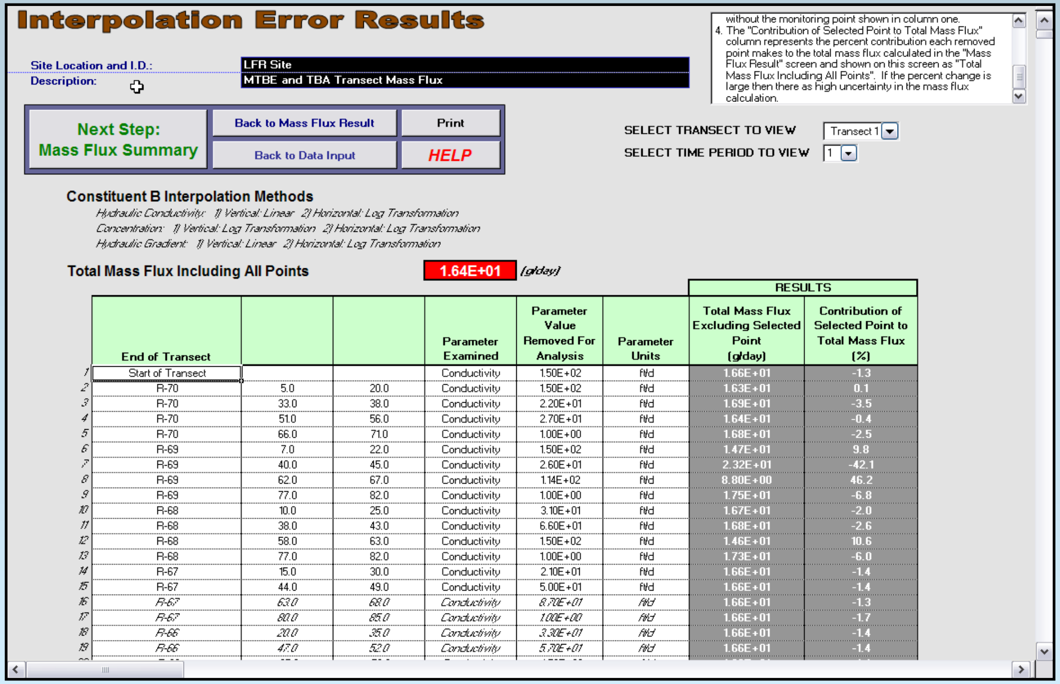


	Monitoring Point	Monitoring Point from Start of Transect (ft)	Sampling Interval (ft bgs) Top	Sampling Interval (ft bgs) Bottom	Plume Top (ft bgs)	Plume Bottom (ft bgs)	Hydraulic Conductivity (ft/d)	Hydraulic Gradient (ft/ft)	Concentration (ug/L) Constituent A	Concentration (ug/L) Constituent B
1	Start of Transect	0							0	0
2	End of Transect	1700							0	0
3	R-70	100	5	20	7.14	81.3	150	0.00071	0.5	10
4	R-70	100	33	38	7.14	81.3	22	0.00071	0.5	10
5	R-70	100	51	56	7.14	81.3	27	0.00071	0.5	10
6	R-70	100	66	71	7.14	81.3	1	0.00071	0.5	10
7	R-69	325	7	22	11.23	92	150	0.002133	2.8	55
8	R-69	325	40	45	11.23	92	26	0.002133	86	310
9	R-69	325	62	67	11.23	92	114	0.002133	7.2	890
10	R-69	325	77	82	11.23	92	1	0.002133	0.5	10
11	R-68	500	10	25	15.81	92	31	0.002133	21	10
12	R-68	500	38	43	15.81	92	66	0.002133	14	10
13	R-68	500	58	63	15.81	92	150	0.002133	17	10
14	R-68	500	77	82	15.81	92	1	0.002133	4.6	30
15	R-67	665	15	30	21.15	95	21	0.002133	11	0.01

ToolKit does not evaluate integral pumping tests

ToolKit Features

- Three types of uncertainty analysis:
  - Interpolation uncertainty
  - Uncertainty due to variability in the input data, using a Monte-Carlo style analysis (Latin Hypercube)
  - Sensitivity of mass flux estimate to each data point (cross validation)



Interpolation Error Results

without the monitoring point shown in column one.
4. The "Contribution of Selected Point to Total Mass Flux" column represents the percent contribution each removed point makes to the total mass flux calculated in the "Mass Flux Result" screen and shown on this screen as "Total Mass Flux Including All Points". If the percent change is large then there as high uncertainty in the mass flux calculation.

Site Location and I.D.: LFR Site
Description: MTBE and TBA Transect Mass Flux

Next Step: Mass Flux Summary | Back to Mass Flux Result | Print | Back to Data Input | HELP

SELECT TRANSECT TO VIEW: Transect 1
SELECT TIME PERIOD TO VIEW: 1

Constituent B Interpolation Methods

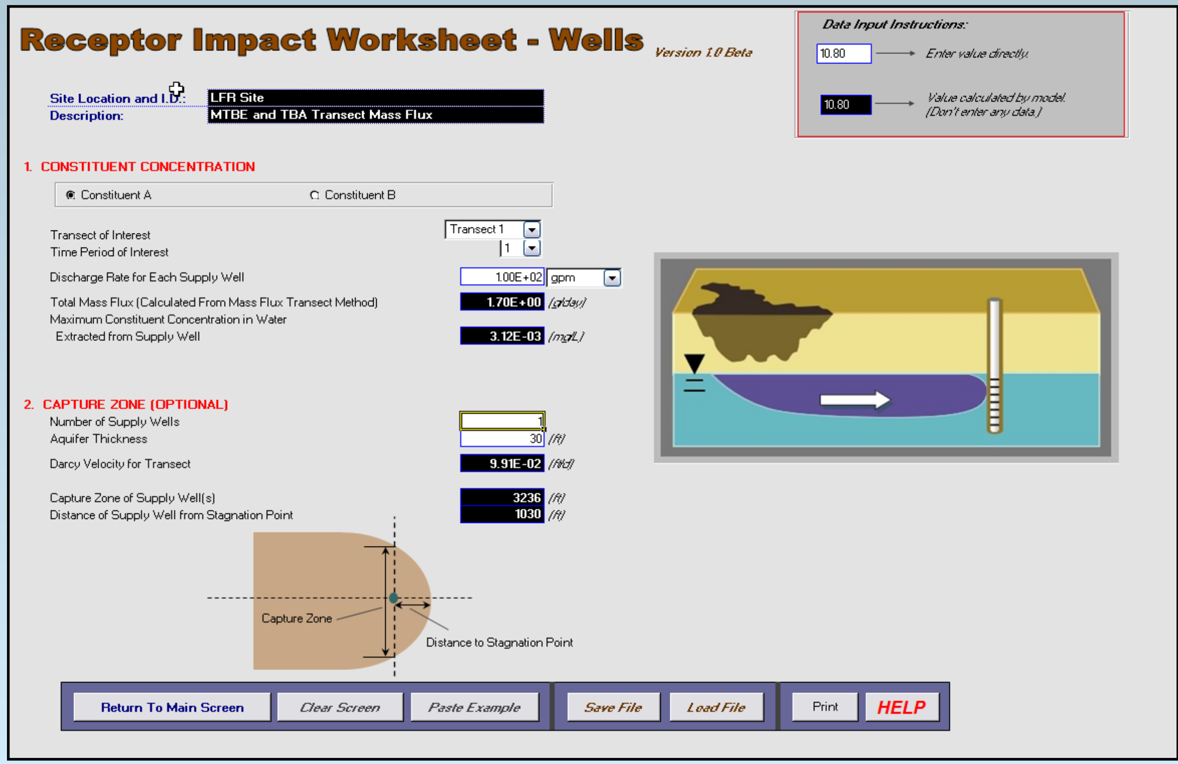
Hydraulic Conductivity: 1) Vertical: Linear 2) Horizontal: Log Transformation
Concentration: 1) Vertical: Log Transformation 2) Horizontal: Log Transformation
Hydraulic Gradient: 1) Vertical: Linear 2) Horizontal: Log Transformation

Total Mass Flux Including All Points 1.64E+01 *(g/day)*

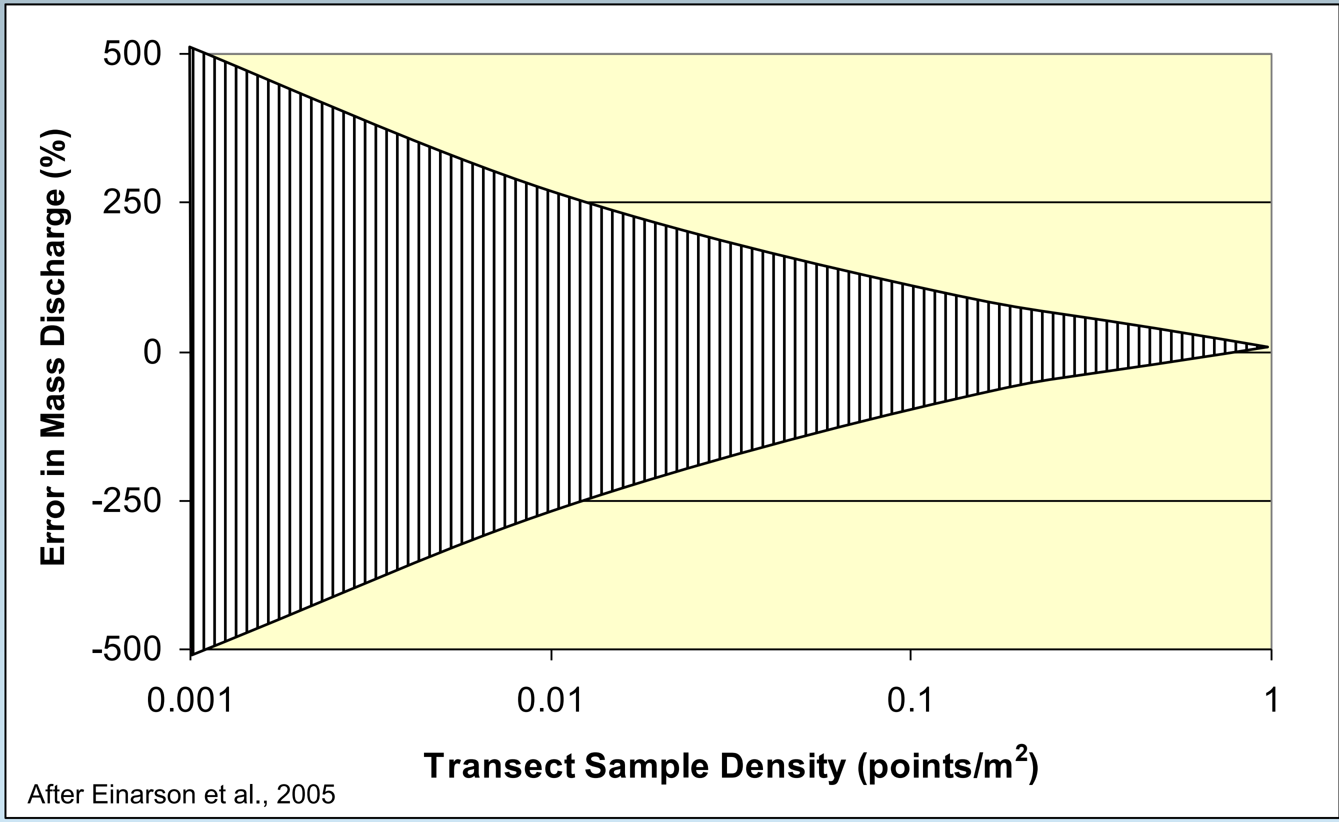
	End of Transect			Parameter Examined	Parameter Value Removed For Analysis	Parameter Units	RESULTS: Total Mass Flux Excluding Selected Point (g/day)	RESULTS: Contribution of Selected Point to Total Mass Flux (%)
1	Start of Transect			Conductivity	1.50E+02	ft/d	1.66E+01	-1.3
2	R-70	5.0	20.0	Conductivity	1.50E+02	ft/d	1.63E+01	0.1
3	R-70	33.0	38.0	Conductivity	2.20E+01	ft/d	1.69E+01	-3.5
4	R-70	51.0	56.0	Conductivity	2.70E+01	ft/d	1.64E+01	-0.4
5	R-70	66.0	71.0	Conductivity	1.00E+00	ft/d	1.68E+01	-2.5
6	R-69	7.0	22.0	Conductivity	1.50E+02	ft/d	1.47E+01	9.8
7	R-69	40.0	45.0	Conductivity	2.60E+01	ft/d	2.32E+01	-42.1
8	R-69	62.0	67.0	Conductivity	1.14E+02	ft/d	8.80E+00	46.2
9	R-69	77.0	82.0	Conductivity	1.00E+00	ft/d	1.75E+01	-6.8
10	R-68	10.0	25.0	Conductivity	3.10E+01	ft/d	1.67E+01	-2.0
11	R-68	38.0	43.0	Conductivity	6.60E+01	ft/d	1.68E+01	-2.6
12	R-68	58.0	63.0	Conductivity	1.50E+02	ft/d	1.46E+01	10.6
13	R-68	77.0	82.0	Conductivity	1.00E+00	ft/d	1.73E+01	-6.0
14	R-67	15.0	30.0	Conductivity	2.10E+01	ft/d	1.66E+01	-1.4
15	R-67	44.0	49.0	Conductivity	5.00E+01	ft/d	1.66E+01	-1.4
16	*R-67*	*63.0*	*68.0*	*Conductivity*	*8.70E+01*	*ft/d*	1.66E+01	-1.3
17	*R-67*	*80.0*	*85.0*	*Conductivity*	*1.00E+00*	*ft/d*	1.66E+01	-1.7
18	*R-66*	*20.0*	*35.0*	*Conductivity*	*3.30E+01*	*ft/d*	1.66E+01	-1.4
19	*R-66*	*47.0*	*52.0*	*Conductivity*	*5.70E+01*	*ft/d*	1.66E+01	-1.4

ToolKit Features

- Evaluates potential impacts of plumes approaching production wells or streams



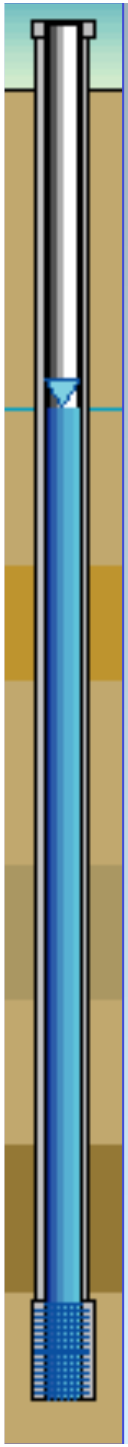
Uncertainty Not Addressed in ToolKit



Example of uncertainty related to transect sampling point density

ToolKit Availability

- Expected release in 2006
- Will be available at
  - http://www.estcp.org
  - http://www.gsi-net.com/Software/

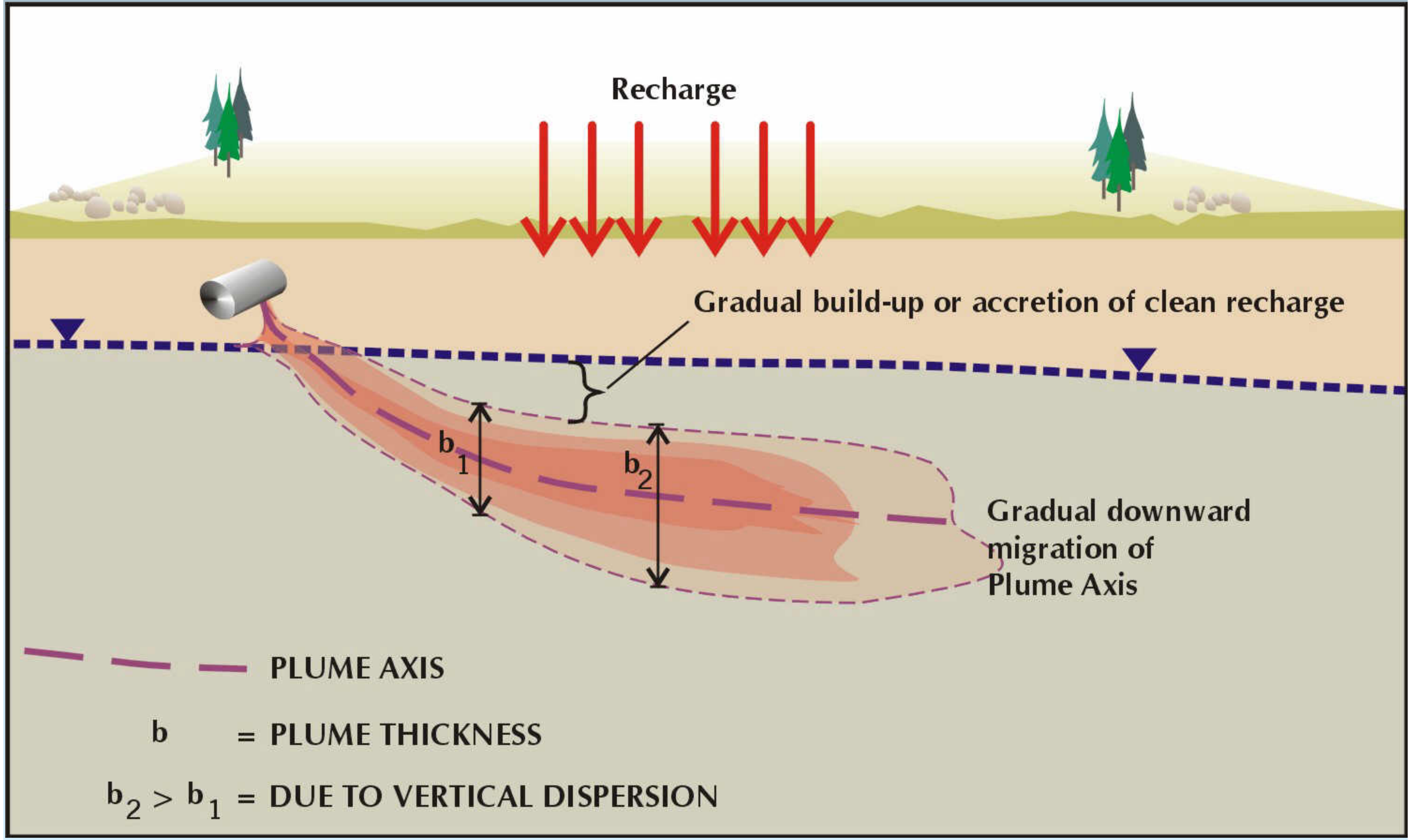


Tools for Diving Plumes

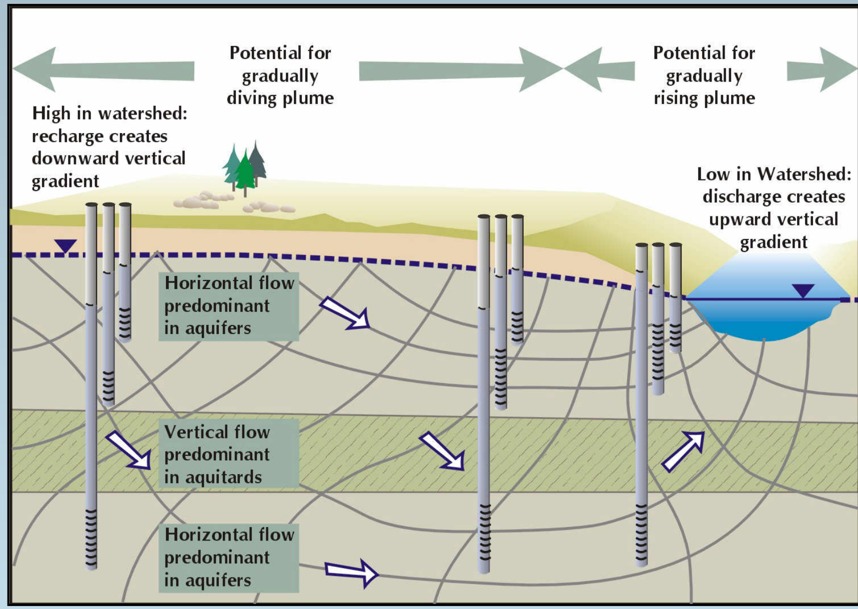
Outils pour Plumes de plongée

Gradually Diving Plume

Plume Graduellement De Plongée



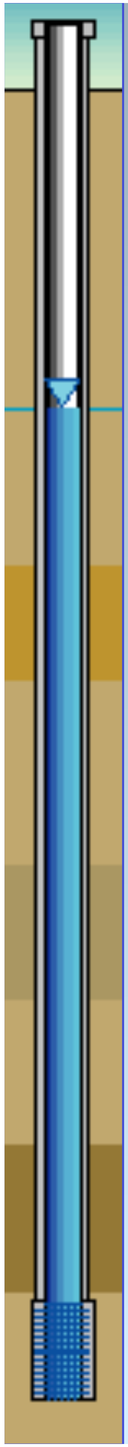
Consequences of Missing Diving Plumes



- Inadequate evaluation of risk to receptors
- Under-designing corrective actions
- Inadequate assessment of remedial performance

“Diving” MTBE Plumes

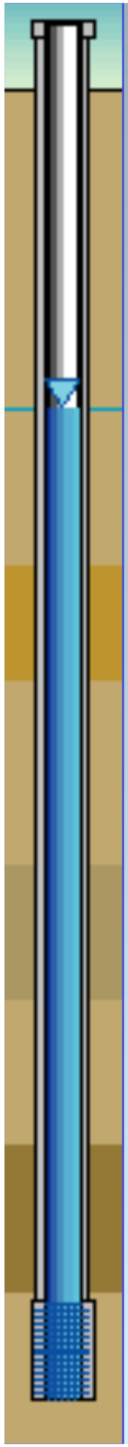
- MTBE is often associated with the phenomena of “diving plumes” because it is
  - highly soluble
  - does not sorb significantly
  - is often slow to biodegrade
- Consequently, MTBE will often migrate greater distances from a source than other LNAPL constituents such as BTEX



API Technical Bulletin

- **Roth, T. and E. Nichols 2006. Diving Plumes: Assessment, Significance, and Implications for Characterization and Monitoring. API Soil and Groundwater Technical Bulletin Number 24.**
- Describes the **phenomena** and its **significance**
- Provides **methods to assess** potential for and magnitude of diving plumes

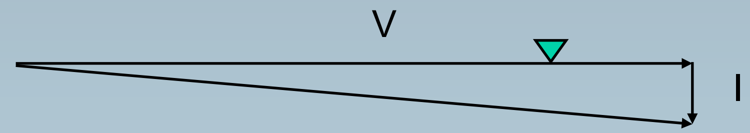
Available soon at **www.api.org/mtbe**



Methods to Assess Potential for and Magnitude of Diving Plumes

- **Analytical and Numerical Models**
- Field Characterization Techniques
- Geochemical Assessment

Screening model: *Ratio of Recharge Rate to Groundwater Discharge Rate*



The slope of plume dive can be estimated by: $$Slope = \frac{I}{V} = \frac{i}{q}$$

Where:

Slope = change in depth per change in horizontal distance, relative to the water table surface [m/m]

I = Accretion rate [m/yr]; recharge rate divided by porosity, where the recharge rate is the net annual recharge to groundwater in m/year

i = recharge rate [m/yr]

V = horizontal groundwater seepage velocity [m/yr]; the specific discharge divided by porosity

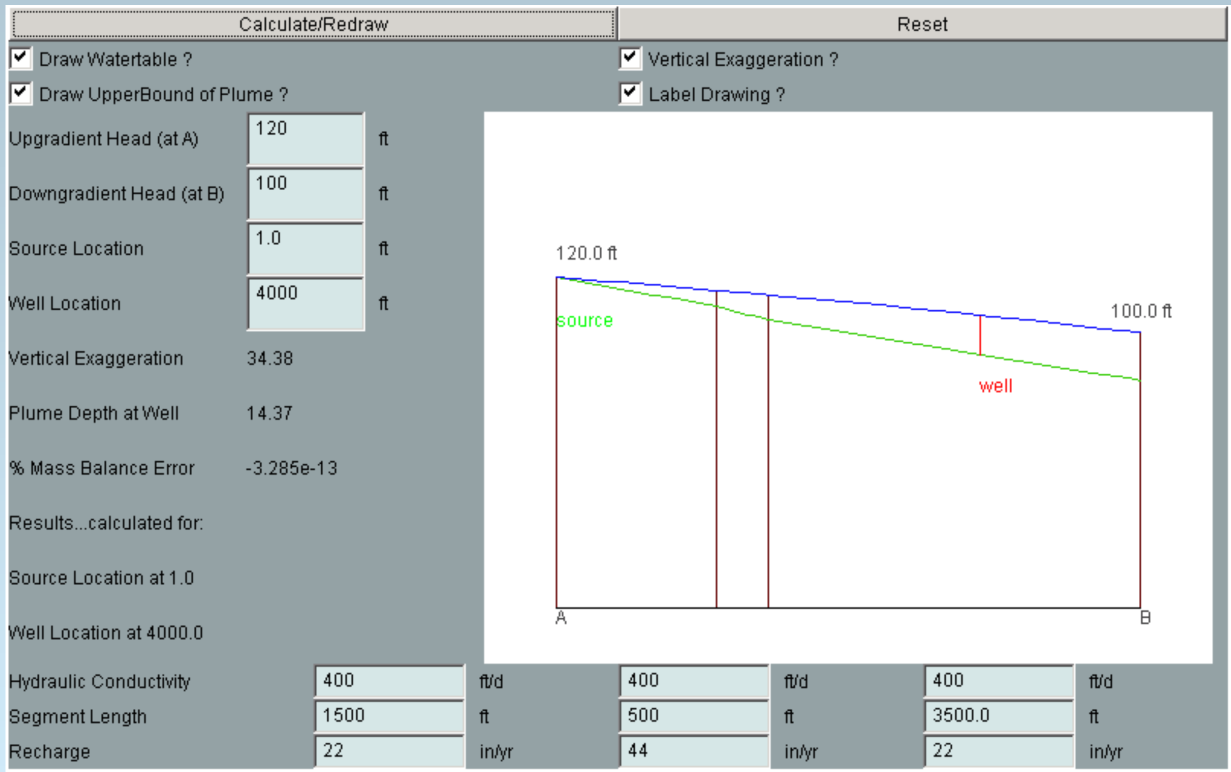
q = specific discharge, also known as Darcy velocity [m/yr]

Assumes:

– evenly distributed recharge
– homogeneous subsurface,
– aquifer is thick relative to the accumulation of recharge
– rate of plume dive is uniform

USEPA Plume Dive Calculator

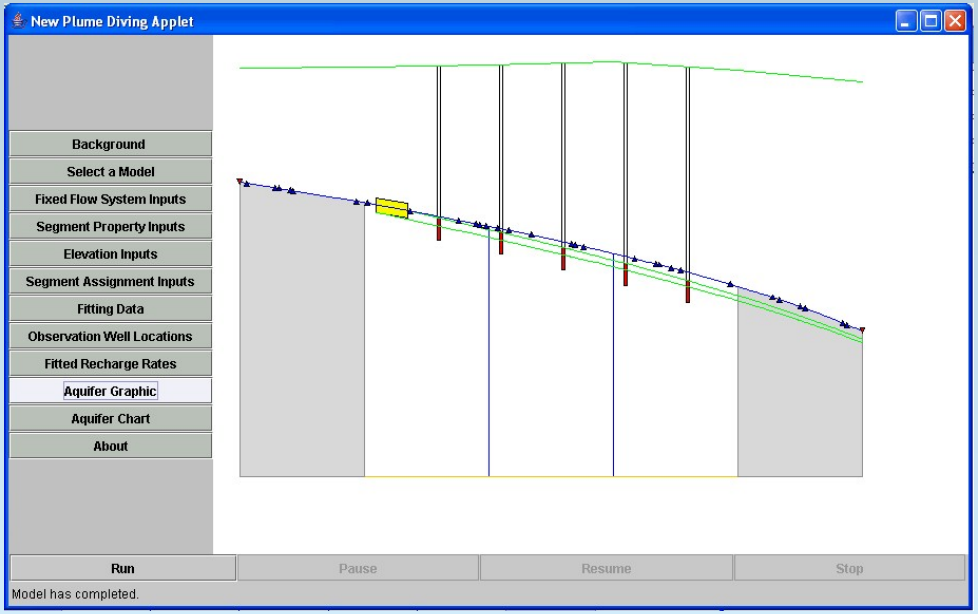
- Current version uses analytical solution of one-dimensional flow to simulate each portion of a segmented aquifer.
- http://www.epa.gov/athens/learn2model/part-two/onsite/diving.htm



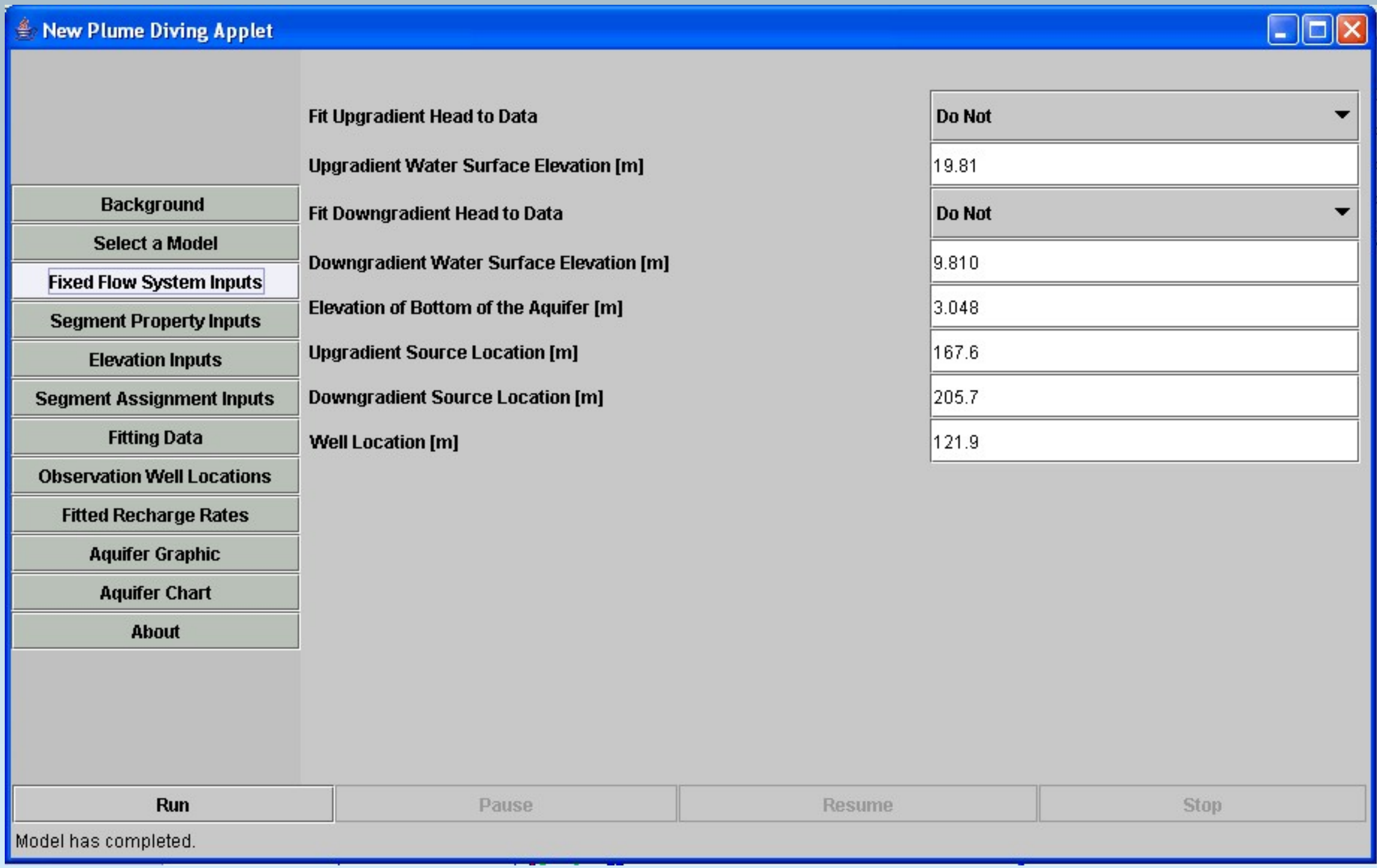
Courtesy of James W. Weaver and Vikenti M. Gorokhovski, U.S. EPA

New Version will be an On-Line Numerical Model

- Previous methods are highly sensitive to recharge rate
- Recharge rate is often uncertain
- New calculator can rely on measured water levels, rather than estimated recharge rates
- Recharge rates are estimated via numerical inversion

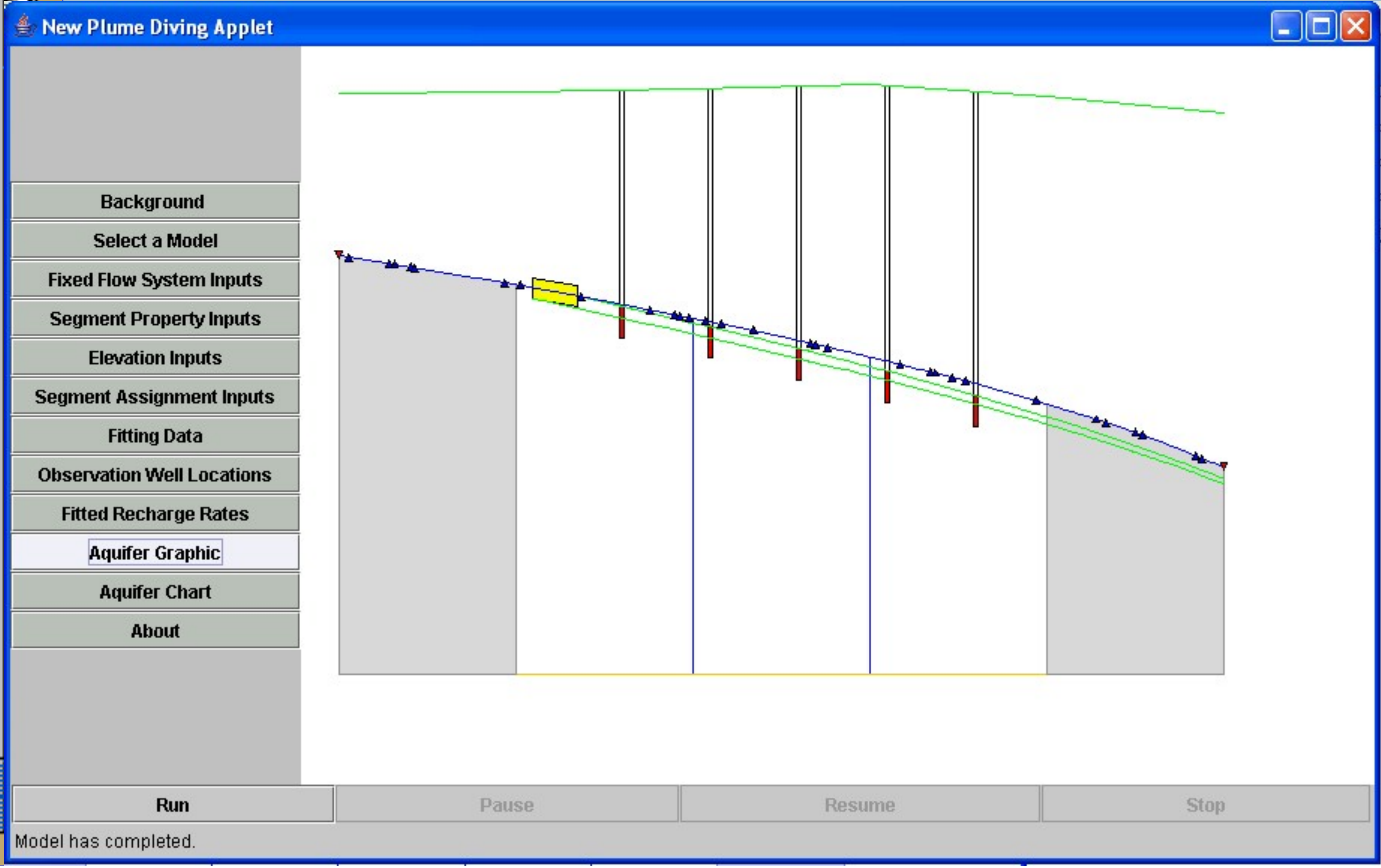


New, Improved Plume Dive Calculator

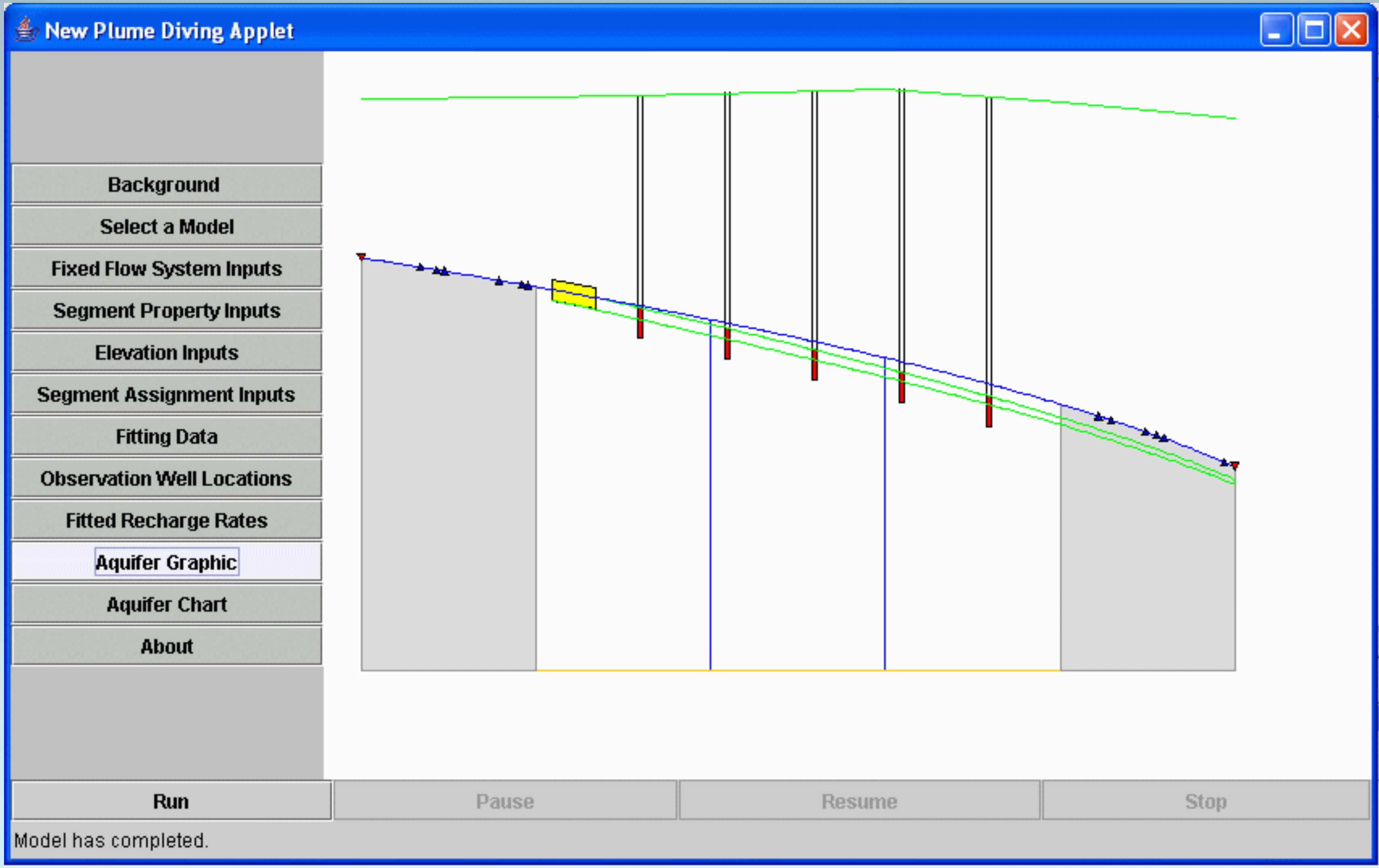


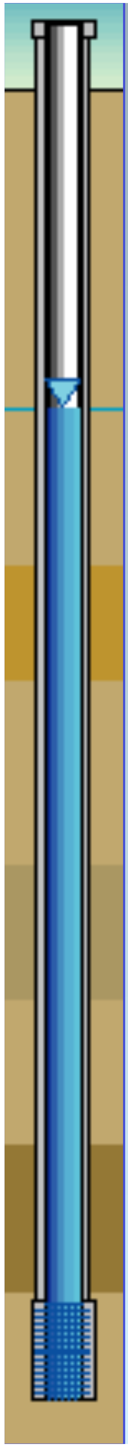
Courtesy of James W. Weaver and Vikenti M. Gorokhovski, U.S. EPA

An On-Line Numerical Model



Estimating Dive in Uncharacterized Segments





New MTBE/TBA Remediation Guidance Documents

Nouveaux Documents De Conseils De Remédiation de MTBE et de TBA

Remediation Guidance from the Interstate Technology and Regulatory Council

- Published in 2005: *Overview of Groundwater Remediation Technologies for MTBE and TBA*
- Release expected in mid-2006: *Overview of Source Zone Remediation Technologies for MTBE and TBA*

http://www.itrcweb.org

Interstate Technology and Regulatory Council

- State-led national coalition of personnel from environmental regulatory agencies
  - 40 states
  - DOD, DOE, EPA
  - Tribes
  - Public and industry stakeholders
- Devoted to reducing barriers to, and speeding interstate deployment of, better, more cost-effective, innovative environmental techniques

ITRC produces guidance documents and provides training

ITRC – Shaping the Future of Regulatory Acceptance

ITRC Internet and Other Training Courses

- MTBE and Other Fuel Oxygenates
- Natural Attenuation
- EISB (Enhanced In Situ Bioremediation)
- Permeable Reactive Barriers (basic and advanced)
- Diffusion Samplers
- Phytotechnologies
- ISCO (In Situ Chemical Oxidation)
- Constructed Treatment Wetlands
- Small Arms Firing Range Characterization and Remediation
- Systematic Approach to In Situ Bioremediation

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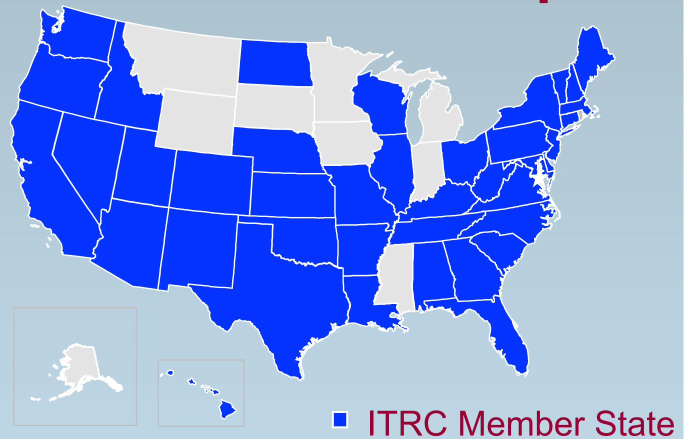
ITRC Membership

States



Federal Partners

DOE DOD EPA

Sponsors

ECOS WGA SSEB

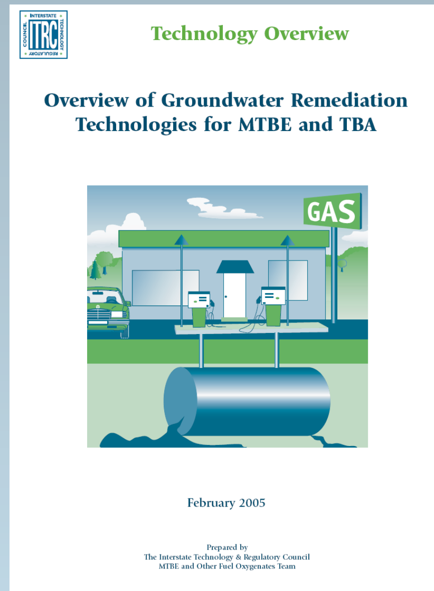
Industry, Academia, Consultants, Citizen Stakeholders

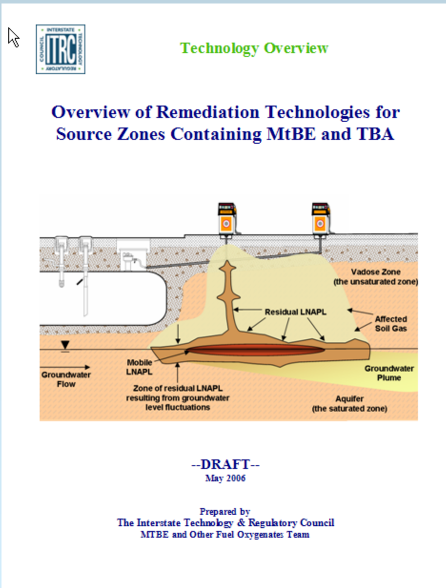
ITRC MTBE and Other Fuel Oxygenates Technical Team

- Current Activities:
  - Finalizing technical overview document "Overview of Source Zone Remediation Technologies for MTBE and TBA"
  - Providing training course "MTBE & TBA: Comprehensive Site Assessment and Successful Groundwater Remediation"

Technical Overview Documents

- 2005 document focuses on remediation of **groundwater**





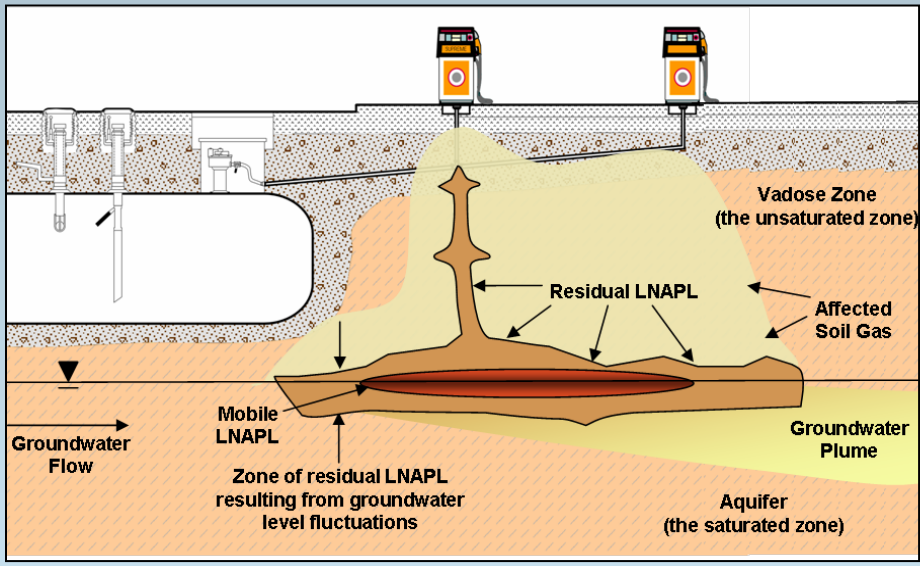
- 2006 document will focus on remediation of **source-zone** media (soil, soil gas, LNAPL)

Overview of Groundwater Remediation Technologies for MTBE and TBA (ITRC, 2005)

- Includes Summaries of:
  - Physical, Chemical and Biological Processes
  - Sample Preservation and Analytical Methods
  - Site Evaluation and Cleanup Requirements
- Detailed Descriptions of Treatment Methods:
  - Groundwater Extraction and Ex-Situ Treatment
  - Air Sparging
  - In-Situ Bioremediation
  - Chemical Oxidation
  - Phytoremediation
  - Monitored Natural Attenuation
- Cost Comparison Summary

Overview of Source Zone Remediation Technologies for MTBE and TBA (ITRC, *in prep.*)

- **Source Zone Considerations**
  - Types of Releases and Source Zones
  - Source Zone Characterization
  - Considerations for Remedy Selection
  - Performance Monitoring



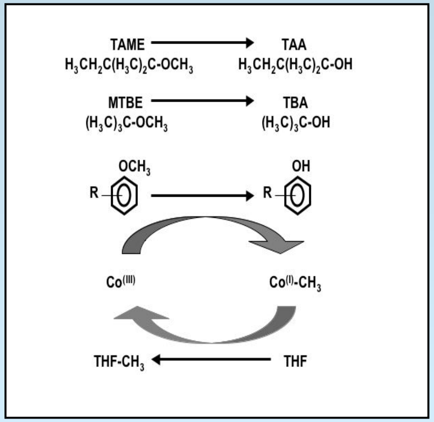
- **Remedial Technologies**
  - Excavation
  - Multi-Phase Extraction
  - Soil Vapor Extraction
  - Air Sparging
  - Enhancements to Air Sparging and Soil Vapor Extraction
  - In-Situ Chemical Oxidation
  - In Situ Bioremediation

What's New in the Source Zone Remediation Document

- Classifies release mechanisms and resulting source zones
- Considers recent research on the significance of small releases at operating UST systems
- Summarizes current understanding of source-zone MTBE and TBA attenuation processes
- Provides extensive information on biodegradation processes

RELEASE CLASSIFICATION	RELEASE CHARACTERISTICS		
	Duration	Rate of Mass Release	Total Mass Released
Acute	Short Term	Low to Moderate	Small
Chronic	Long Term	Low	Small to Large
Catastrophic	Short Term	High	Large

Release Classification Matrix



Training Courses

- Previous courses:
  - New Hampshire October 2003
  - New York December 2003
  - New Jersey May 2004
  - Colorado December 2004
  - Denmark May 2005
  - Leipzig June 2005
  - California August 2005
  - Nevada March 2006

References

- **Mass Flux**
  - Einarson, M., D. Mackay, N. de Sieyes, L. Jacobson, M. Noske, and L. Justice 2005. *Evaluation of Point Measurement and Pumping Techniques for Calculating Contaminant Mass Flux at a Nonsteady State MTBE Plume in California*. NGWA Ground Water Summit, San Antonio, Texas. April 20.
  - Einarson, M. and D. Mackay, 2001. *Predicting the Impacts of Groundwater Contamination*, Env. Sci. Technol., 35(3): 67A:73A.
  - Farhat, S.K., C.J. Newell, E.M. Nichols, and E.S.K. Becvar. *In preparation*. Mass Flux Toolkit To Evaluate Groundwater Impacts, Attenuation, and Remediation Alternatives. User's Manual, Version 1.0.
  - Nichols, E. and T. Roth. 2004. Flux Redux: Using Mass Flux to Improve Cleanup Decisions. L.U.S.T. Line, New England Interstate Water Pollution Control Commission, Lowell MA. Bulletin 46, March. http://www.neiwpcc.org/lustline.htm.
  - Ptak, T. and G. Teutsch. 2005. *An Integral Mass Flux Based Cyclic Approach for the Quantification and Remediation of Subsurface Contamination*. NGWA Ground Water Summit, San Antonio, Texas. April 20.
- **Diving Plumes**
  - Acree, S., J.T. Wilson and G. Alvarez. 2003. Predicting Diving Plume Behavior. *In* Proceedings of the NGWA Focus Conference On MTBE: Assessment, Remediation and Public Policy; National Ground Water Association, June 5-6, 2003, Baltimore; p. 171-172.
  - Alvarez, G. 2003. "Predicting Diving MTBE Plume Behavior" Presentation at the National Ground Water Association Conference on MTBE: Assessment, Remediation, and Public Policy, Baltimore, Maryland. June 5-6.
  - American Petroleum Institute (API). 2000. Strategies for Characterizing Subsurface Releases of Gasoline Containing MTBE, Health and Environmental Sciences Department, API Publication Number 4699. Prepared by E.M. Nichols, M.D. Einarson, and S.C. Beadle for API, Washington, D.C. February 15. http://www.api.org/mtbe.
  - Roth, T. and E. Nichols. 2006. Diving Plumes: Assessment, Significance, and Implications for Characterization and Monitoring. API Soil and Groundwater Technical Bulletin Number 24.
  - Weaver, James W., 2004, On-line Tools for Assessing Petroleum Releases, United States Environmental Protection Agency, Washington, D.C., EPA 600/R-04/101.
  - Weaver, J.W. and J.T. Wilson, 2000, Diving Plumes, L.U.S.T.Line, New England Interstate Water Pollution Control Commission, 36(12-15).
  - Weaver, J.W, J.T. Haas, and J.T. Wilson, 1996, Analysis of the gasoline spill at East Patchogue, New York, Proceedings of Non-Aqueous Phase Liquids (NAPLs) in Subsurface Environment: Assessment and Remediation, ed. L. Reddi, American Society of Civil Engineers, Washington, D.C., November 12-14, pp. 707-718.
  - Wilson, J.T., R. Ross, and S. Acree, 2005, Using Direct-Push Tools to Map Hydrostratigraphy and Predict MTBE Plume Diving, Ground Water Monitoring and Remediation, 25(3), 93–102.
- **Cleanup Guidance**
  - ITRC MTBE-1. 2005. Overview of Groundwater Remediation Technologies for MTBE and TBA. Interstate Technology and Regulatory Council, (ITRC) a committee of the Environmental Council of States. www.itrcweb.org.
  - ITRC MTBE-2. *in draft*. Overview of Remediation Technologies for Source Zones Containing MTBE and TBA. Interstate Technology and Regulatory Council, (ITRC) a committee of the Environmental Council of States. www.itrcweb.org.