Addressing the Challenges…

Large and Dilute Plumes of Chlorinated Solvents – Challenges and Opportunities

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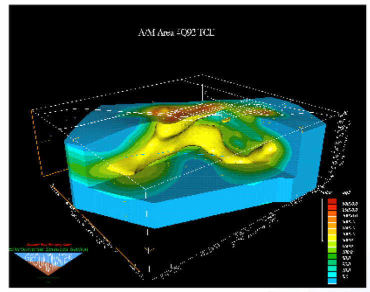


Clu-In Webinar

May 2013

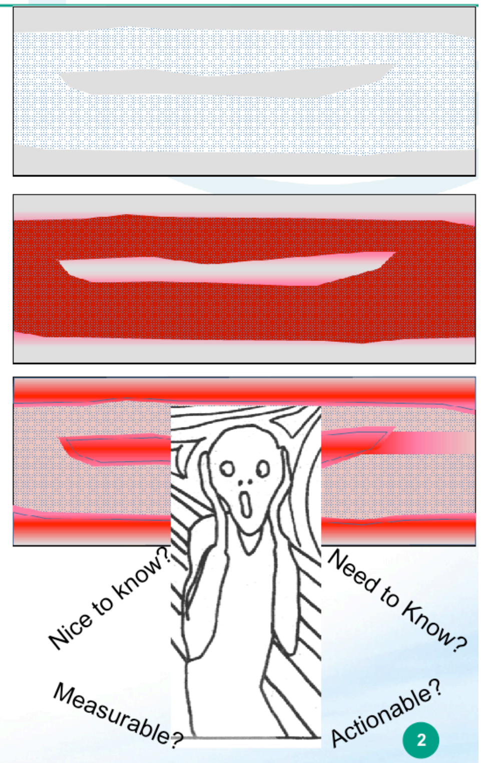
If mass transfer is the final challenge

Interface targeted reagents

- For sites where mass transfer limited flux/ release is maintaining concentrations above final RAOs, focus on the problem (interfaces)
- Consider deployment strategies, density viscosity, etc. for in situ design to limit flux

Work from what is known

- Make sure characterization data are actionable
- Select and build remediation systems that are robust to site conditions
- Do not be paralyzed by the many things you do not know



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An example "Large and Dilute Plume" – A/M Area of SRS

video

Attenuation Processes in Large Dilute (Aerobic) Plumes

- Degradation?
- "Dispersion?"
- Sorption?

2005 on…

- Parametric analysis to evaluate the relative importance of different attenuation processes (collaboration with Frank Chappelle)
- Lessons from REMchlor (journal articles and collaboration with Ron Falta and Chuck Newell)

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General Approach….

A parametric study is a mathematical exercise. Start simple and then add on additional factors to figure out what is important under different conditions….

$x = \frac{v_s}{R} t = v_c t$ & $(C/C_0) = e^{-\lambda t}$

plug flow w/ sorption — degradation

$$x = \frac{v_s}{R\lambda}\ln\left(\frac{C}{C_0}\right) = -L_\lambda \ln\left(\frac{C}{C_0}\right)$$

steady state plume

Full plume differential equation

$$R\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + \alpha_L\frac{\partial^2 C}{\partial x^2} + \alpha_T\frac{\partial^2 C}{\partial y^2} + \alpha_Z\frac{\partial^2 C}{\partial z^2} - \lambda C$$

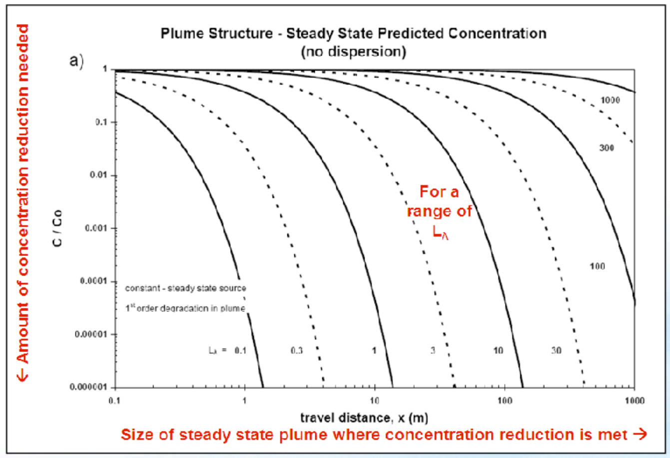
Assume steady state, neglect dispersion

$$0 = -v\frac{\partial C}{\partial x} - \lambda C \qquad \frac{dC}{dx} = -\lambda/v\, C$$

$$at\ x = 0,\quad C = C_0$$

Solution

$$\ln\frac{C}{C_0} = \frac{-\lambda x}{v}$$



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What does the math tell us…

The magnitude of concentration reduction needed is a key determinant of maximum plume size and the timeframe of plume cleanup

The rates of attenuation processes in the plume strongly impacts the ultimate size of the plume

Confirmed EPA preference for degradation processes. Degradation is a dominant natural attenuation mechanism, but any mechanism (anaerobic, aerobic or abiotic) can contribute.

Source decay and source remediation can reduce plume size (but not as much as you might expect)

Sorption is not a dominant mechanism unless the source is very short lived (and is mathematically less important if the sorbed material is assumed to be not degrading)

Longitudinal dispersion is not an important attenuation mechanism and can increase plume length in some cases

Transverse dispersion can contribute to attenuation if there is a basis for the spreading – but only for large plumes > about 1000 m

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What does this math tell us…

For Large and Dilute Plumes the size and scale of the steady state plumes will be larger than anaerobic sites. Best case aerobic plumes (weak sources and half lives of about 10 years) will stabilize within 1,000m (less than 1 mile) and "worst case" aerobic plumes (strong sources and half lives of 30 years) will stabilize within about 5,000 to 10,000m (about 3 to 6 miles)

This is what we see in real-world plumes!

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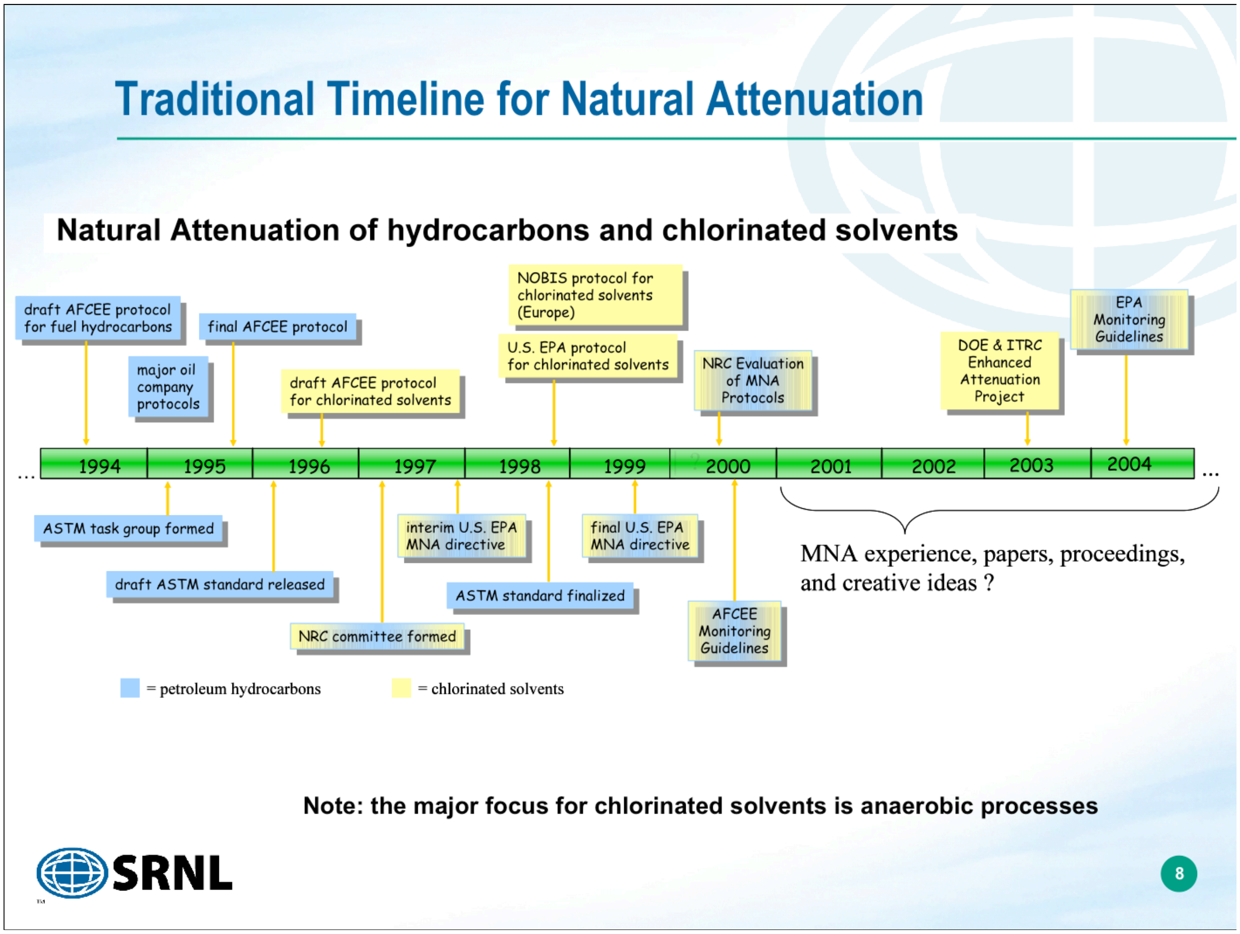
Traditional Timeline for Natural Attenuation
Natural Attenuation of hydrocarbons and chlorinated solvents
draft AFCEE protocol for fuel hydrocarbons
major oil company protocols
final AFCEE protocol
draft AFCEE protocol for chlorinated solvents
NOBIS protocol for chlorinated solvents (Europe)
U.S. EPA protocol for chlorinated solvents
NRC Evaluation of MNA Protocols
DOE & ITRC Enhanced Attenuation Project
EPA Monitoring Guidelines
... 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 ...
ASTM task group formed
draft ASTM standard released
NRC committee formed
interim U.S. EPA MNA directive
ASTM standard finalized
final U.S. EPA MNA directive
AFCEE Monitoring Guidelines
MNA experience, papers, proceedings, and creative ideas ?
= petroleum hydrocarbons
= chlorinated solvents
Note: the major focus for chlorinated solvents is anaerobic processes
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Dominant chlorinated solvent degradation mechanism(s) in aerobic aquifers based on recent literature

abiotic degradation with reactive mineral phases such as iron sulfides, magnetite (applicable to trichloroethene, carbon tetrachloride, etc.)

John Wilson et al. (EPA Laboratory Ada Oklahoma)

aerobic cometabolism (trichloroethene, etc.)

Hope Lee, et al (PNL Richland WA)

aerobic direct metabolism (dichloroethene, vinyl chloride, etc.)

Paul Bradley, et al. (USGS Columbia SC)

hydrolysis (carbon tetrachloride, etc.)

Peter Jeffers, et al. (SUNY-Cortland)

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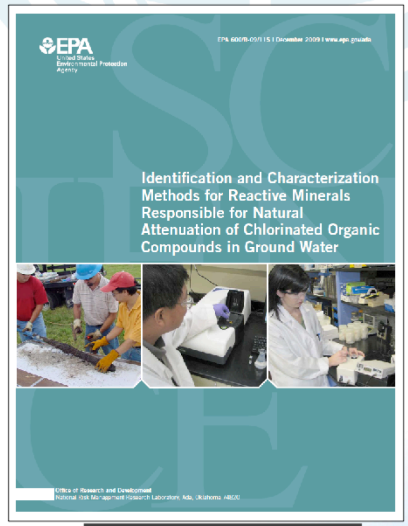
Abiotic Degradation – reactions dissolved plume with mineral phases

- Types of minerals
  - reactive iron(II) minerals such as pyrite, mackinawite (sulfides), Siderite (carbonate)
  - mixed iron(II) / iron(III) minerals such as magnetite, green rusts, and goethite
  - mixed iron(II) / titanium (IV) minerals such as ilmenite
- For several real sites, significant attenuation has been documented due to magnetite and rates have been correlated to inexpensive magnetic susceptibility measurements -- half lives of 3 to 6 years measured at sites with magnetite present



EPA 600/R-09/115

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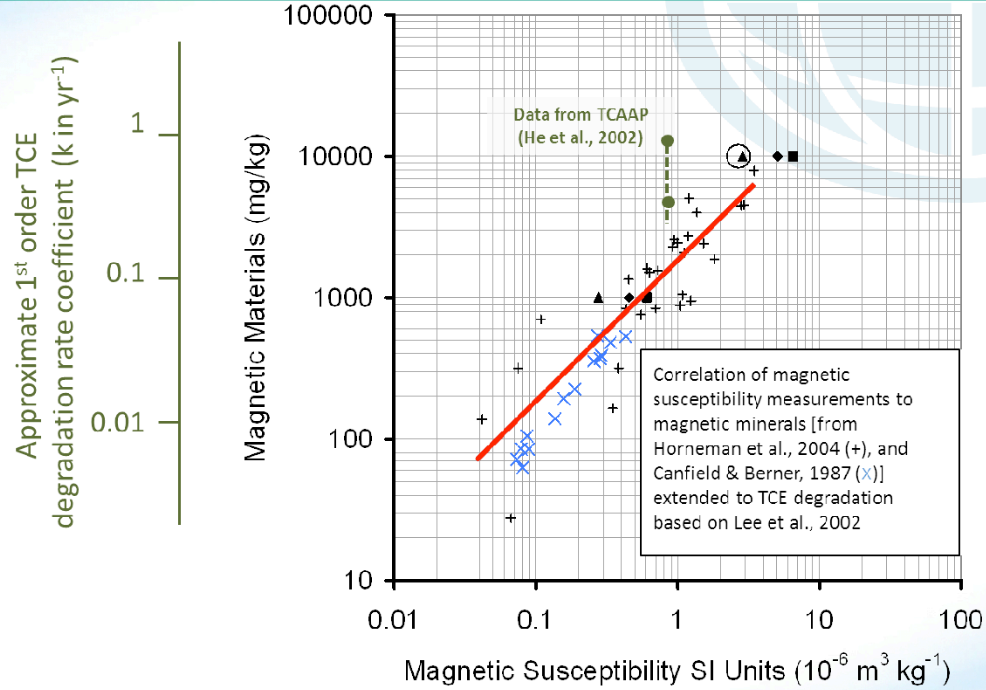
Preliminary data evaluation – developing a rule of thumb



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Order of Magnitude Impact of Abiotic Degradation

One approach to incorporate geochemical data into the models is to develop correlations that relate data/measurements to 1st order degradation coefficients

For example, the preliminary evaluation suggests that abiotic 1st order degradation coefficients can be estimated from reactive mineral content (e.g., mass content of reactive minerals such as magnetite) using the following approximation:

$$k \text{ in } yr^{-1} \cong (10^{-4})(\text{mg/Kg of reactive minerals})$$

For example, the approximate 1st order decay coefficient in an aquifer material containing 0.1% magnetite (1000 mg/Kg) would be in the range of 0.1 yr^{-1} (which is equivalent to a half life of about 7 years)

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Abiotic Degradation

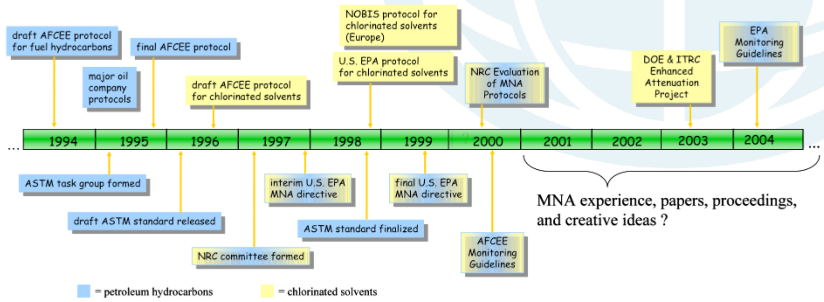
various reduced and mixed iron minerals participate

	Mineral	Key Elements and Oxidation States	
iron oxides	hematite	Fe(III)	Cr C
	magnetite	Fe(II) - 2 Fe(III)	Crystal Common or microb
	ilmenite	Fe(II) - Ti(IV)	Crystallin Common a and ign
	uvospinel	2 Fe(II) - Ti(IV)	Crystallin Common a
iron sulfides*	greigite	Fe(II) - 2 Fe(III)	Crystallin
	pyrrhotite and troilite	Fe(II/III)	Crys
	makinawite	predominantly Fe(II)	Crystall
	amorphous iron sulfide	Fe(II)	Noncrysta
	pyrite and marcasite	Fe(II)	C
	siderite	Fe(II)	Crystallin soluble
			Lay

	Mineral	Key Elements and Oxidation States	Description	Magnetic Properties	Recognized in EPA Guidance (He et al., 2009)	abiotic degradation potential (chlorinated solvents)	magnetic susceptibility / fractionation in proposed separation method
iron oxides	hematite	Fe(III)	Crystalline iron(III) oxide (Fe_2O_3). Common oxidized iron mineral.	nonmagnetic	--	o	"none" / heavy minerals
	magnetite	Fe(II) - 2 Fe(III)	Crystalline "spinel" iron(II,III) oxide (Fe_3O_4). Common mineral that can form either abiotically or microbially (sometimes observed in samples as "black sand" or "iron sand").	magnetic	✓	+	strong / ferromagnetic minerals
	ilmenite	Fe(II) - Ti(IV)	Crystalline "spinel" iron titanium oxide ($FeTiO_3$). Common accessory mineral found in metamorphic and igneous rocks and associated sediments.	weakly magnetic	--	+	weak / heavy minerals
	uvospinel	2 Fe(II) - Ti(IV)	Crystalline "spinel" iron titanium oxide (Fe_2TiO_4). Common accessory mineral found in metamorphic and igneous rocks.	weakly magnetic to diamagnetic	--	+	weak / heavy minerals
iron sulfides*	greigite	Fe(II) - 2 Fe(III)	Crystalline "spinel" iron(II,III) sulfide (Fe_3S_4) akin to magnetite.	weakly magnetic	✓	+	weak / heavy minerals
	pyrrhotite and troilite	Fe(II/III)	Crystalline iron sulfide mineral ($Fe_{1-x}S$)	weakly magnetic to nonmagnetic	✓	+	weak / heavy minerals
	makinawite	predominantly Fe(II)	Crystalline iron(II,III) sulfide mineral ($Fe_{1+x}S$).	not magnetic	✓	+	"none" / heavy minerals
	amorphous iron sulfide	Fe(II)	Noncrystalline iron(II) precipitate or mineral (FeS)	not magnetic	✓	+	"none" / heavy minerals
	pyrite and marcasite	Fe(II)	Crystalline iron(II) sulfide (FeS_2)	diamagnetic	✓	+	"none" / heavy minerals
	siderite	Fe(II)	Crystalline iron(II) carbonate ($FeCO_3$). Relatively soluble - not a common accessory mineral in undisturbed aerobic materials.	not magnetic	✓	+	"none" / heavy minerals
	green rust	Fe(II)	Layered mixed valence iron mineral $(Fe^{2+}, Mg)_6 Fe_2^{3+}(OH)_8 \cdot 4H_2O$ reactive mineral. $Fe(OH)_2$ layers alternate with interlayers of anions (chloride, sulfate, or carbonate) and water molecules - not a common accessory mineral in undisturbed aerobic materials.	not magnetic	✓	+	"none" / heavy minerals
	goethite	Fe(III)	Crystalline iron(III) oxyhydroxide (FeOOH) with minimal inherent reactivity unless Fe(II) is sorbed to surface	not magnetic	✓	o	"none" / heavy minerals
	phyllosilicate clays and associated reduced metals	Fe(II/III)	layered mixed valence iron mineral with potential reactivity if they contain Fe(II) in the structure or sorbed to the surface	not magnetic	✓	+ / o	"none" / heavy minerals
✓	Identified in EPA guidance (He et al., 2009) and the scientific literature.						
--	not identified in EPA guidance (He et al., 2009) and the scientific literature.						
o	minimal / no reactivity						
+	= reactivity recognized in EPA guidance (He et al., 2009) and the scientific literature.						
+ (blue)	= suggested by data in EPA guidance (He et al., 2009) and the scientific literature.						
*	= for all sulfides: May form abiotically by hydrothermal processes and/or biotically by magnetotactic and sulfate reducing bacteria under reducing conditions in fine grained river sediments. These minerals may be less common than the oxides in the geologic conditions typical of large aerobic plumes.						
	These mineral phases may be less prevalent in the geologic materials characteristic of large aerobic groundwater plumes/systems but may be present in the vicinity of redox based treatment systems (e.g., mulch wells, iron wells and electron donor additions) and in aquitards and clay lenses.						

Aerobic Cometabolism Research Pre-Dates Traditional MNA Timeline

Natural Attenuation of hydrocarbons and chlorinated solvents



Aerobic Cometabolism

Wilson, J.T., and Wilson, B.H., 1985, Biotransformation of trichloroethylene in soil: Applied and Environmental Microbiology, v. 49, no. 1, p. 242-243.

McCarty, Semprini, Hazen, Alvarez-Cohen, Fries, …   Lee, Wymore, Looney, …

no toxic daughter products accumulate, maintains high aesthetic water quality…

So why did virtually all natural attenuation and bioremediation research for chlorinated solvents shift to anaerobic? (aerobic slow, indirect process -- active bioremediation difficult to design and not sustainable using typical hydrocarbon reagents…)

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Cometabolism for Chlorinated Solvents

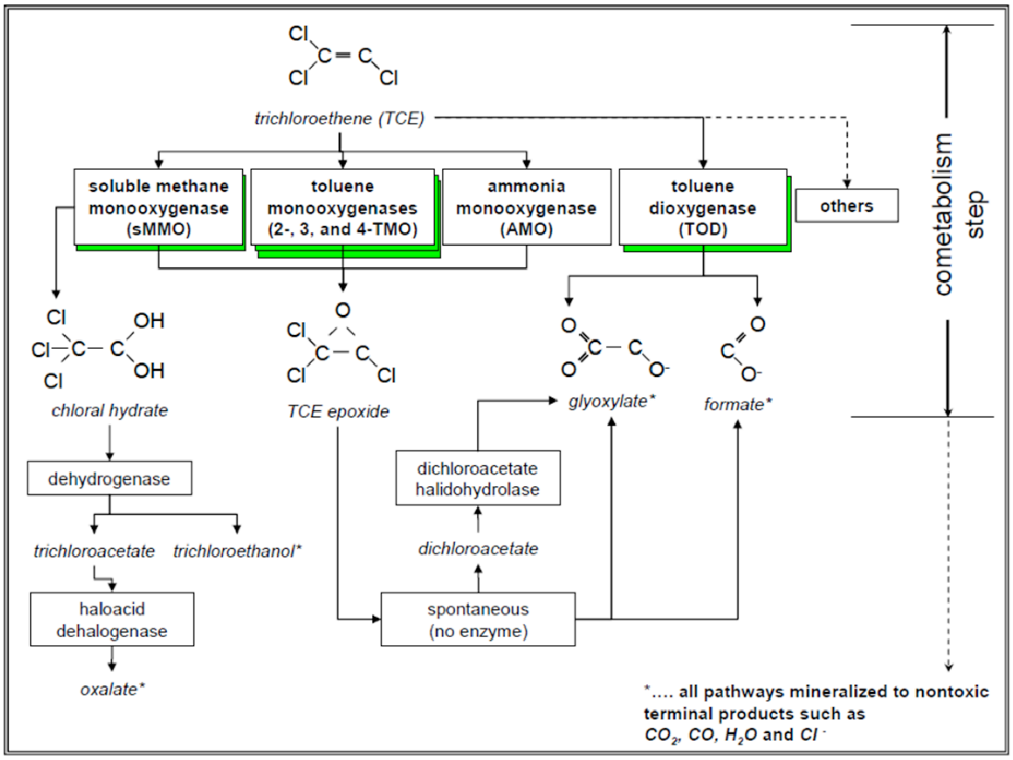

Figure 4. Some of the cometabolic pathways for TCE

(this figure represents a compilation of pathways documented in the University of Minnesota Biocatalysis/Biodegradation Database, http://umbbd.msi.umn.edu/)

EAP assays available for the highlighted items

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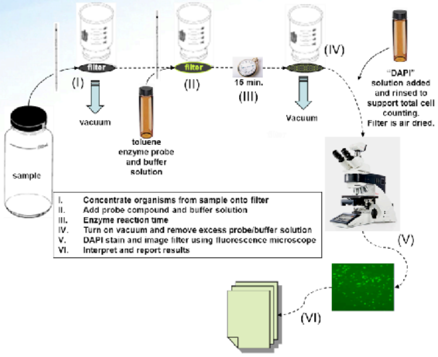
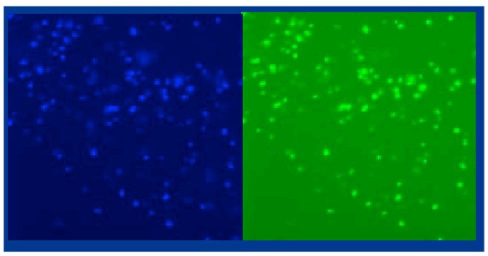
Evidence for cometabolic degradation of chlorinated solvents

Enzyme Activity Probes (Hope Lee)





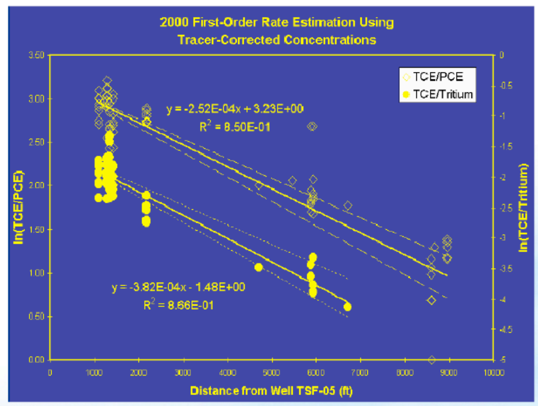
qPCR (targeted DNA)

Table 2. Cultured organisms, oxygenase genes to be targeted, and select qPCR target primers.

Organism	Oxygenase of Interest	qPCR Primers
Pseudomonas putida F1	toluene 2,3 dioxygenase	TOD
P. f lourescens CFS215	toluene 2,3 dioxygenase	TOD
Pseudomonas mendocina KR1	toluene 4-monooxygenase	TMO, RMO, PHE
Ralstonia pickettii PKO1	toluene 3-monooxygenase	XYL, RMO, PHE
Burkholderia cepacia G4	toluene 2-monooxygenase	PHE
Pseudomonas putida mt-2	toluene side chain monooxygenase	TOL
Methylosinustrichosporium OB3b	soluble & particulate methane monooxygenase	mmoX, pmoA
Mycobacterium vaccae JOB-5	propane monooxygenase	alkB
Burkholderia cepacia E1	phenol hydroxylase or 2-monooxygenase	PHE

. . .

Field data (INL)



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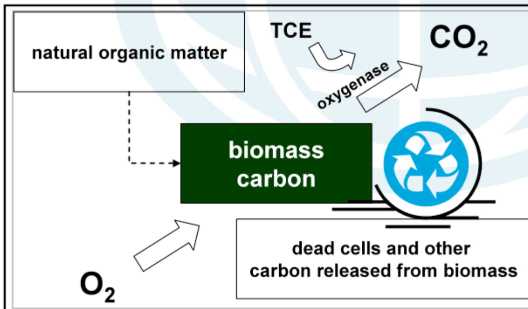
Summary of aerobic cometabolism research

- Half lives of about 10 to >40 years have been measured
- Based on current conceptual model the natural attenuation processes appear sustainable and are consistent with the expected microbial ecology of oligotrophic (nutrient limited) systems
- SRNL/INL/PNL team currently working on long-lived "natural organic carbon" amendment technology to sustainably enhance aerobic cometabolic rates in L&D settings



Conceptual "Microbial Ecology" Model: We have shown that oligotrophic aquifers typically have significant numbers of organisms that are producing cometabolic oxygenase enzymes – approximately 10^4 (10^3 to 10^5) cells per mL. Since recycle of carbon is not 100% efficient (i.e., O_2 to CO_2), slow oxidation of natural organic matter provides the organic carbon necessary to sustain the microbial communities. Aromatic-rich natural organic matter induces the expression of oxygenases that have been documented to cometabolize TCE and other solvents. For large aerobic plumes, understanding this and other aerobic degradation processes and rates is crucial to successful environmental management because it bounds the requirements for source and primary plume treatment needed and facilitates transition to natural attenuation.

hypothesis

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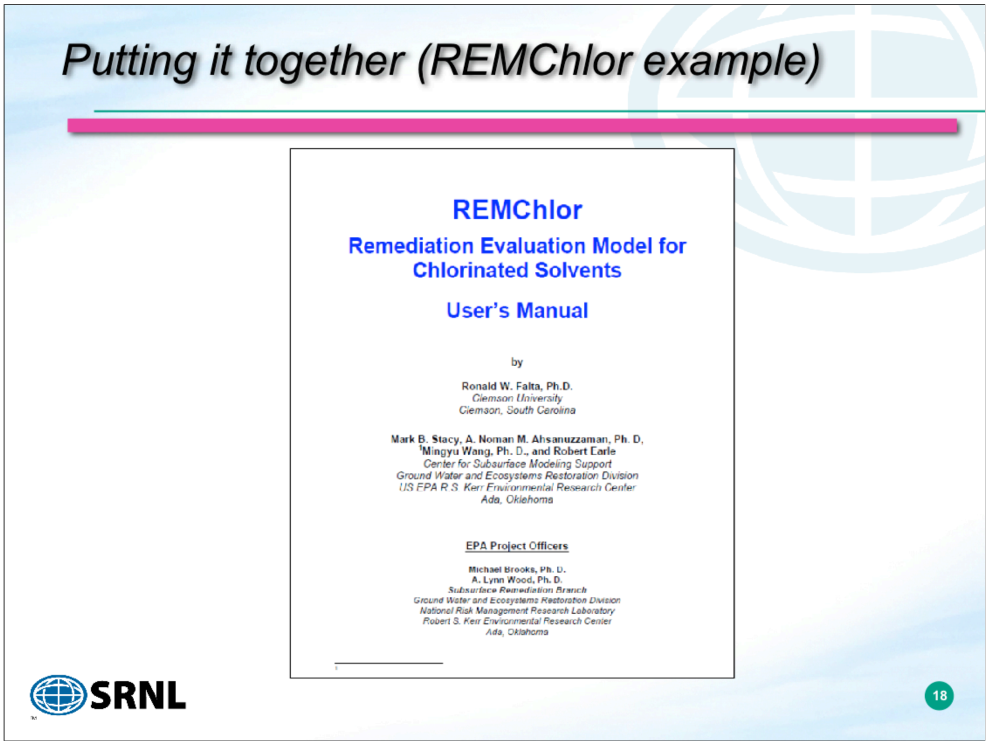

Putting it together (REMChlor example)
REMChlor
Remediation Evaluation Model for Chlorinated Solvents
User's Manual
by
Ronald W. Falta, Ph.D.
Clemson University
Clemson, South Carolina
Mark B. Stacy, A. Noman M. Ahsanuzzaman, Ph. D,
[1]Mingyu Wang, Ph. D., and Robert Earle
Center for Subsurface Modeling Support
Ground Water and Ecosystems Restoration Division
US EPA R.S. Kerr Environmental Research Center
Ada, Oklahoma
EPA Project Officers
Michael Brooks, Ph. D.
A. Lynn Wood, Ph. D.
Subsurface Remediation Branch
Ground Water and Ecosystems Restoration Division
National Risk Management Research Laboratory
Robert S. Kerr Environmental Research Center
Ada, Oklahoma
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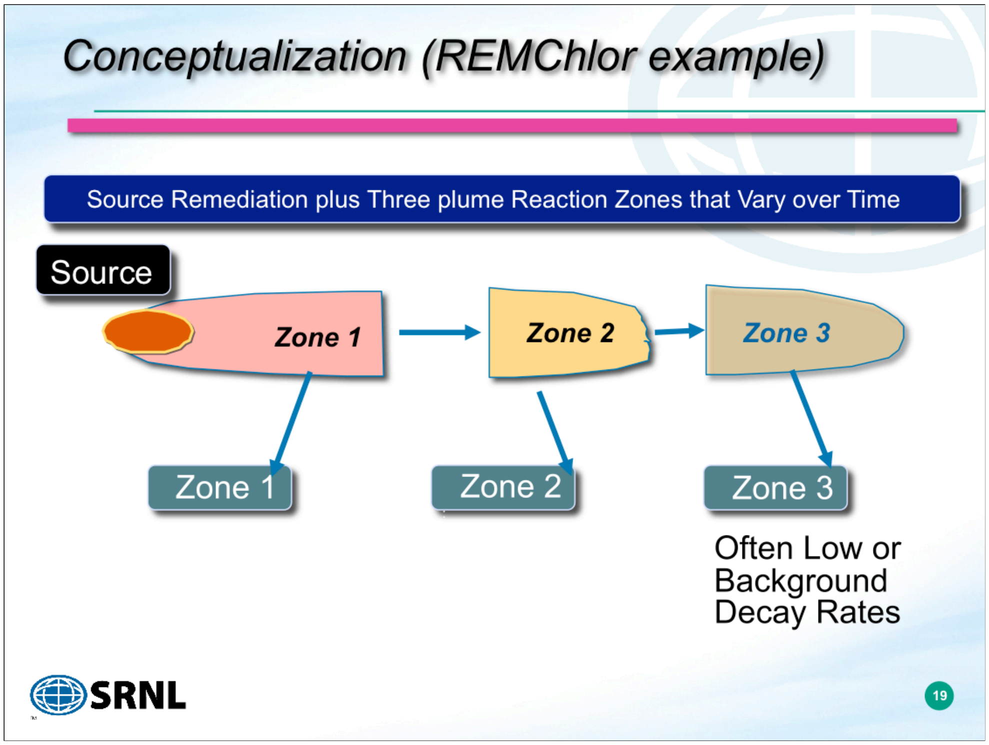
Conceptualization (REMChlor example)
Source Remediation plus Three plume Reaction Zones that Vary over Time
Source
Zone 1
Zone 2
Zone 3
Zone 1
Zone 2
Zone 3
Often Low or Background Decay Rates
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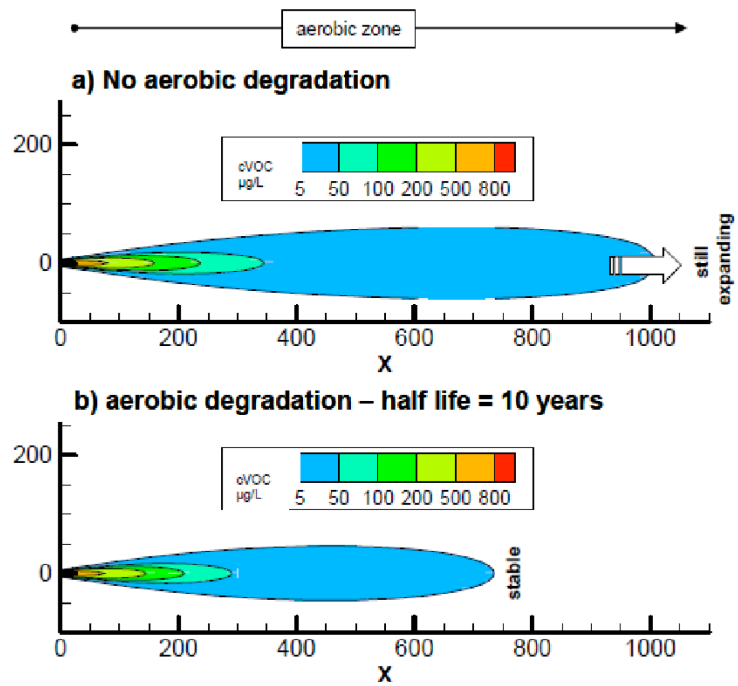
Simple example for natural attenuation

- 200 kg release
- Co = 1000 ug/L
- Pore velocity = 60 m/yr
- Anaerobic …0 to 20 m
- Remainder … aerobic

- A conservative assumption of no degradation in the aerobic zone results in plume expansion for approximately 60 years (plume length > 1000m)

- An assumed aerobic zone half life of 10 years stabilizes the plume earlier (plume length about 750m)



plume snapshots at 40 years

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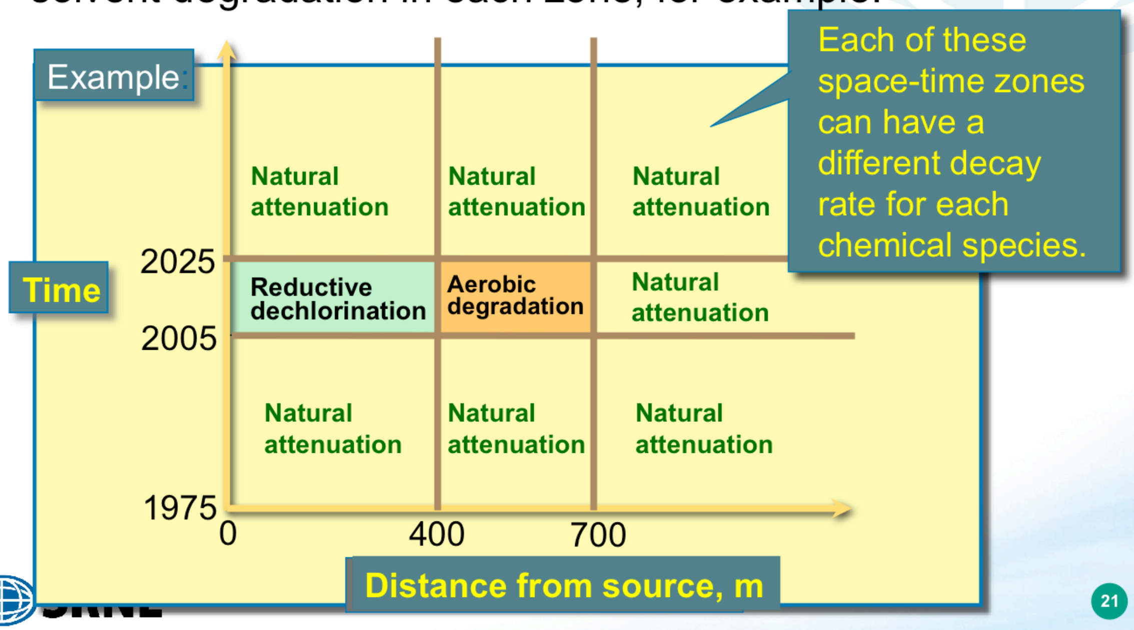
REMchlor "space-time structure"

Divide space and time into "reaction zones", solve the coupled parent-daughter reactions for chlorinated solvent degradation in each zone; for example:



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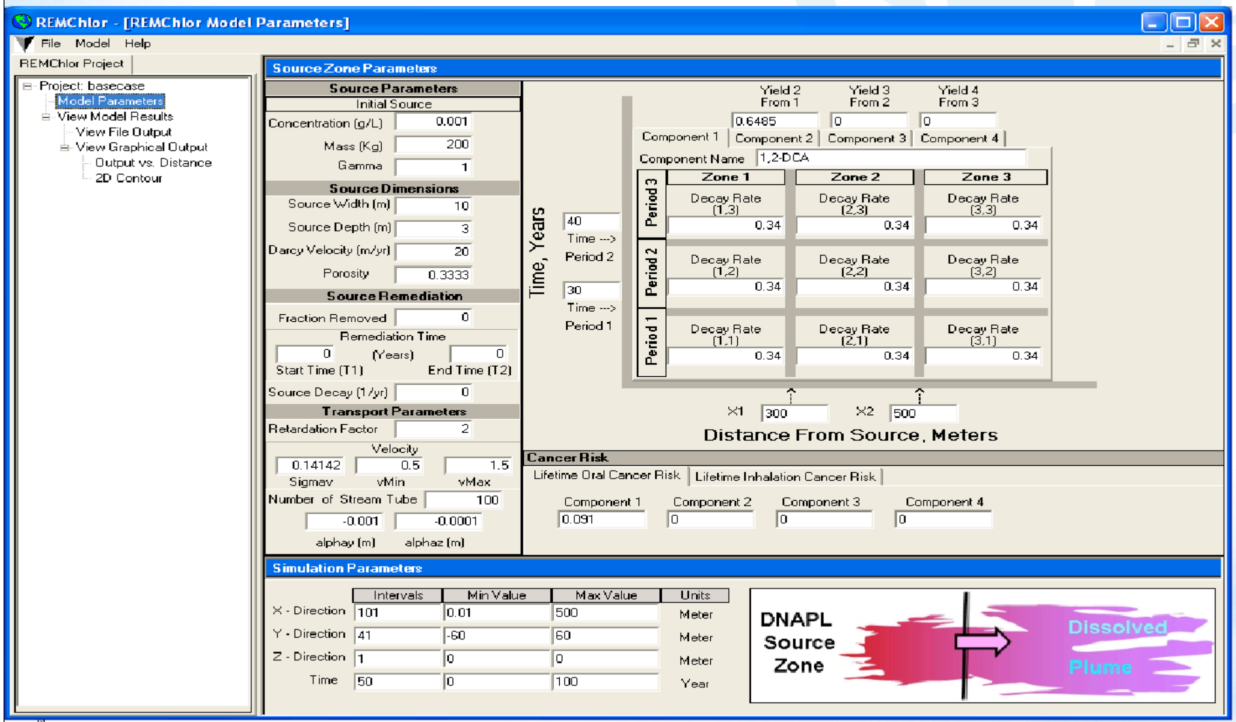
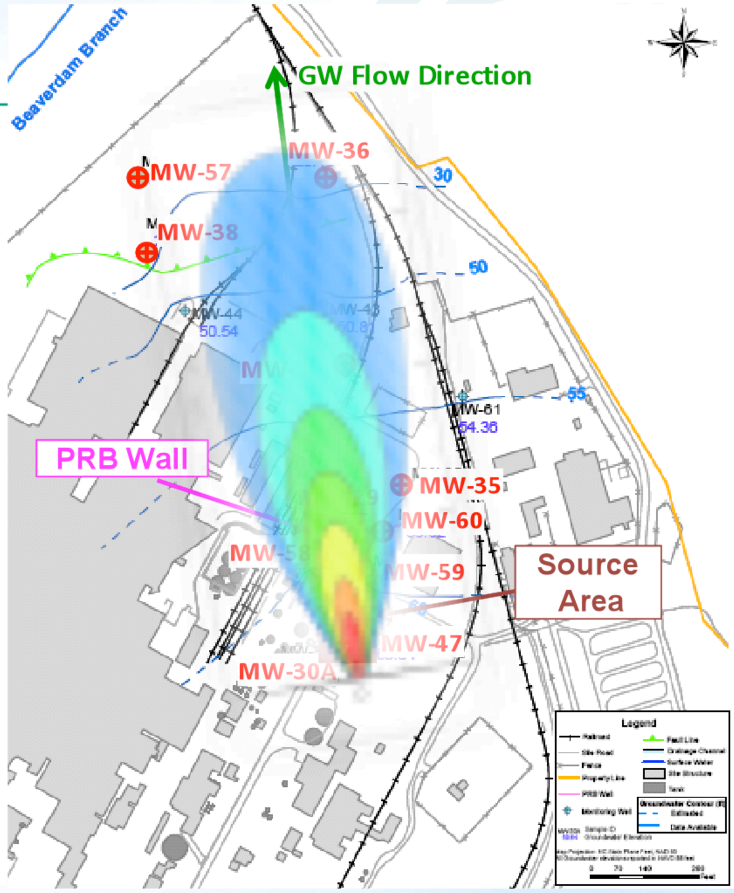
RemChlor Input Screen



Simulated TCE concentrations In 1999 prior to source remediation or PRB wall installation

Contours at 5, 20, 50,100, 200, 500, and 1000 ug/L



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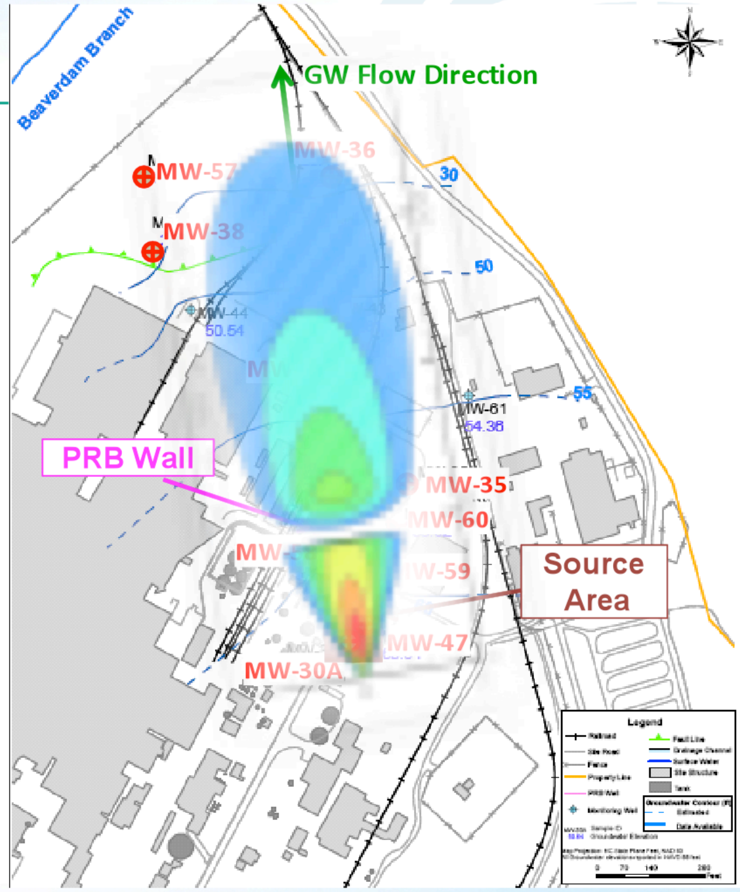
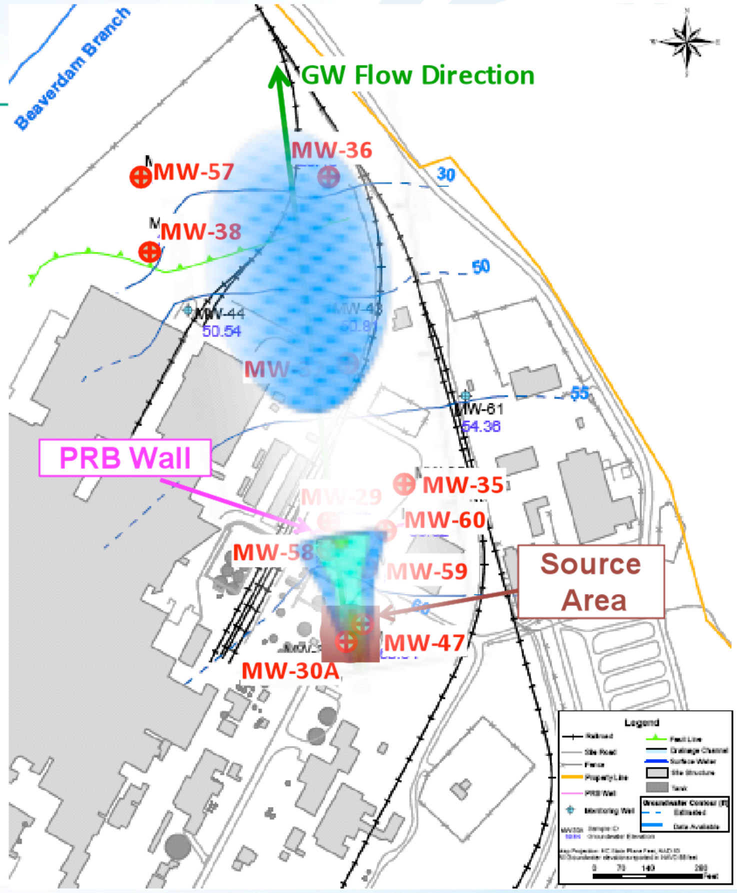
Simulated TCE concentrations In 2001, 2 years after source remediation and PRB wall installation

Contours at 5, 20, 50,100, 200, 500, and 1000 ug/L



Simulated TCE concentrations In 2009, 10 years after source remediation and PRB wall installation

Contours at 5, 20, 50,100, 200, 500, and 1000 ug/L



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Describing a plume's "space-time story"

REMChlor allows plume to develop for any number of years before remediation (Neat and important).

You can simulate three natural reaction.

You can simulate a source removal action

You can "remediate" all or part of the plume by increasing degradation rates for three specific time periods

The plume will respond to all of these factors:

natural attenuation processes
+ plume remediation
+ source decay
+ source remediation

EPA recently completed CLU-IN web based training covering REMChlor and REMFuel and the five modules are online

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Some trends in recent modeling results

The concentration reduction required to meet interim or final goals is linked to the amount of source removal needed

The solubility of the source DNAPL strongly impacts the remediation timeframe (e.g., timeframe for PCE >> TCE)

A 90% source reduction does not reduce plume size by 90% -- this type of reduction often has little effect on the ultimate size of the 5ppb contour but a relatively large impact on the 100ppb contour.

Modeling confirms the value of source remdiation (combined remedies) but effects on the distal portion of the plume requires time for the impacts to wash through – mass transfer will further extend timeframes

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Overarching Goal Setting Concepts (from the REMchlor workshops)

The goal of remediation is to protect human health and the environment to the extent practicable.

The ultimate objective is to restore the impacted resource and the services that the resource provides (ecological, drinking water, etc.)

A binary metric (pass-fail) for success may discourage clean-up

A variety of metrics for interim goals were explored -- mass flux is an example metric to link source treatment and plume impacts – new concepts such as the “Plume Magnitude Scale” are emerging – risk reduction – optimization functions – etc.

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Summary for Goal Setting

Interim source/mass balance objectives may be useful for DNAPL source treatments and tie into "combined remedy" constructs

"impacts on the 5 ppb contour are a weak metric for success of a source or central plume treatment"

"mass flux to the plume to a predetermined level may be a good interim metric"

"impacts on plume structure (e.g., the 100 ppb contour) are more diagnostic metrics of the success of source treatment"

Other regulatory and legal constructs may be needed (e.g., natural resource damage assessment) to effectively compensate for lost resources/services.

Need to apply realistic timeframes

Technical impracticability ? ☹

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Finishing up -- M Area Example from the DOE Savannah River Site

Quick facts:

2013 is the 30th anniversary of pump and treat at this site

15 years of soil vapor extraction

Thermal remediation (steam) of solvent storage tank and M Area Basin

Pilot testing of air sparging, cometabolic bioremediation, Electrical resistance heating, radio frequency heating, oxidants, etc.

Finish up with a quick final look at a real large dilute plume remediation

Start with an early mass balance model for source and plume remediation and compare to some current inventories

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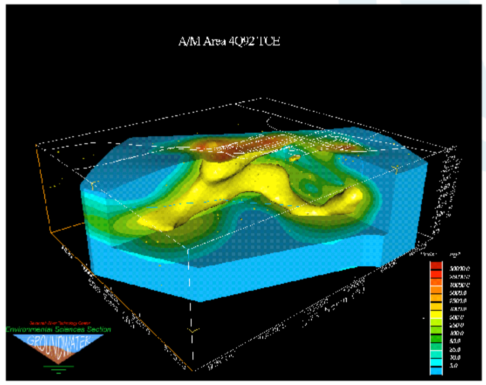
M Area – DOE Savannah River Site



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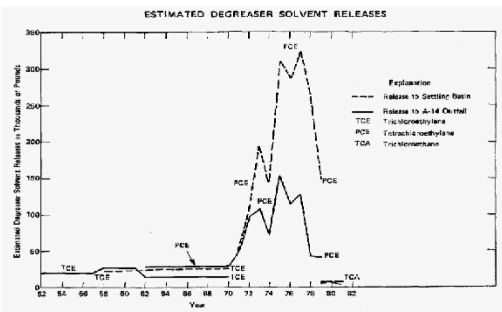
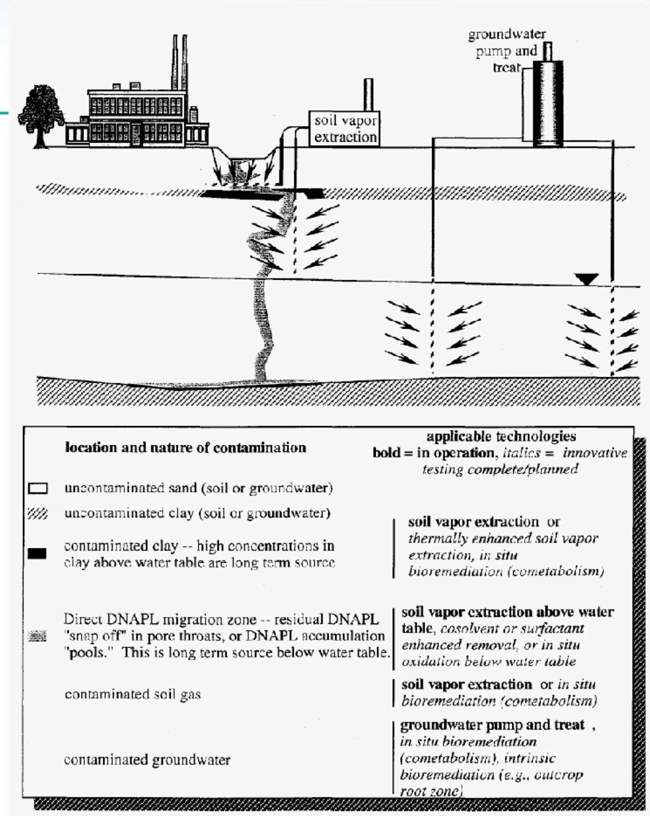
Early Mass Balance

$$M_{s,t} = \sum_{t=0}^{t}(inputs - outputs)$$
$$= \sum_{t=0}^{t}(M_R - (M_{SVE} + M_{P\&T}))$$

A simple 1st order equation was developed for each input and output and calibrated to about 9 years of remediation operation





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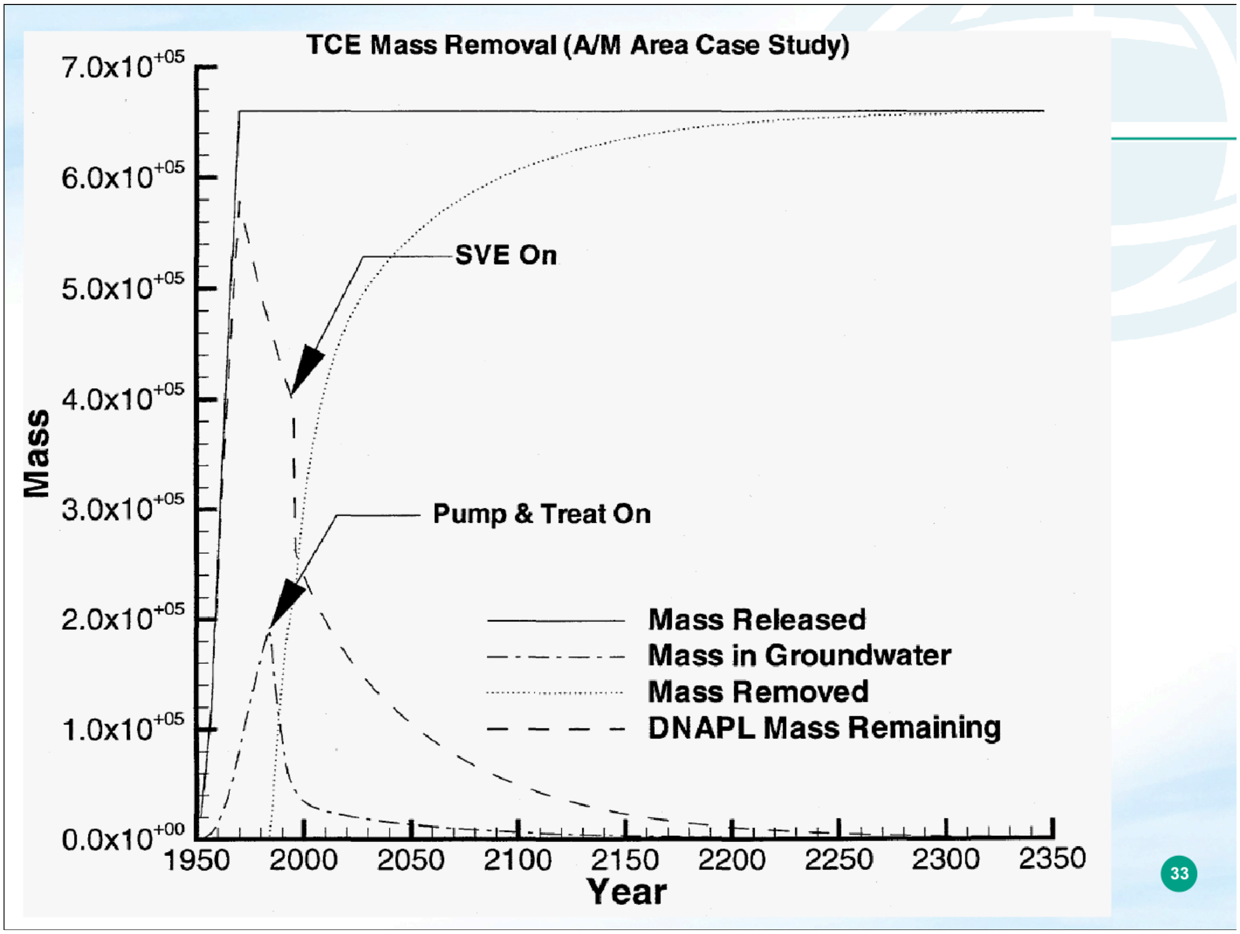
TCE Mass Removal (A/M Area Case Study)
Mass
7.0x10+05
6.0x10+05
5.0x10+05
4.0x10+05
3.0x10+05
2.0x10+05
1.0x10+05
0.0x10+00
1950
2000
2050
2100
2150
2200
2250
2300
2350
Year
SVE On
Pump & Treat On
Mass Released
Mass in Groundwater
Mass Removed
DNAPL Mass Remaining
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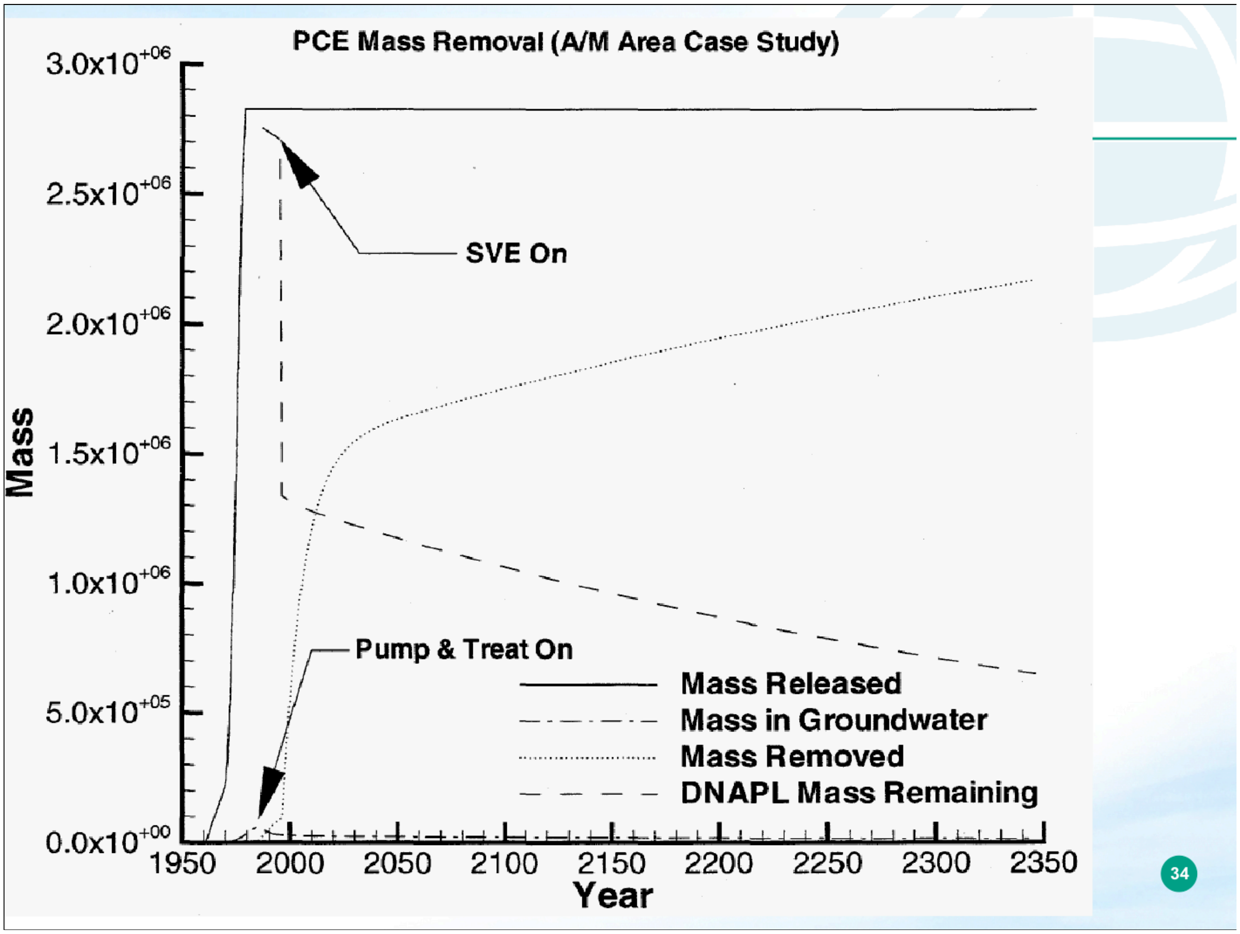
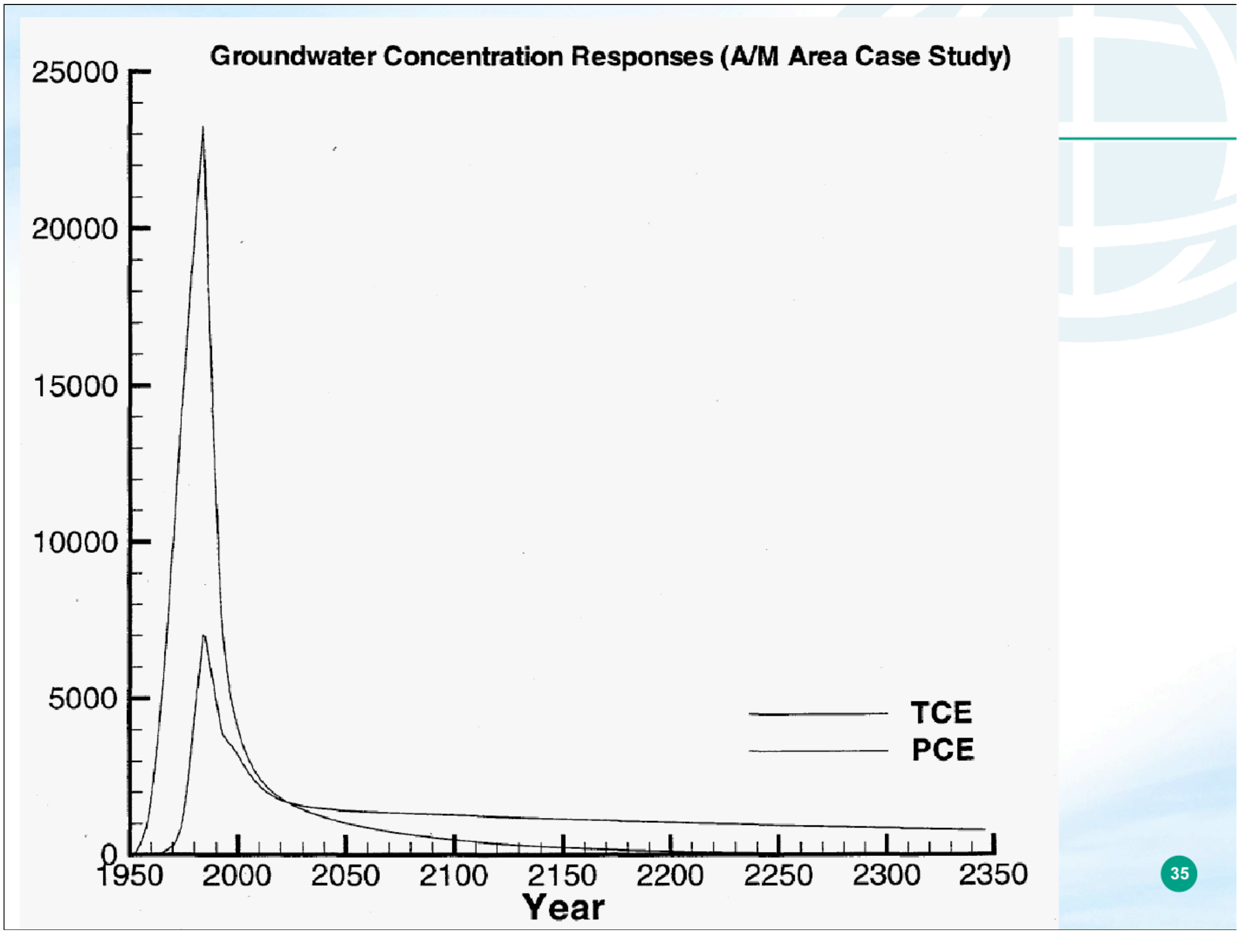


PCE Mass Removal (A/M Area Case Study)
Mass
Year
3.0x10+06
2.5x10+06
2.0x10+06
1.5x10+06
1.0x10+06
5.0x10+05
0.0x10+00
1950
2000
2050
2100
2150
2200
2250
2300
2350
SVE On
Pump & Treat On
Mass Released
Mass in Groundwater
Mass Removed
DNAPL Mass Remaining
34


Groundwater Concentration Responses (A/M Area Case Study)
25000
20000
15000
10000
5000
0
1950
2000
2050
2100
2150
2200
2250
2300
2350
Year
TCE
PCE
35

M Area totals

Dennis Jackson is currently preparing a paper on M Area (in honor of the 30th anniversary). Preliminary tally numbers…

	lbs	% removal based on total from active treatments	% removal based on total est. release of 3.5 million lbs
Pump and Treat	490000	33%	14%
Soil Vapor Extracton	448000	30%	13%
Field Testing	36000	2%	1%
Recirculation Wells	5700	0.40%	0.20%
Steam / Thermal	508163	34%	15%
Total from all active	1490000	100%	42%
MNA (40 yr half life)	1230000	na	35%
Grand Total	2717098	na	78%

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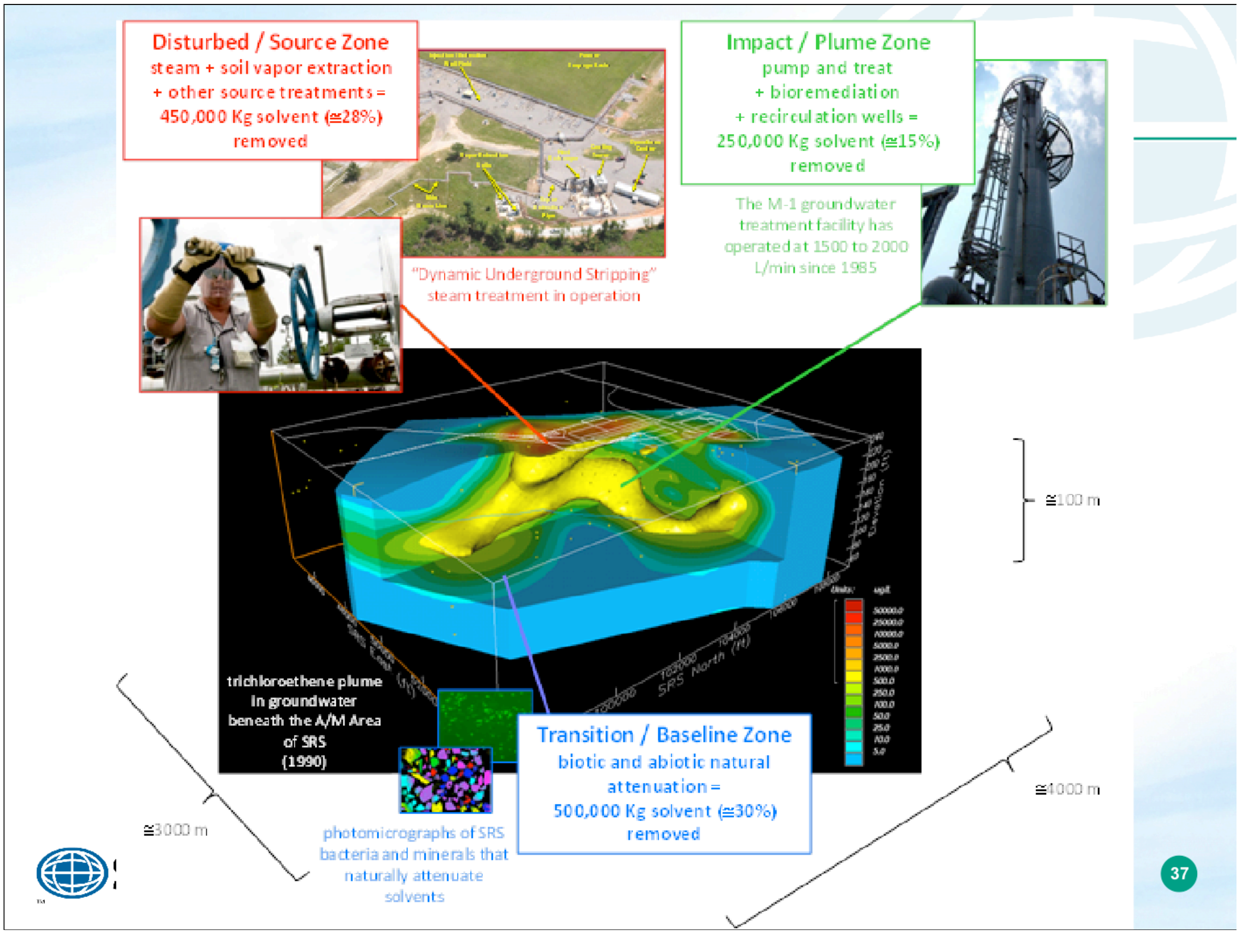
Disturbed / Source Zone
steam + soil vapor extraction
+ other source treatments =
450,000 Kg solvent (≅28%)
removed
"Dynamic Underground Stripping"
steam treatment in operation
Impact / Plume Zone
pump and treat
+ bioremediation
+ recirculation wells =
250,000 Kg solvent (≅15%)
removed
The M-1 groundwater
treatment facility has
operated at 1500 to 2000
L/min since 1985
≅100 m
trichloroethene plume
in groundwater
beneath the A/M Area
of SRS
(1990)
Transition / Baseline Zone
biotic and abiotic natural
attenuation =
500,000 Kg solvent (≅30%)
removed
photomicrographs of SRS
bacteria and minerals that
naturally attenuate
solvents
≅3000 m
≅4000 m
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Conclusions – Challenges

Large and Dilute!

Aerobic – relatively slow (“weak”) attenuation rates for chlorinated solvents

Deep

Persistent plumes with long tails due to mass transfer processes

Requires clean-up of source zones coupled with other actions and time

Any treatment must provide sustainable (long-lived) performance and be deployable to impact a large area for a reasonable cost

Treatments should avoid large scale adverse collateral impacts when possible

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Conclusions -- Opportunities

Remediation "successes" will:

- match technology and deployment to site specific conditions
- focus on actionable characterization data for a reasonable cost
- set technically-based, realistic and achievable goals
- link source treatment to desired impacts in the downgradient plume
- combine technologies as needed

Weak to moderate source strength, high permeability, presence of reduced iron minerals, presence of microorganisms that produce oxygenase enzymes, and other factors increase the potential for success in these challenging plumes

The is lots of emerging science: Abiotic processes may be "significant" at some/many sites; aerobic cometabolism occurring at most sites and rates appear to be related to microbial measurements

The breadth of work on remediation amendments may lead to attenuation enhancement materials that are viable for L&D conditions

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Questions and Discussion

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or
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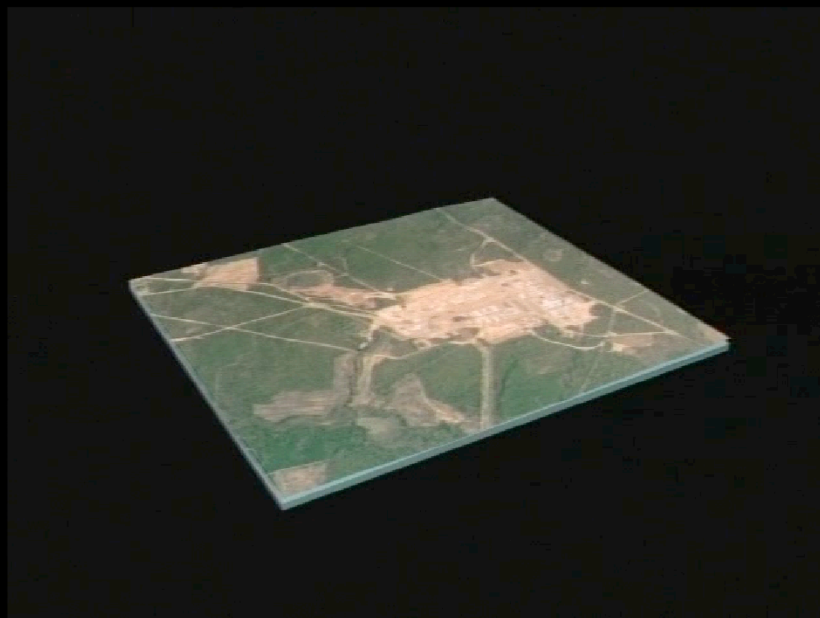
An example "Residual Source"
process sewer line at the A/M Area of SRS



video