Large and Dilute Plumes of Chlorinated Solvents –
Challenges and Opportunities

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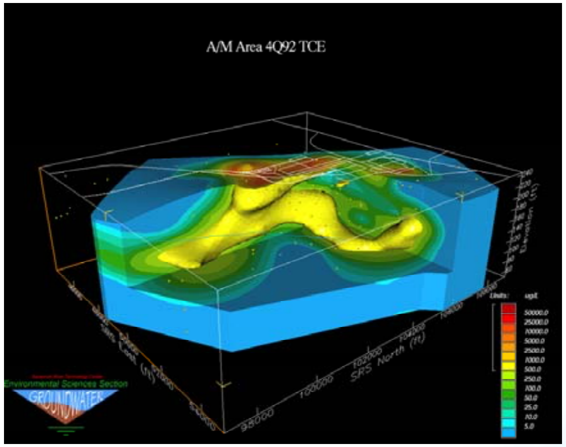

Federal Remediation Technologies Roundtable

Washington DC – June 2012

Informal Definition…

Large and Dilute (L&D) Plume:

A plume of relatively low concentration that extends over a large area – many L&D plume lengths measured in "km" or "miles"

A Key Perspective on L&D Plumes: SERDP Research Program

What conditions create L&D plumes?

Permeable aquifers, generally with low organic carbon contents and low biomass

Aerobic systems where influx of electron acceptors makes it difficult to establish and maintain reducing conditions

Attenuation processes are generally slow (e.g., degradation half-lives more than 1 to 2 years)

Often deep

Often affected by mass transfer in/out of less-transmissive compartments (clay/silt layers)

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L&D Plumes: SERDP Research Program (cont.)

So What's the Problem?

There is a desire to actively remediate

High costs and technical difficulties involved in treating large volumes of water and large areal footprint

Sometimes plumes are too deep for cost-effective interdiction or containment (hard to implement PRBs…)

Concentrations will exceed standards for a long time with or without treatment

Significant contaminant mass often present relatively inaccessible ("immobile") zones, resulting in "secondary sources" and persistent concentrations after primary source mass is removed

Large scale manipulation of the geochemical environment over an entire plume can be very difficult, expensive and undesirable

DOE Examples

M-Area – DOE Savannah River Site

- TCE, approximately 2 square miles and extending to 200 feet deep, initial source concentration → DNAPL

200 Area – DOE Hanford Site

- Carbon tetrachloride, approximately 3 square miles and extending to 350 feet deep, initial source concentration → DNAPL

Northwest Plume – DOE Paducah Gaseous Diffusion Plant

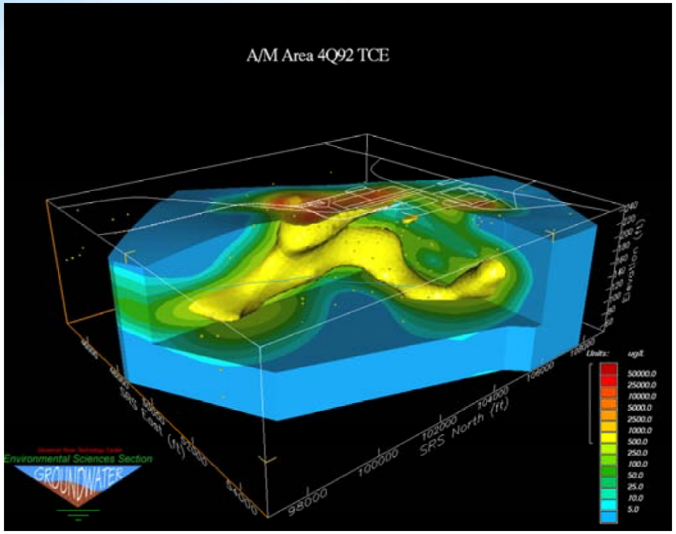
- TCE, approximately 1 square mile extending 75 feet deep, initial source concentration → DNAPL

Test Area North – DOE Idaho National Laboratory

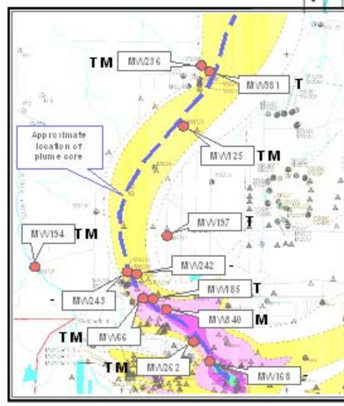
- TCE, approximately 1 square mile and extending to 350 feet deep, initial source concentration → DNAPL

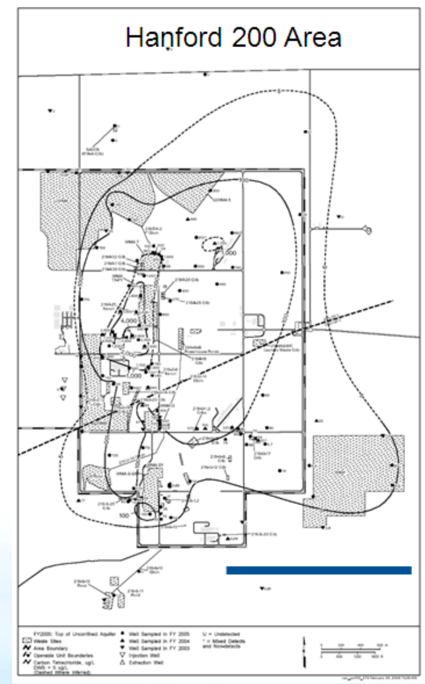
Many DOD examples (Hill AFB, Tinker AFB, MMR, Tooele, etc.) and industrial facilities

A few example plume maps from DOE sites



Paducah
Gaseous
Diffusion
Plant (KY)





bold bar = 1.60934 km

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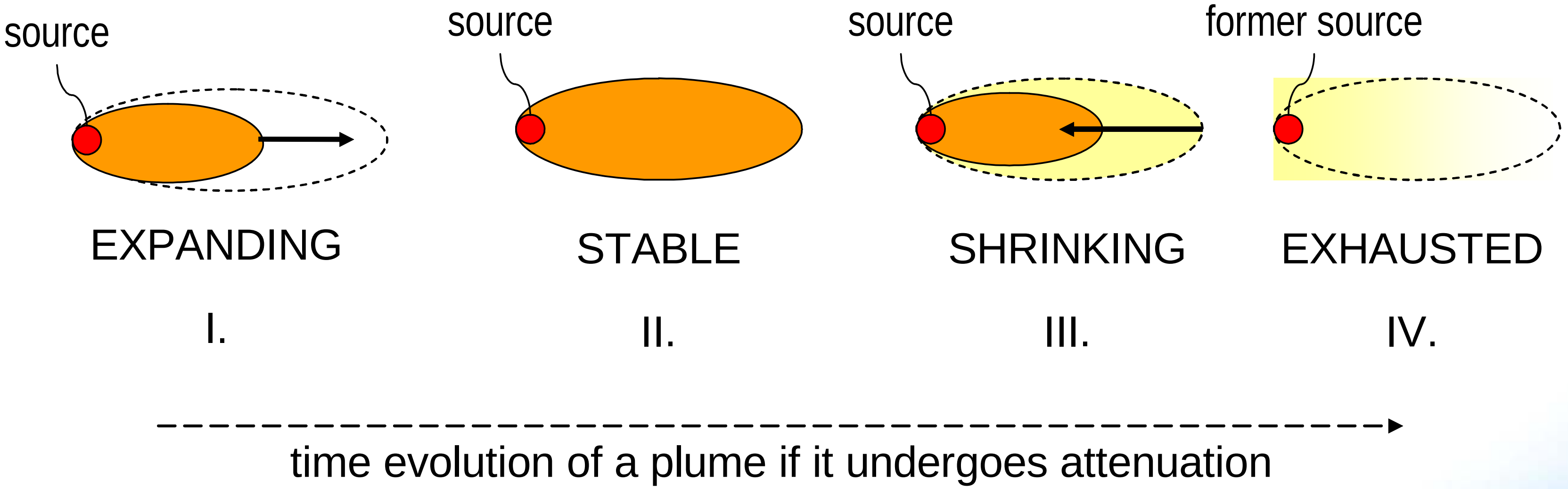
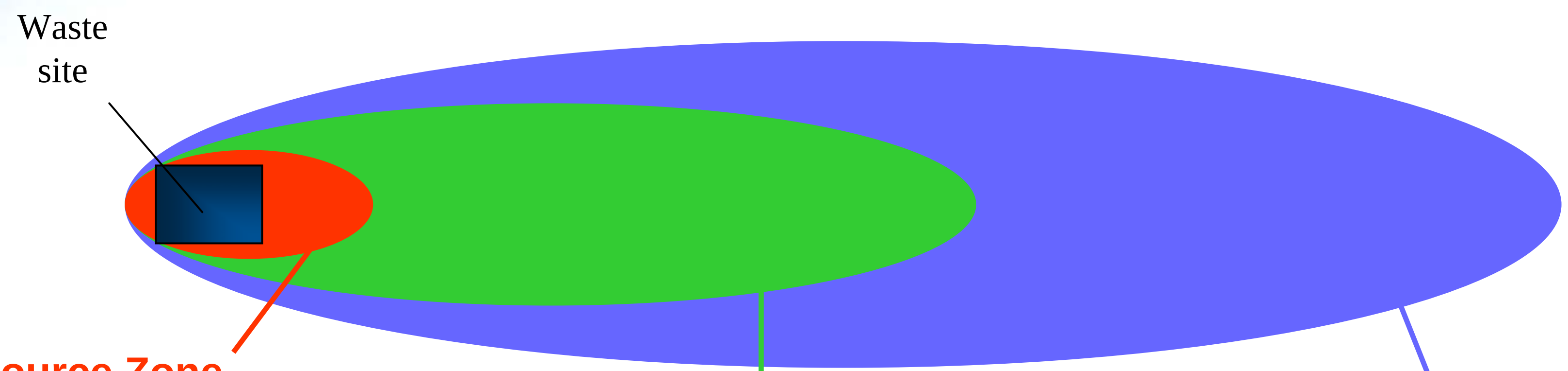
Lifecycle of a Contaminant Plume

Contaminants released into the soil and groundwater will form a "plume".

As contaminants are attenuated by natural processes the plume will stabilize and then shrink.



Anatomy of a Contaminated Site



Source Zone

Characteristics:
DNAPL and high Concentrations

Need:
Aggressive technologies to limit long term damage

Examples:
destruction or stabilization in place; heat/steam; chemical oxidation or reduction; immobilization.

Primary Groundwater / Vadose Zone Plume

Characteristics:
Moderate to high aqueous/vapor phase concentrations

Need: Baseline methods or moderately aggressive alternatives

Examples: pump (gas or water) and treat; recirculation wells; enhanced bioremediation

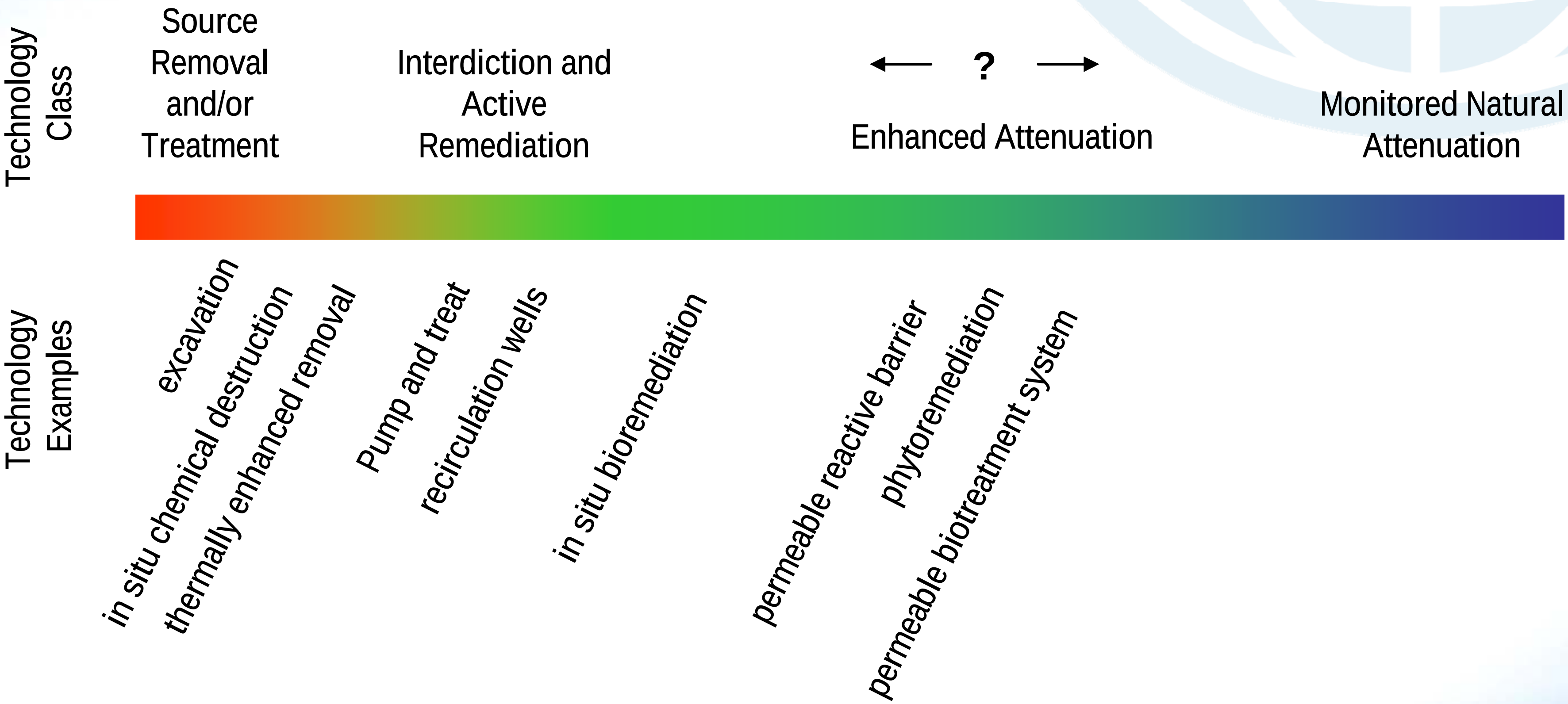
Dilute Plume / Fringe

Characteristics:
Low aqueous/vapor phase concentrations;
Large water volume.

Need: innovative technologies - sustainable low energy concepts

Examples: MNA, Passive pumping (siphon, barometric, etc.); enhanced attenuation

Continuum of Treatment Technologies for DNAPL sources and resulting plumes



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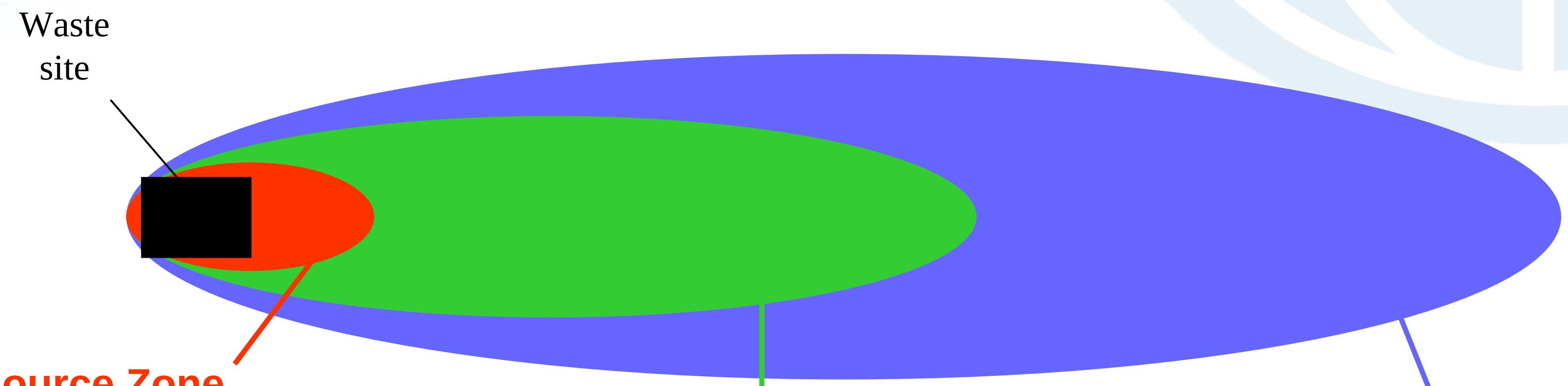
Treating a Contaminated Site



Source Zone

<u>Costs:</u>
$/lb contaminant or $/cu yd. Removal examples:
< *$50-$100/cu yd or*
< *$100/lb for chlorinated solvents*

hot spot characterization reduces cleanup volume

Primary Groundwater/Vadose Zone Plume

<u>Costs:</u>
$/treatment volume (gallon/cu ft)
example:
<$0.5-$10 / 1000 gallons

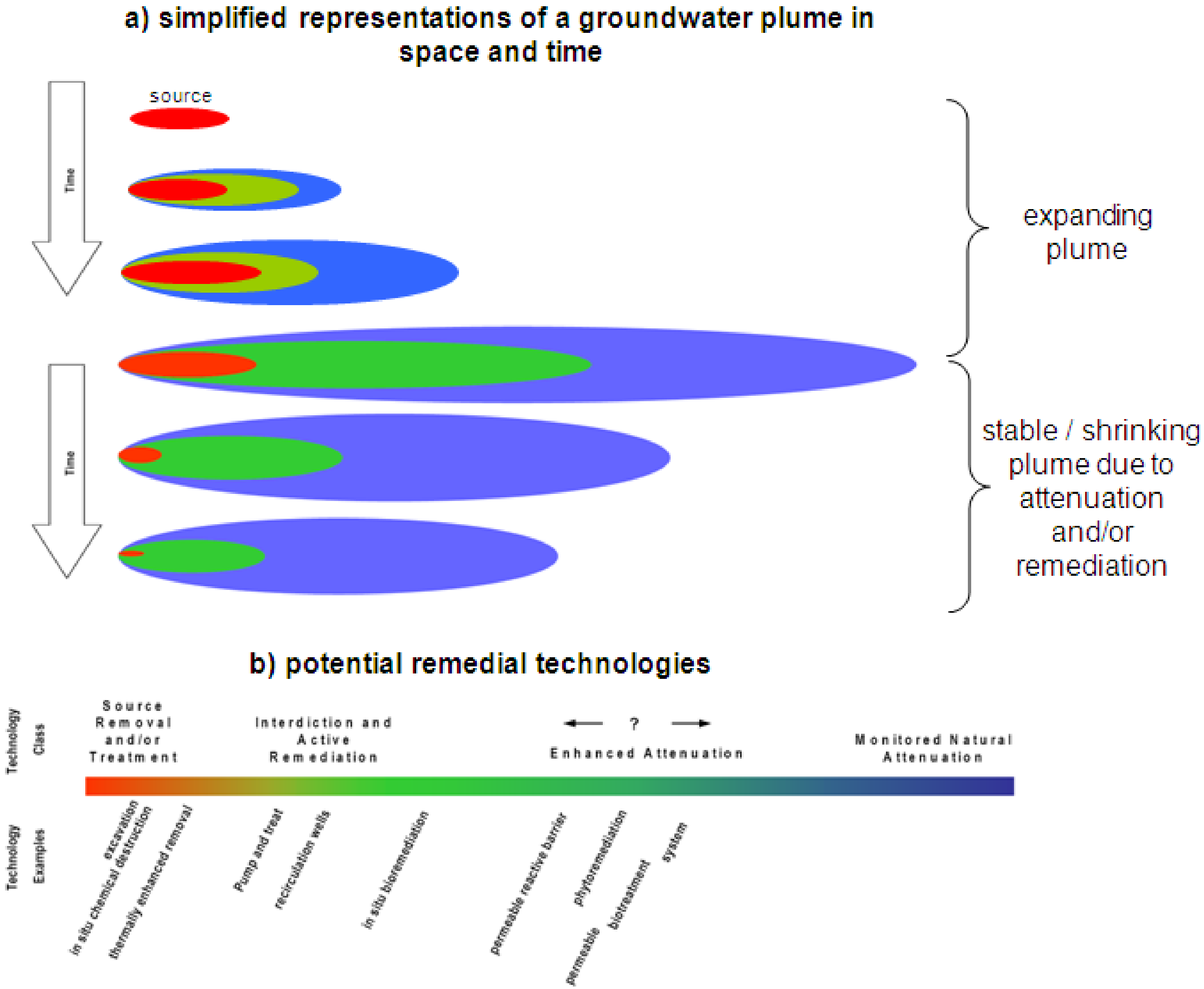
zone of capture characterization needed, optimize extraction to reduce treatment volume

Dilute Plume/Fringe

<u>Costs:</u>
Operation and maintenance costs $/time

mass transfer and flux characterization needed

Updated Lifecycle of a Contaminant Plume



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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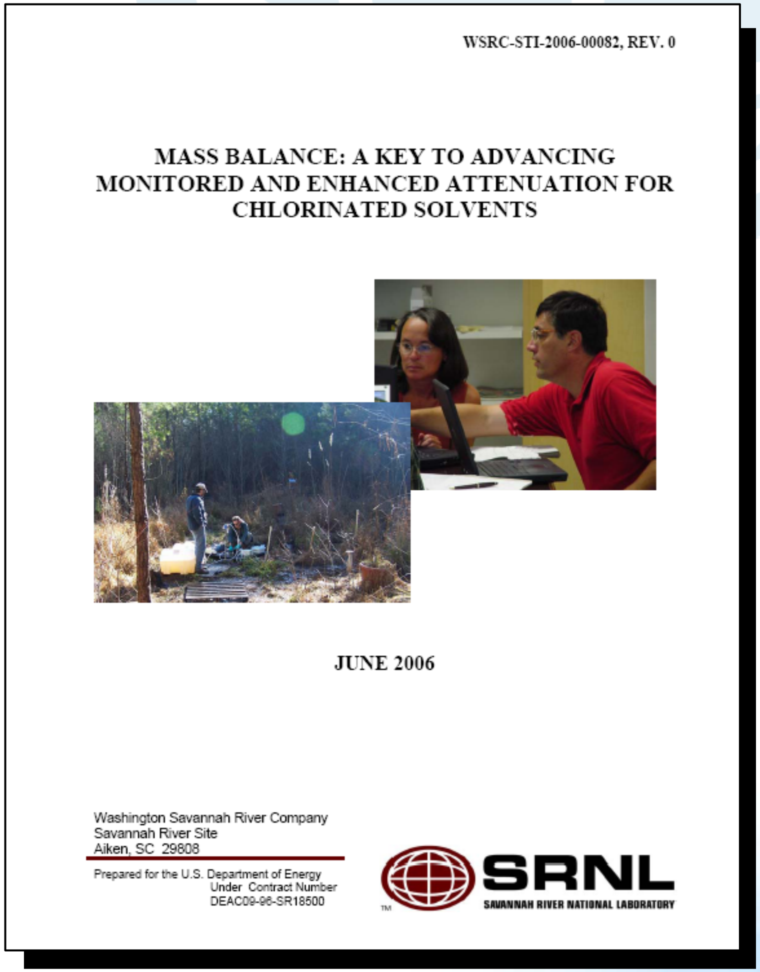
Attenuation Processes in Large Dilute (Aerobic) Plumes

Degradation?

Dispersion?

Sorption?

We performed a parametric analysis to demonstrate the relative importance of the different processes.



WSRC-STI-2006-00082, REV. 0

MASS BALANCE: A KEY TO ADVANCING MONITORED AND ENHANCED ATTENUATION FOR CHLORINATED SOLVENTS

JUNE 2006

Washington Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy
Under Contract Number
DEAC09-96-SR18500

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SAVANNAH RIVER NATIONAL LABORATORY

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Start with Sorption and Degradation….

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

$$x = \frac{v_s}{R} t = v_c t$$

plug flow w/ sorption

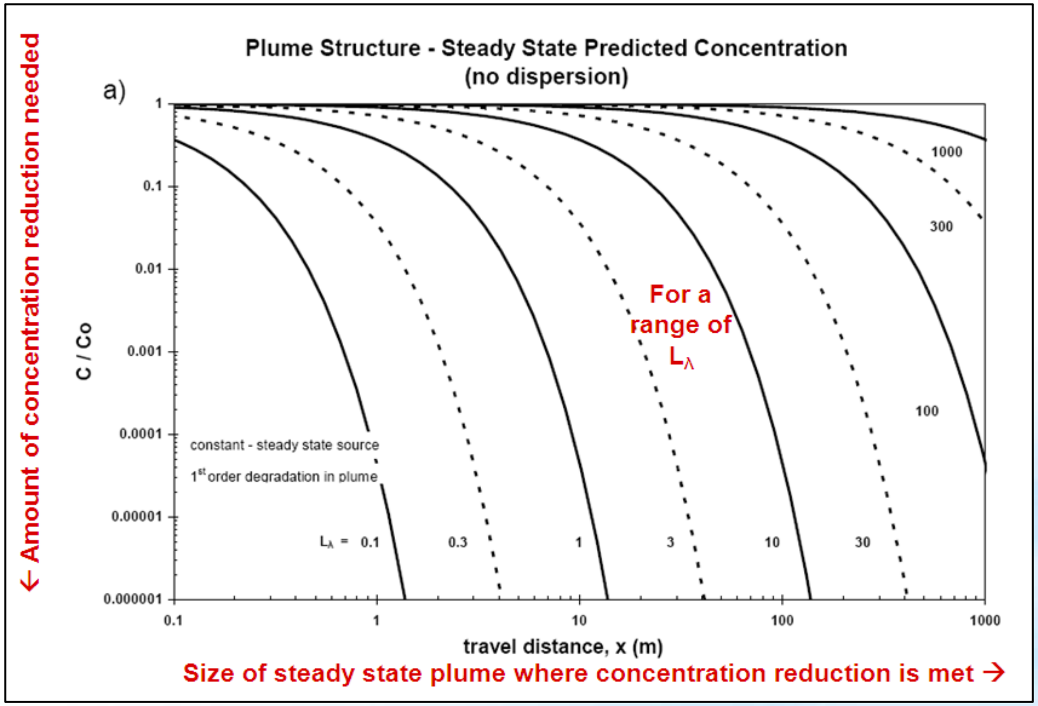
&

$$(C/C_0) = e^{-\lambda t}$$

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



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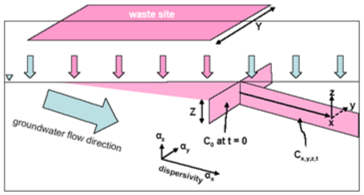
Add dispersion and source degradation…



source decay

$$C_{(x,y,z,t)} = C_0 e^{-k_s t} \frac{f_x}{2} \frac{f_y}{2} \frac{f_z}{2}$$

flow and longitudinal dispersion

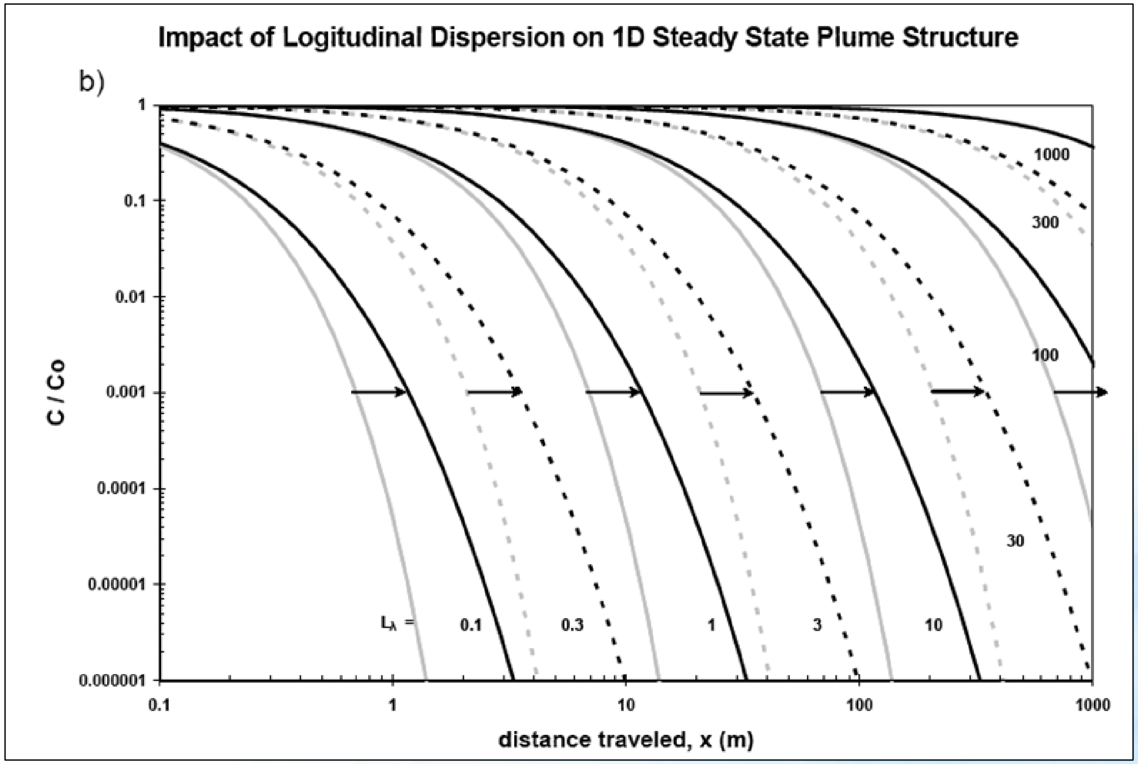
transverse dispersion

$$f_x = \exp\left[\frac{x\left(1-\sqrt{1+4\alpha_x(\lambda-k_s)/v_c}\right)}{2\alpha_x}\right] * erfc\left[\frac{x-v_c t\left(1-\sqrt{1+4\alpha_x(\lambda-k_s)/v_c}\right)}{2\sqrt{\alpha_x v_c t}}\right] +$$

$$\exp\left[\frac{x\left(1+\sqrt{1+4\alpha_x(\lambda-k_s)/v_c}\right)}{2\alpha_x}\right] * erfc\left[\frac{x+v_c t\left(1-\sqrt{1+4\alpha_x(\lambda-k_s)/v_c}\right)}{2\sqrt{\alpha_x v_c t}}\right]$$

$$f_y = erf\left[\frac{y+Y/2}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{y-Y/2}{2\sqrt{\alpha_y x}}\right]$$

$$f_z = erf\left[\frac{y+y/2}{2\sqrt{\alpha_y x}}\right] - erf\left[\frac{y-y/2}{2\sqrt{\alpha_y x}}\right]$$



What does this math tell us…

The rate of attenuation in the plume strongly impacts the ultimate size of the plume

Confirmed EPA preference for degradation processes. Degradation was a dominant natural attenuation mechanism, but any degradation (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 less important if the sorbed material is not degrading)

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

Transverse dispersion can contribute to attenuation – but only for large plumes > about 1000 m

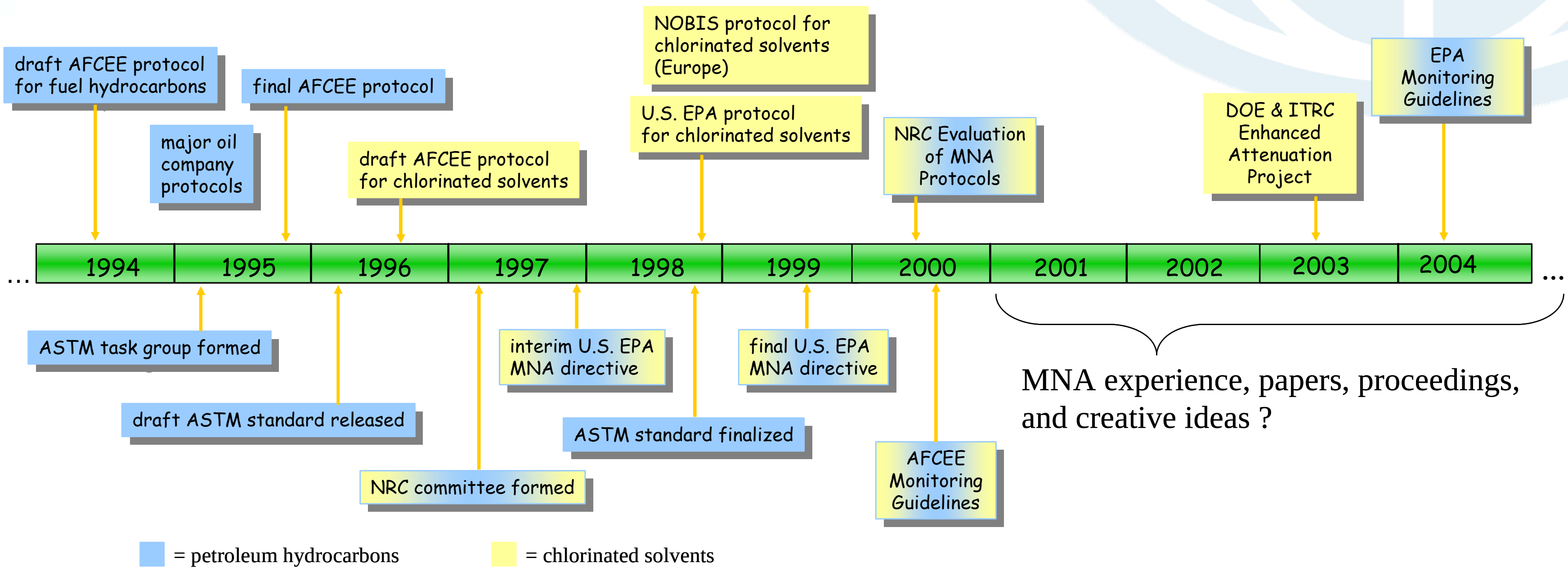
What does this math tell us…

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!

Traditional Timeline for Natural Attenuation

Natural Attenuation of hydrocarbons and chlorinated solvents



Note: major focus for chlorinated solvents on anaerobic processes

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Dominant chlorinated solvent degradation mechanism(s) in aerobic aquifers

abiotic degradation with reactive mineral phases such as iron sulfides, magnetite (applicable to TCE, CT, etc.)

John Wilson et al.

aerobic cometabolism (TCE etc.)

Hope Lee, et al.

aerobic direct metabolism (DCE, VC, etc.)

Paul Bradley, et al.

hydrolysis (carbon tetrachloride etc.)

Peter Jeffers, et al.

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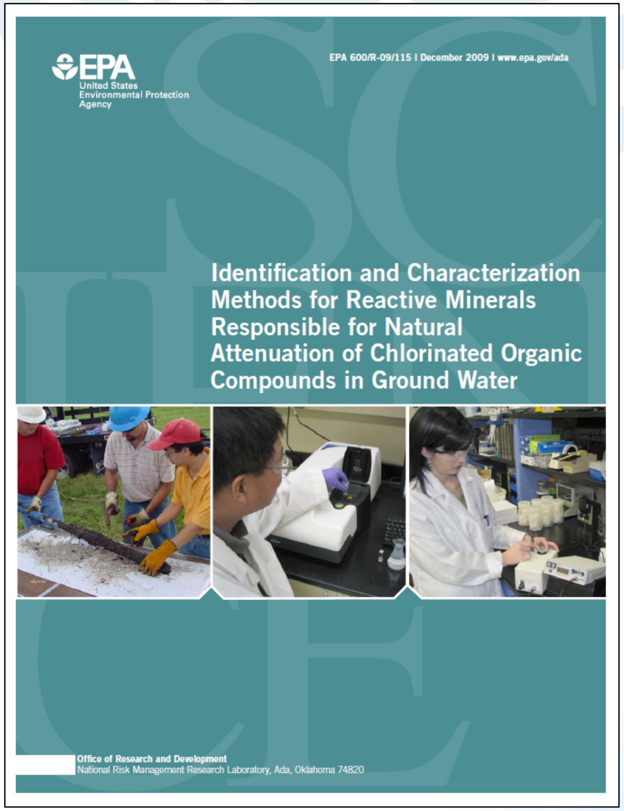
Abiotic Degradation – reactions with mineral phases

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

For several sites, significant attenuation has been documented for magnetite and rates have been correlated to inexpensive magnetic susceptibility measurements -- half lives of 4 to 6 years measured at sites with magnetite present



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Aerobic Cometabolism Research Pre-Dates Traditional MNA Timeline

Natural Attenuation of hydrocarbons and chlorinated solvents

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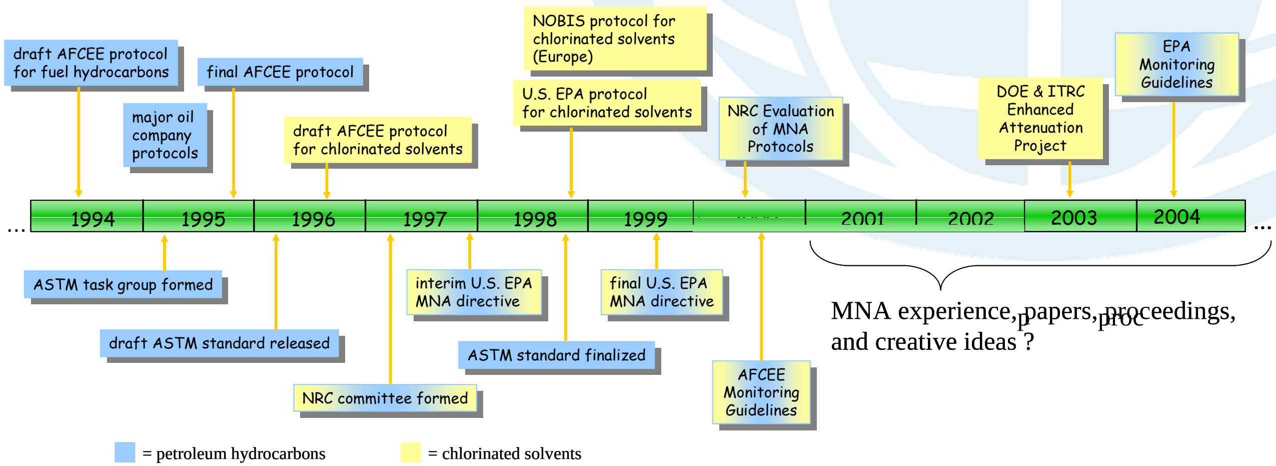

Aerobic Cometabolism

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 hydrocarbon and aromatic reagents…)

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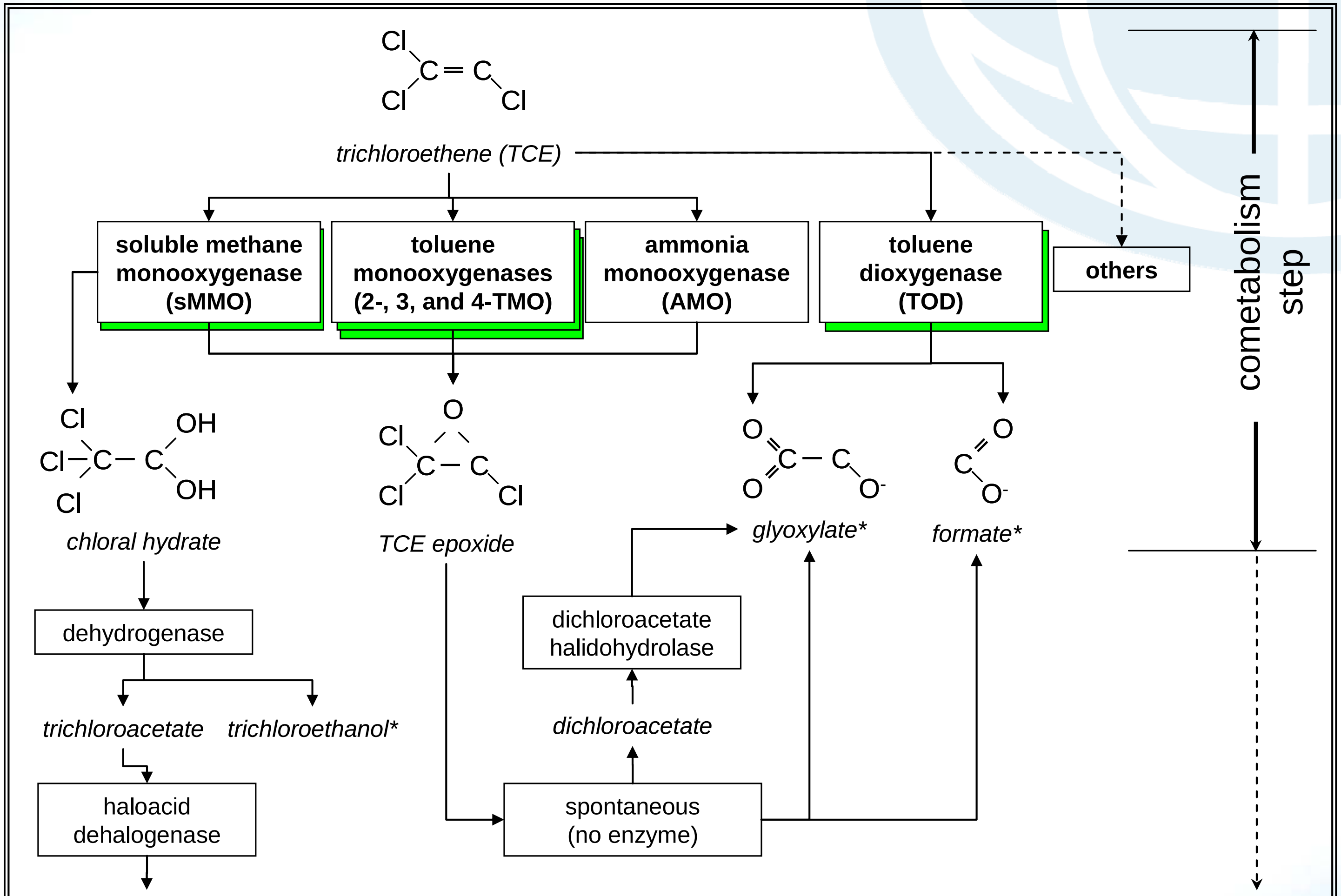
Cometabolism for Chlorinated Solvents



…. all pathways mineralized to nontoxic terminal products such as *CO_2, CO, H_2O* and *Cl^-

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Summary of aerobic cometabolism research

Half lives of about 6 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 amendment technology to sustainably enhance aerobic cometabolic rates in L&D settings

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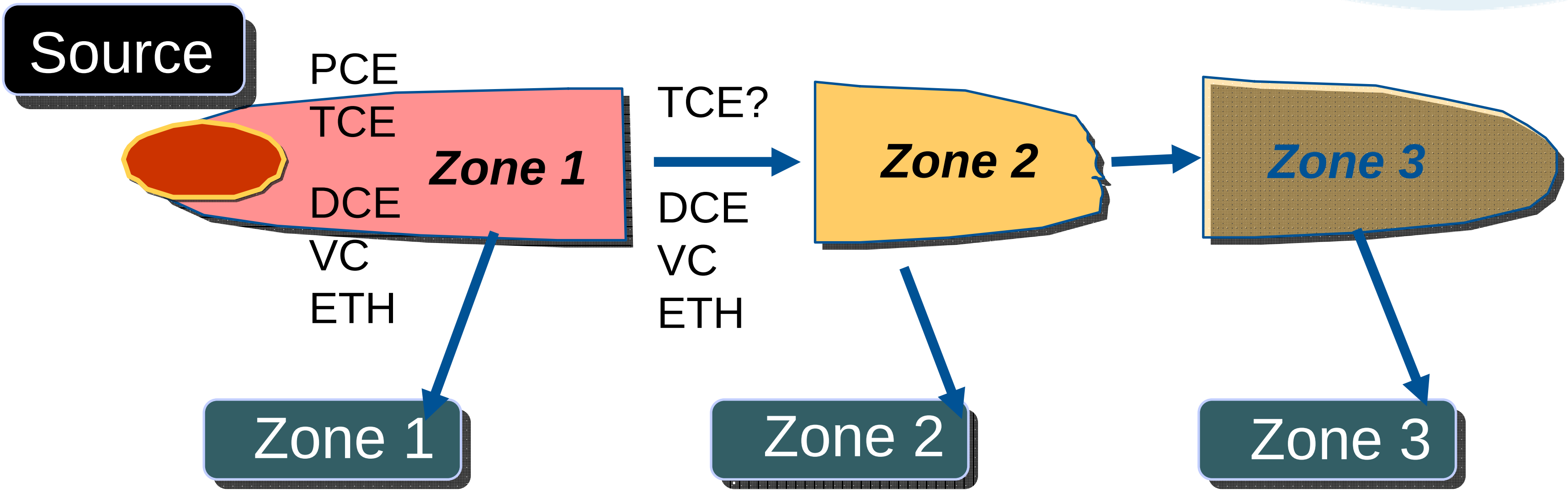
Putting it all together (REMChlor)

Three Reaction Zones for Mixed Sites



High Anaerobic Decay Rates
(Carbon Present)

Possible Enhanced Aerobic Decay

Low or Background Decay Rates

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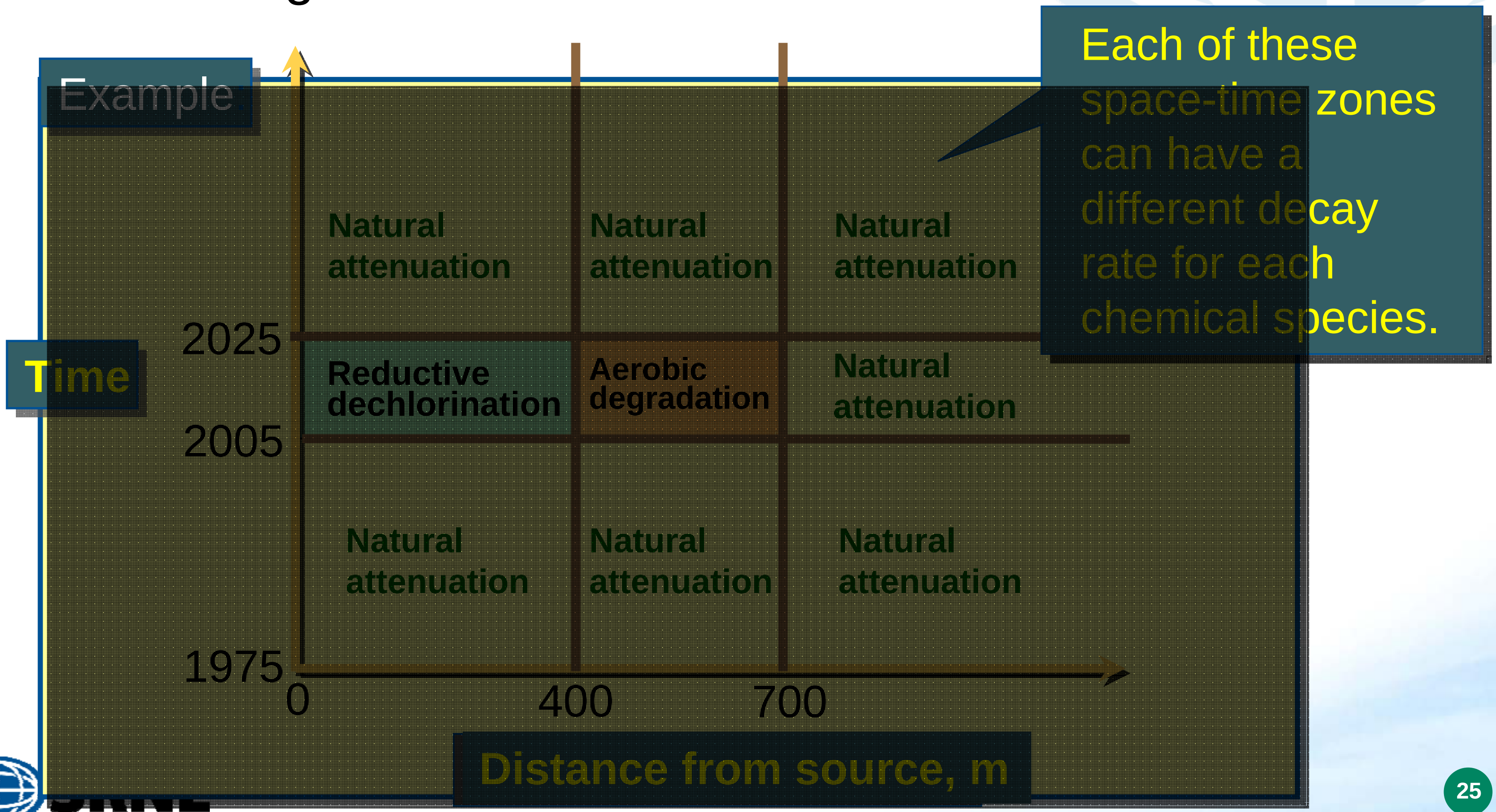
Plume Remediation Model

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



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 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 currentlypl anning training workshop
throughC LU-INc overingR EMChlor and
REMFuel

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.

Overarching Goal Setting Concepts (modeling workshop)

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 are currently being explored -- Mass flux an example metric to link source treatment and plume impacts (but only if cost-effective and reliable flux measuring methods are available) – new concepts such as the “Plume Magnitude Scale” are emerging

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 the 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.

Technical impracticability ? ☹

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

2013 is the 30th anniversary of p&t

15 years of SVE

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

Air sparging, cometabolic bioremediation, ERH and RF heating, oxidant, etc.

Finish up with a quick final look at the real remediation site

We will examine an early mass balance model for source and plume remediation and some current totals

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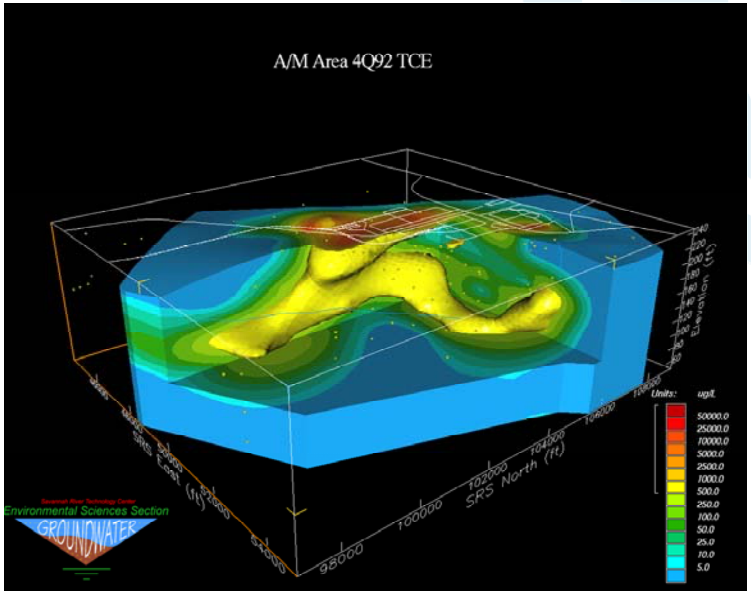
M Area – DOE Savannah River Site



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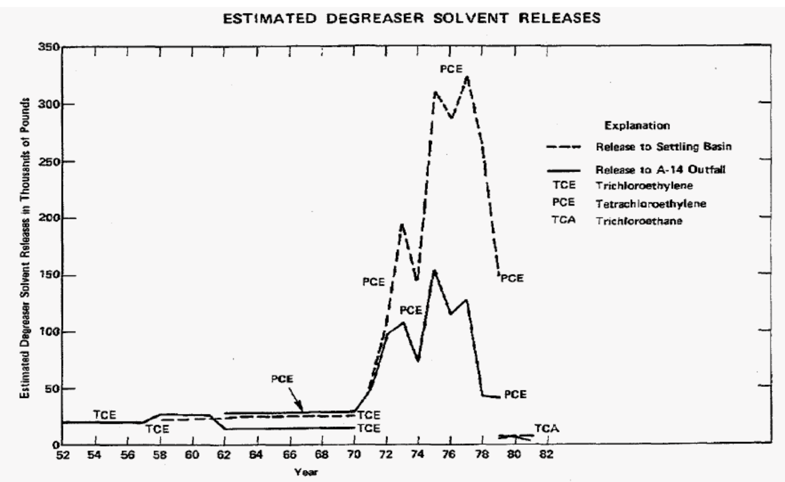
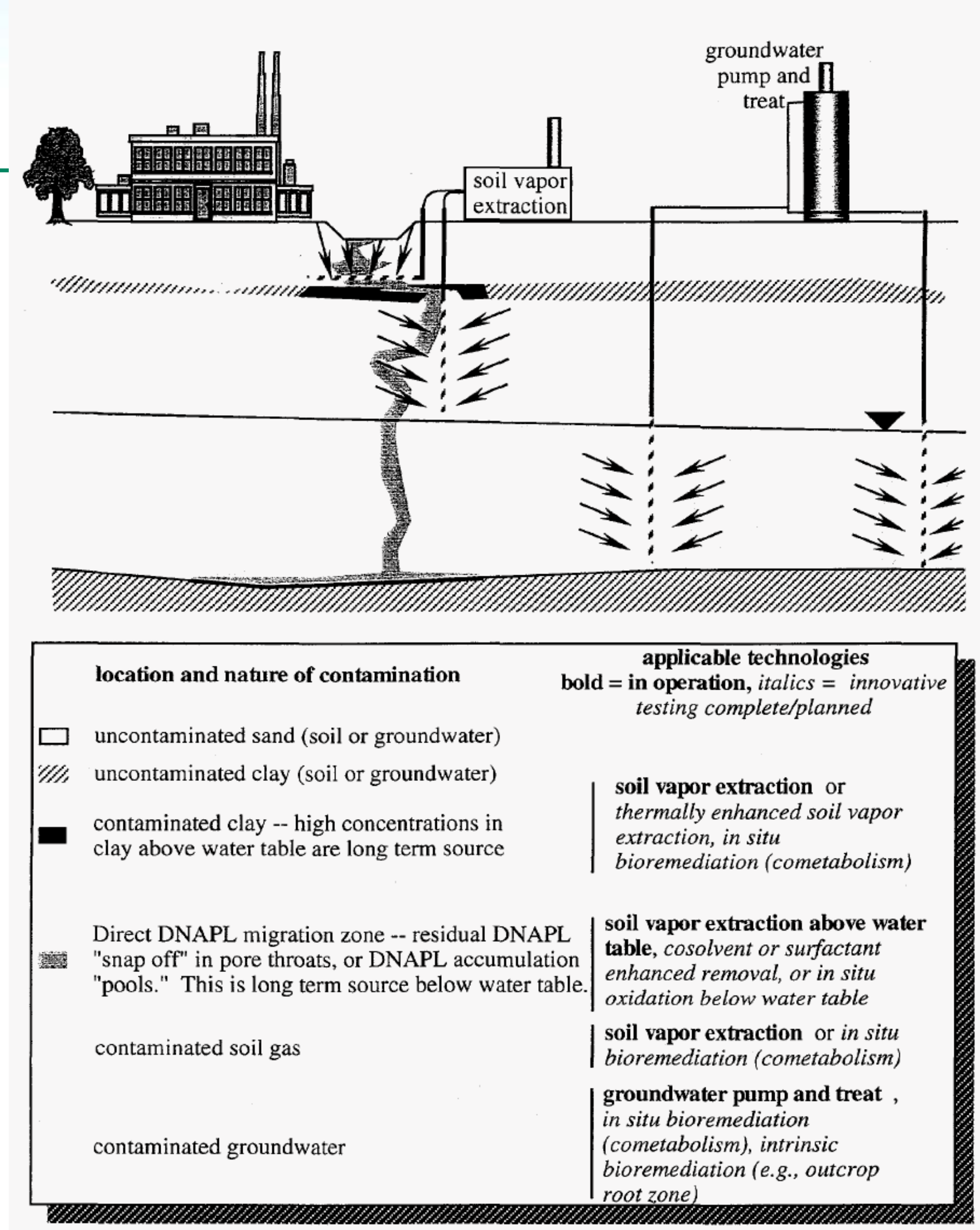
Early Mass Balance

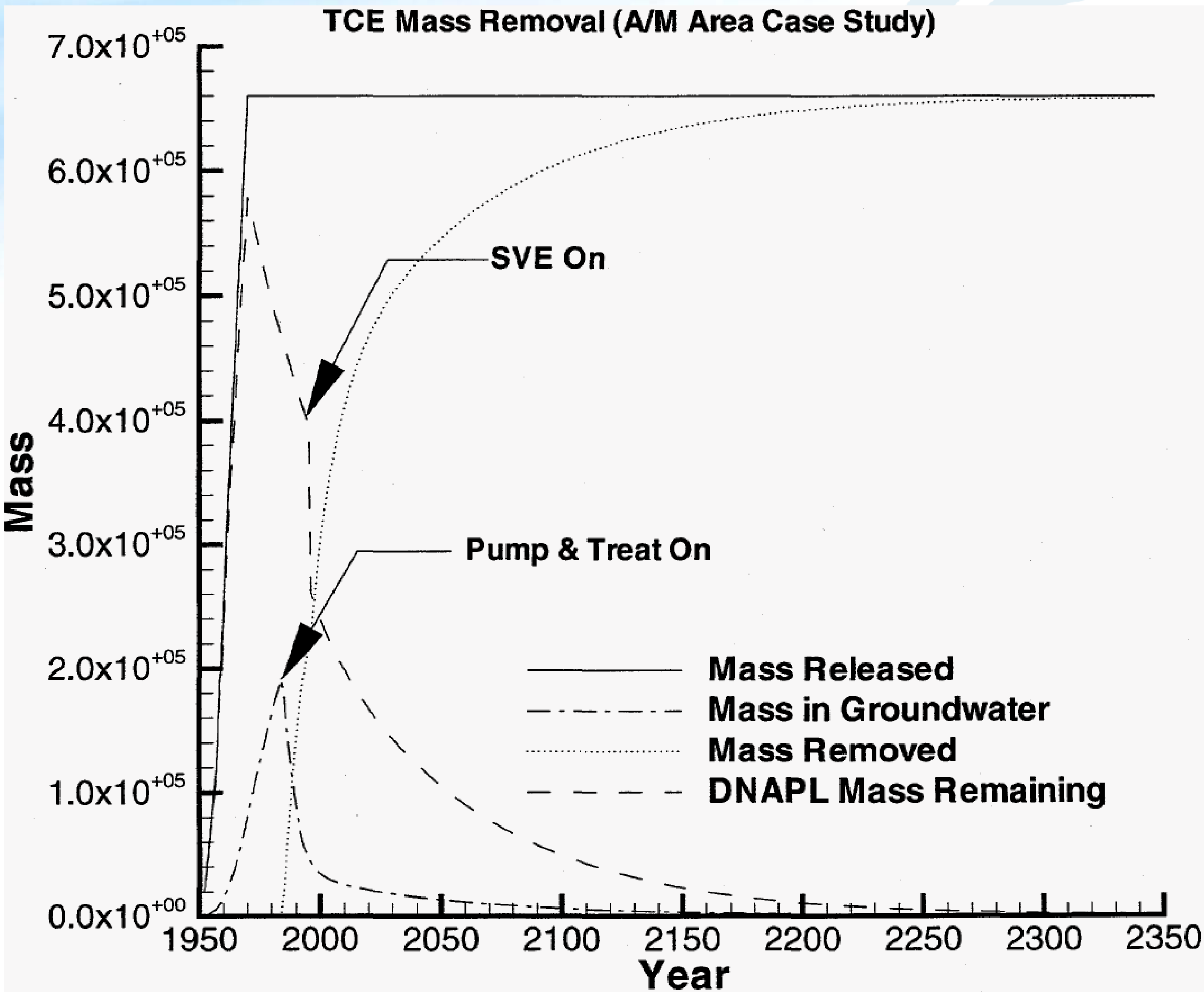
$$M_{s,t} = \sum_{t=0}^{t}(inputs - outputs)$$

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

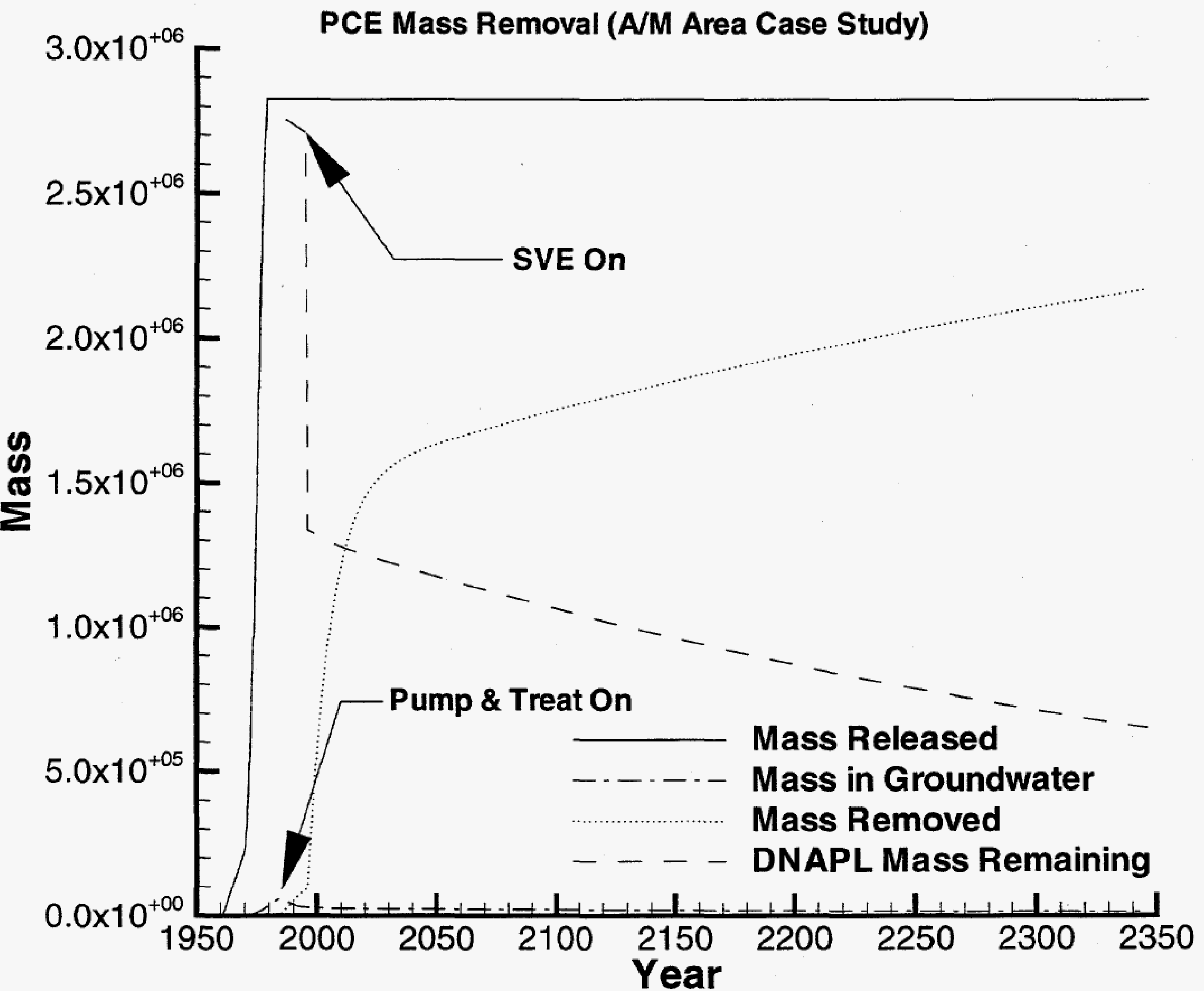
A simple 1st order equation was developed for each activity and calibrated to about 9 years of remediation operation

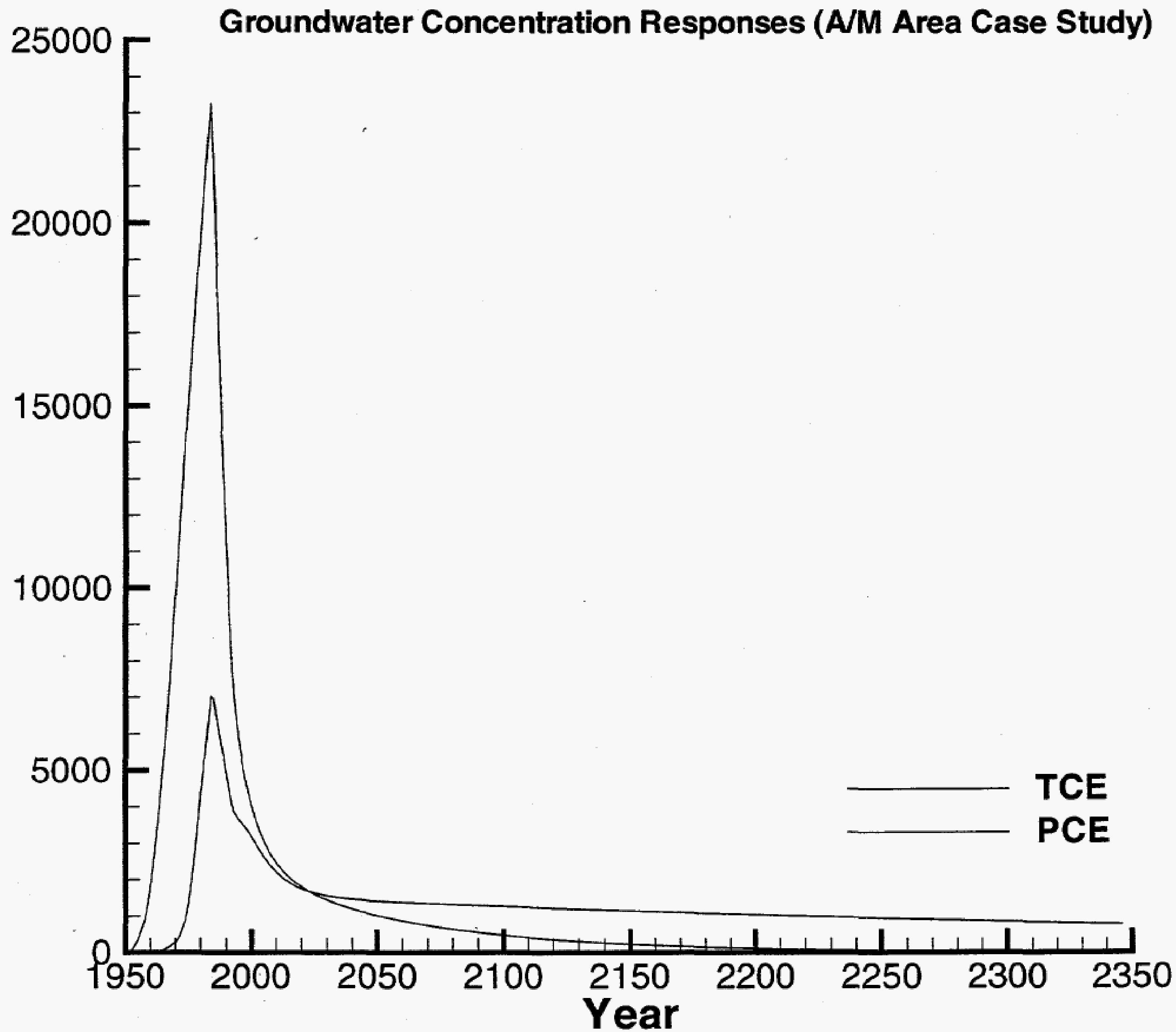






TCE Mass Removal (A/M Area Case Study)
Mass
Year
7.0x10+05
6.0x10+05
5.0x10+05
4.0x10+05
3.0x10+05
2.0x10+05
1.0x10+05
0.0x10+00
1950
2000
2050
2100
2150
2200
2250
2300
2350
SVE On
Pump & Treat On
Mass Released
Mass in Groundwater
Mass Removed
DNAPL Mass Remaining


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


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

M Area totals

- Dennis Jackson is currently preparing a paper on M Area (in honor of the 30th anniversary)
- Here are some 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%

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

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

Treatments should avoid large scale adverse collateral impacts when possible

Conclusions -- Opportunities

remediation "successes" will:

- match technology and deployment to site specific conditions
- focus on actionable 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

The is lots of emerging science for the plume: 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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