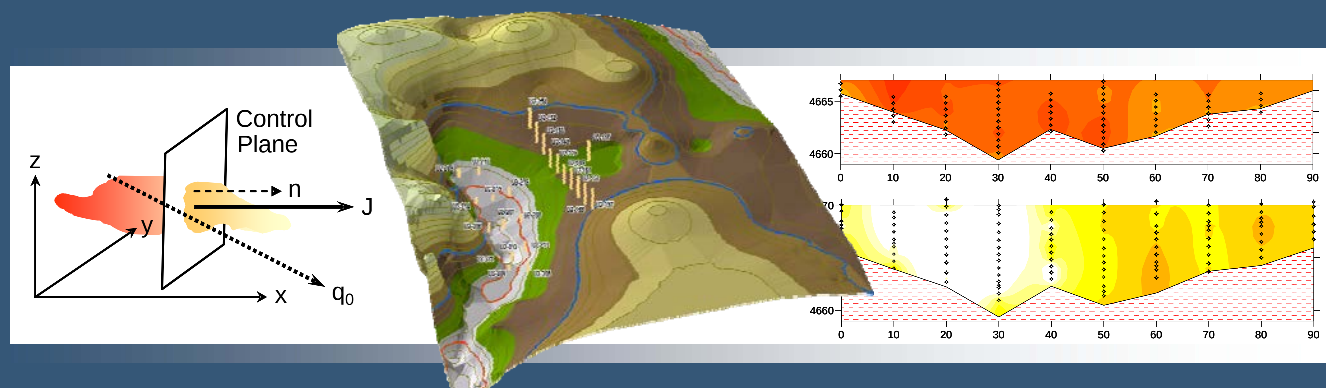
Triad Conference – June 10, 2008

Flux-Based DNAPL Site Remediation: Field Case Studies

Suresh Rao, School of Civil Engineering, Purdue University



Office of Research and Development
National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division, Ada, Oklahoma

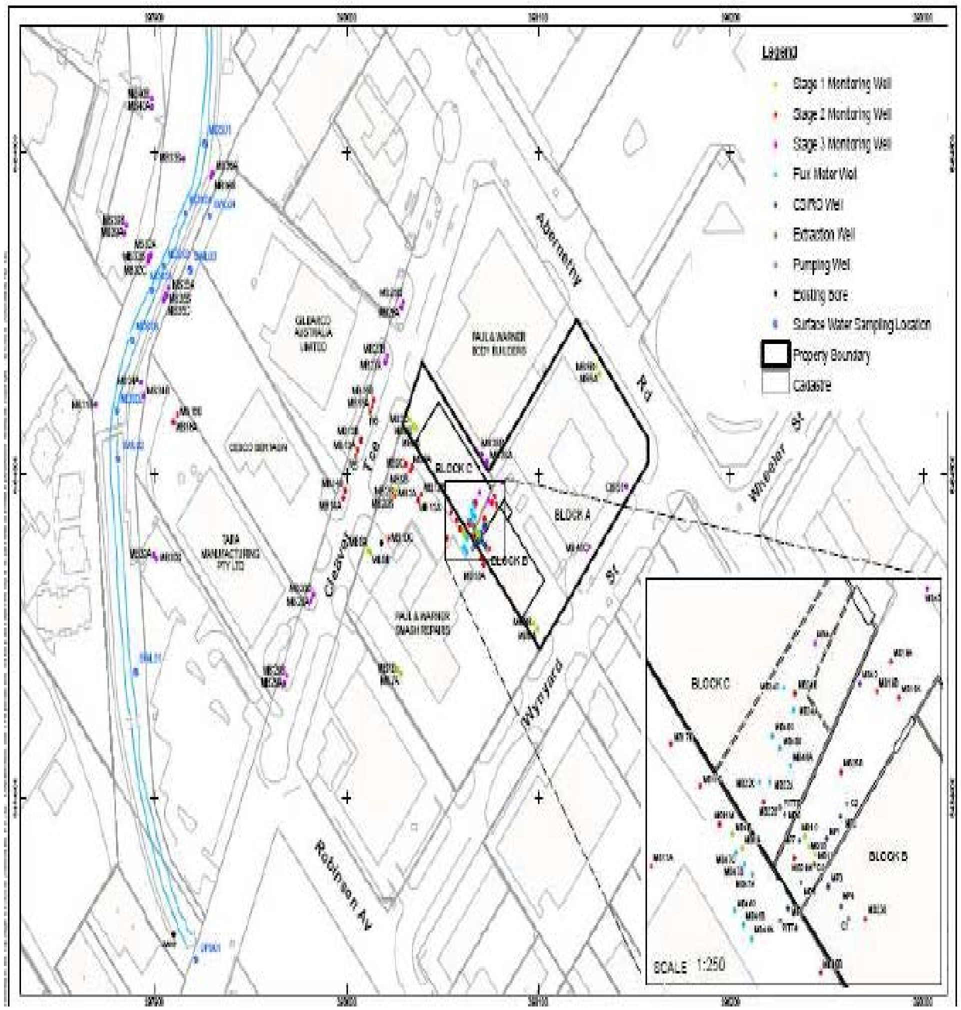
Flux-Based Characterization at ~30 Field Sites

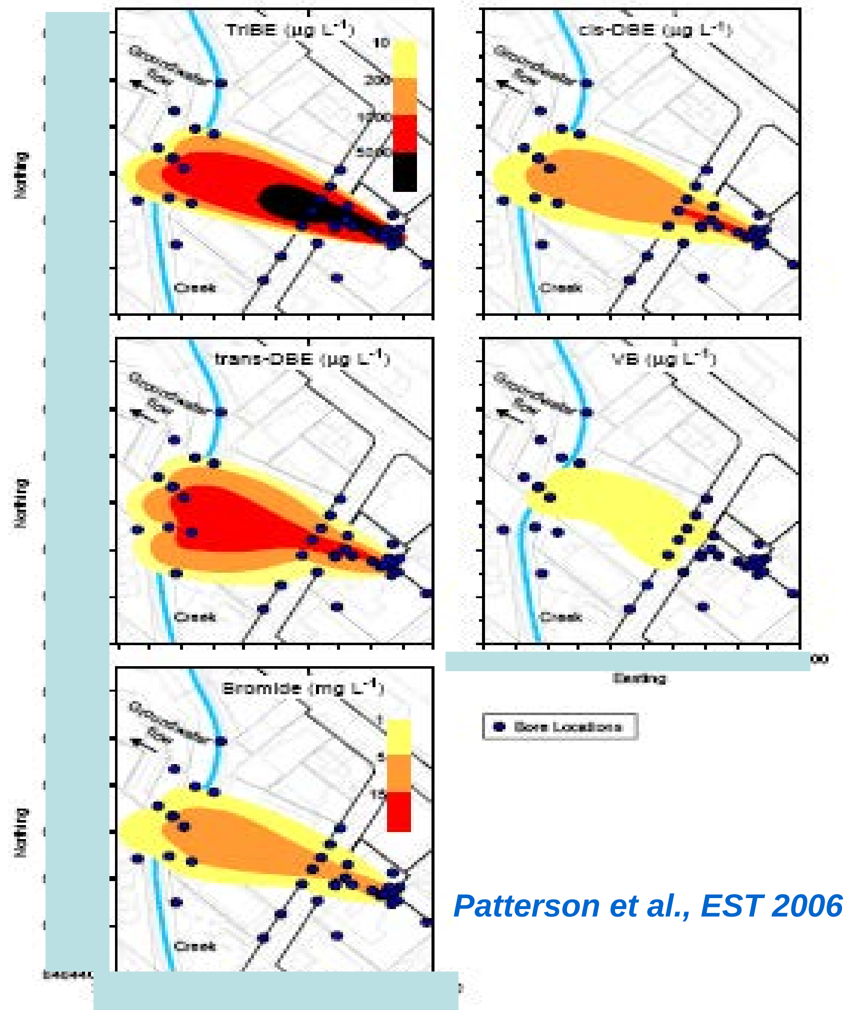
- **Federal Sites**
  - Hill AFB; Patrick AFB; Dover AFB; Vandenberg AFB; Ft Lewis; Ft Devin; Indian Head; Port Hueneme; Paris Island; Cape Canaveral; Charleston; SRS; NASA
- **Other Sites**
  - Manufacturing Facilities in Indiana & Illinois
  - Dry Cleaner sites in Florida & Indiana
- **International Sites**
  - Borden CFB, Canada
  - Wales, UK
  - Australia (4 sites)

Four DNAPL Case Studies

- Three large sites, one small site
- Two source zones treated, one under consideration
- All sites had considerable archived data
- At all sites new flux measurements made, PFM deployments & Integral Pump Tests conducted
- We will examine:
  - Source & plume characterization
  - Source remediation performance assessment
  - Source & plume treatment options
  - Implications to long-term stewardship

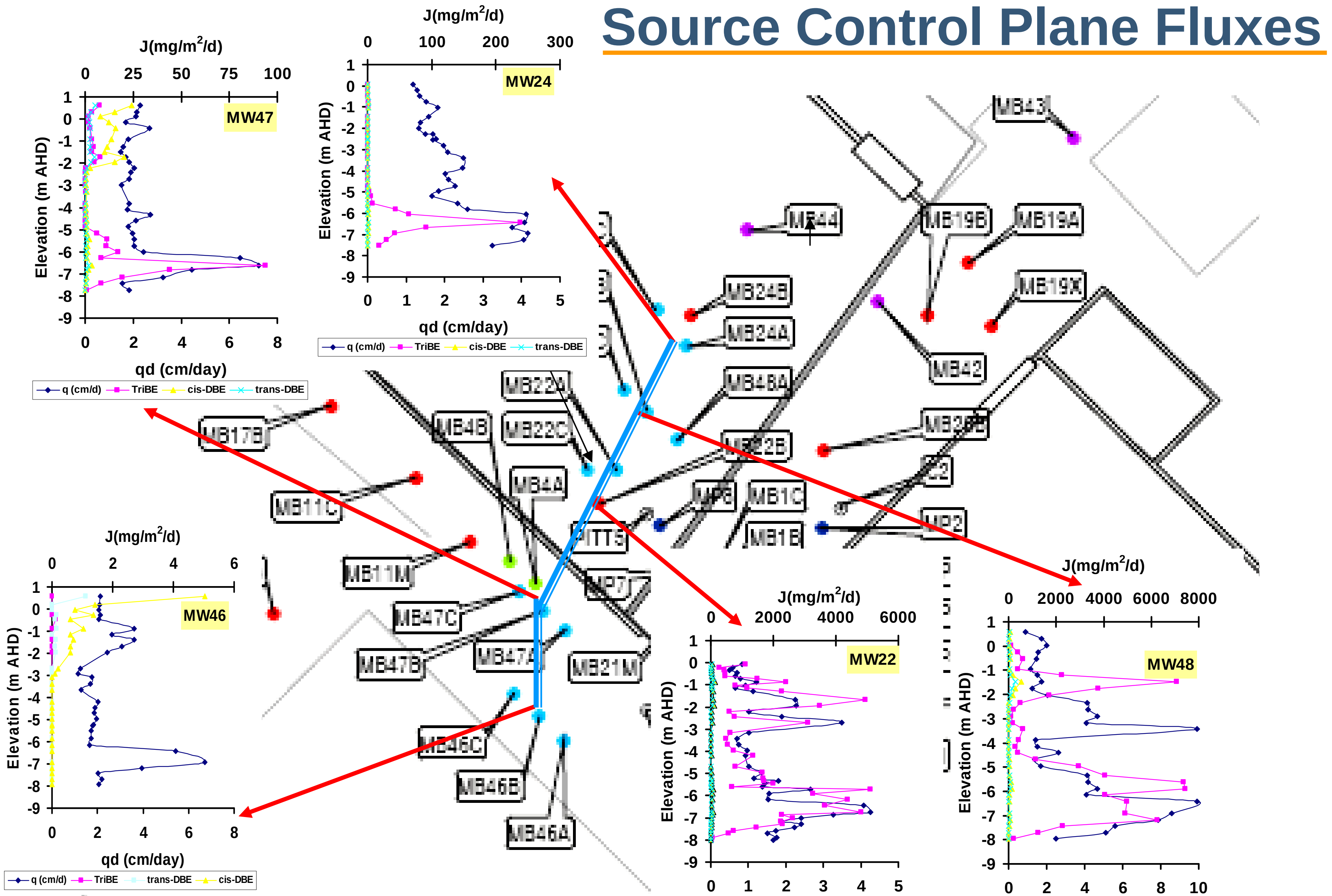
DNAPL Site - 1





Patterson et al., EST 2006

Source Control Plane Fluxes



Unpublished Data: Do Not Cite or Distribute

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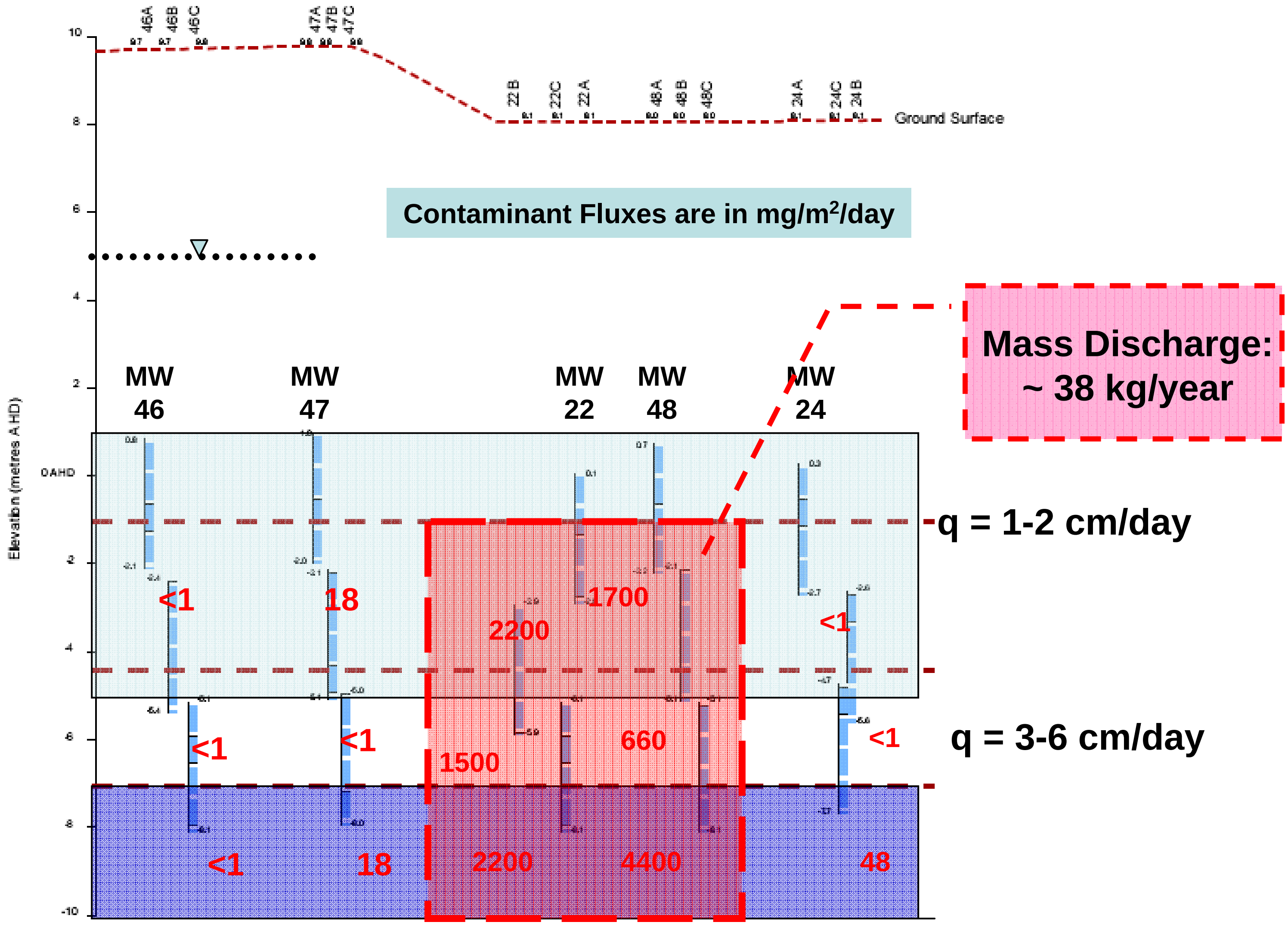
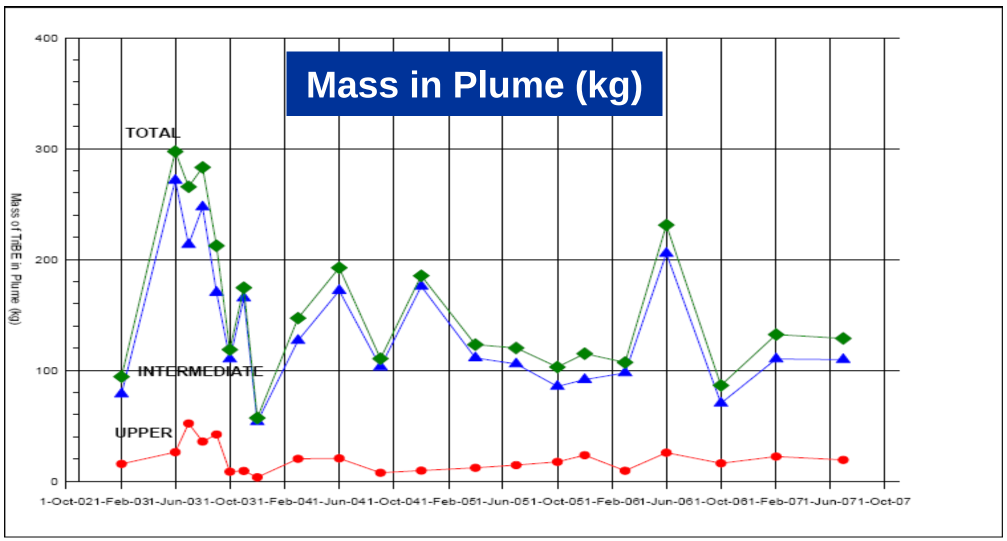
Cross Section of Source Transect



DNAPL Plume Mass

- **Plume mass (M_p) was estimated from integration of plume data (monitoring over 2002-2007 period)**
- **Most of the TriBE mass is found in the Intermediate aquifer**
- **Total mass of TriBE has stabilized at ~100-200 kg (additional mass in sorbed phase; R=??)**
- **Might be approaching "steady-state" conditions; stable plume??**
- **Need to consider mass of DBE, VB, Br.**



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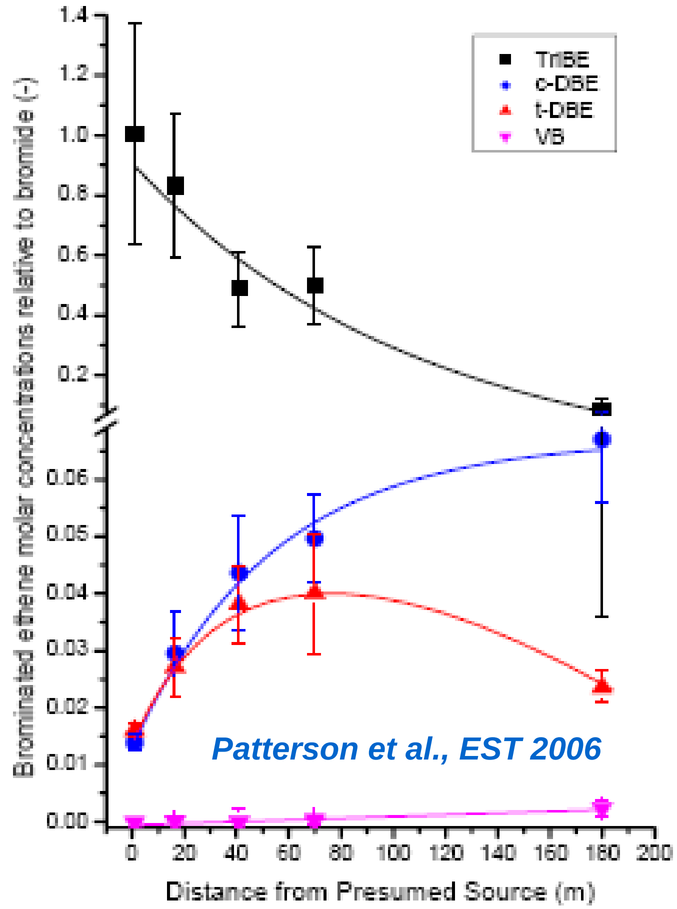


Lessons Learned: DNAPL Site 1

- Source mass: ~1.5-3 mT? (500-1,000L?)
- Contaminant mass discharge from a small area of control plane
- Archived data integrated with flux data for an improved Conceptual Site Model
- Partitioning Inter-well Tracer Tests & Integral Pump Tests recently completed
- Aggressive source remediation & plume management planned
- Post-remediation monitoring to establish effectiveness & design long-term stewardship

DNAPL Site-2

History

TCE plume created due to activities associated with the production of detonators from the Second World to the 1970s

Hydrogeology

- Multiple interconnected aquifers
- 4 quaternary aquifers and three tertiary aquifers
- v = 20 – 40 m/yr
- Water table ~ 10 to 15 m bgs

Plume Characterization

- Plume monitored since 1996
- 1,500 m long, 300 m wide and 16 m deep

Remediation driven by:

- Industrial redevelopment
- Flexible regulatory environment
- Cost constraints (passive vs aggressive)

Remedial activities to date

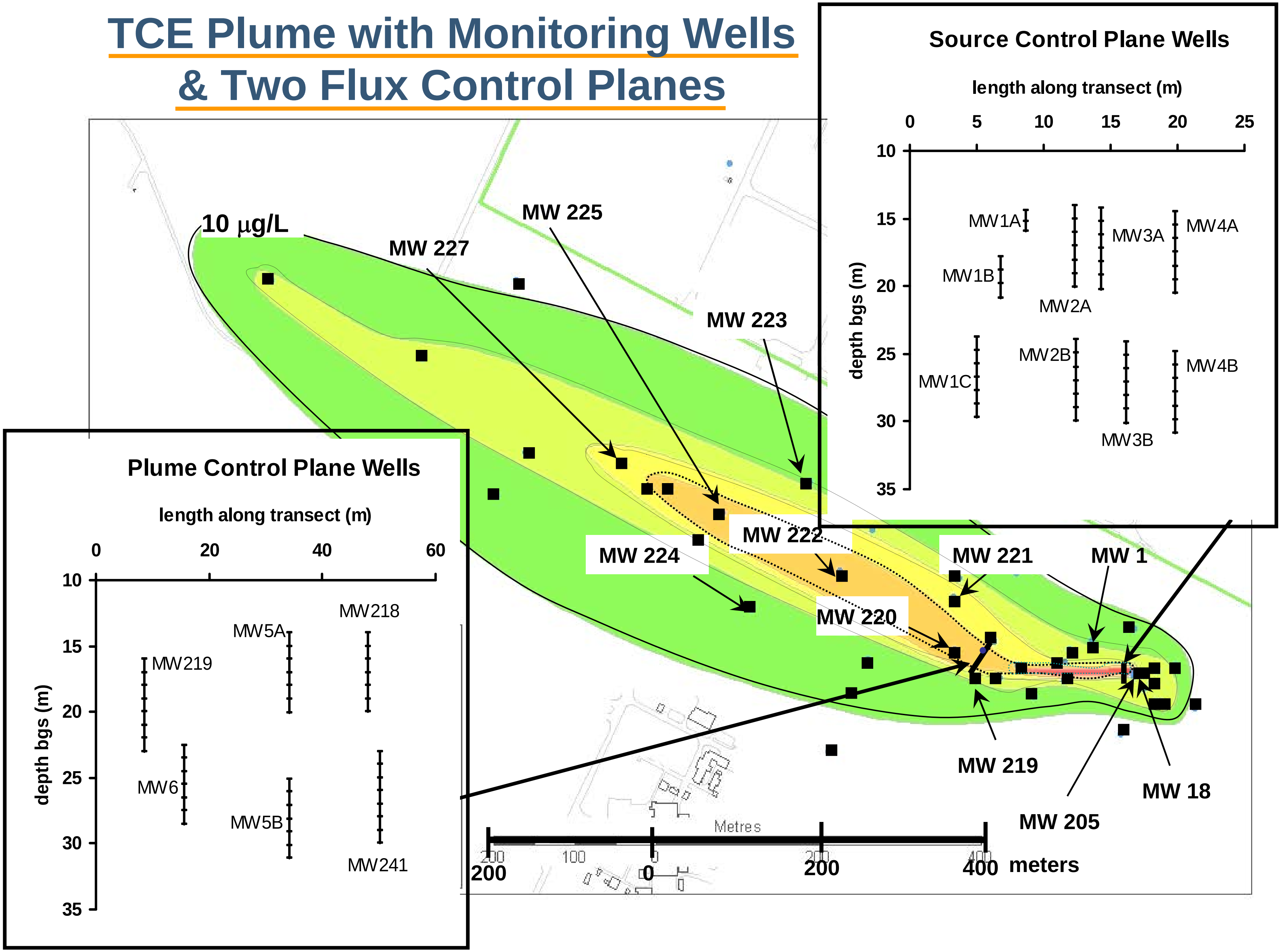
Shallow excavation in source area

Proposed Site Remediation

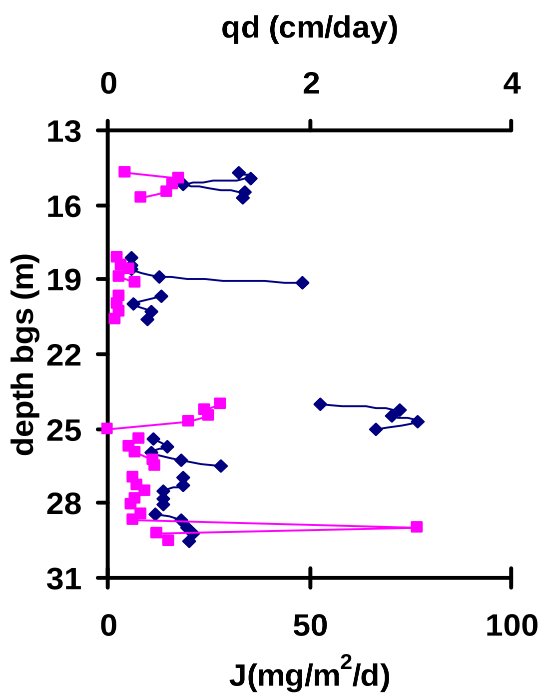
Chemical oxidation of source??

Permeable Reactive Barrier??

TCE Plume with Monitoring Wells & Two Flux Control Planes

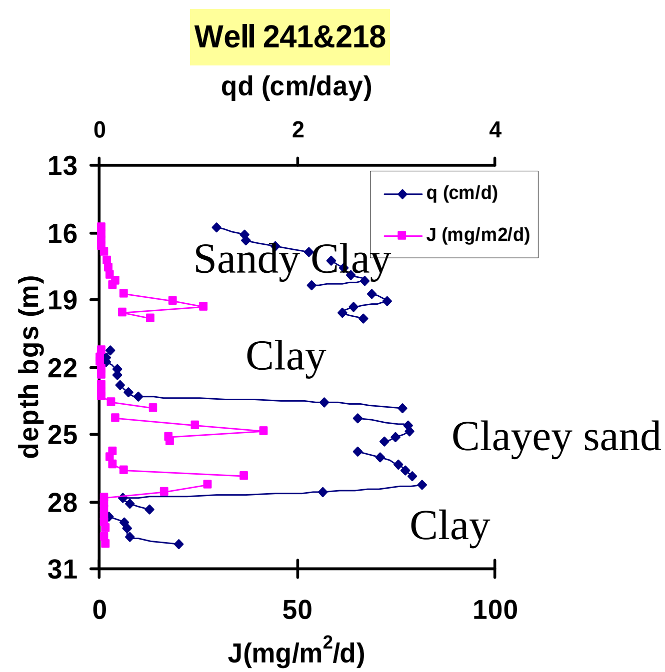


TCE & Groundwater Flux Profiles: PFM Deployments



Source Transect Well

- Source Strength = 3 g/day (other sites: 100 – 400 g/day)
- Negative Correlation

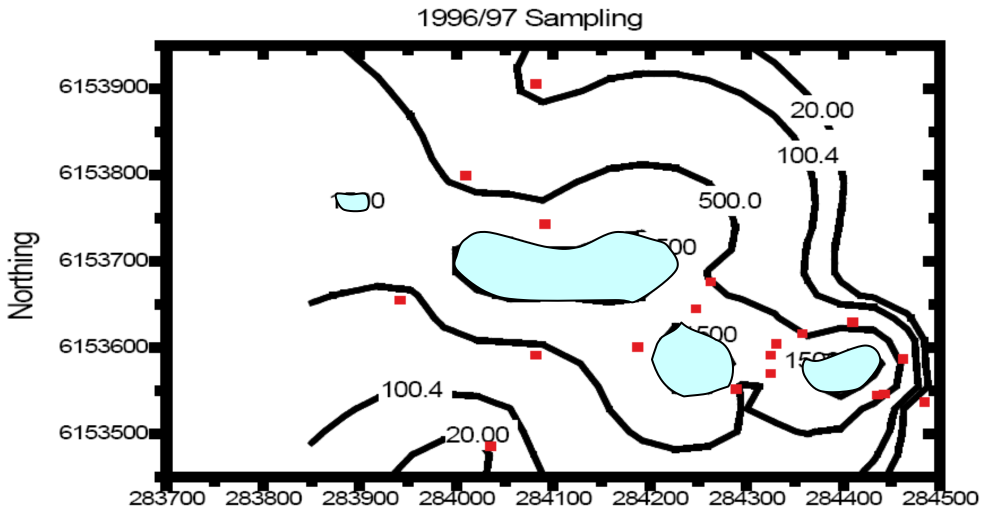


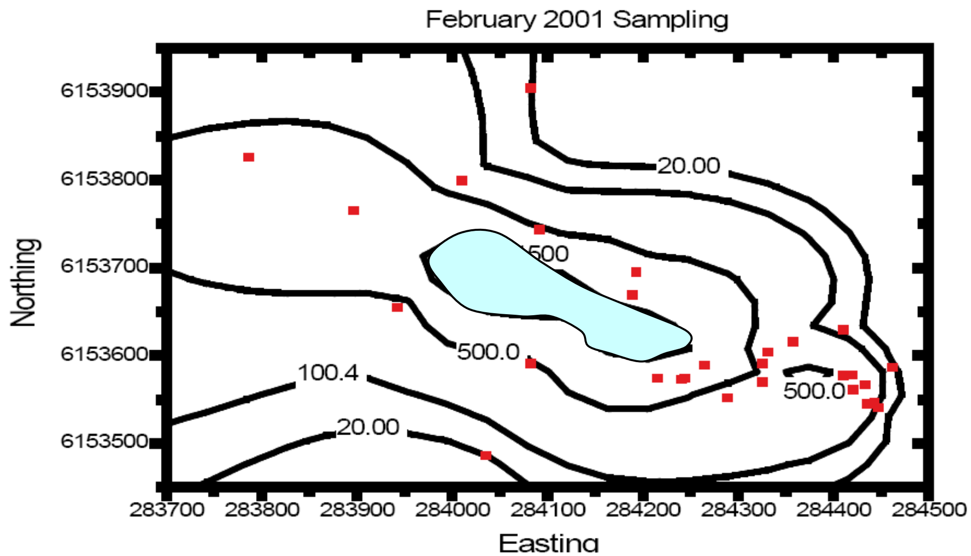
Plume Transect Well

- Plume Strength = 6 g/day
- Positive Correlation
- No degradation

Basu et al., JCH 2008 (in review)

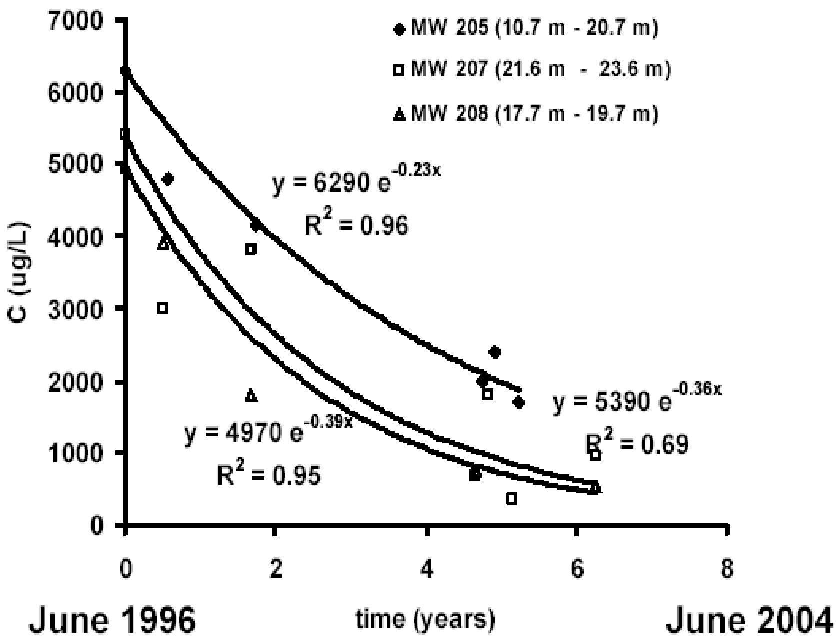
TCE Plume Dynamics





- Several small areas with conc >1500 ug/L
- Plume disconnecting from a depleted source zone
- Some shifts in plume shape
- Decrease in source mass discharge

Source Mass Estimation



Method A:

$$M_{2006} = M_{1996} \exp(-10k)$$

$$= (V_d A C_{t=1996} / k) \exp(-10k)$$

M_{2006} = present source mass

< 10 kg

Method B:

$$M_P = \int_0^t M_{D,0} \exp\left(-\frac{M_{D,0}}{M_0} t\right) dt = 2250 kg$$

$$M_{D,t} = M_{D,0} \exp\left(-\frac{M_{D,0}}{M_0} t\right) = 1 kg / year$$

M_0 = 2,260 kg

$M_{D,0}$ = 170–365 kg/yr

M_{2006} ~ 10 kg

Integration of Historic Data with Mass Flux Measurements

Proposed Remediation at Site: Chemical Oxidation of Source

Observations

1. Source strength small compared to other sites (3 g/day)
2. Flux data indicate negatively correlated source distribution – high concentrations in low flow regions
3. Mass discharge at source and plume control planes of similar magnitude: plume degradation rates ~ 0
4. Source concentrations are decaying and will attain irrigation standards in <10 years
5. Source mass <10 kg, Plume mass ~ 3800 kg

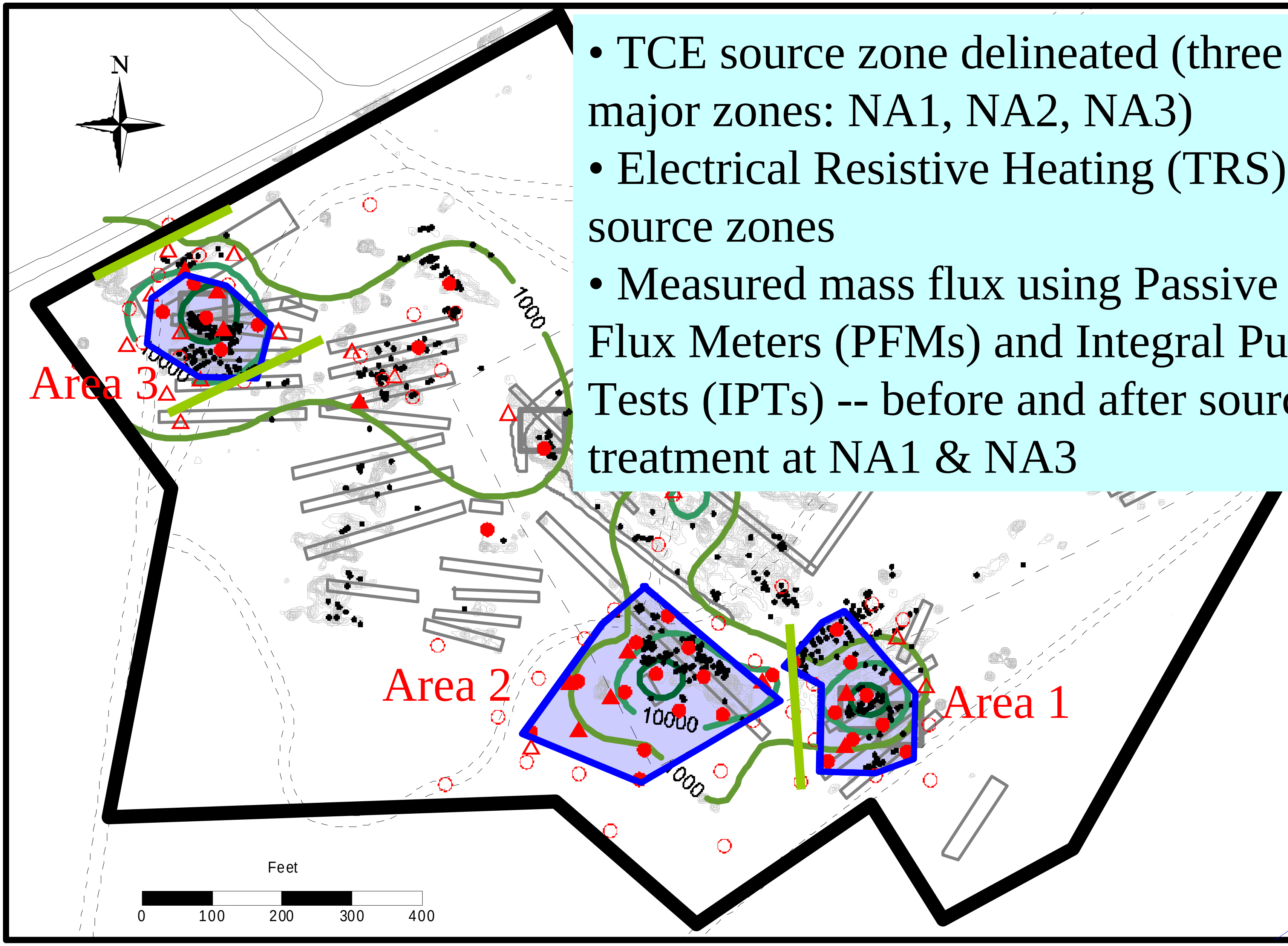
Interpretations

1. Source removal is not important at this site??
2. Source treatment maybe inefficient due to accessibility of isolated ‘hotspots’
3. Plume remediation or containment is vital
4. Source removal is not important?
5. Plume remediation more important than source

Recommendations:

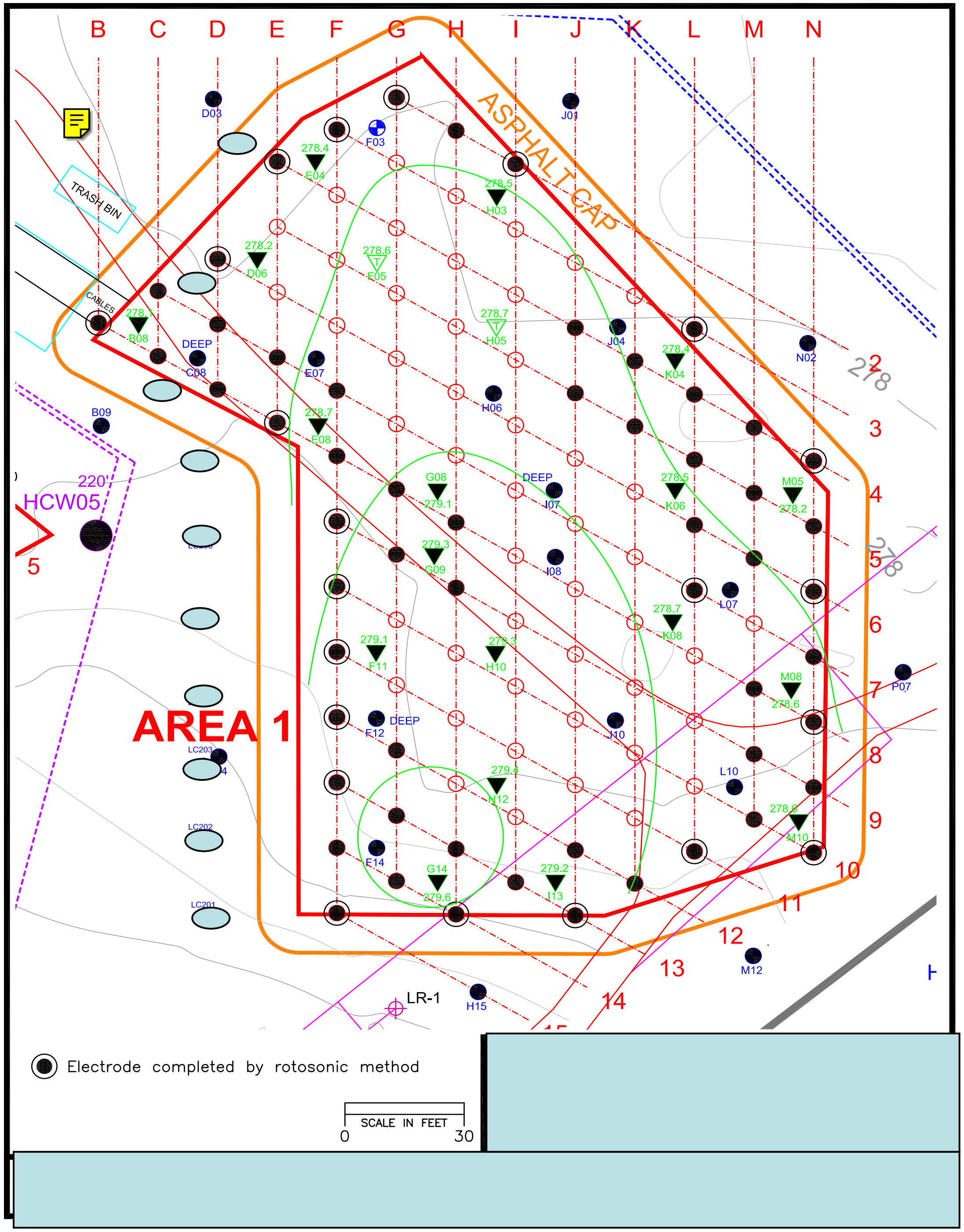
1. No source removal is necessary
2. Plume treatment or containment maybe required

Ft Lewis, WA



- TCE source zone delineated (three major zones: NA1, NA2, NA3)
- Electrical Resistive Heating (TRS) of source zones
- Measured mass flux using Passive Flux Meters (PFMs) and Integral Pump Tests (IPTs) -- before and after source treatment at NA1 & NA3

NA1 Source Area



Flux Transect Wells

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Hill AFB OU2

History

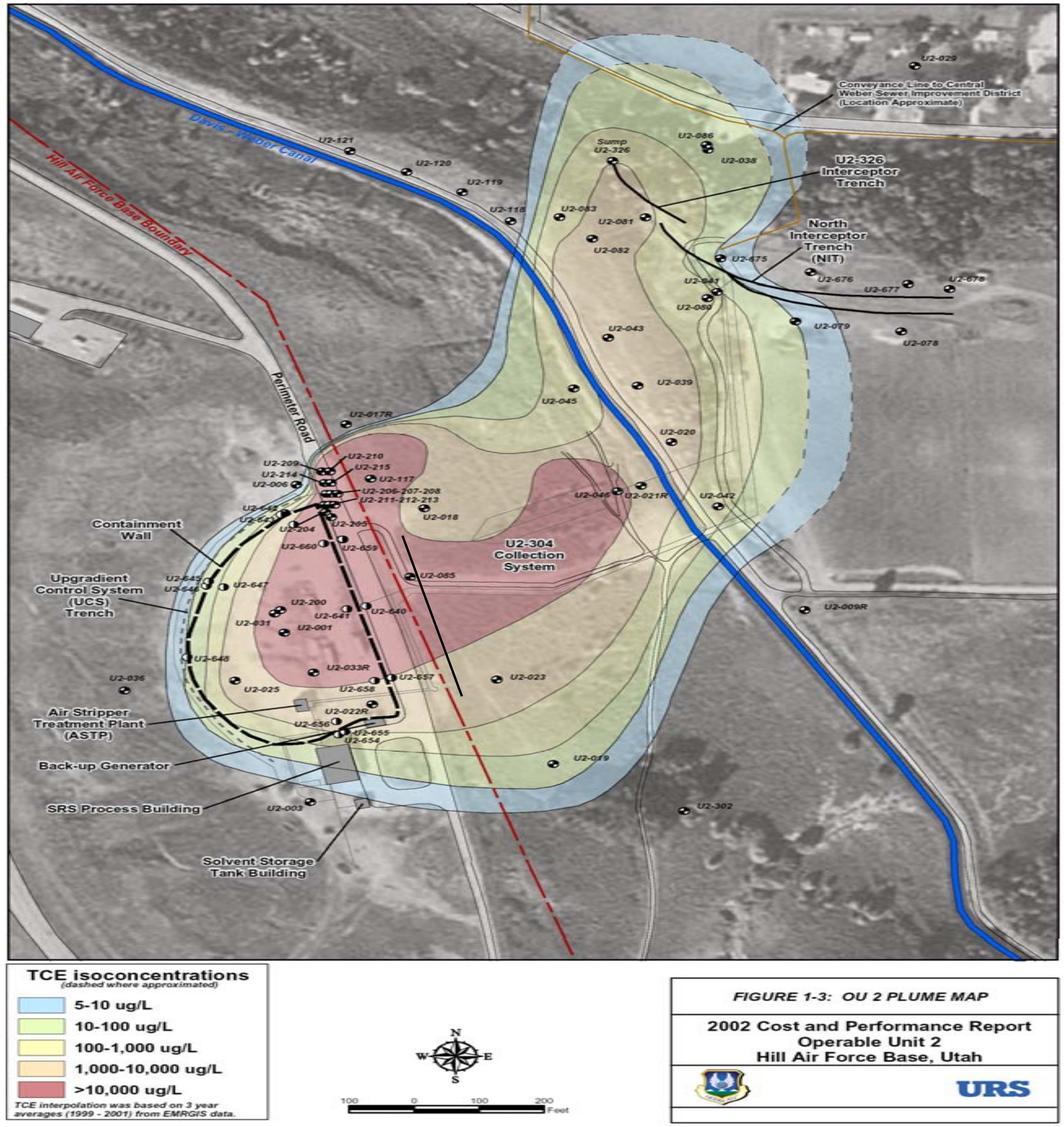
Created due to disposal of chlorinated solvents from degreasing operations during 1967 to 1975

Hydrogeology

- **Shallow unconfined aquifer**
- **K ~ 2 m/day**

Plume Characterization

- **DNAPL pooled in the paleo-channel forming a source**
- **900 m long, 150 m wide, and 10 m deep plume**



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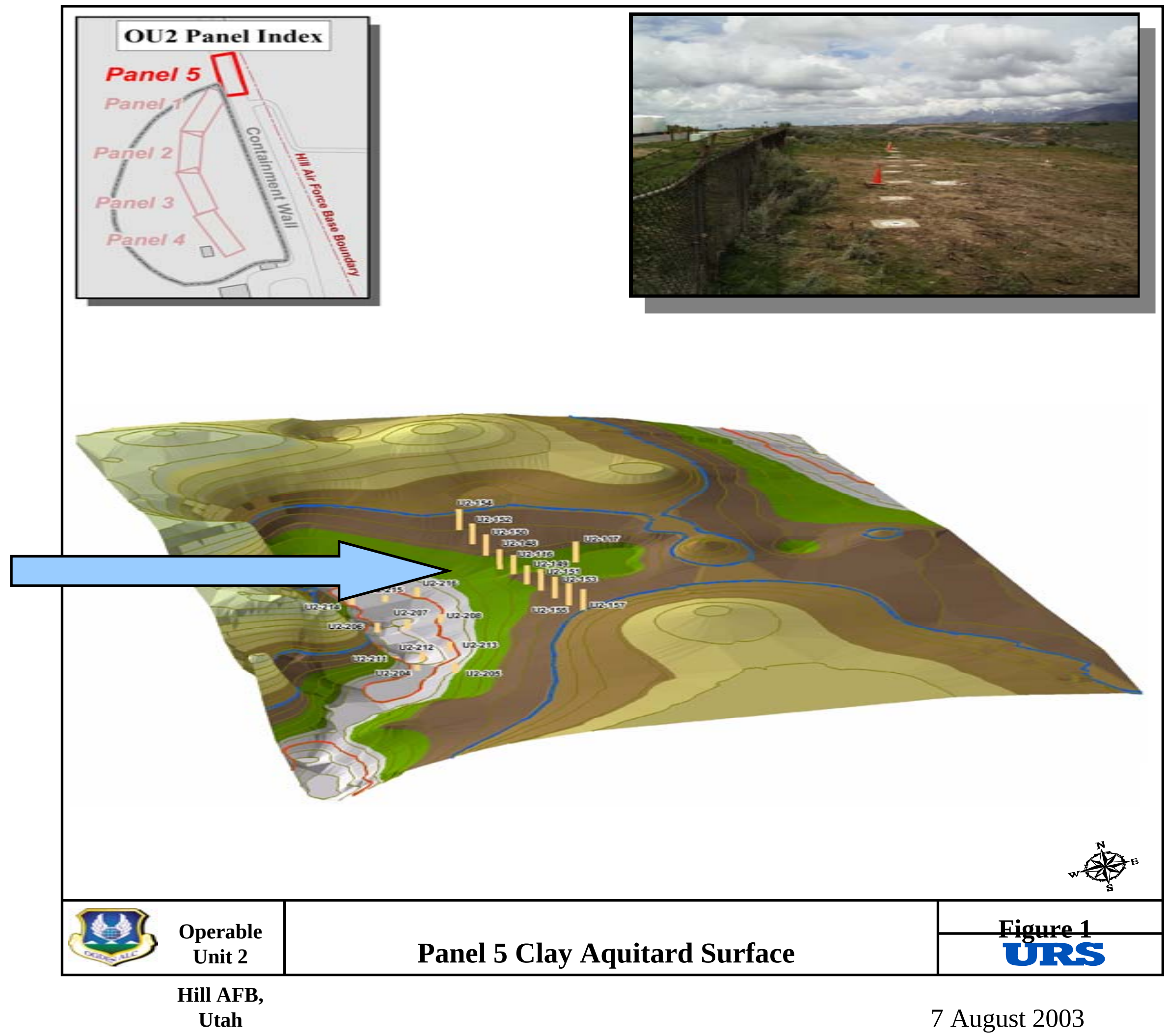
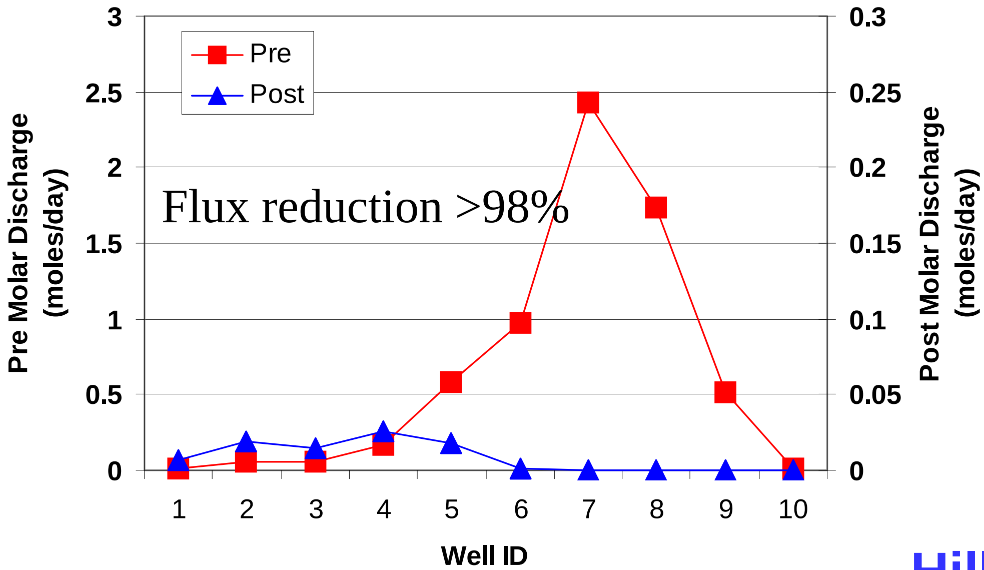
Source Remediation Activities

- **40,600 gallons DNAPL recovered**
- **In 1996 containment wall constructed around the source area**
- **In 1997, additional DNAPL discovered in a depression in the clay surface, just north of the containment wall in Panel 5.**
- **Study initiated to investigate effects of mass removal on mass discharge**
- **SEAR resulted in TCE mass depletion 1,300-2,200 kg; >70% reduction??**



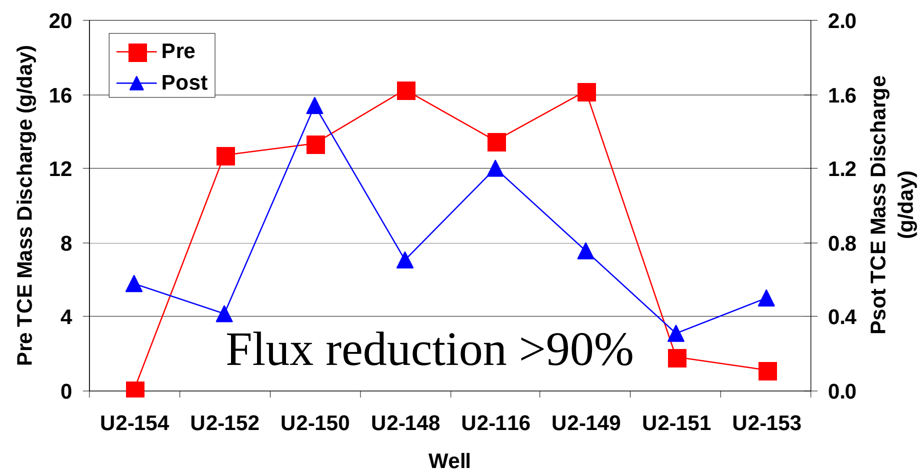
Effect of Source Remediation

Ft Lewis Thermal Remediation



Field studies indicate significant decrease in mass discharge from source zones after DNAPL mass removal.

Hill AFB Surfactant Remediation



Brooks et al. JCH In review

DNAPL Mass Depletion:
Ft Lewis EGDY Thermal

Area 1			
	TCE (Kg)	c-DCE (Kg)	TPH (Kg)
Estimated Mass Removed	2,580	410	40,170
Area 2			
	TCE (Kg)	c-DCE (Kg)	TPH (Kg)
Estimated Mass Removed	1,090	250	11,340
Area 3			
	TCE (Kg)	c-DCE (Kg)	TPH (Kg)
Estimated Mass Removed	840	280	530

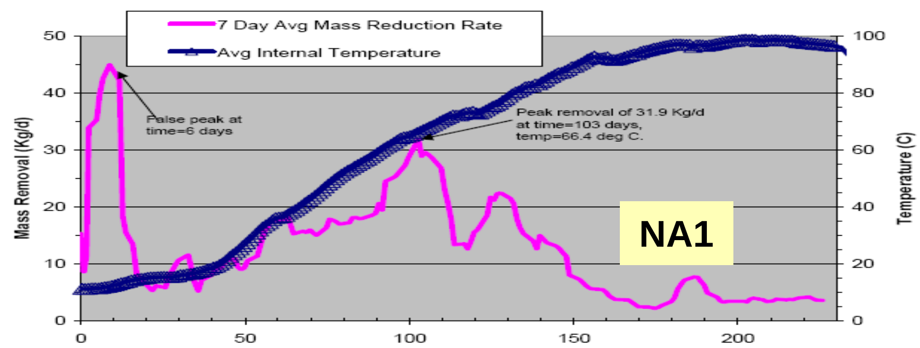
Notes:

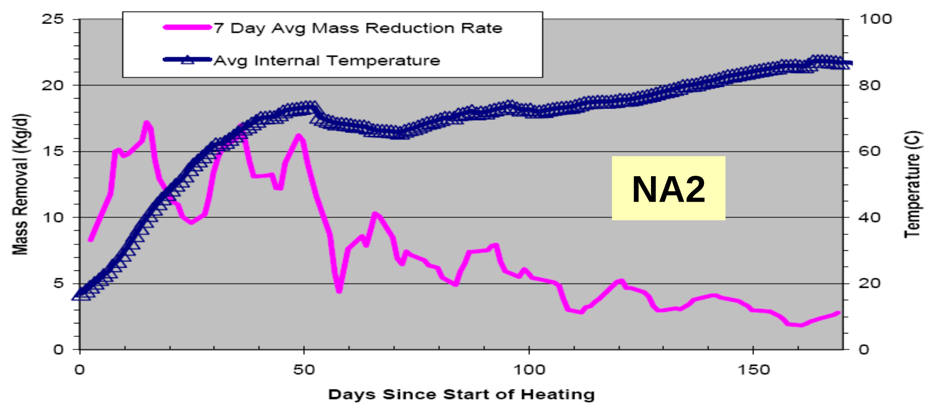
Numbers provided in table are rounded.

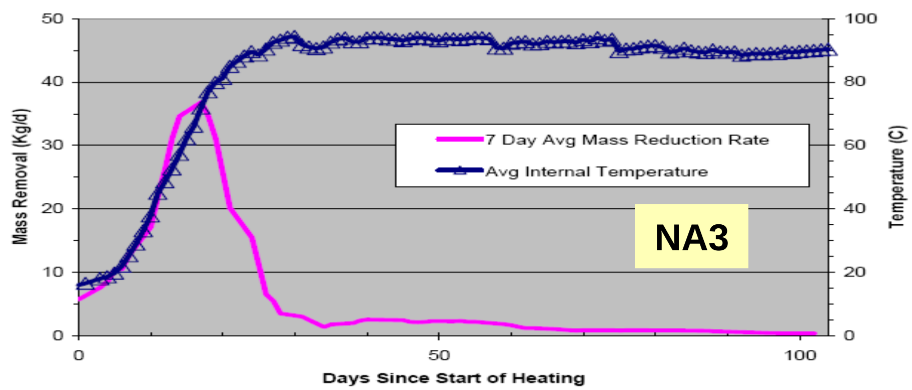
NA2 configuration changed; all estimates based on revised configuration.

Total mass removal estimates based on stoichiometric means.

Thermal treatment objective to maximize CVOC (TCE, cis-DCE) removal, not TPH removal.

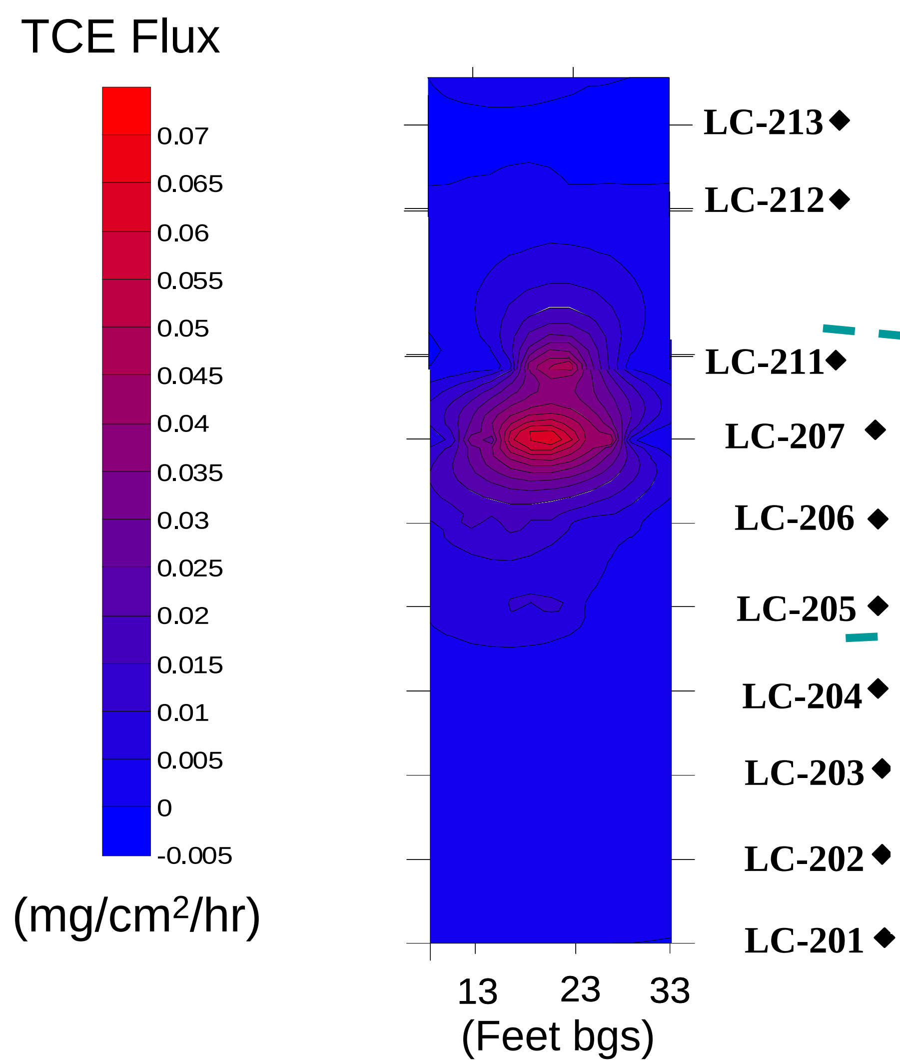


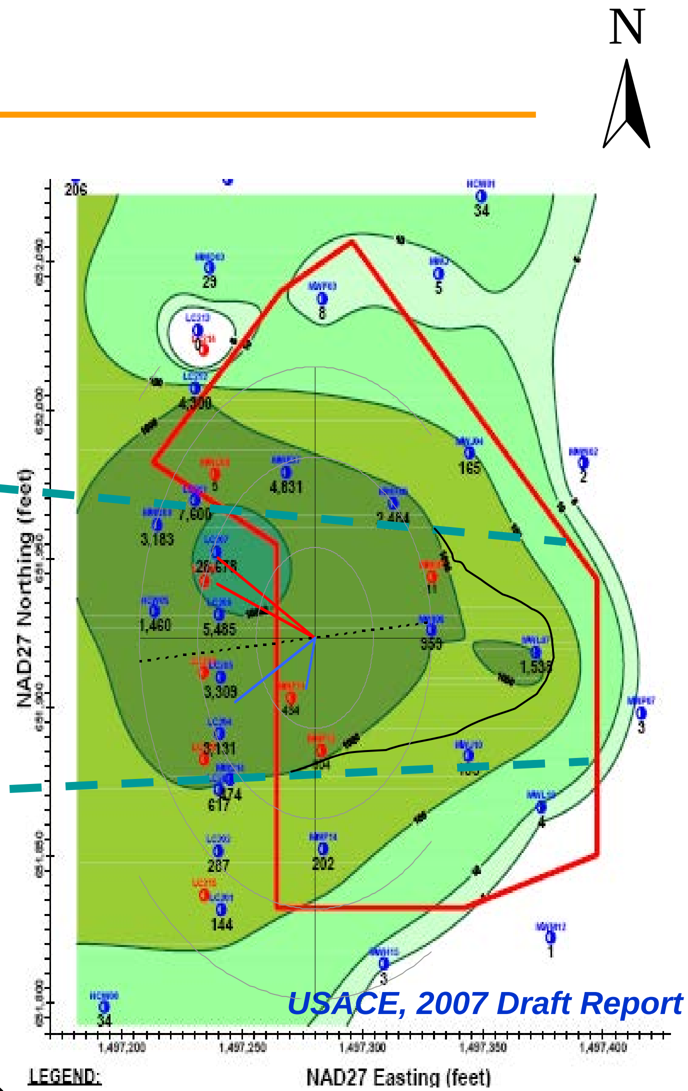




USACE, 2007 Draft Report

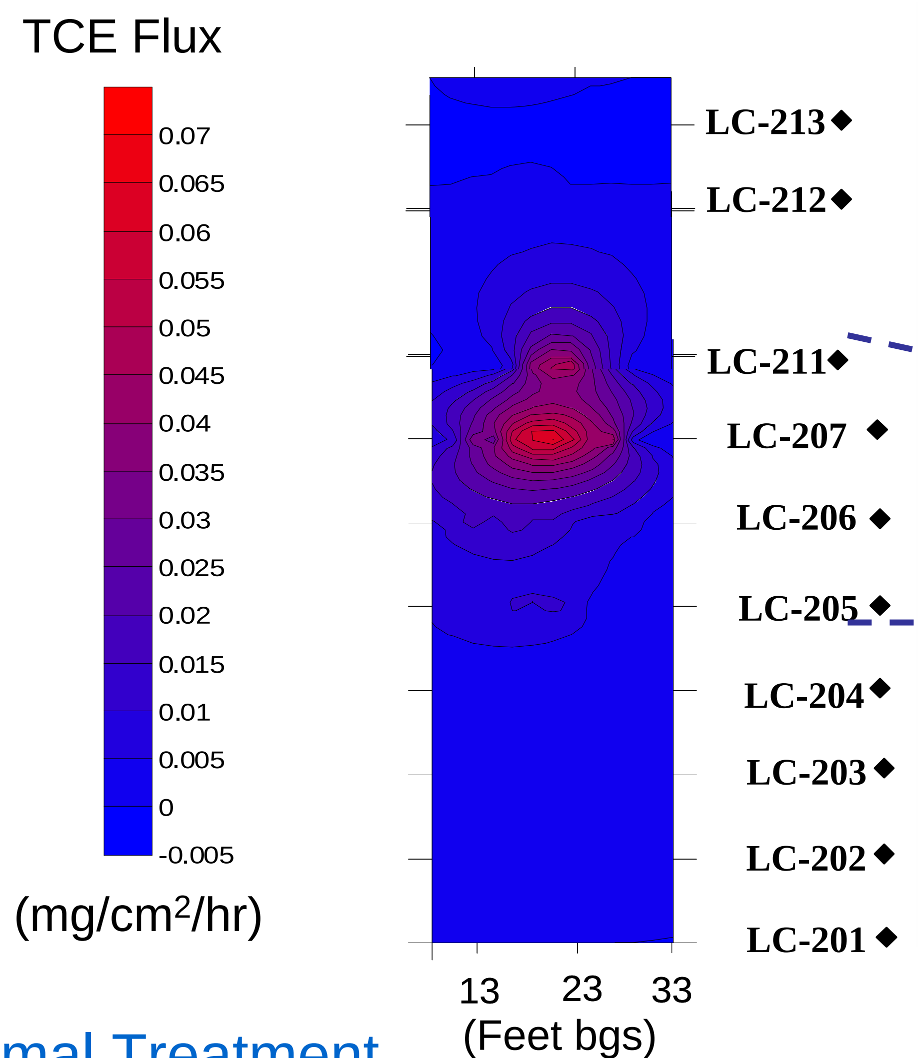
Fort Lewis EGDY NA1

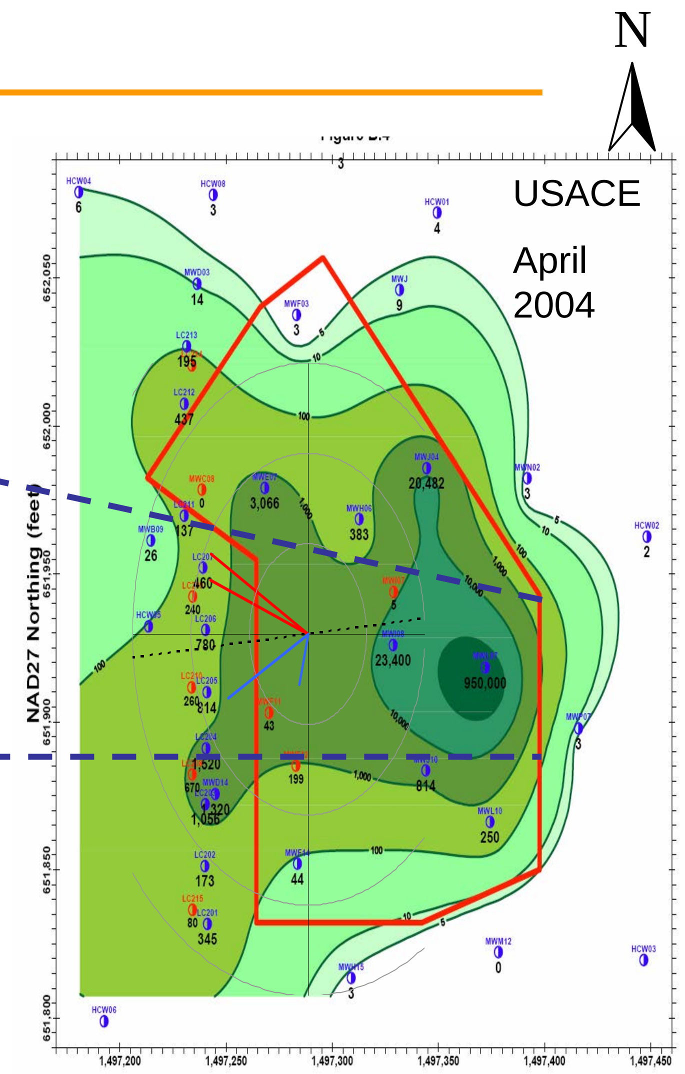




Pre-Remediation (Baseline GW Data)

Fort Lewis EGDY NA1





Peak-Thermal (Performance Monitoring)

Thermal Treatment

Cost ≈ $6M; Flux cost ≈ 2%

USACE, 2007 Draft Report

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Lessons Learned: Ft Lewis EGDY

- Detailed site characterizations required to locate and delineate sources (cost & level of effort?)
- Initial NAPL mass estimates; later revised with additional analysis & interpretation.
- Thermal treatment of NA1, NA2, NA3
- ~2,600 kg TCE recovered during thermal treatment (~70% reduction)
- GW fluxes are large (q ~ 25 cm/day)
- **Thermal treatment reduced (>95%) TCE & DCE mass discharge**
- Flux distributions across NA1 source control plane show small area contributed most of mass discharge
- **How would the source remediation decisions have changed if the flux distribution data were used?**

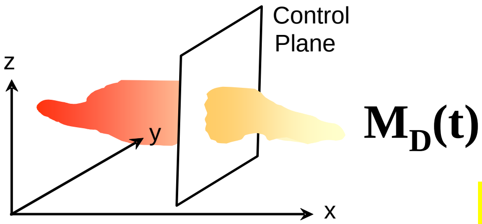
Lesson Learned: Hill AFB OU2

- TCE Mass discharge estimates using three methods are in agreement.
- TCE mass discharge is across a fraction of the source control plane.
- Source treatment (SEAR) resulted in TCE mass depletion (1,300-2,200 kg removed; ~70% reduction) and an associated decrease (>90%) in TCE mass discharge.
- Increase in DCE mass discharge suggests increased biodegradation after SEAR.
- How does the source treatment influence plume evolution?

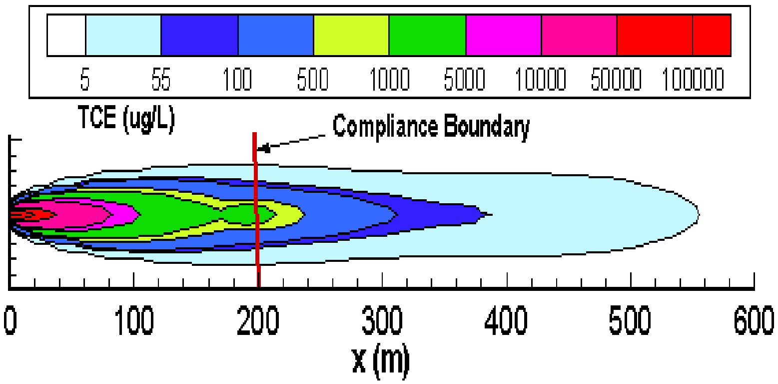
DNAPL Site Attributes

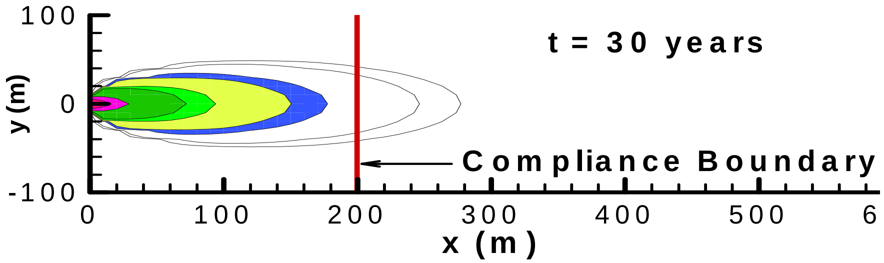
SITE PARAMETERS	Northwest US	Midwest US	Oz-1	Oz-2
Site Hydrogeology				
Groundwater Flux, q (cm/day)	30	10 (6 & 40)	2.5 (1 & 13)	5 (3 & 20)
Current Source				
Mass, m_0 (kg)	~5,000	??	<100	~2,500
Max. Conc., C_{max} (mg/L)	~10	70	~5	~150
Mass Discharge, M_D, (g/day)	~800	~300	~3	~100
Depletion Rate Constant, α (yr^{-1}), $\alpha=[qA_{cp}C_0/M_0]$	0.2	0?	0.4	~0.1
Control Plane, A_{cp} (m^2)	70x12 = 840	10x5 = 50	25x15 = 375	30 x 10 = 300
Current Plume				
Dimensions (m x m x m)	5,000x500x50	500x120x15	1500x40x11	250x50x15
Mass, M_p (kg)	~10,000	~1,000	~3,800	~500
Avg. Deg Rate Constant, k (yr^{-1})	~0??	~1	0	~1
Site Management				
Source Remediation	ERH (99%+)	ChemOx?	None?	Flushing?
Plume Remediation Recommendation	P&T	None?	None?	P&T

REMChlor Simulations of Management Options

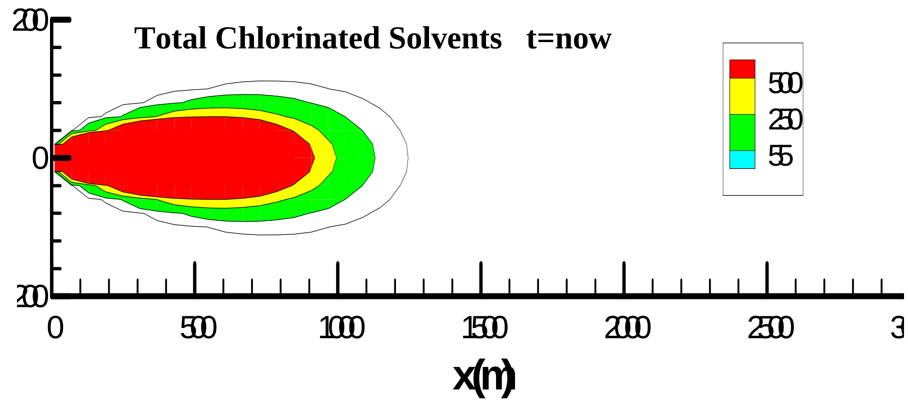


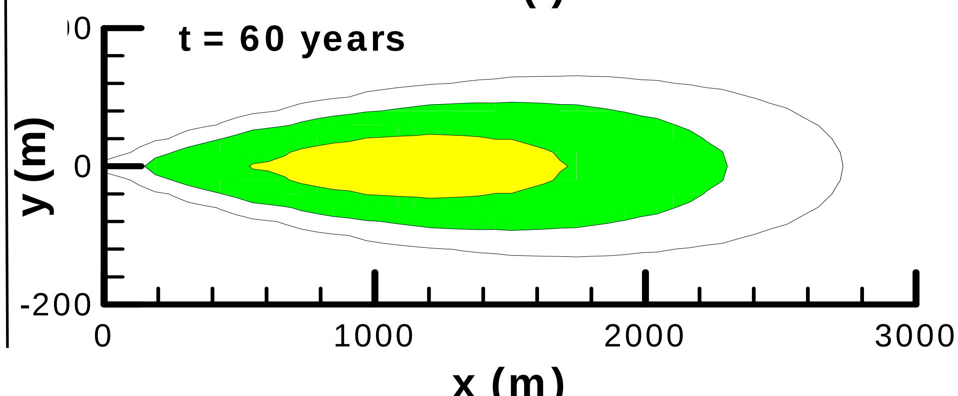
SITE 1





SITE 2





Plume shrinks at both ends

Plume marches on at leading edge

Both cases 90% mass depletion

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What Guides Remediation Choices?

1. **Remedial Objectives**
   - Compliance boundary ("everywhere" or at specified POC?)
   - Performance Metrics:
     - concentration or flux?
     - Mass depletion & residual mass
   - Source and/or plume**?**
2. **Remediation timeframe**
   - Short-term responses
   - Long-term site stewardship
3. **Site Characteristics**
   - Source strength and longevity
   - Degradation rates in the plume

Source Remediation Options?

options	Stable $M_D(t) = \lambda(t)$	Advancing $M_D(t) > \lambda(t)$	Shrinking $M_D(t) < \lambda(t)$
1. No remediation	M_D (t) decreases over time (exponential?); so, if λ (t) is constant (?), eventually all plumes start shrinking– ** requires long term stewardship for at least a century		
2. Reduce source mass through some aggressive source depletion action (e.g., flushing, chem ox, thermal, etc) $M_D(t) \downarrow$	Plume "pinched off" at the head; tail starts shrinking when reduced M_D reaches it	Plume "pinched off" at the head but tail continues to move forward – split plumes?	Plume shrinks inwards from both ends
3. Reduced Source Flux as in the case of n-ZVI or enhanced bio	Plume response similar to 2; but, since the source mass hasn't been reduced, the source treatment has to be maintained for a very long time		
4.Integrated "Treatment Train" Approach: (2) + (3) → Implement "aggressive" short-term action to deplete most of the source mass (say, ~80%?), and then use the "passive" source treatment (nZVI or eZVI) to sustain essentially zero source flux, or a low-grade "chaser" of say chem ox			

Summary Comments

- Groundwater & contaminant flux characterization at DNAPL source control planes provides critical information needed in source remedy selection and performance assessment.
- “Source Strength” can be used to compare sites, and the required source strength reduction through mass depletion can be determined based on likely plume response.
- Regulatory framework and policy guidance lacking for adoption.

Discussion Items

- How much longer will we debate the benefits/limitations of partial mass removal for DNAPL source zones?
- If "MCL everywhere" can't really be achieved "at reasonable cost and in reasonable time," what are the alternatives for site remediation?
- If some DNAPL mass is left behind in the source zone, what are the implications to site stewardship (costs, risks, liabilities, etc)?
- How do short-term *dis*counting procedures influence site remediation decisions at government & corporate sites?

Questions?