

# *Arsenic in Ground Water at Waste Sites*

Robert Ford

U.S. Environmental Protection Agency  
Office of Research and Development

Collaborators:

Richard Wilkin, Frank Beck, Patrick Clark, Cynthia Paul, Steven Acree, Randall Ross, Brad Scroggins, Kirk Scheckel, Aaron Williams, Jack Creed, Joseph LeMay, Bill Brandon

SBRP Arsenic in Landfills - Boston, MA

October 4, 2006

# ***Factors Controlling As Mobilization***

- Solid phase association
  - Partitioned in reduced or oxidized forms
  - Present as separate phase or a trace component (adsorption/coprecipitation) in soil/sediment minerals
- Ground-water geochemistry (e.g., oxidizing, reducing, pH, anions)
- Microbial activity and the supply of electron donors and acceptors
  - Manipulation of system redox chemistry (C, Fe, S)
  - Direct transformation of As speciation
- *Rate of fluid flow relative to the rates of abiotic or biotic processes influencing aquifer chemistry...*

# *Example Waste Sites*

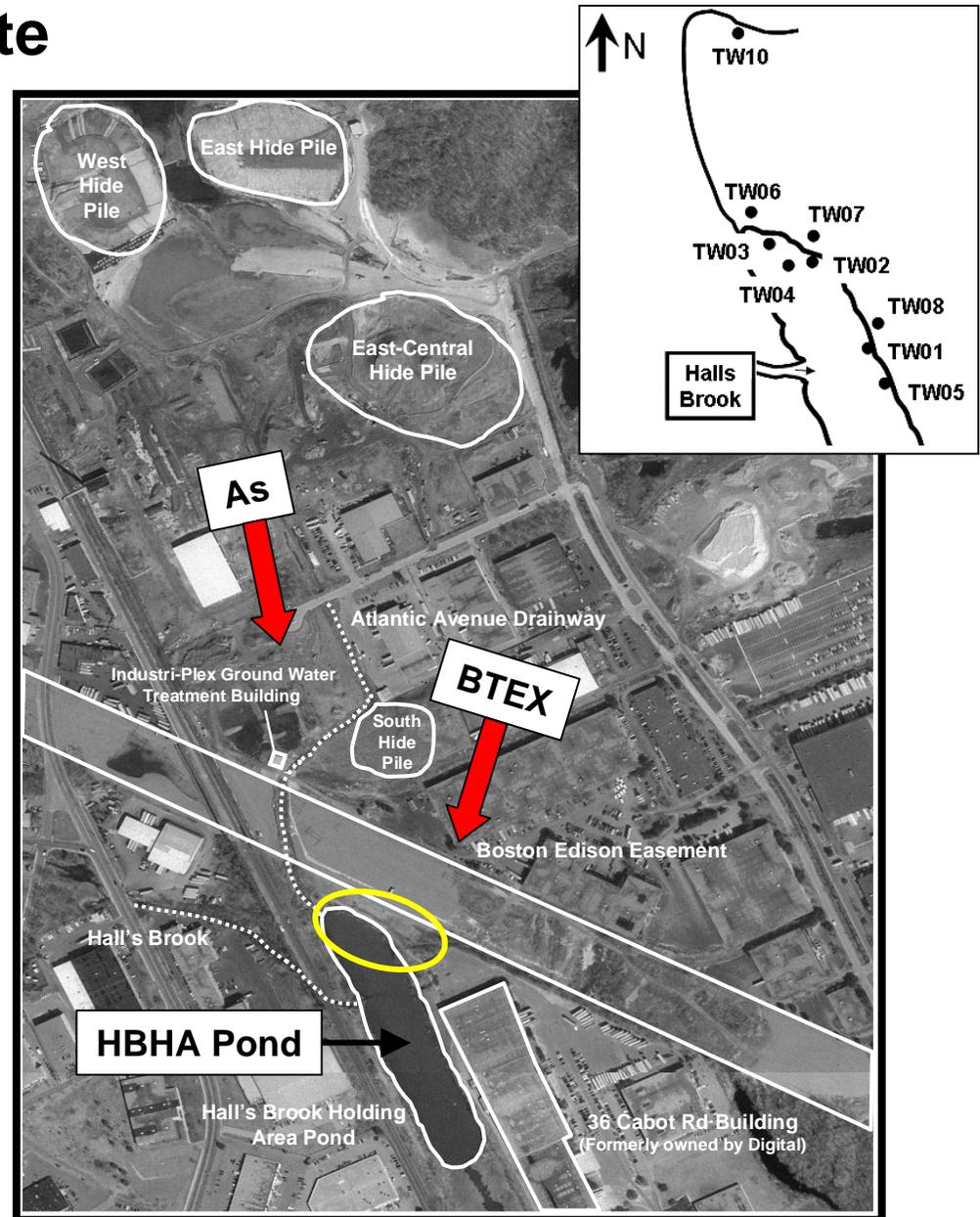
- Industri-Plex Superfund Site
  - Anthropogenic sources of arsenic
  - ‘Unlimited’ supply of electron donors and acceptors
- Shepley’s Hill Landfill (Fort Devens)
  - Possible anthropogenic & natural sources of arsenic
  - Sufficient supply of electron donors and acceptors to maintain As mobility
- *Do these sites provide a useful analog for assessing future conditions at operational landfills?*

# Industri-Plex Superfund Site

Woburn, MA (Region 1)

Joseph LeMay, RPM

- Land disposal of waste products from production of sulfuric acid, lead arsenical pesticides, various organic compounds and leather tanning
- Continual leaching into shallow ground water and transport to downgradient wetland
- Primary GW plume discharges into Halls Brook Holding Area (HBHA) Pond prior to transport down watershed
- GW contains high concentrations of C (including BTEX), Fe, and SO<sub>4</sub> and near-neutral pH

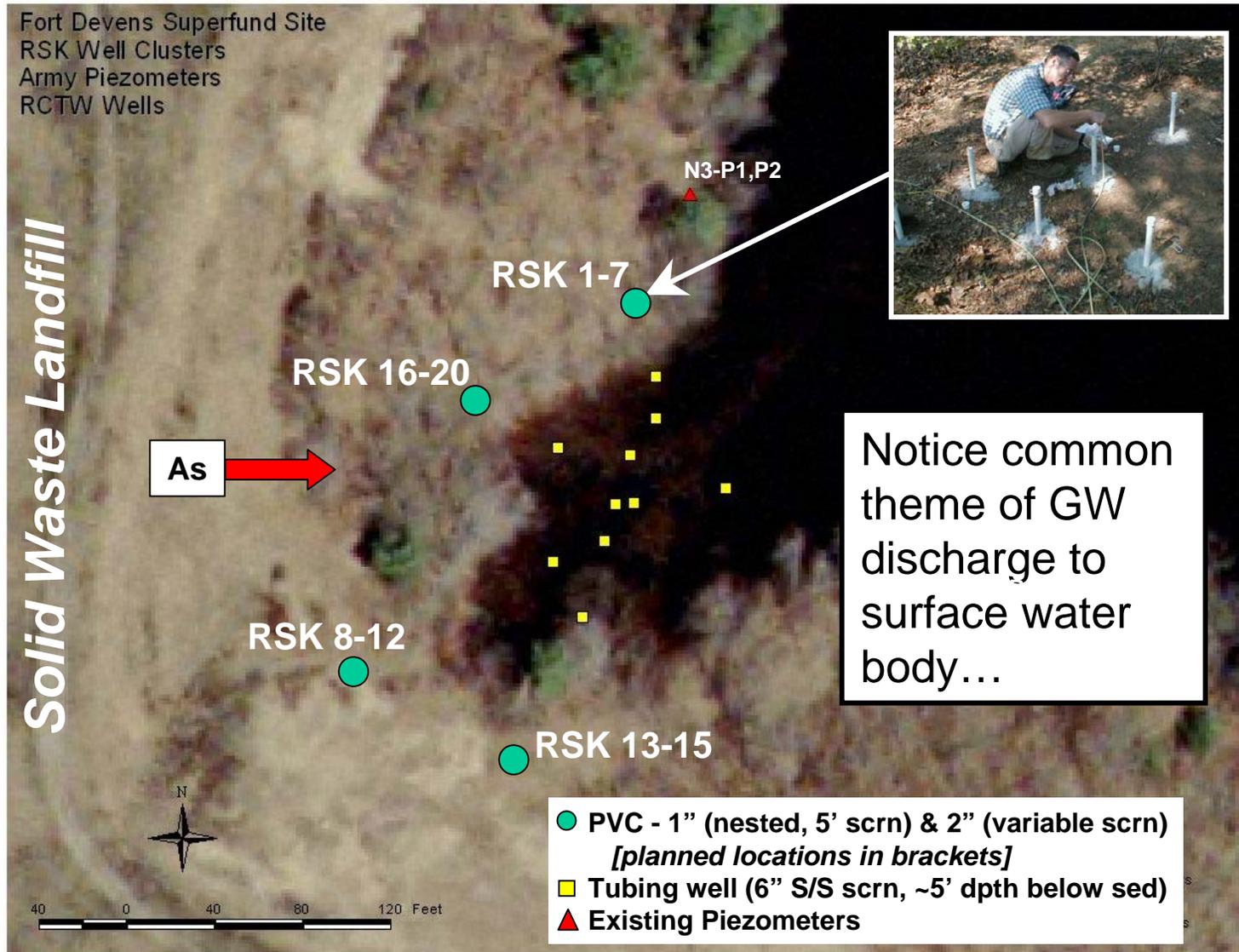


RESEARCH & DEVELOPMENT

*Building a scientific foundation for sound environmental decisions*

# Fort Devens Superfund Site

Devens, MA (Region 1)  
Ginny Lombardo, RPM



RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions

# Comparison of 'Leachate' Chemistries

Parameter	Landfills <sup>1</sup>	Industri-Plex	Shepley's Hill
pH	4.5-9	5.6-8	6.3-7
Specific conductivity ( $\mu\text{S cm}^{-1}$ )	2500-35 000	500-12 000	280-630
Total organic carbon (TOC)	30-29 000	9-390	1-14
<b>Inorganic macrocomponents</b>			
Chloride	150-4500	70-250	8-30
Sulphate	8-7750	5-3600	0.05-16
Hydrogencarbonate	610-7320	170-5350	200-300
Sodium	70-7700	70-2200	7-25
Potassium	50-3700	10-100	3-13
Ammonium-N	50-2200	4-85	1-10
Calcium	10-7200	20-600	22-65
Magnesium	30-15 000	10-100	3-10
Iron	3-5500	1-70	22-60
Manganese	0.03-1400	0.5-2.5	1-4
<b>Inorganic trace elements</b>			
<b>Arsenic</b>	<b>0.01-1</b>	<b>0.04-2.3</b>	<b>0.25-1.1</b>
Chromium	0.02-1.5	<0.05	<0.001
Zinc	0.03-1000	<0.7	<0.03

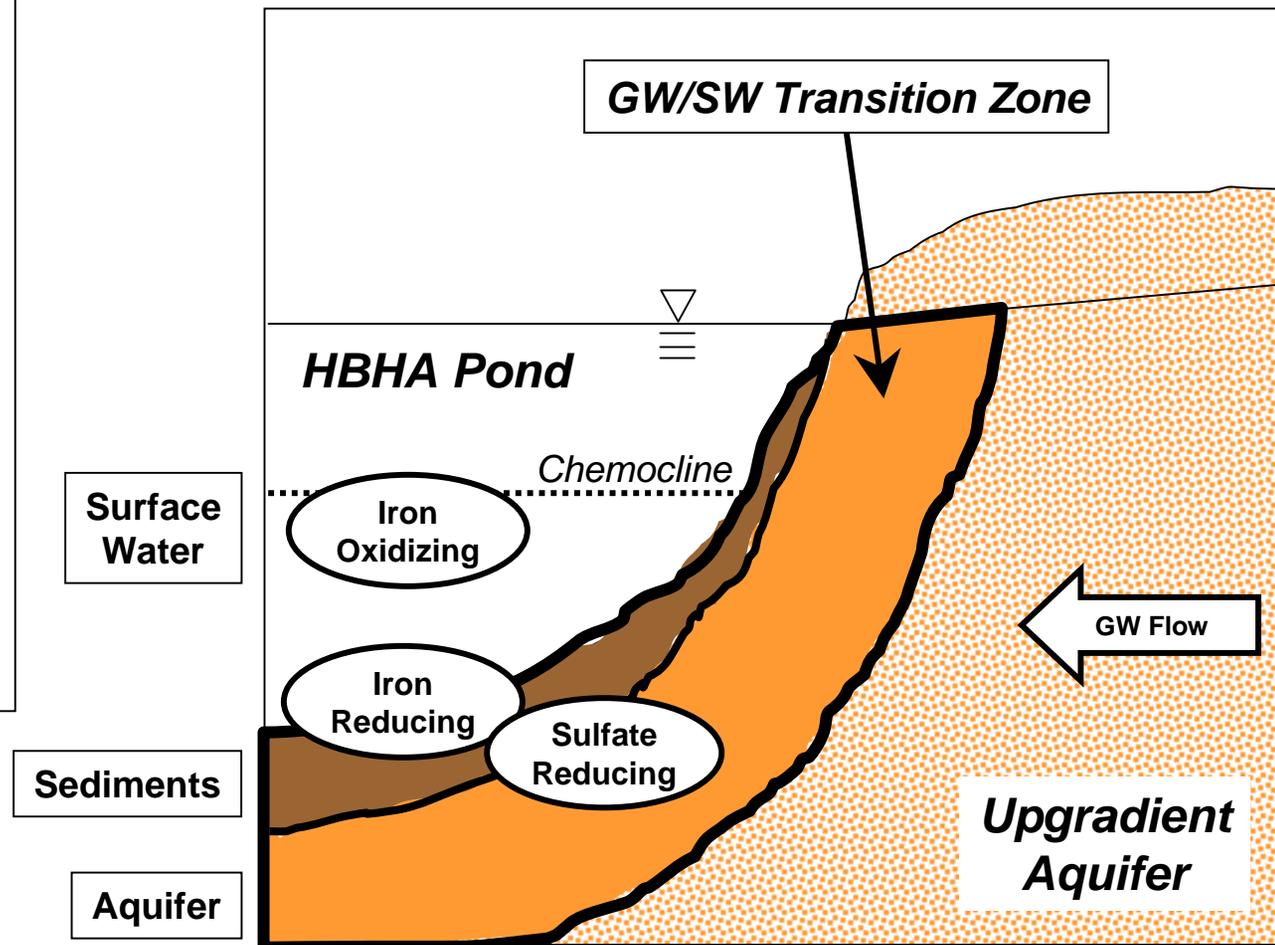
*As assessed via down-gradient or side-gradient wells.*



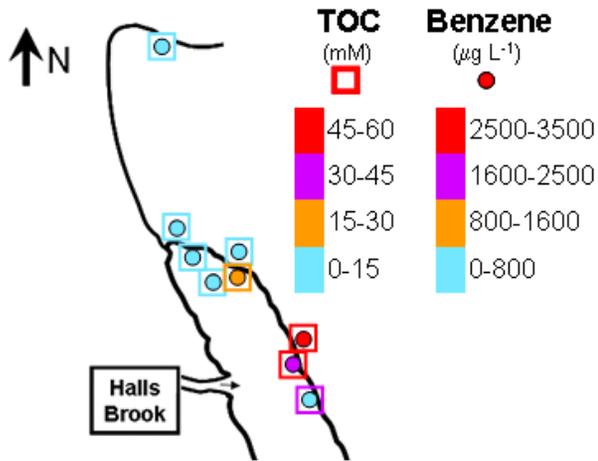
<sup>1</sup> Christensen et al. (2001) Biogeochemistry of landfill leachate plumes: Applied Geochemistry, v. 16, p. 659-718.

# Industri-Plex Site: Conceptual Model of Critical Redox Processes

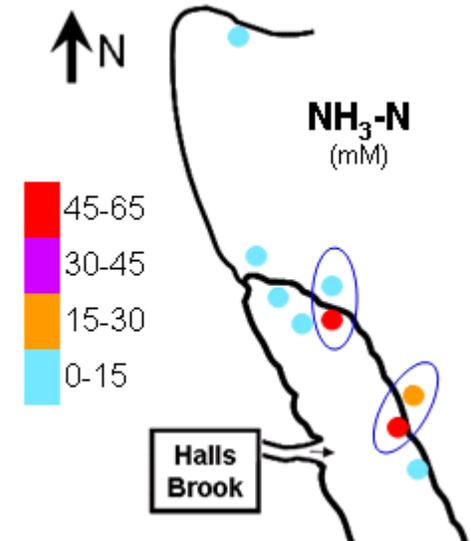
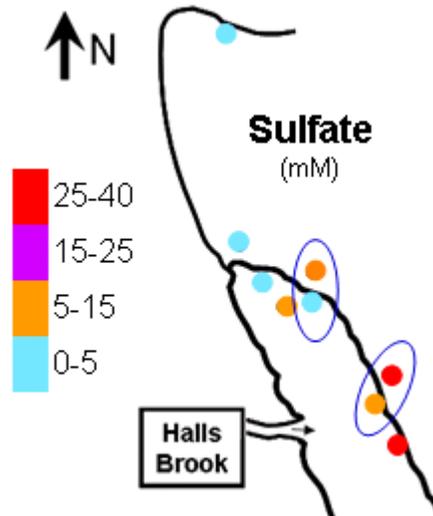
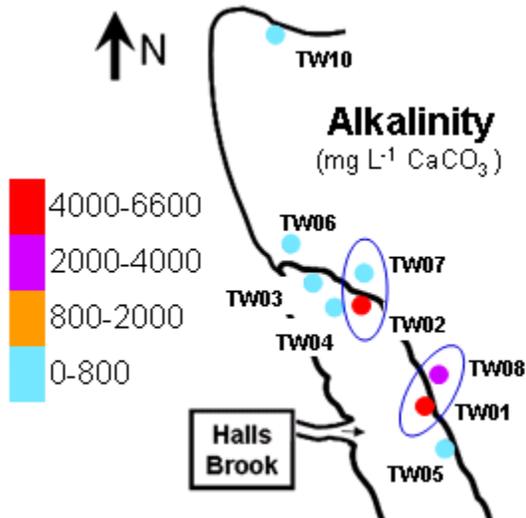
- Possible absence of acidogenesis and/or methanogenic phases
- Fe reduction-oxidation and  $\text{SO}_4$  reduction important, but possibly not for landfills – accept gypsum debris
- *Q: Are Fe- and  $\text{SO}_4$ -reduction not observed in landfills?*



# Patterns in GW Chemistry



- Region of highest alkalinity corresponds with region of highest BTEX concentrations
- Circled well pairs indicate regions of sulfate reduction and ammonia production – BTEX stimulation
- Arsenic aqueous speciation dominated by inorganic w/ periodic occurrences of MMA, DMA, and DMTA (BTEX region)



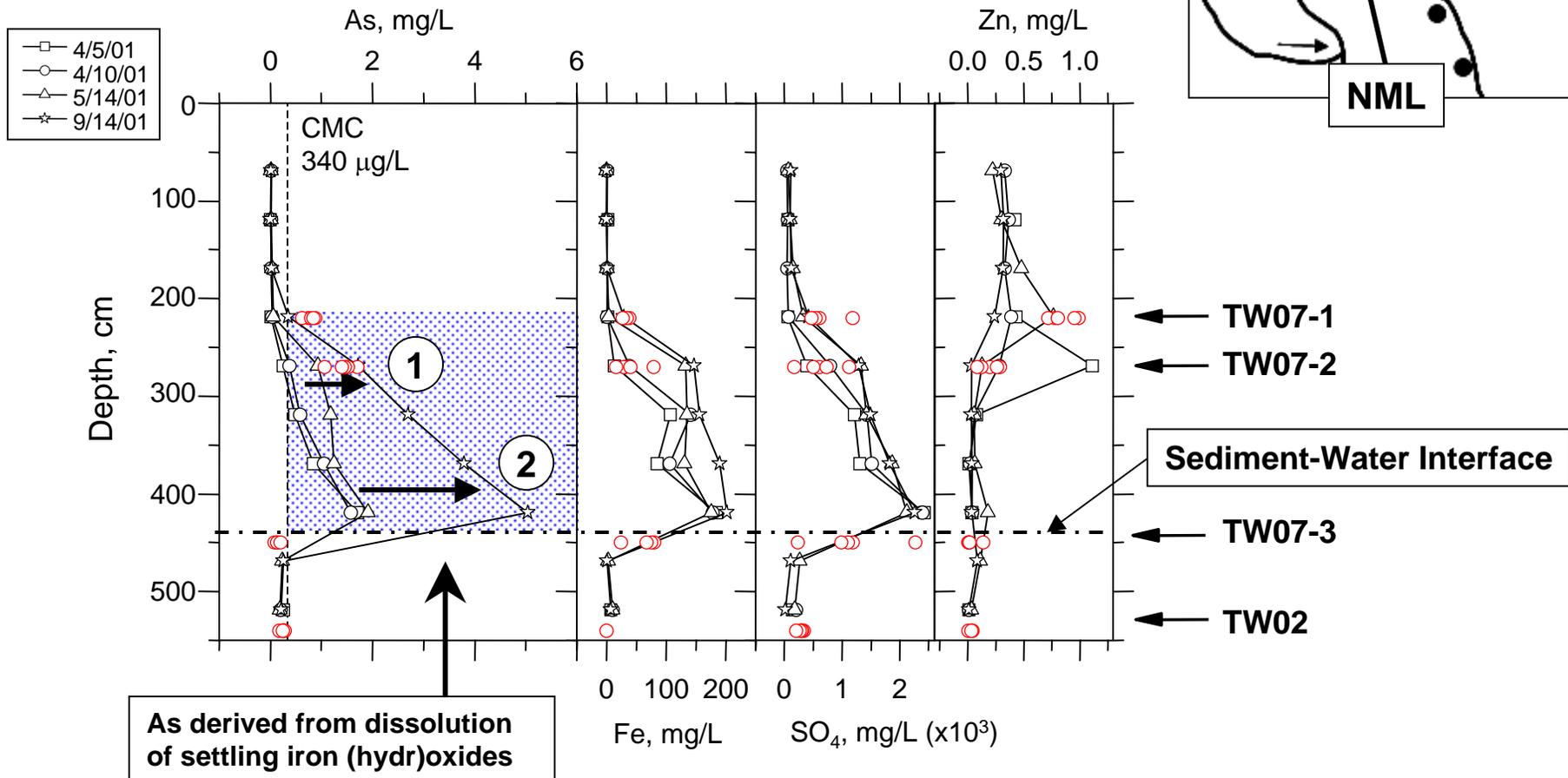
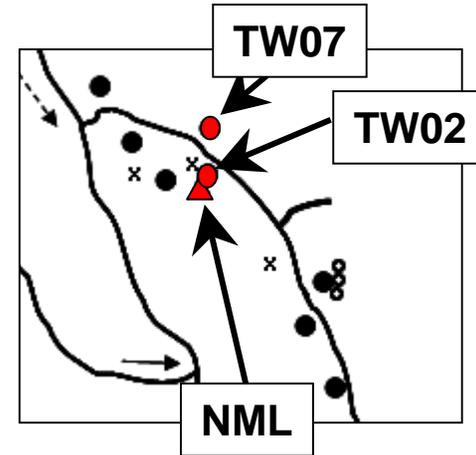
# Sources of As to HBHA Pond water column?

(1) GW Discharge

(2) Sediment Dissolution

○ Surface Water & Sediments

○ Ground Water Wells

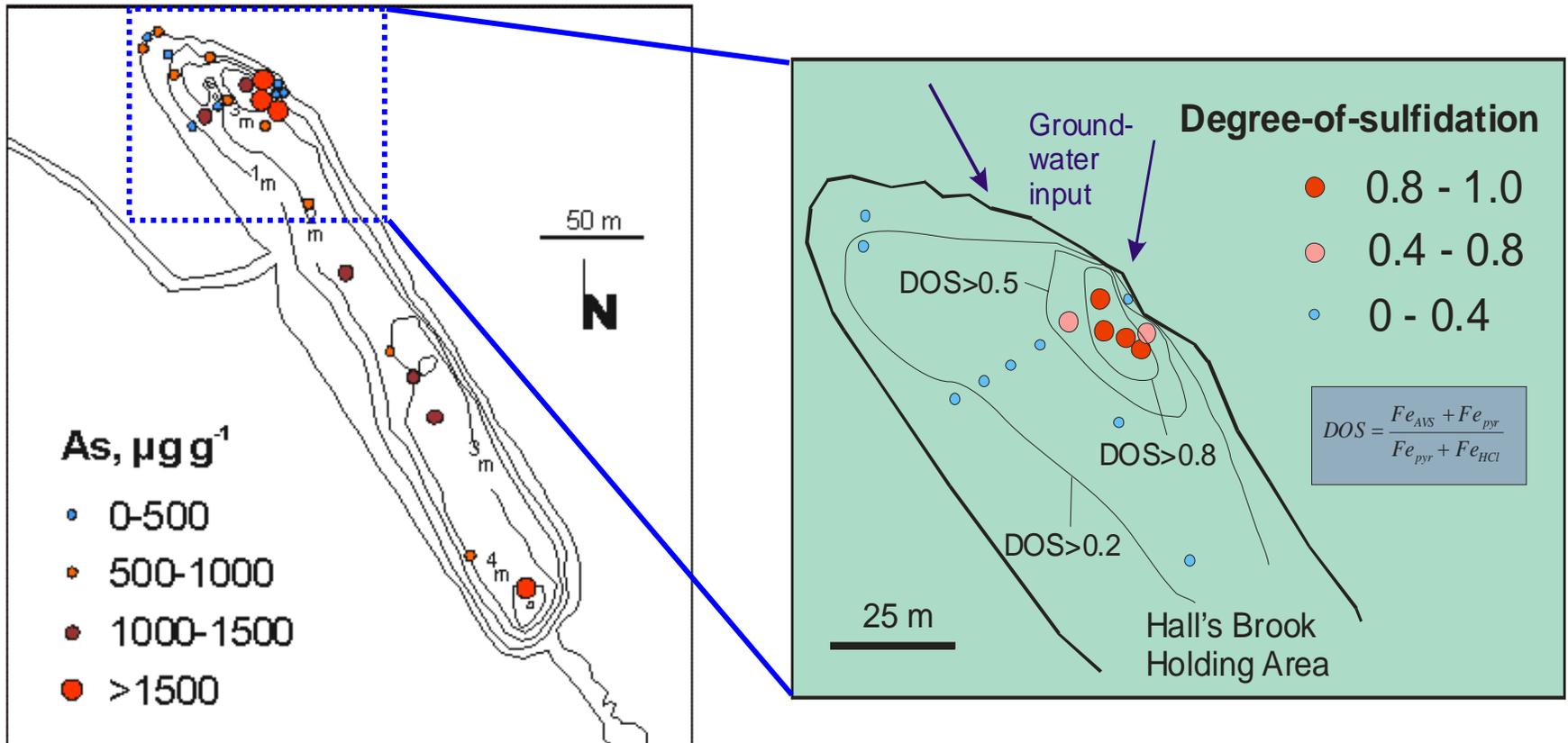


# ***What is the analogous landfill situation?***

- Infiltration of precipitation during operational lifetime ('oxic reaction front')
- Internal fluctuations in water table for closed landfill
  - Cause alternation between oxidizing and reducing conditions
- Internal redox shifts within landfill mass during degradation of waste material coupled with seasonal fluctuations in microbial activity
- *Cyclic fluctuations will tend to maintain arsenic mobility (metastable solid phases) – unidirectional changes may be of less concern*

# Spatial Pattern in As & Sediment Mineralogy

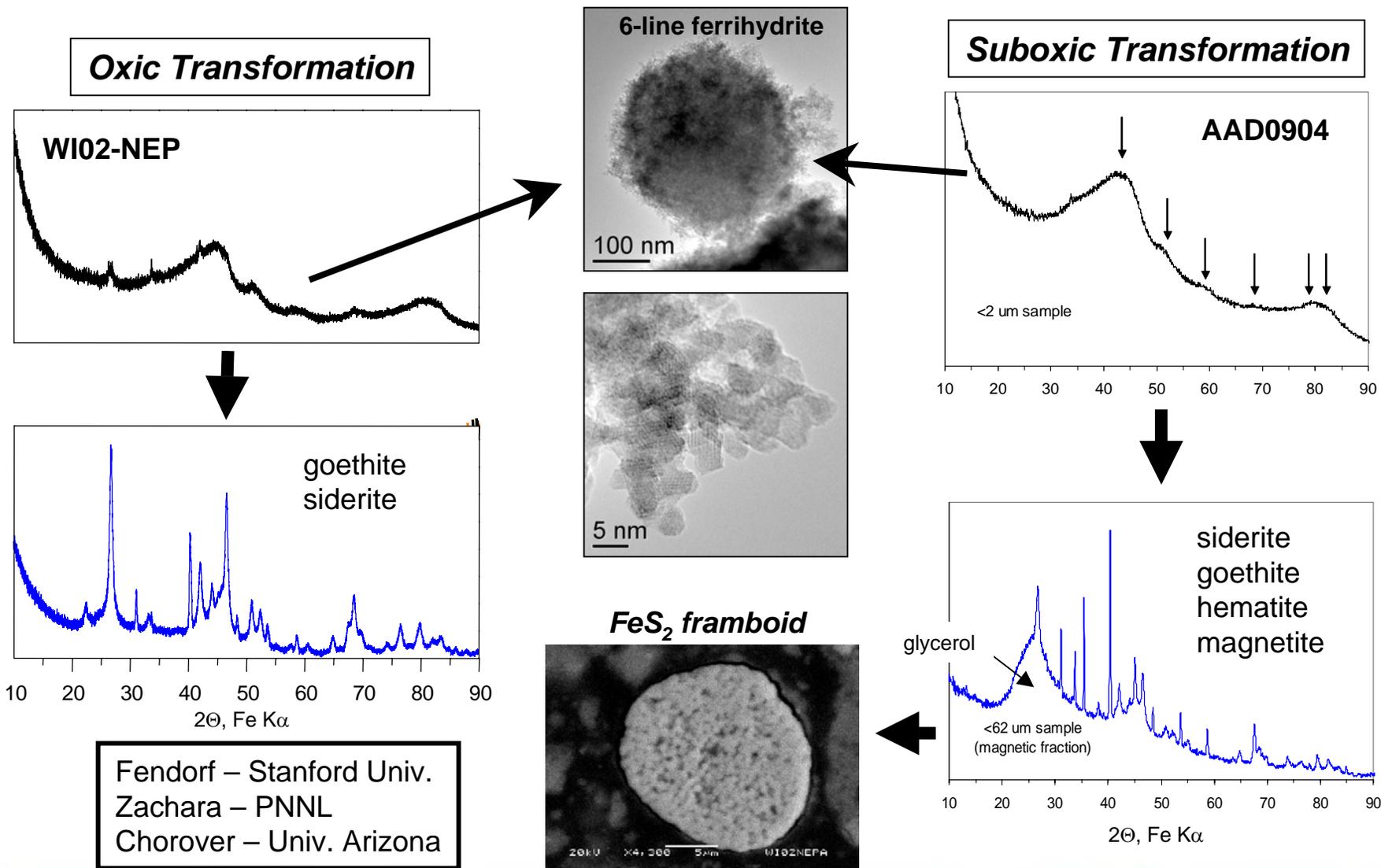
- As accumulation maximum in region of most intense AVS production co-located with primary discharge of benzene and toluene



# *Implication for landfills?*

- Strongly reducing conditions may be beneficial to As immobilization, i.e., sulfate reduction and beyond (As sulfides or Fe sulfides)
- Marginally reducing conditions, i.e., predominantly Fe reduction may enhance As mobility
- *Suggests that management of landfill geochemistry following closure could be a beneficial strategy – treat the ‘closed’ landfill as a engineering system (“bioreactor”) & manage As flux*

# What are possible fates for metastable iron oxyhydroxides (other than dissolution)?



Fendorf – Stanford Univ.  
Zachara – PNNL  
Chorover – Univ. Arizona

# *Implication for landfills?*

- Not all Fe reduction processes will cause loss of reactive mineral mass available for As sequestration
- Development of a more complete understanding of the Fe biogeochemical cycle in the context of mineral transformations will help reduce the uncertainty of projecting As mobility
- *Note that iron oxyhydroxides formed in-situ will likely have properties distinct from treatment residuals (e.g., GFH = mainly akaganeite)*

# Summary

- Our conceptual model should account for both aqueous and solid phase chemistry observed within a system

aqueous 

solid 

- Multiple lines of evidence provide the best underpinning for the conceptual model developed for the landfill environment
- Since landfills and organic contaminant plumes share some common biogeochemical signatures, there is an opportunity to improve projections of ‘landfill’ arsenic behavior through analysis of ‘plumes’ at various life stages

# Session-Specific Synthesis Questions

- 1) How prevalent is arsenic contamination...landfills?
  - European studies suggest similar concentrations to those observed at waste sites.
- 2) What is the arsenic content of iron floc deposits? Risks?
  - Arsenic captured at the time of Fe precipitation can result in weight percent contents. Subsequent risk is dependent on ultimate depositional environment (oxic – OK; reduced – labile)
- 3) Effectiveness of engineered cap?
  - Works towards minimizing infiltration of precipitation; does not prevent interaction with subsurface ground-water flow field for landfills interacting with shallow water table or positioned within depressions that are located within drainage basin.
- 4) Comparison of impact of arsenic wastes vs. naturally occurring arsenic?
  - Depends on geologic setting (mineralogy, physical characteristics); anticipate that anthropogenic sources would generate higher concentrations.
- 5) Arsenic as a concern at C&D debris landfills?
  - Landfill construction conducive to generating worst-case scenario, e.g., wall board has both a degradable organic carbon source and an abundant source of electron donor (sulfate).