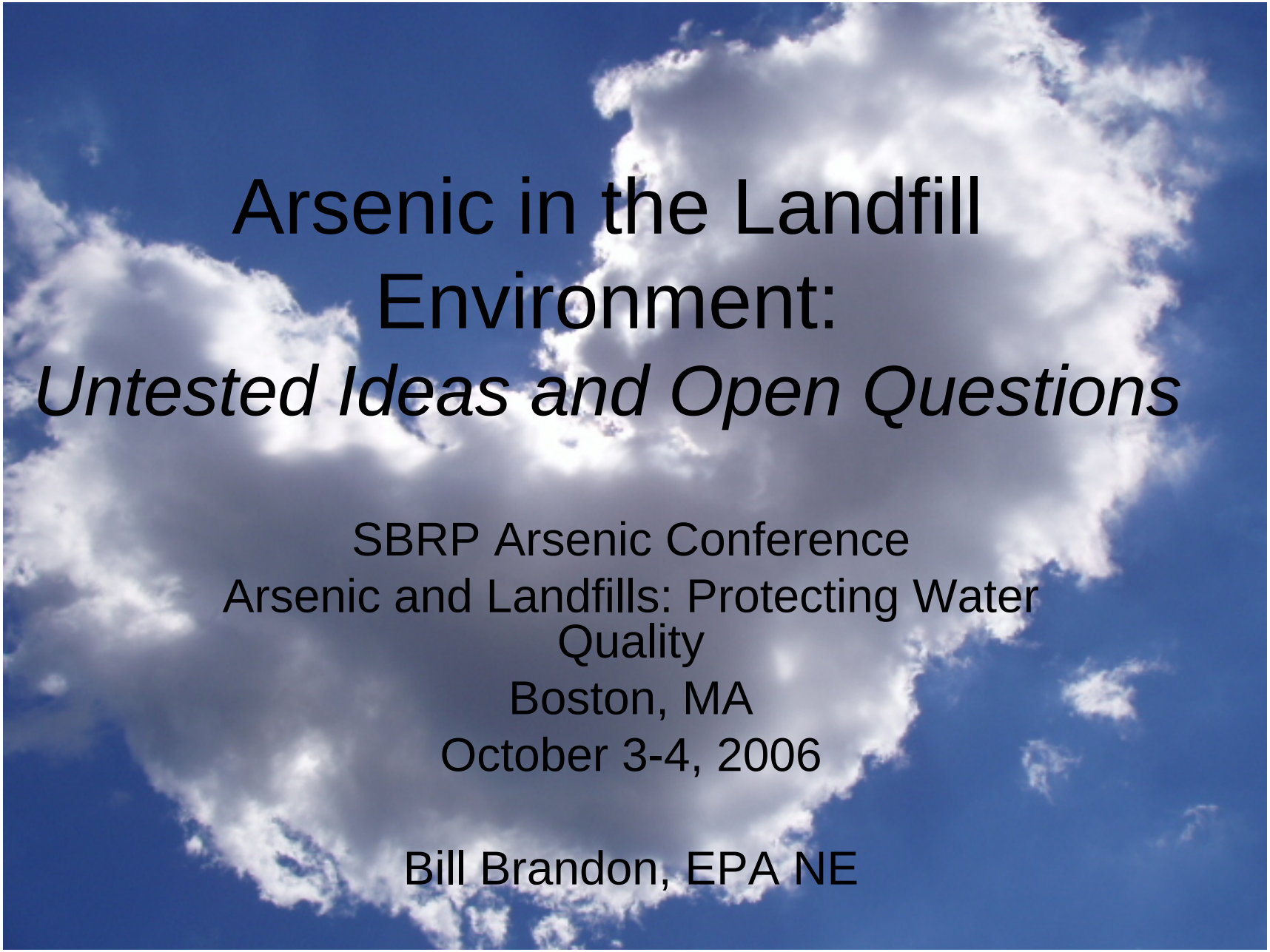


Arsenic in the Landfill Environment:
Untested Ideas and Open Questions

SBRP Arsenic Conference

Arsenic and Landfills: Protecting Water Quality

Boston, MA

October 3-4, 2006

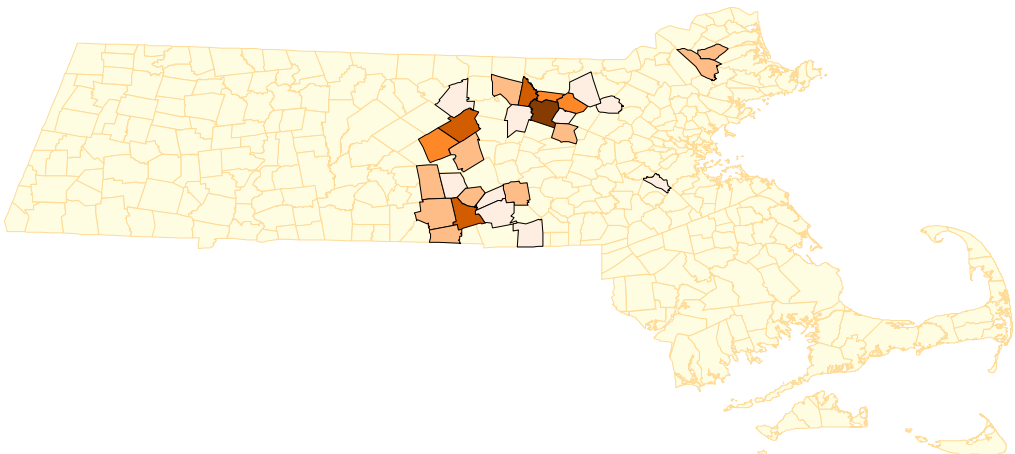
Bill Brandon, EPA NE

Acknowledgements

- EPA ORD
- Boston College
- Dave McTigue, G-F
- Carol Stein, G-F
- Devens BCT
- Region 1 Tech Support
- Region 1 Laboratory
- USGS

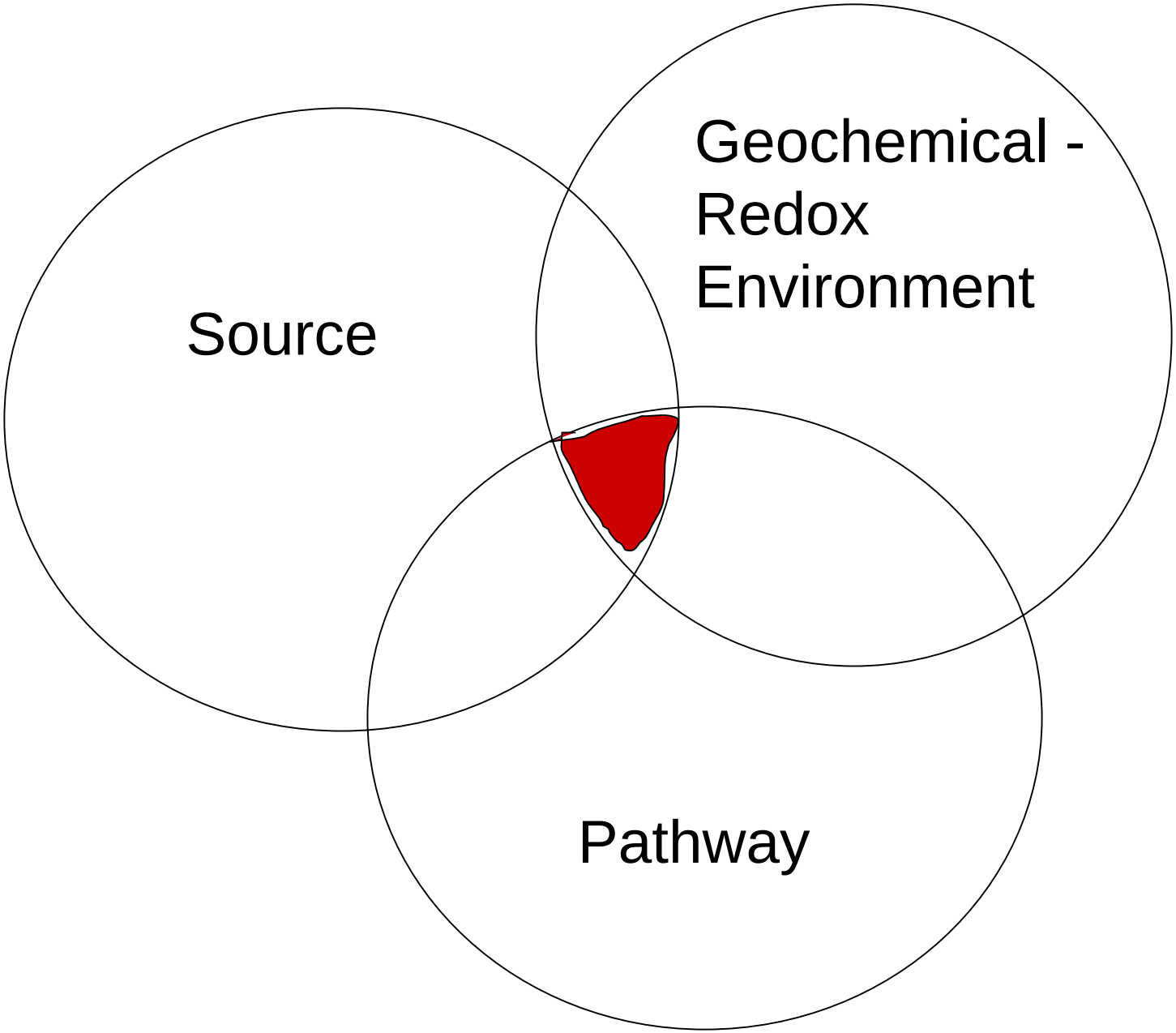
Introduction

- Central Mass. Landfill Averages on the order of 500 ppb….
- SHL (As up to 6000+ ppb)….
- What is Different about SHL ??



Introductory Questions

- Source = Waste Materials ?
- Source attributable to Particular Geologic Circumstances ?
- Both ?
- Or, Is this landfill just better characterized than the norm ??
- Does “Solvent Plume” paradigm hamper Conceptual Site Model (CSM) development ?
- Significance of Redox Environment ?


Source
Geochemical -
Redox
Environment
Pathway

Conceptual Site Models (CSMs)

- ‘Popular’ CSMs have emerged but none fully supported by data

- ‘Overlap’ of existing CSMs
  - Some elements common to more than one

- We don’t have all the answers!
  - “Challenge questions” posed

CSM Inputs

- Sources
- Geologic Characterization/Solid Phases
- Hydraulic Characterization/System
- Redox Environment/System
- Contaminant Migration Pathways
- Contaminant Transformation Pathways
- Intermediate Contaminant Fate - Accumulation
- Receptors – Risk Assessment
- Other ?

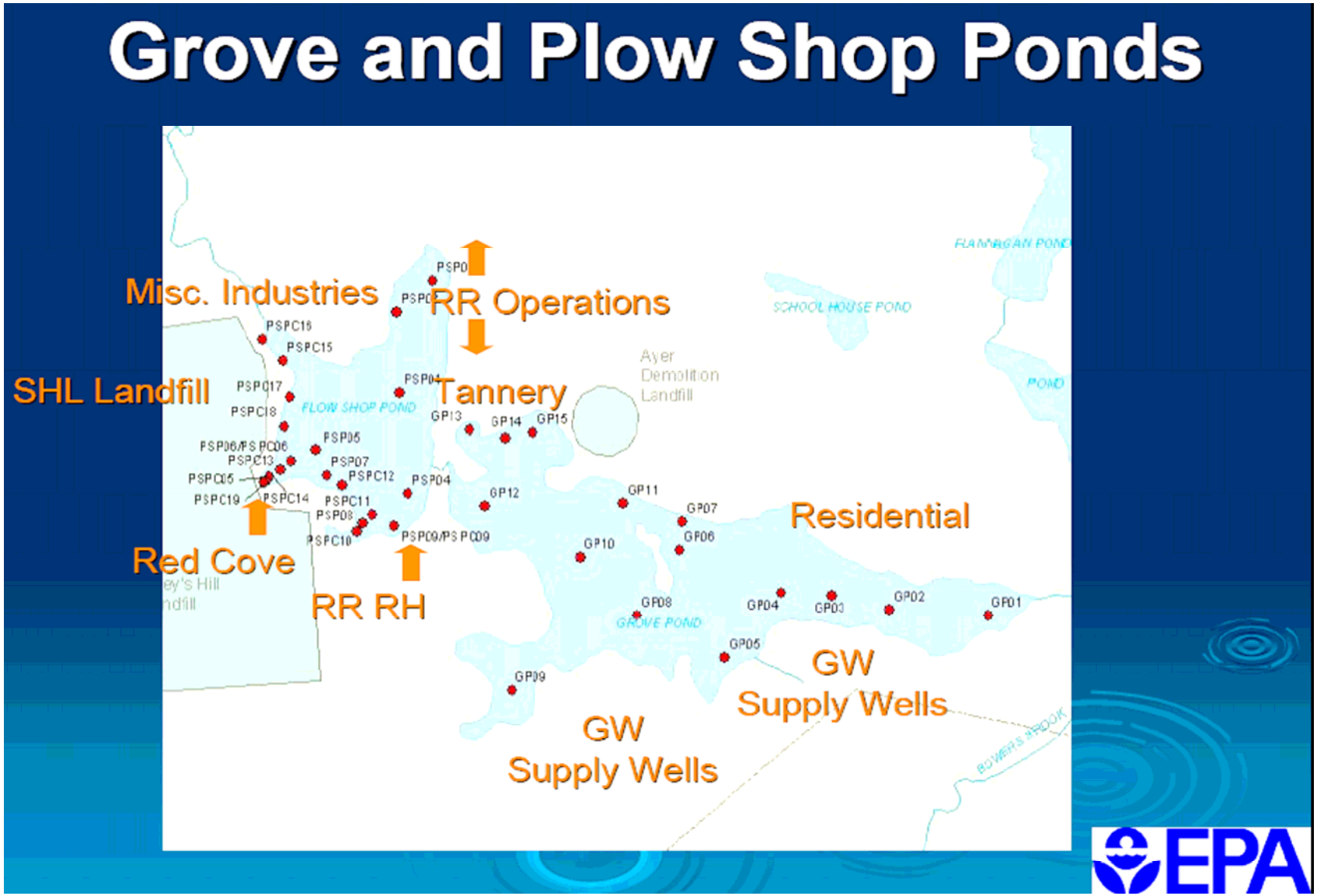
When MNA Isn't Working… (CSM Updates Needed)…

- increase in concentrations
- detection of contaminants outside of known plume boundary
- rate of decrease is not as expected
- changes in land and/or groundwater use

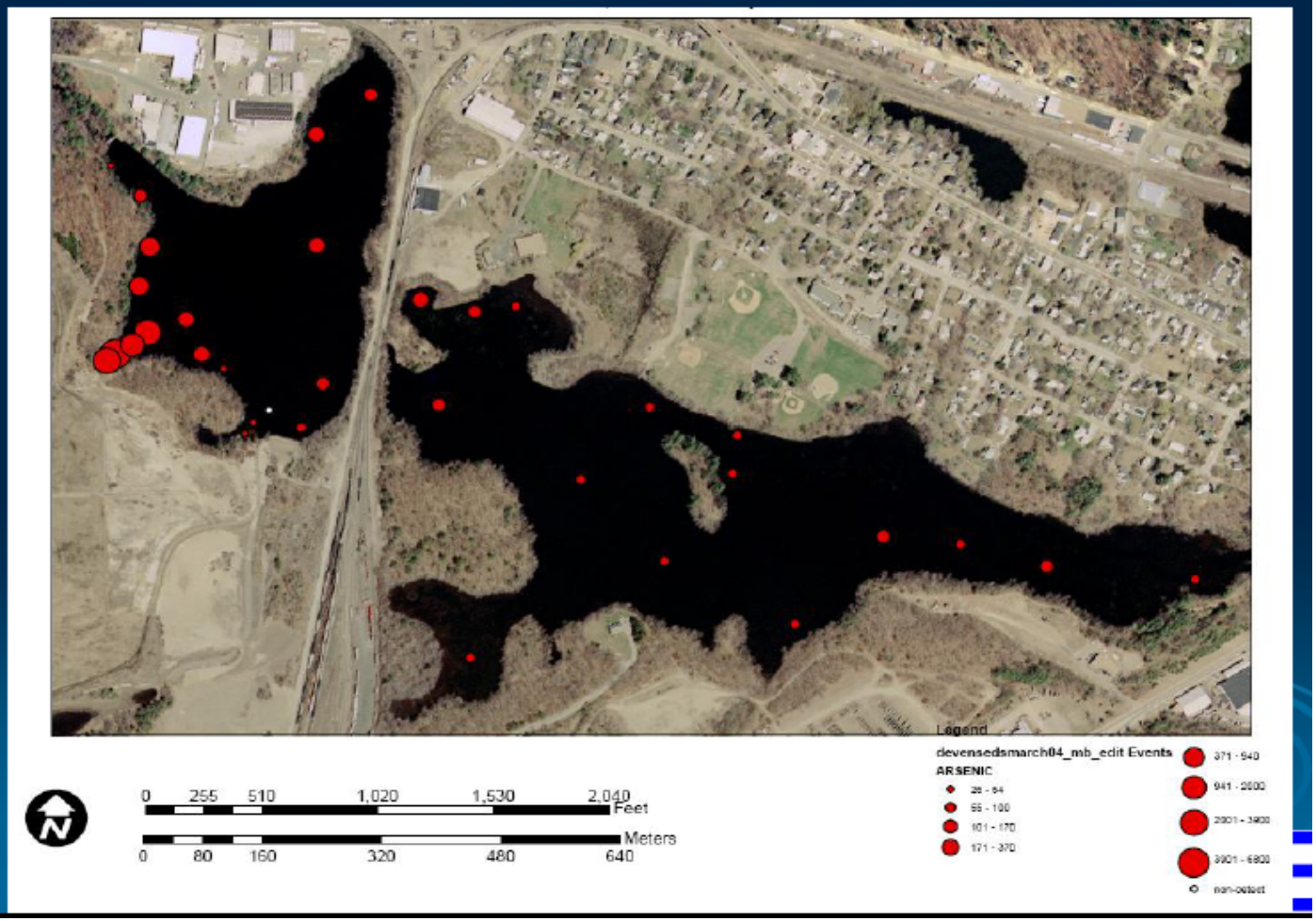
CSM - v.1

Tannery
Orchard
N
W
E
S
Contaminated
Sediment
Water-supply
wells
0
Feet
1000
Superfund site

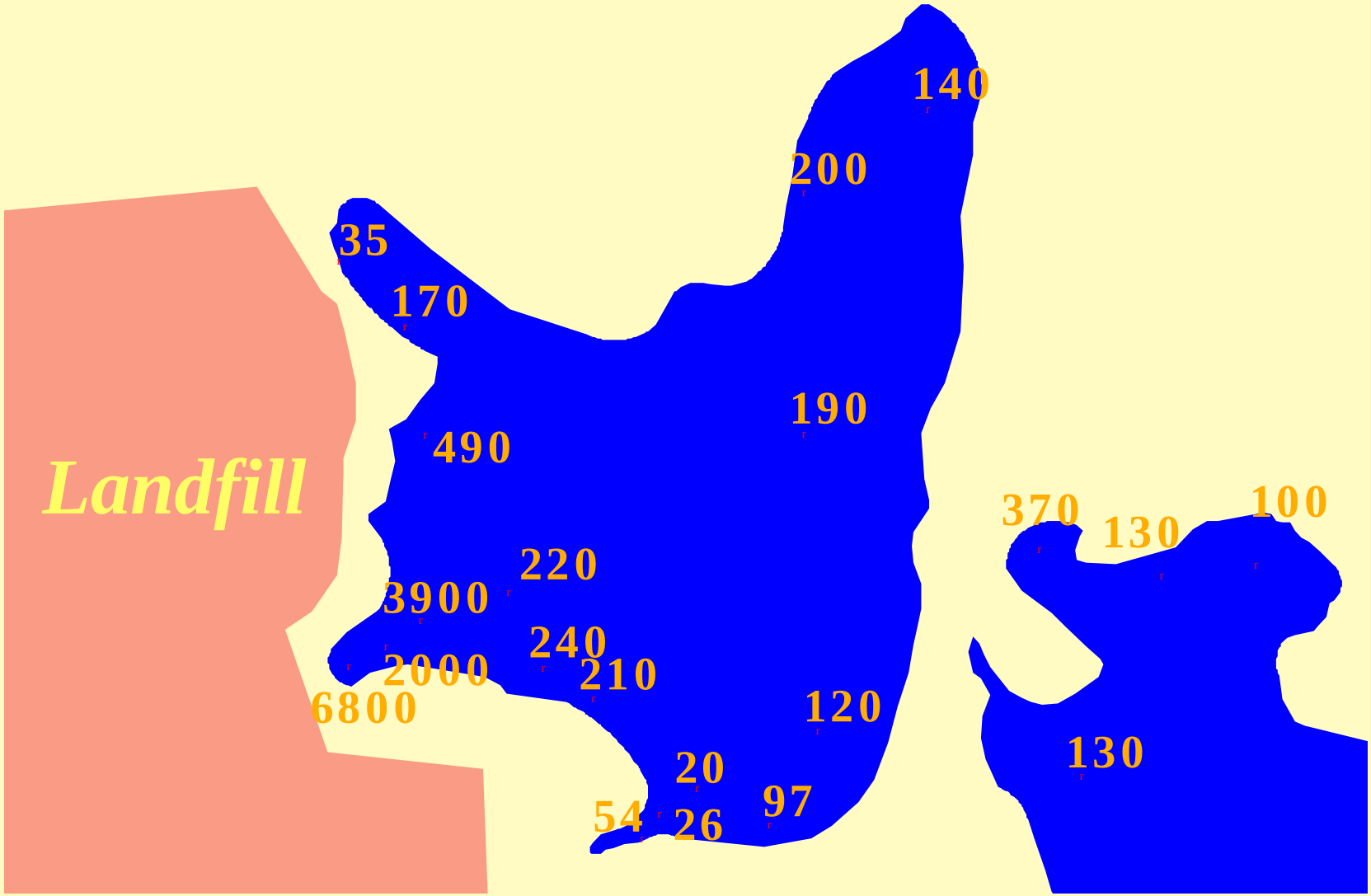
CSM – v.1.2


Grove and Plow Shop Ponds
Misc. Industries
RR Operations
SHL Landfill
Tannery
Red Cove
RR RH
Residential
GW
Supply Wells
GW
Supply Wells
FLANNIGAN POND
SCHOOL HOUSE POND
Ayer
Demolition
Landfill
FLOW SHOP POND
GROVE POND
BOWERS BROOK
PSP01
PSP02
PSP03
PSP04
PSP05
PSP06/PSPC06
PSP07
PSP08
PSPC09/PSPC09
PSPC10
PSPC11
PSPC12
PSPC13
PSPC14
PSPC15
PSPC16
PSPC17
PSPC18
PSPC19
GP01
GP02
GP03
GP04
GP05
GP06
GP07
GP08
GP09
GP10
GP11
GP12
GP13
GP14
GP15
EPA

Relative Arsenic Concentrations in Grove an Plow Shop Ponds



Arsenic in Bottom Sediments mg/Kg

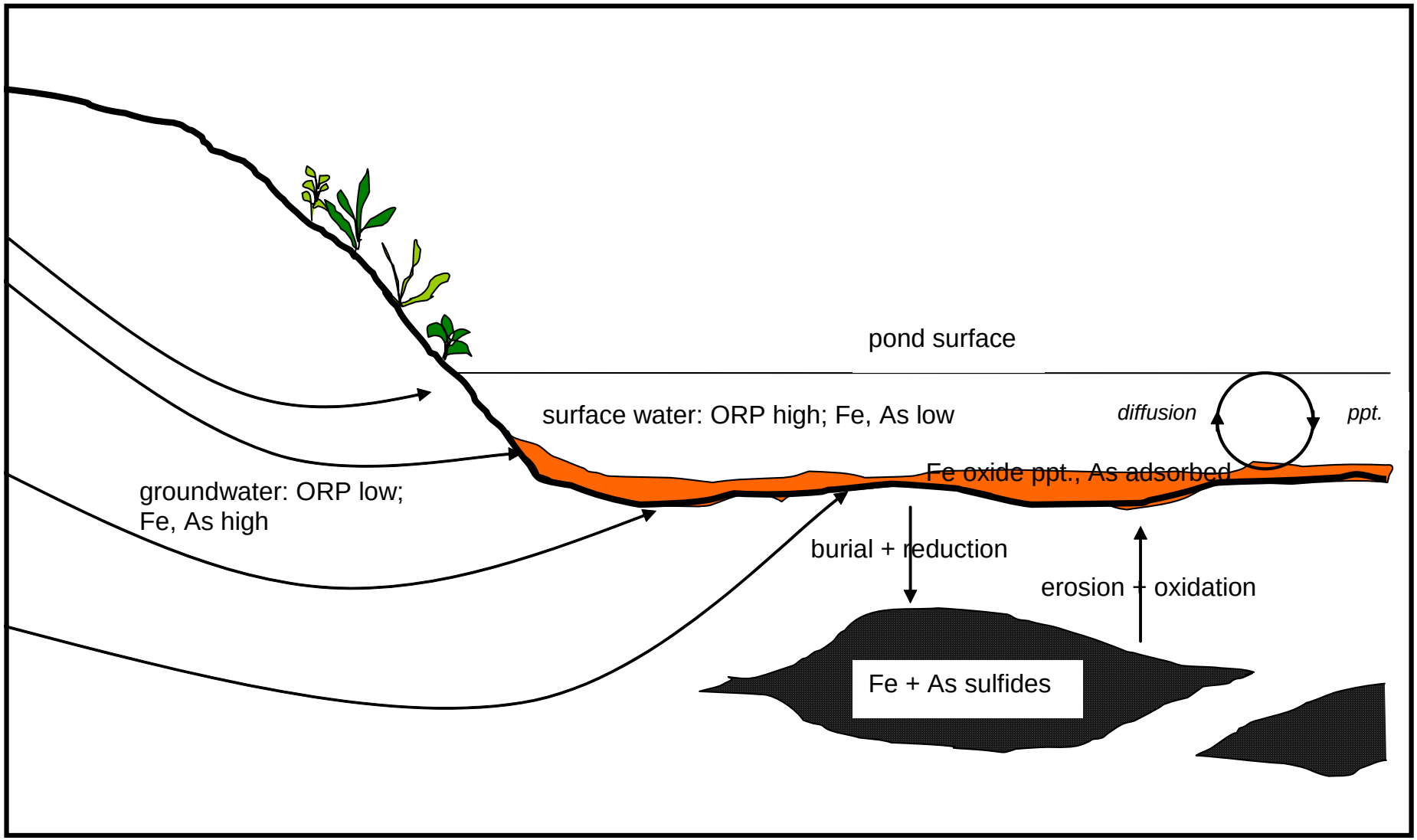


Toxicity Test Results

Working Conceptual Model #1

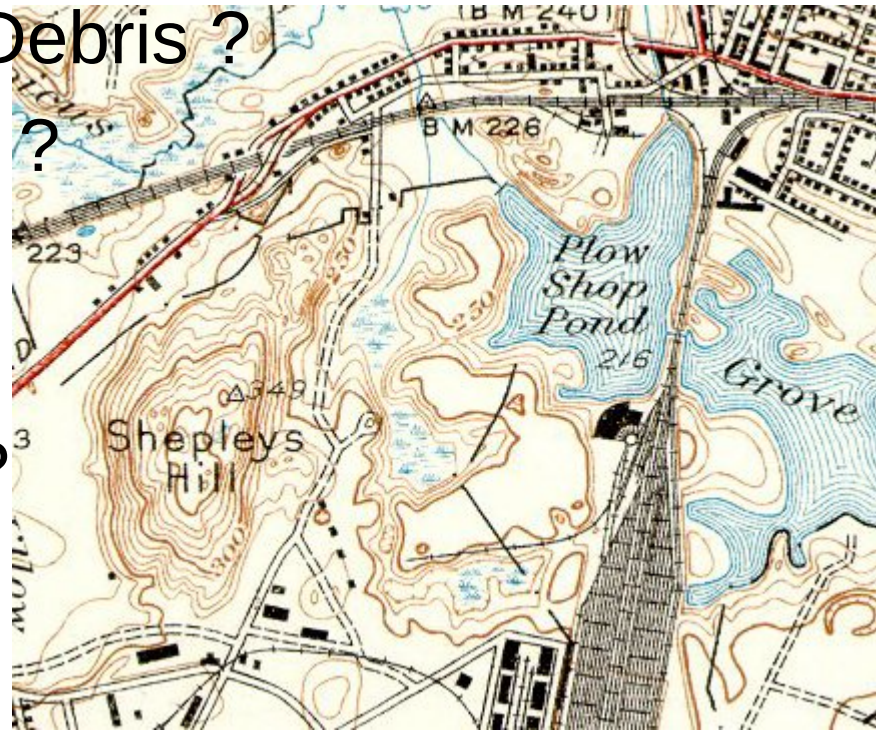
- Arsenic is present in some bedrock lithologies
- Glacial transport and postdepositional alteration redistribute Fe and As
- As is sorbed by hydrous ferric oxides (HFO) in overburden
- Landfills lower ORP of downgradient groundwater by oxidation of organics
- HFO dissolves (“reductive dissolution”), liberates arsenic

Unified Conceptual Model- Red Cove



Potential Anthropogenic Sources Need Additional Consideration

- Coal Ash (locomotives) ?
- CCA treated wood/Ash (on-site incinerator) ?
- Wall Board/Construction Debris ?
- Treatment Plant residuals ?
- Arsenical Pesticides ?
- Rat Poison (As_2O_3)?
- Other Hazardous Waste ?
- Other ?

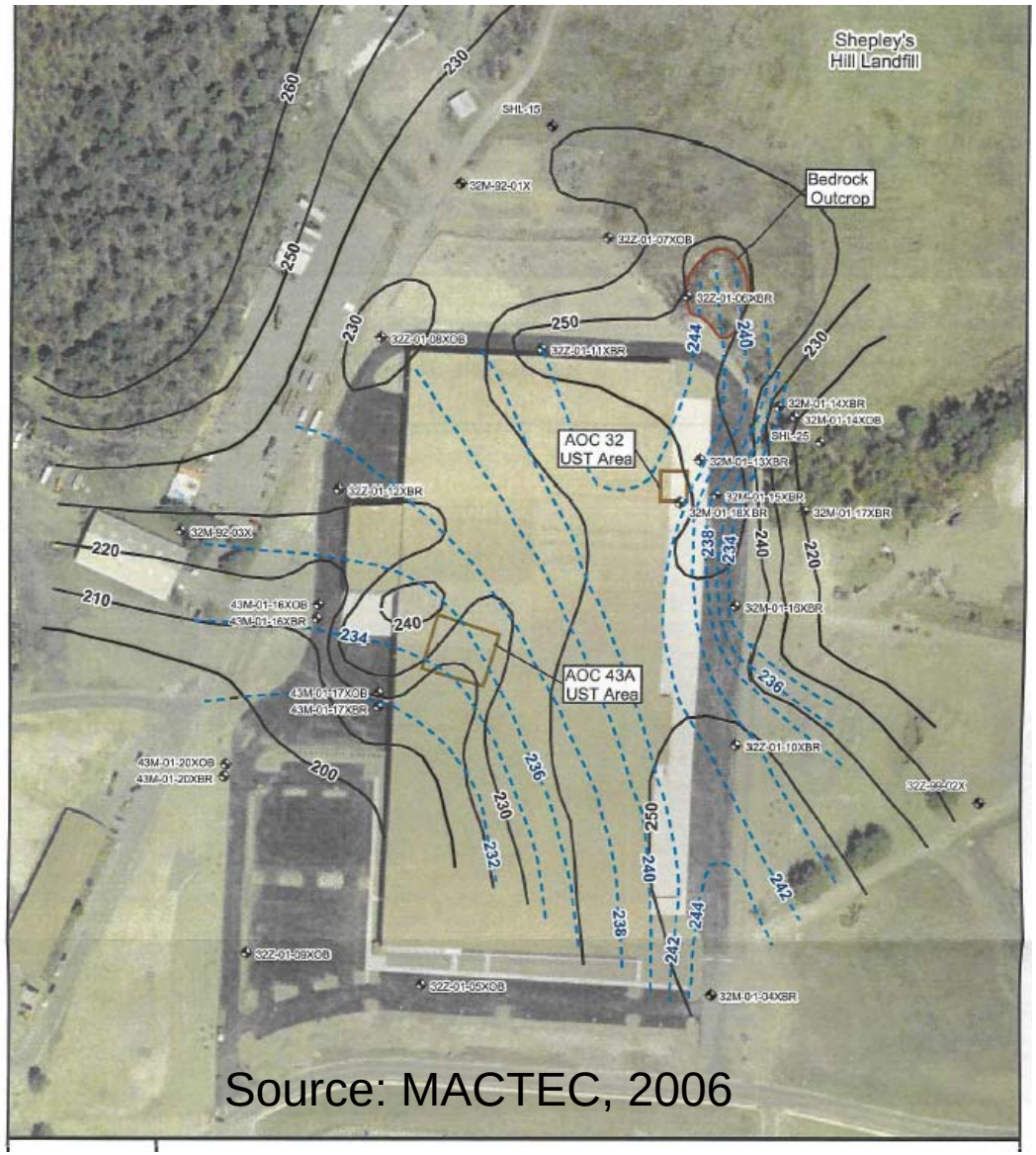


Potential Geologic Sources

- HFO coatings on outwash sand grains ?
- Rock Chips in outwash sands ?
- Bedrock Fractures Coatings (oxides) ?
- Disseminated Sulfides ?
- Mineralized zones (veins, shear zones, etc.) ?
- All of the above ?
- Effects of Blasting ?

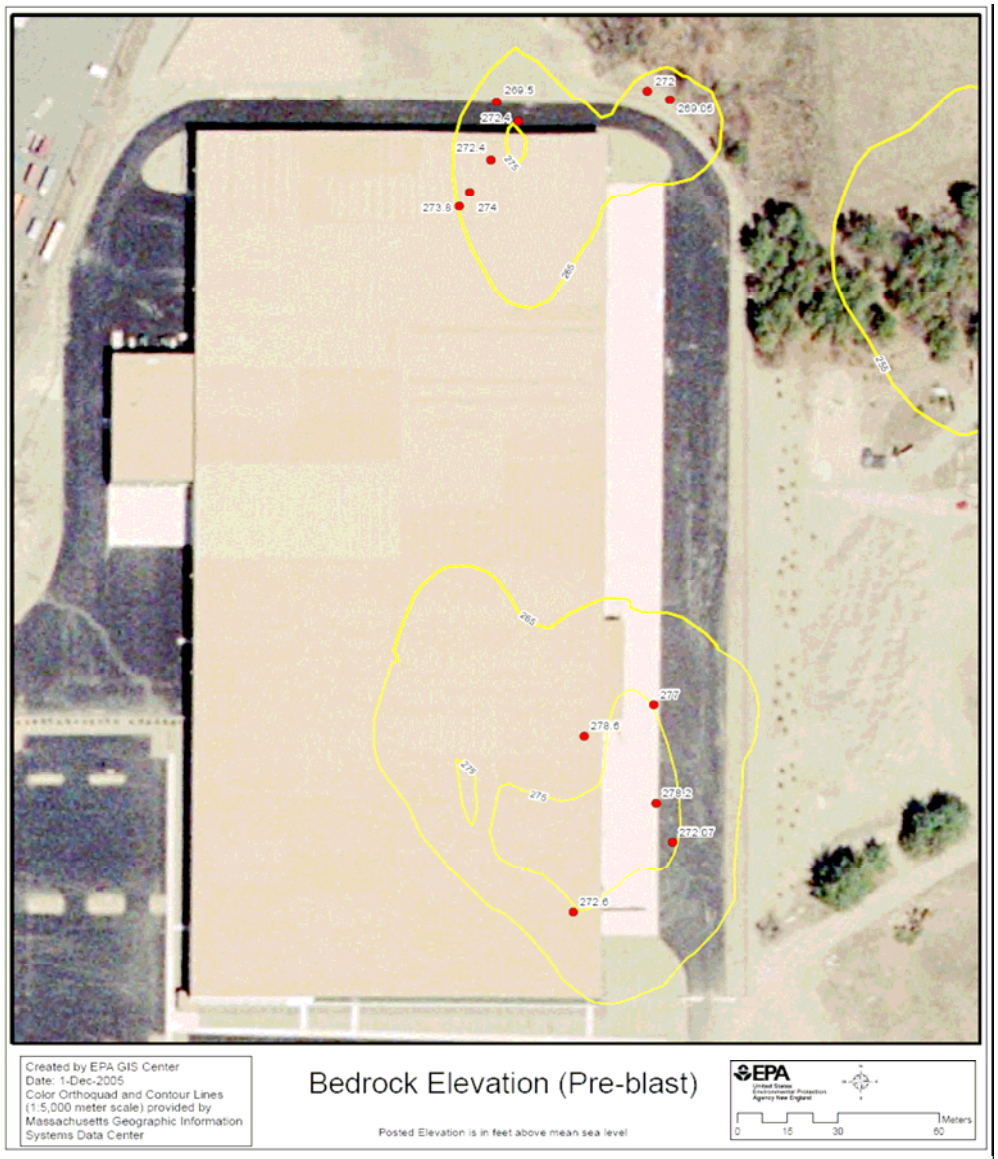
Blasting Presents Fresh Exposures

Interpretive Bedrock Groundwater Surface Map, October 7, 2004



Source: MACTEC, 2006

Bedrock Elevation (Pre-Blast)



Pre-Blast Bedrock Exposures at SE Corner of Building Area

Hydrologic Issues

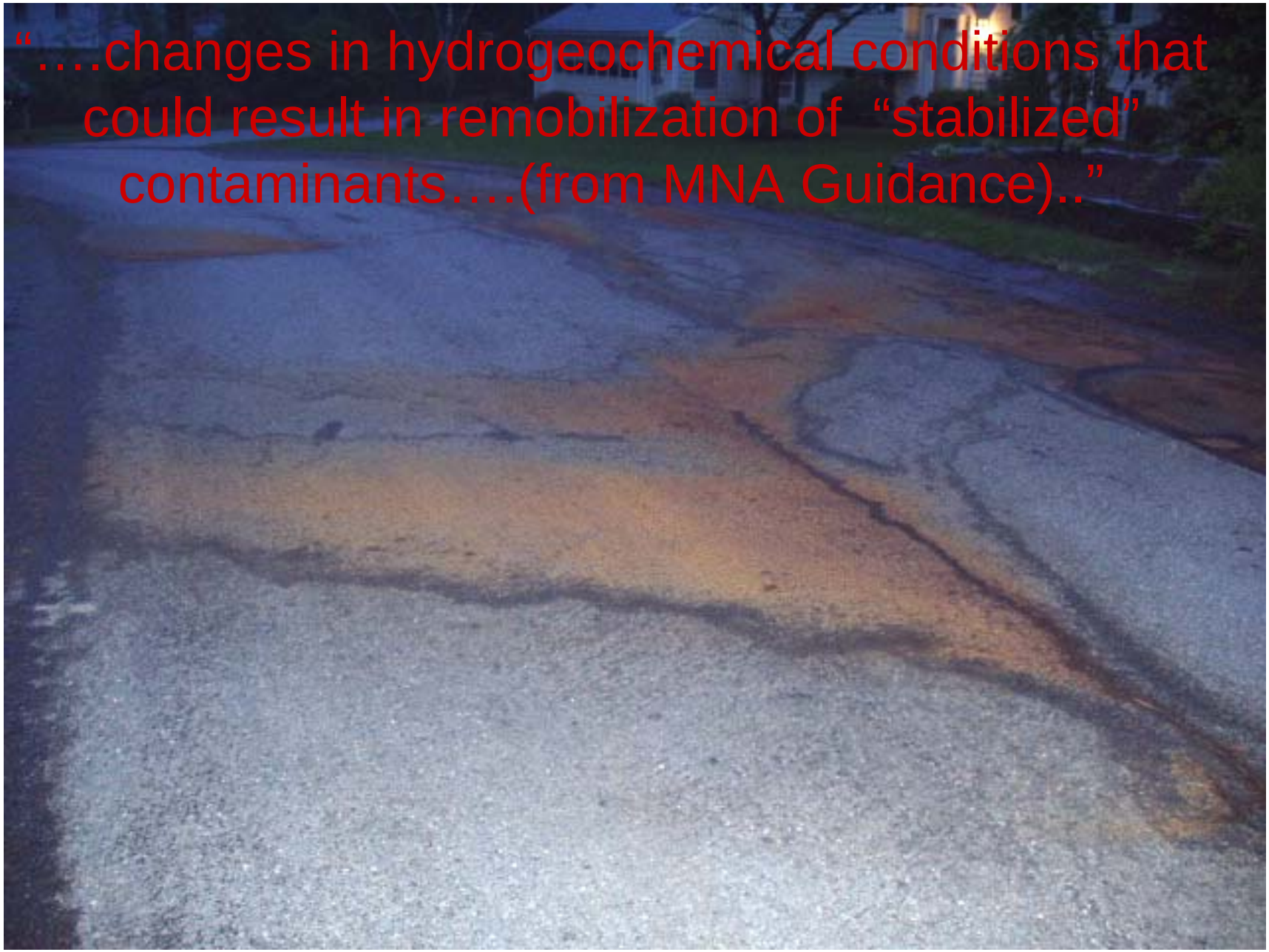
- Impoundments
- Cap Performance ?
- “Run-under” from Shepley’s Hill
- Pumping Wells
- Engineered Drainage
- Impervious Surfaces
  - Pavement
  - Landfill caps
- TIME SCALES !??

Storm Drain Installation

Fill Emplacement
SW of Building Footprint

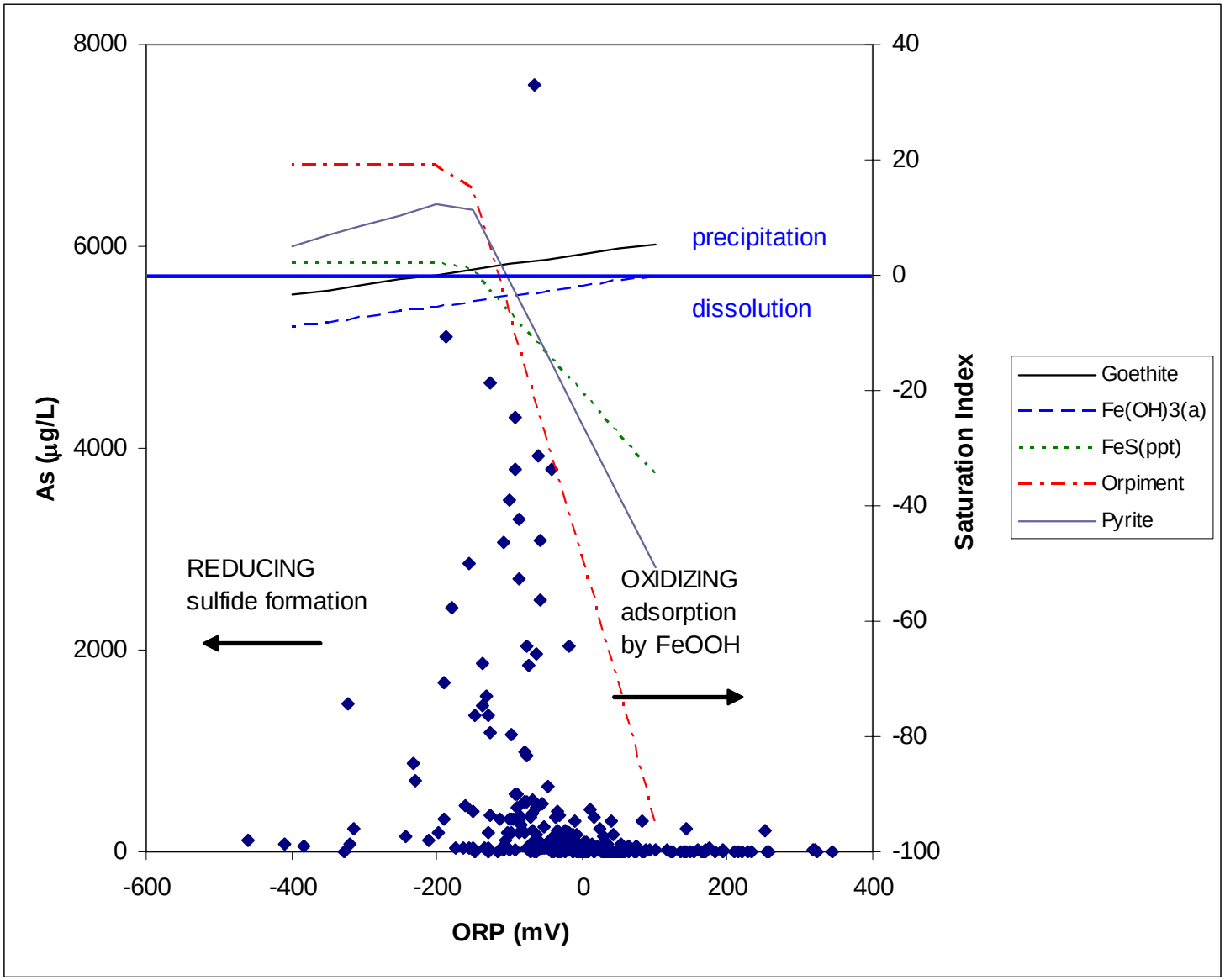
Hydrology Affects Geochemistry
(R. Ford, SFBR, 2006)

- Infiltration of precipitation during operational lifetime ('oxic reaction front')
- 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
- *Dynamic fluctuations will tend to maintain arsenic mobility*

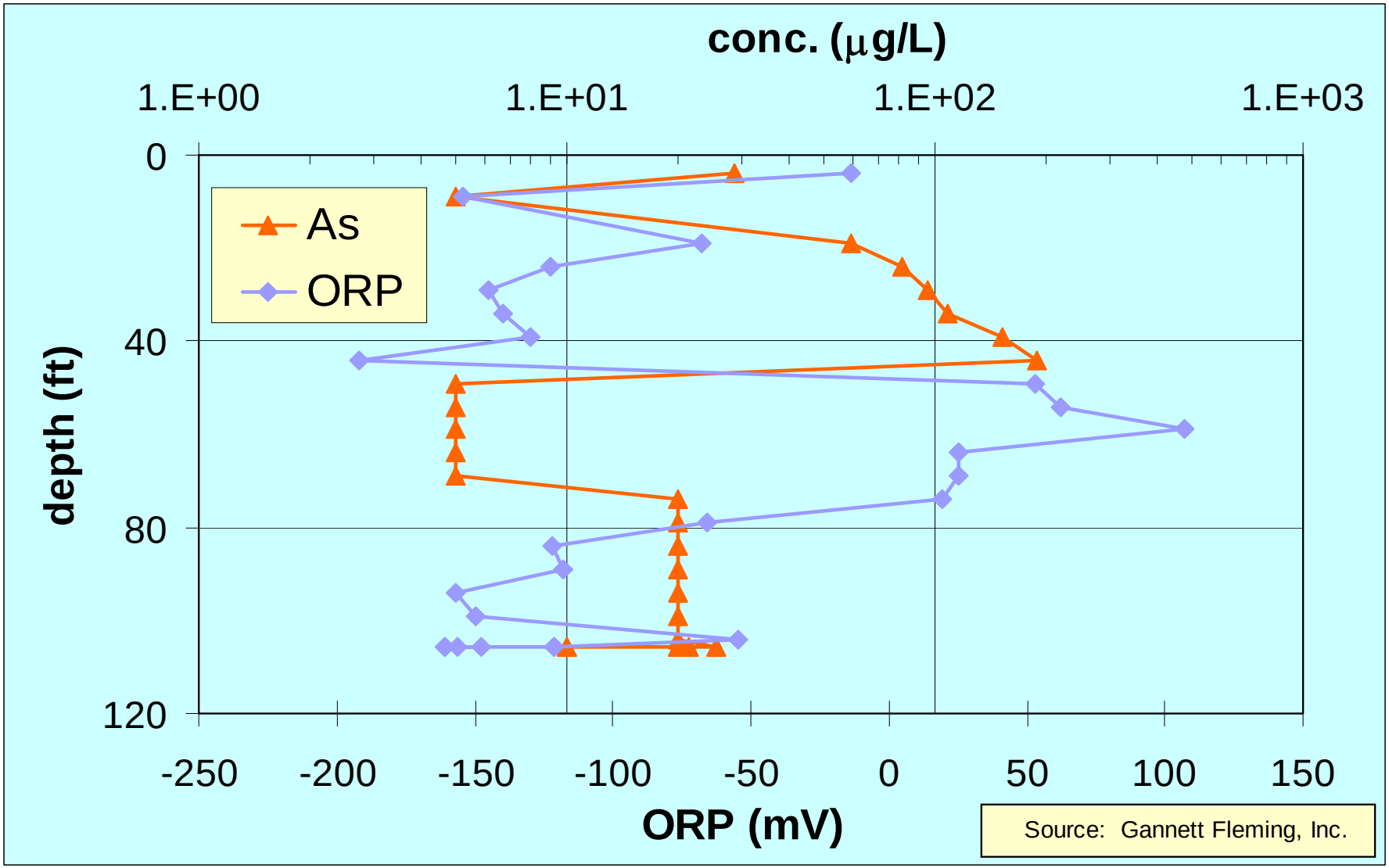

“….changes in hydrogeochemical conditions that could result in remobilization of “stabilized” contaminants….(from MNA Guidance)..”

SHL Groundwater Geochemistry

DANGER ZONE

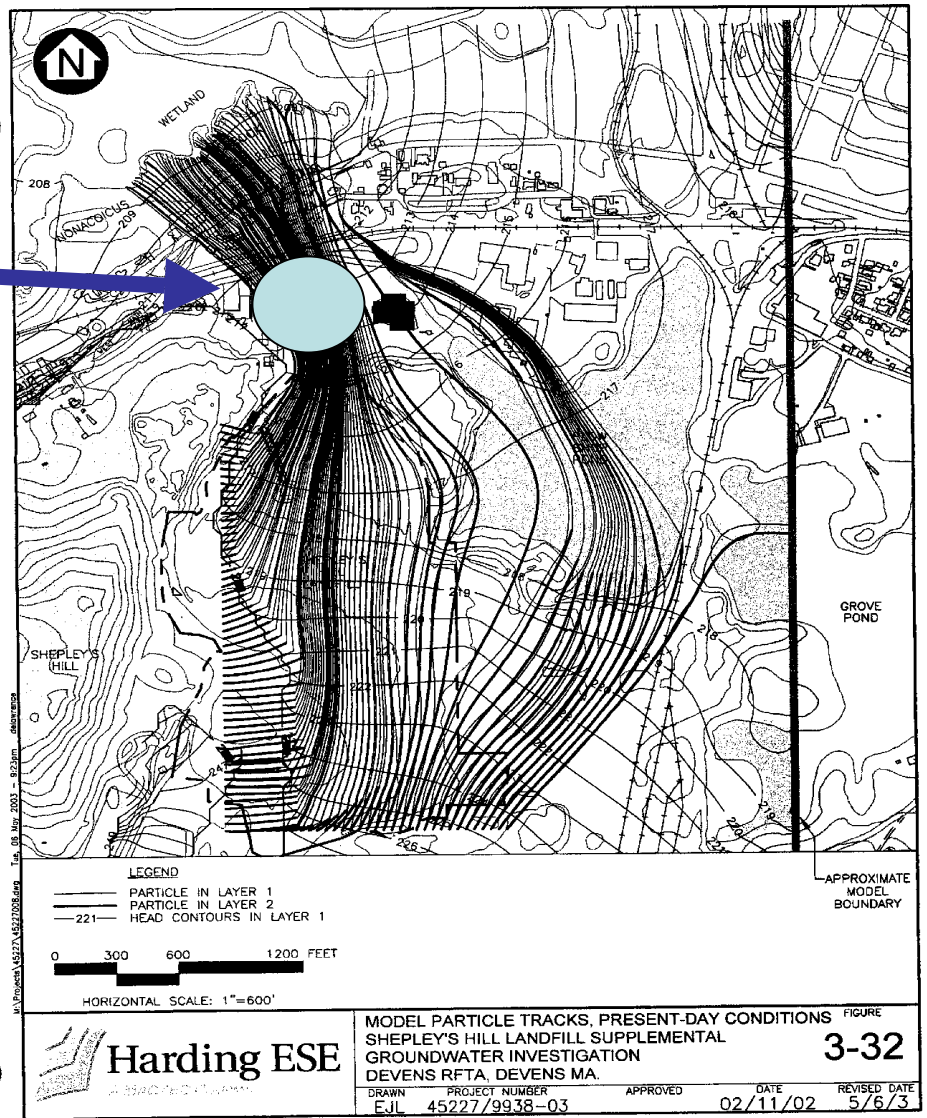


As and ORP in Ground Water

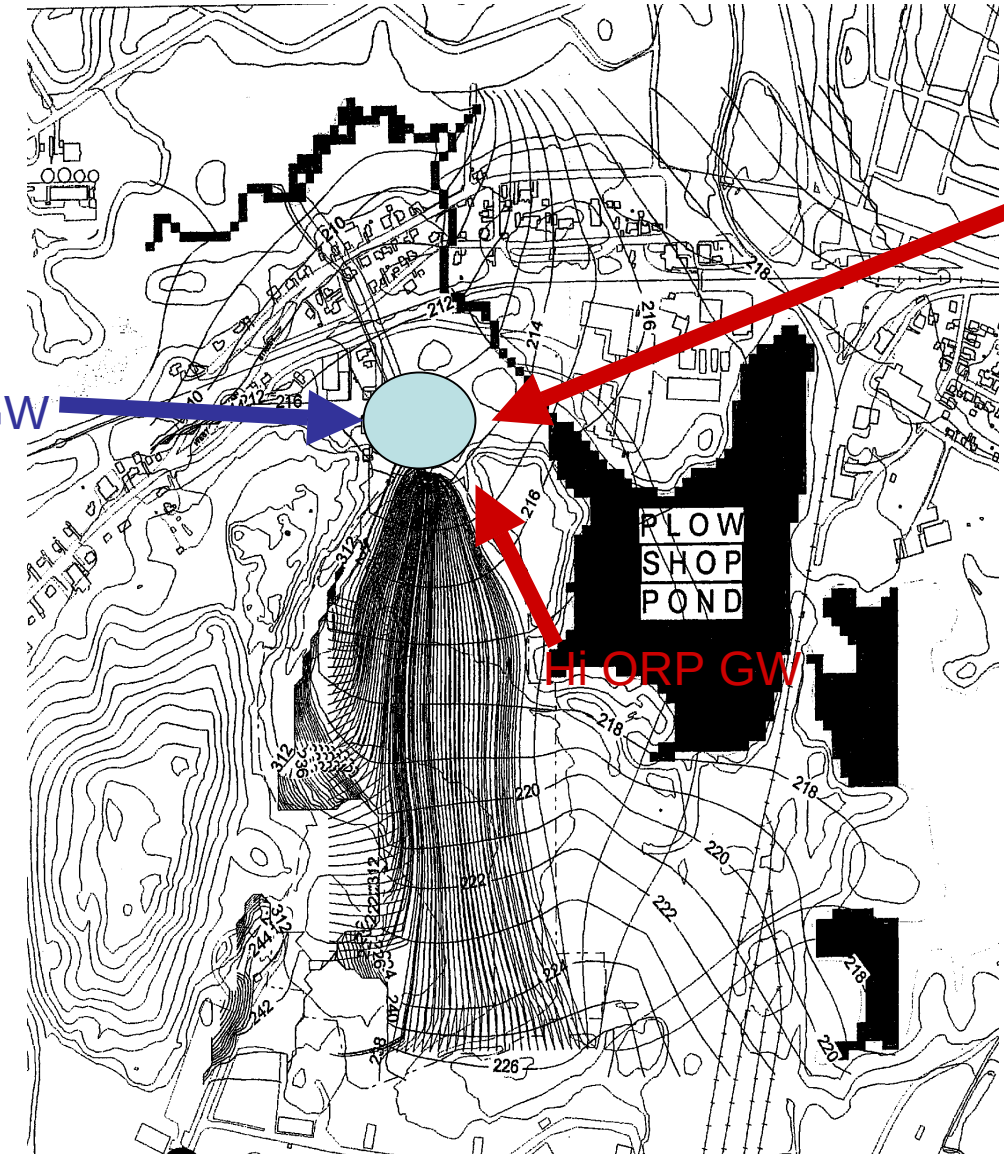


SHEPLEY'S HILL LANDFILL
MODELED PARTICLE TRACKS, CURRENT CONDITIONS

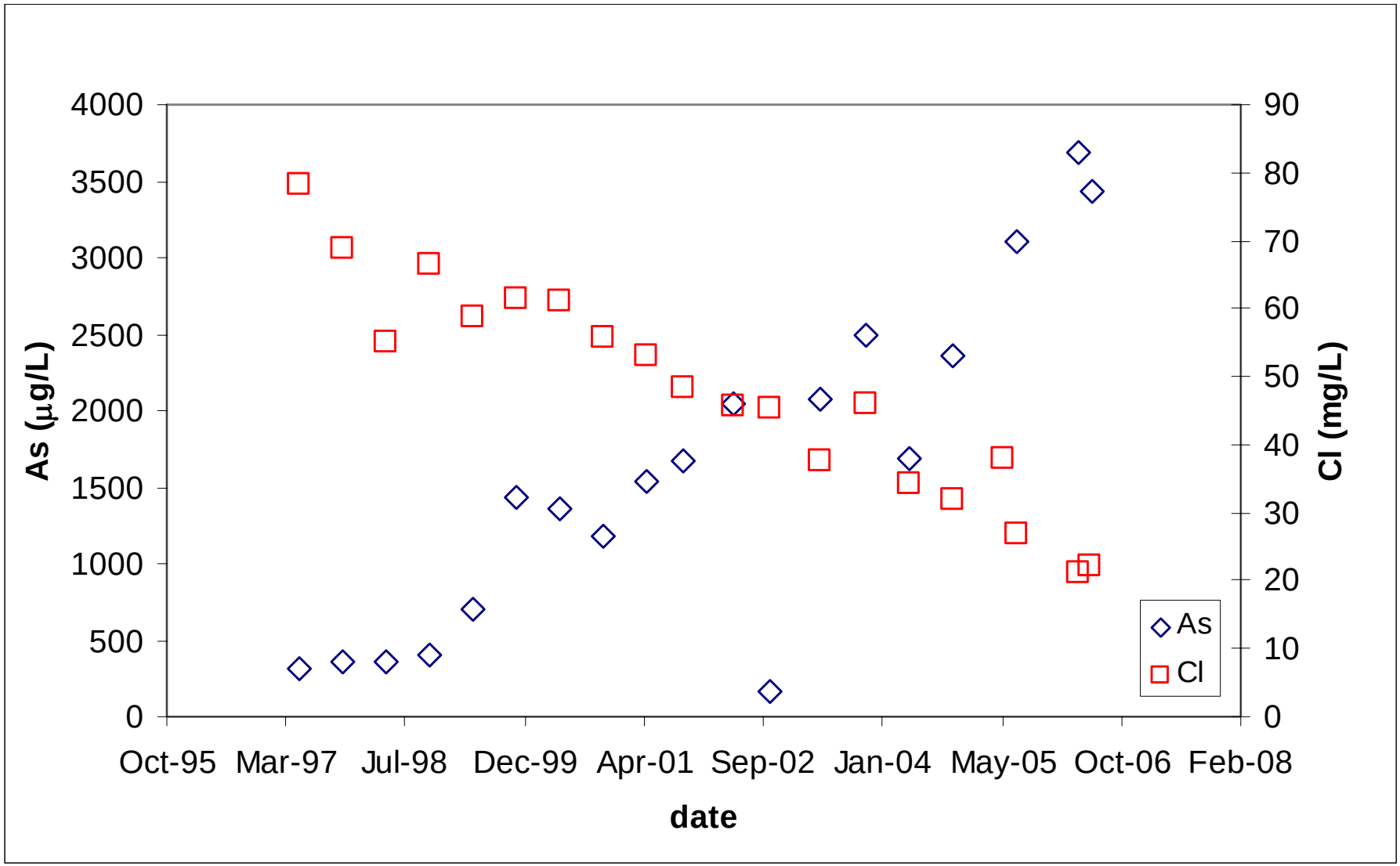
Highly Reduced GW



SHEPLEY'S HILL LANDFILL
MODELED PARTICLE TRACKS, RUN 106C, 50 gpm



SHM-96-22B


4000
3500
3000
2500
2000
1500
1000
500
0
As (µg/L)
90
80
70
60
50
40
30
20
10
0
Cl (mg/L)
Oct-95
Mar-97
Jul-98
Dec-99
Apr-01
Sep-02
Jan-04
May-05
Oct-06
Feb-08
date
As
Cl

Characterization "Quality" Issue

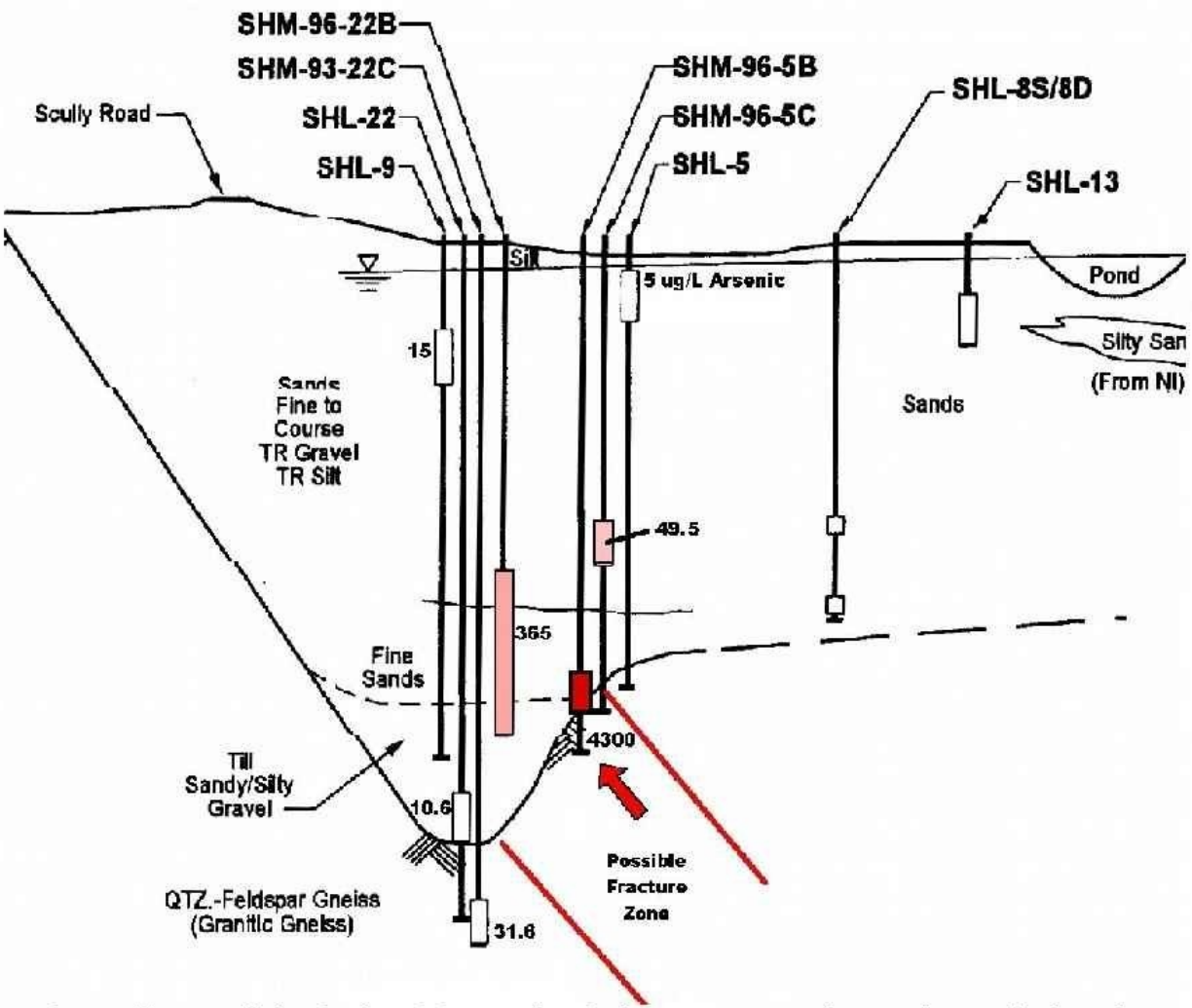
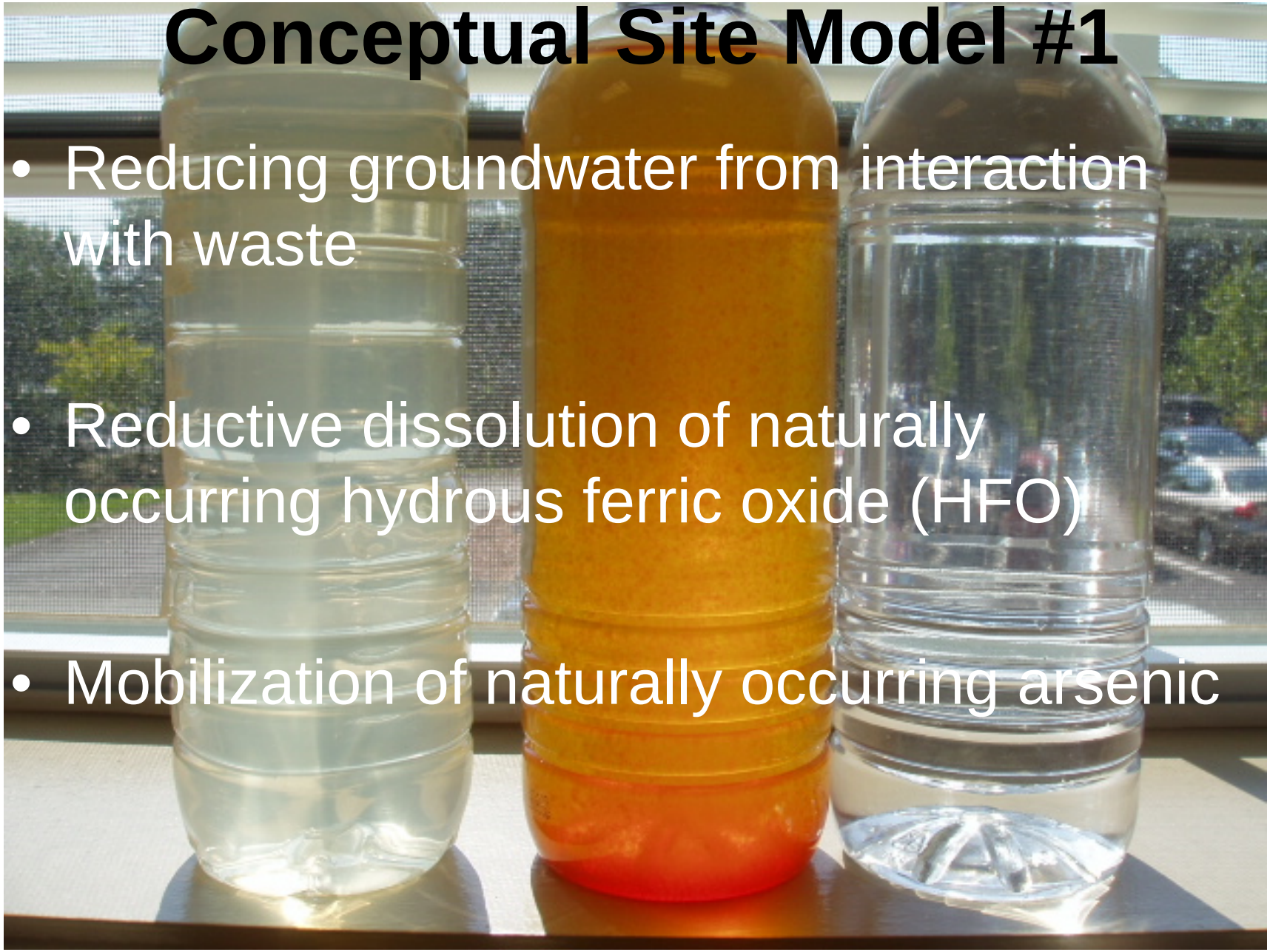


Figure 3. Spatial relationships and relative concentrations of arsenic-bearing wells on the northern boundary of Shepley's Hill Landfill. Deeper red translates to greater arsenic concentration.

Conceptual Site Model #1



- Reducing groundwater from interaction with waste
- Reductive dissolution of naturally occurring hydrous ferric oxide (HFO)
- Mobilization of naturally occurring arsenic

Conceptual Site Model #1 Questions

- What data support/refute cause of reducing conditions (waste vs. naturally occurring)?
- If waste/GW interaction generates low-ORP 'plume'
  - Can 'plume' be mapped self-consistently?
  - Is 'plume' consistent with other leachate indicators, e.g. Cl, conductance?
- Why is As deep?
  - Density flows?
- Other tracers for waste interaction?
  - Rationalize SHM-96-22B (As increasing, Cl decreasing)

Conceptual Site Model #2

- Arsenic source present in waste
  - Suggested by unusually high As at SHL
  - Incomplete waste characterization
- Adds to naturally occurring As mobilized by reductive dissolution (CSM#1)

Conceptual Site Model #2 Questions

- What are candidate materials?
  - Coal ash: Where are associated trace elements? Why only elevated As?
  - Pesticides (e.g., As_2O_3): Why correlated with Fe in soil and groundwater? Is gross mass balance consistent with pesticide application? Surface application, now capped, cannot be continuing source to groundwater ?
- Why is high As found in deep GW, when waste interaction is shallow?

Conceptual Site Model #3

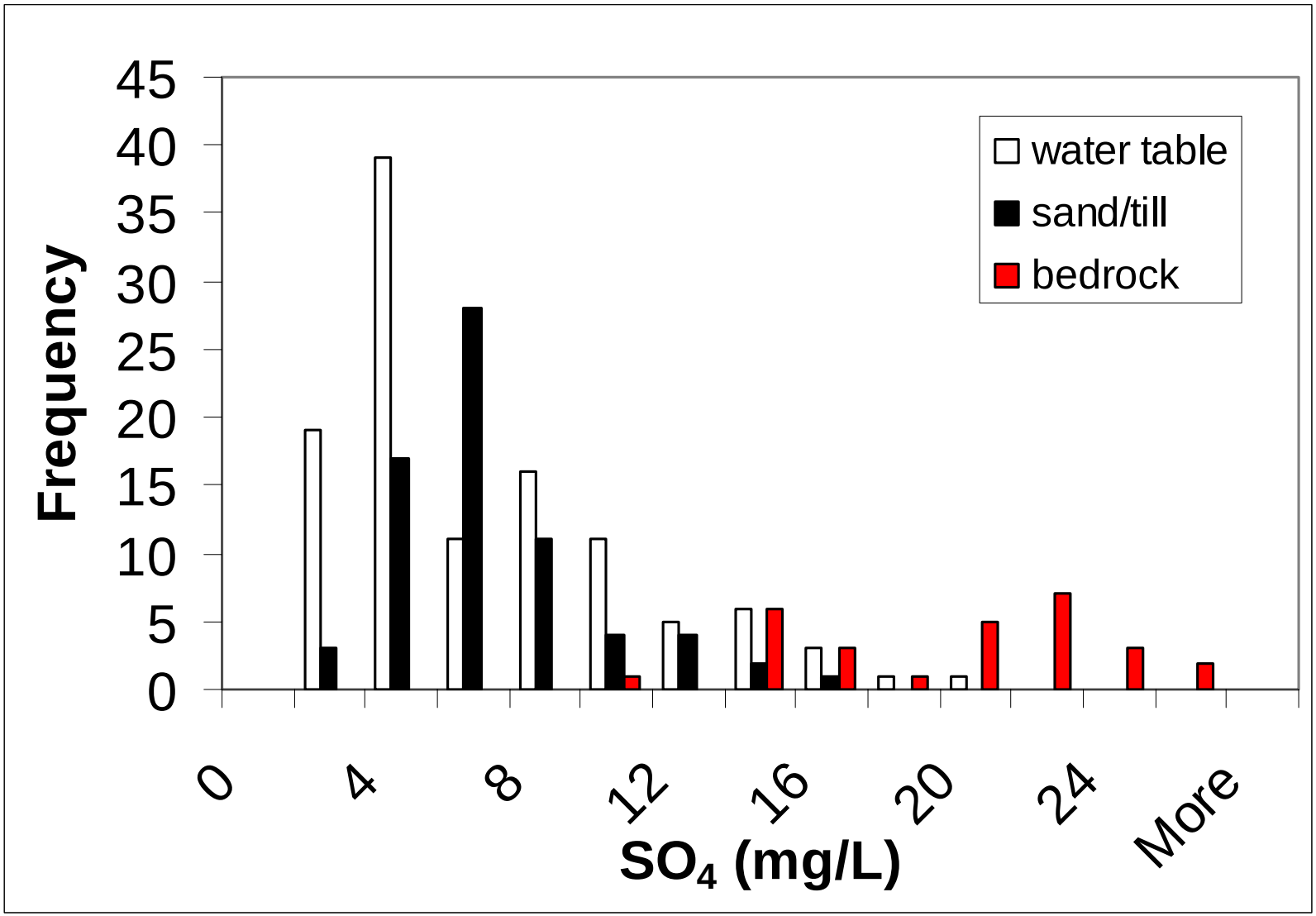
- Bedrock arsenic source
  - Does not preclude CSM#1
  - Little mineralogical information available
  - Mobilization mechanism(s), transport pathway(s) unknown
- What (if any) is association with deep methane?

Overarching Questions Regarding Waste-Groundwater Interaction

- Little apparent geochemical signature of waste interaction
  - Relatively little physical interaction (small saturated volume)
  - Waste is relatively chemically unreactive
- General increase with depth: major-element concentration, TDS, sp. cond., alkalinity, etc.
  - Density?
  - Universal observation: deeper = older, longer residence time (Freeze and Cherry, 1979, p. 241)

Your
Thoughts ?

LTMP Geochemical Data



Groundwater Characteristics

	Specific Conductance (mS/m)	Alkalinity (mg/L $CaCO_3$)	Chloride (mg/L)	Na (mg/L)	Ca (mg/L)	SO_4 (mg/L)
Wisconsin landfills [1]	**284 – 1585**	**960 - 6845**	**180 - 2651**	**12 - 1630**	**200 - 2100**	**8.4 - 500**
SHL [2]	**2.1 – 148**	**3 - 670**	**1U - 65**	**2U - 48**	**1.8 - 140**	**1.1 - 20.9 [3]**
Grove Pond [4]	**21 - 364**	**20.2 - 182**	**0.5 - 111**	**16 – 54.3**	**2.9 – 74.5**	**0.1 – 44.2**

[1] From Fetter, 1994; typical ranges of site medians
[2] SHL PMP/LTMP data
[3] Average of LTMP data, by well, 5/98-6/05
[4] From *Grove Pond Arsenic Investigation*, Gannett Fleming 2002

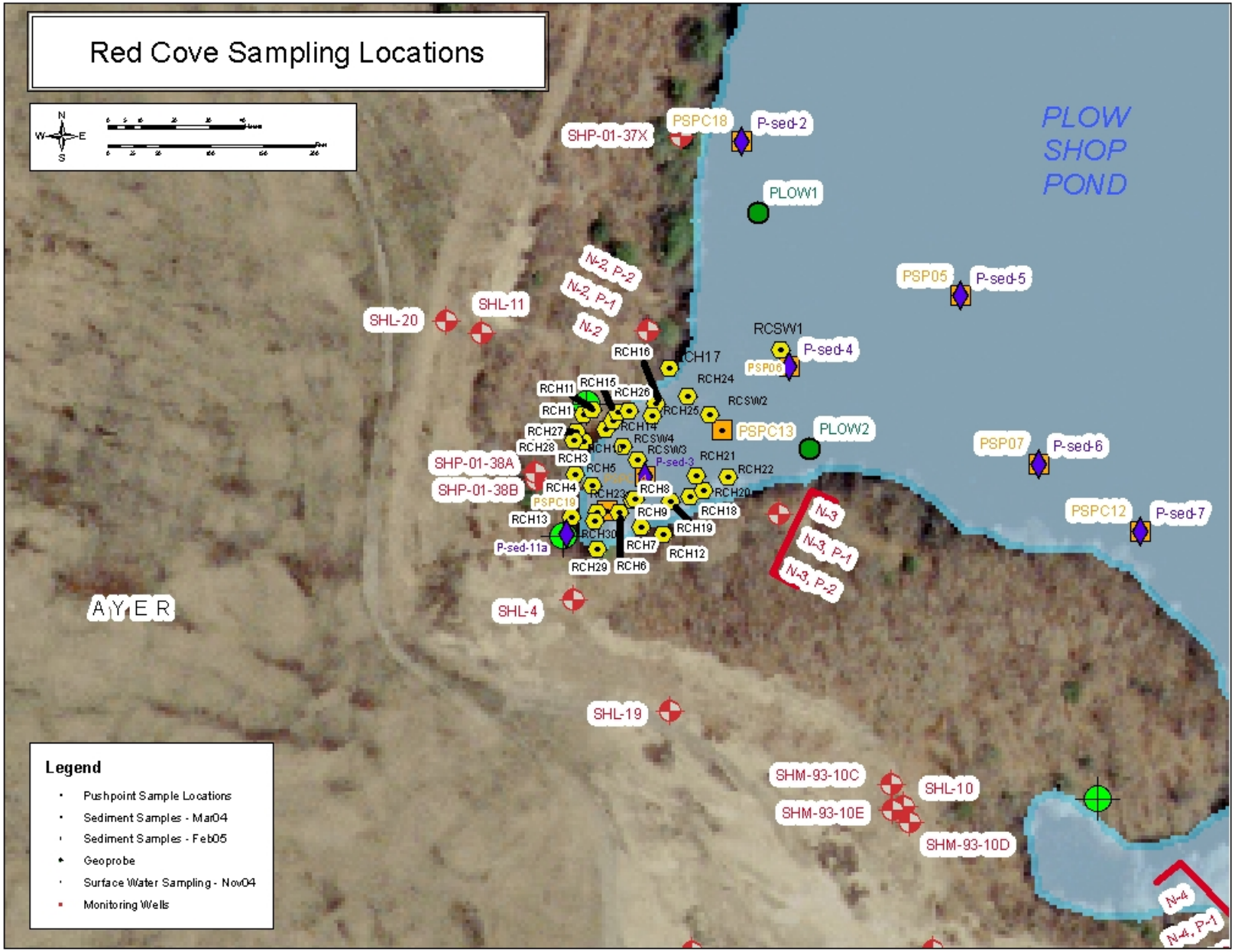
Arsenic Speciation

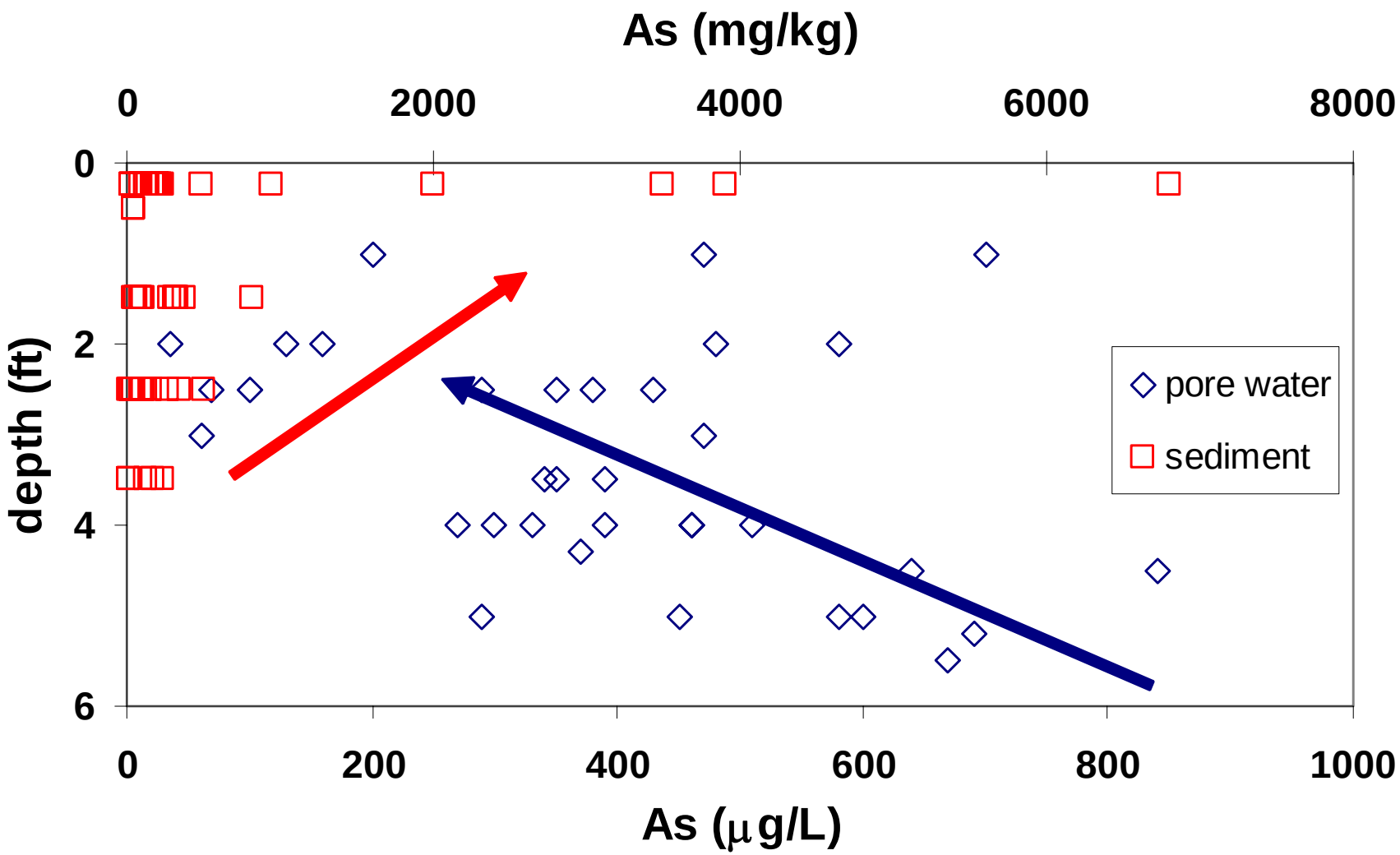
- Inorganic Species
  - As(III): $H_3AsO_3^0$
  - As(V): $H_2AsO_4^-$, $HAsO_4^{-2}$
- Organic Species
  - Monomethyl arsenic (MMA)
  - Dimethyl arsenic (DMA)
  - Arsenobetaine (AsB)

Which forms will be analyzed?

Questions Addressed by Arsenic Speciation Analysis

- Arsenic sources?
  - From waste?
  - Reductive dissolution of HFO?
- Carbon source (for organic species)?
  - C in waste vs. C in peat (“young” vs. “old”)?
- Risk issues
  - Bioavailability (organic or inorganic species)?
- How will data be used?
- Sampling and analytical considerations


Red Cove Sampling Locations
N
W
E
S
PLOW
SHOP
POND
PSPC18
P-sed-2
SHP-01-37X
PLOW1
PSP05
P-sed-5
N-2, P-2
N-2, P-1
N-2
SHL-11
SHL-20
RCSW1
P-sed-4
PSP06
RCH16
RCH17
RCH24
RCH11
RCH15
RCH26
RCSW2
RCH1
RCH25
PSPC13
PLOW2
RCH14
RCH27
RCSW4
RCH28
RCH10
RCSW3
PSP07
P-sed-6
SHP-01-38A
RCH3
P-sed-3
RCH21
RCH22
RCH5
SHP-01-38B
RCH4
RCH8
RCH20
RCH23
PSPC19
RCH18
PSPC12
P-sed-7
RCH9
RCH13
RCH19
RCH30
N-3
N-3, P-1
N-3, P-2
P-sed-11a
RCH7
RCH12
RCH29
RCH6
AYER
SHL-4
SHL-19
SHM-93-10C
SHL-10
SHM-93-10E
SHM-93-10D
N-4
N-4, P-1
Legend
Pushpoint Sample Locations
Sediment Samples - Mar04
Sediment Samples - Feb05
Geoprobe
Surface Water Sampling - Nov04
Monitoring Wells

Red Cove

Sediment and Pore Water Arsenic