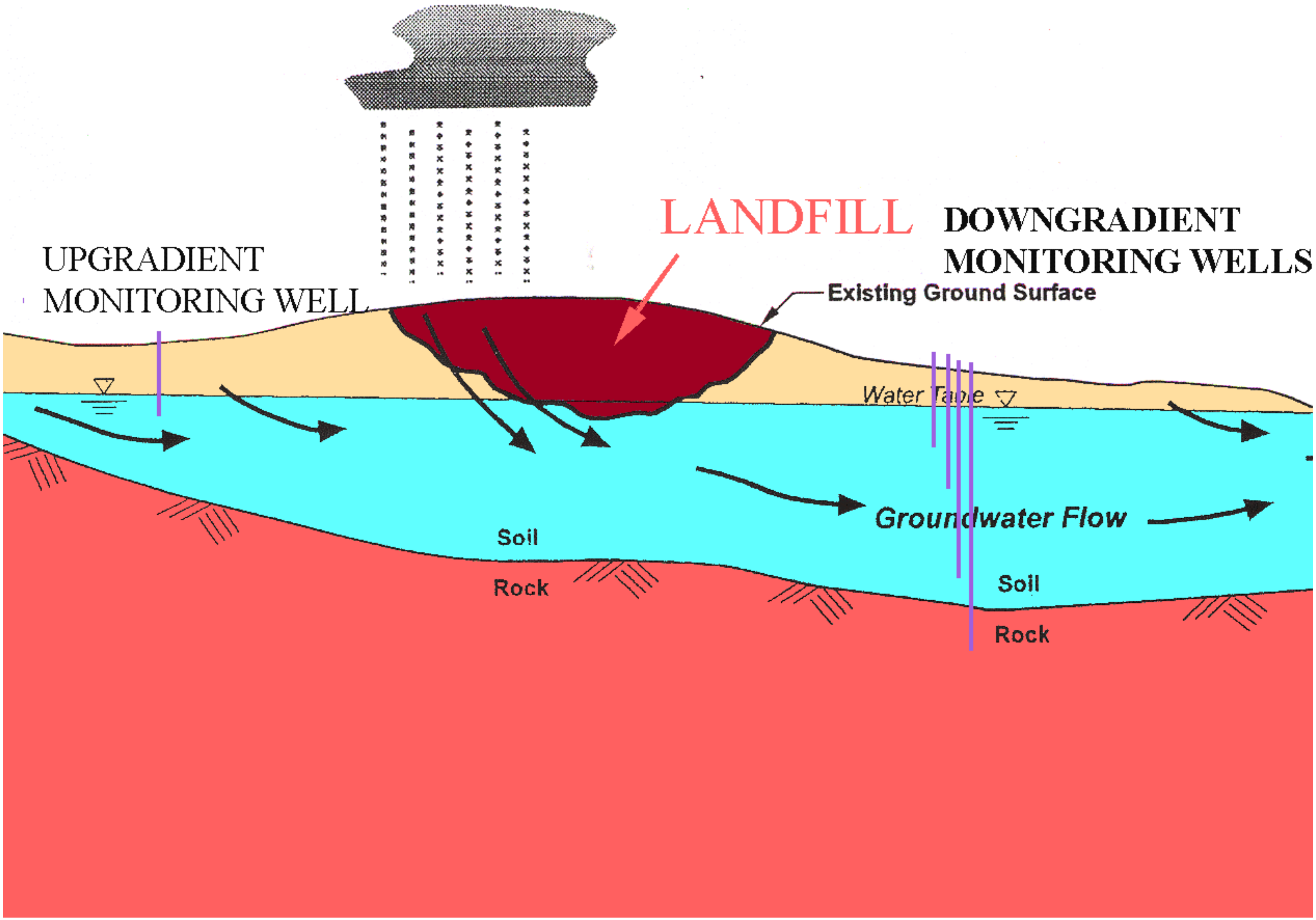
Case Studies of Arsenic Mobilization Related to Landfills and Superfund Sites

- Multi-group presentation
  - Columbia University SBRP and NYSDEC Region 3
  - Boston College and USEPA Region 1
  - Dartmouth College SBRP
- Steven Chillrud, Rudi Hon, Ben Bostick and their many colleagues

Arsenic in plumes of old landfills- analog for what may happen in landfill



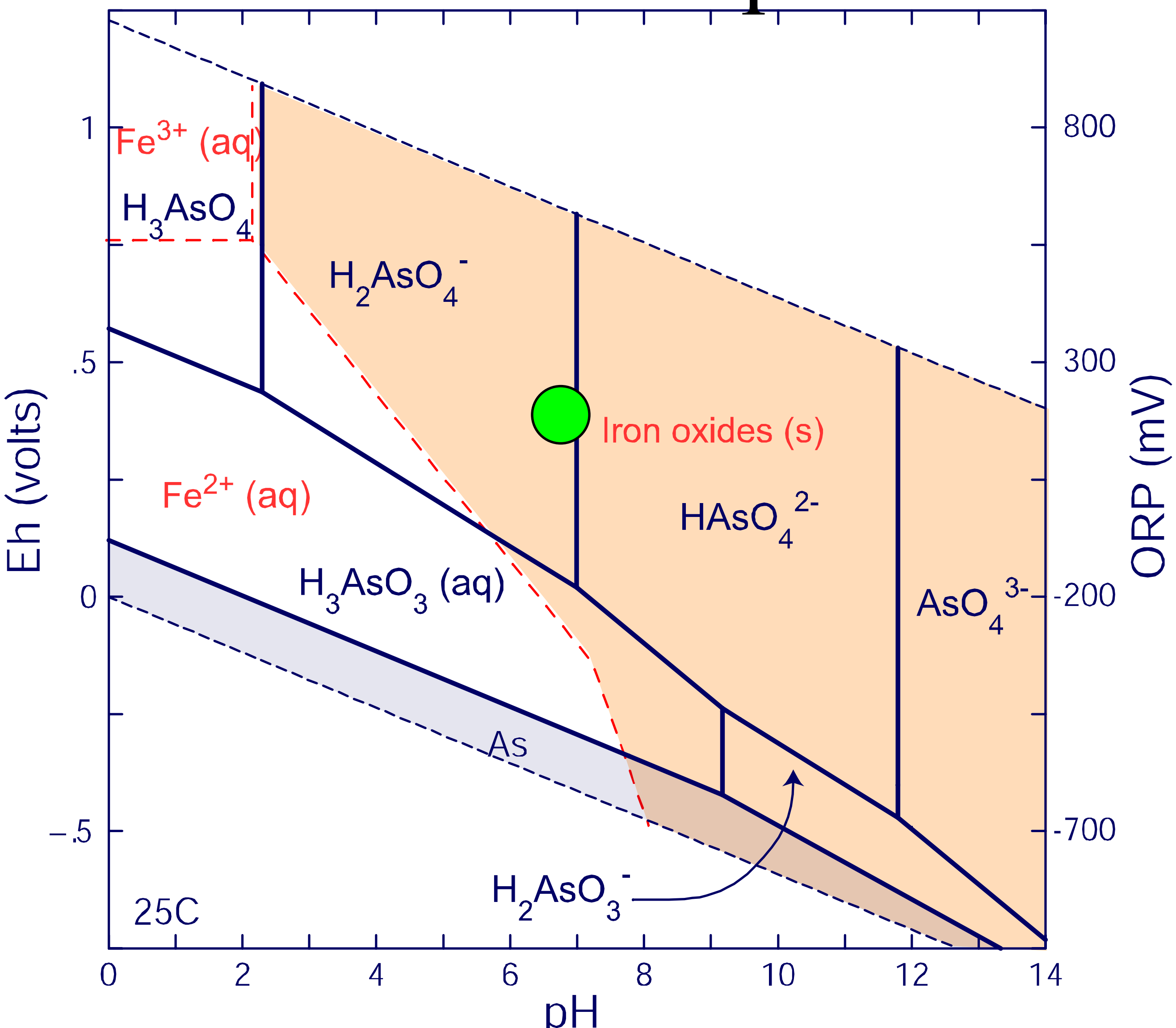
Implications for landfill leachates

- Arsenic mobilization coupled to iron mobil.
- Mobilization tied to organic carbon sources in landfill wastes
- Regional variations of As levels in natural soils can lead to variations in gw [As], if Fe

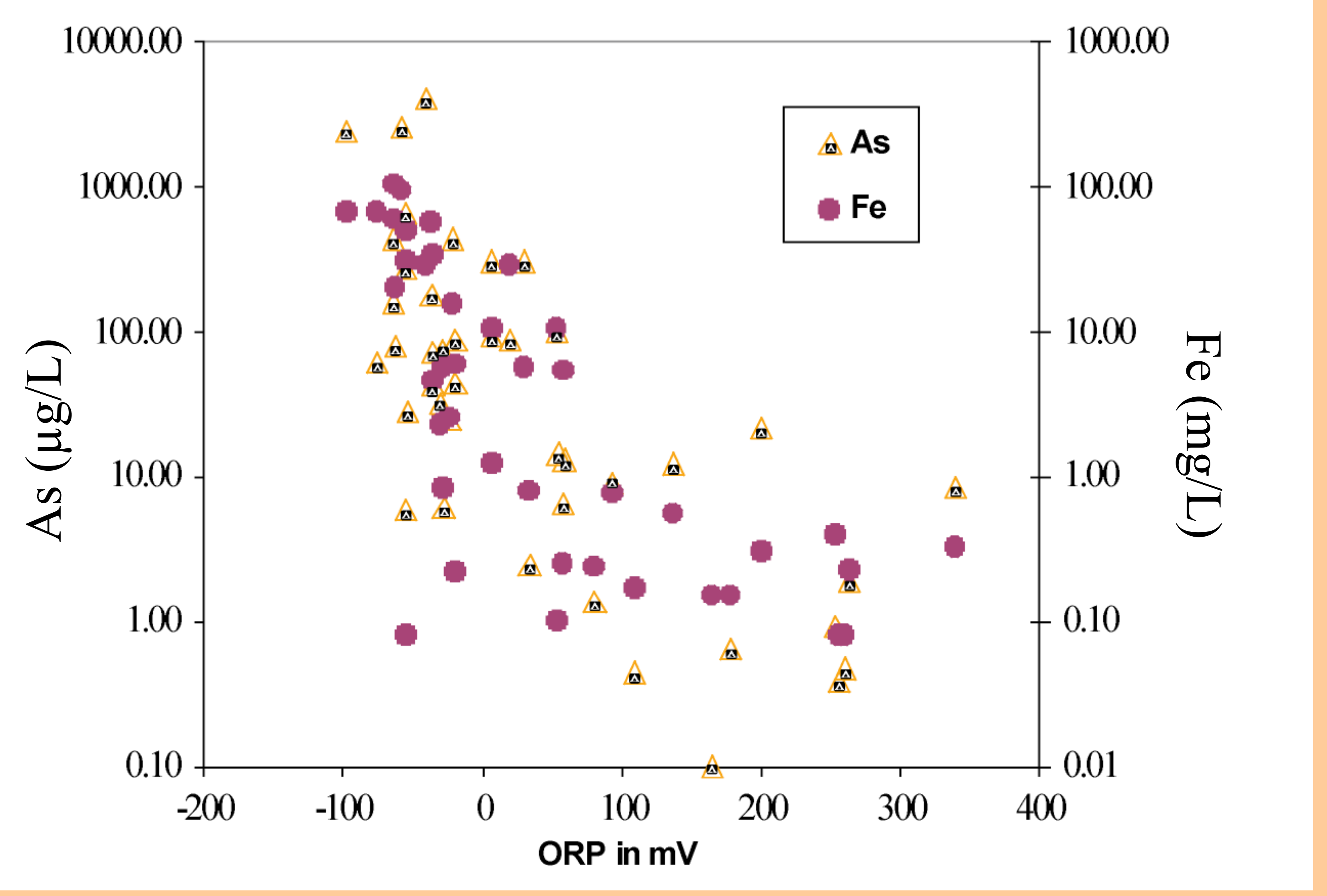
Causes of Arsenic Contamination

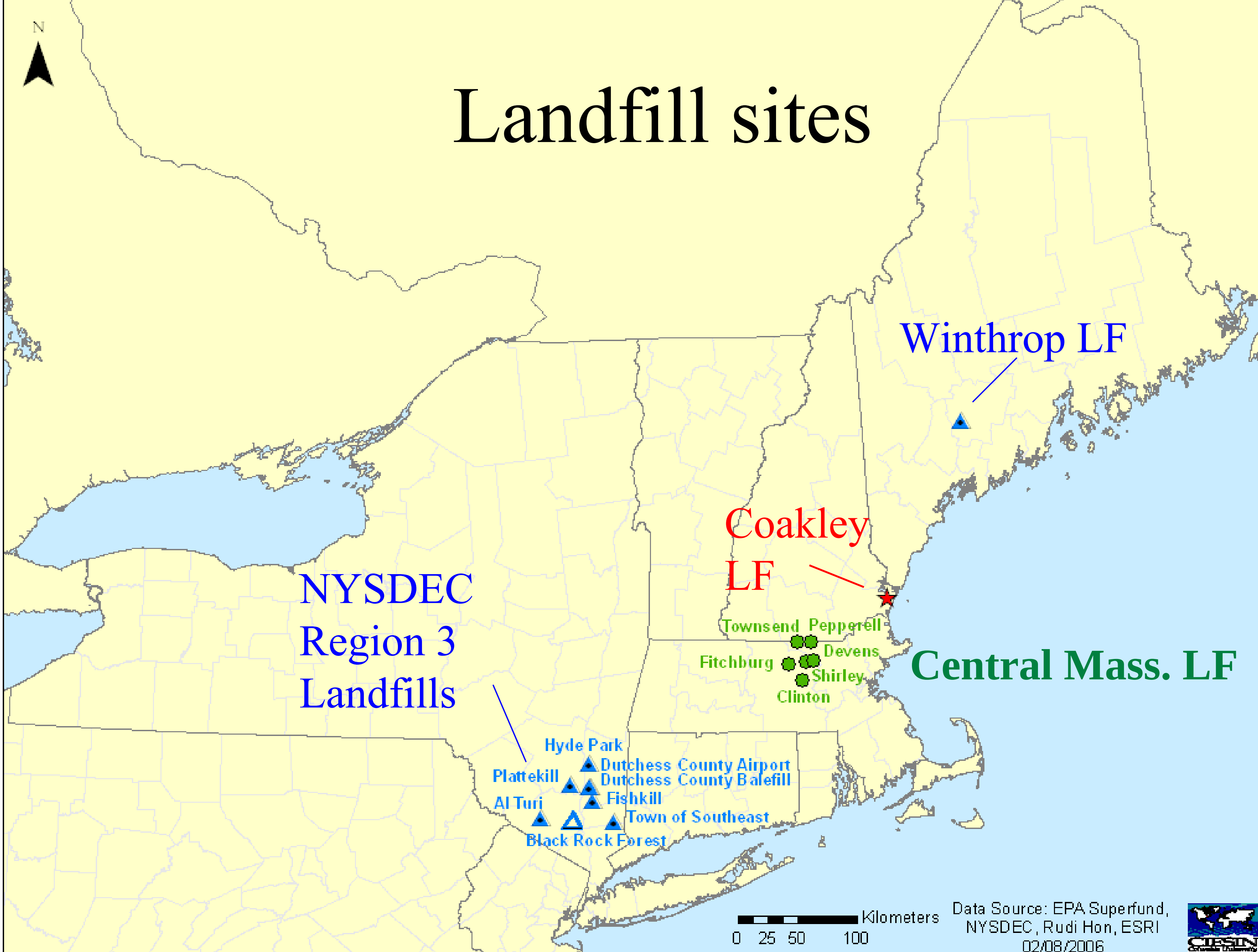
- Entirely natural:
  - Arsenic in solid phase released to waters
- Entirely anthropogenic:
  - Human activities release As and contaminate soil and groundwater
- **Anthropogenically induced mobilization of naturally-occurring-Arsenic:**
  - **Changes to groundwater chemistry allow natural As to be released from sediment to groundwater (coupling of Fe and As)**
- **Combination of above**

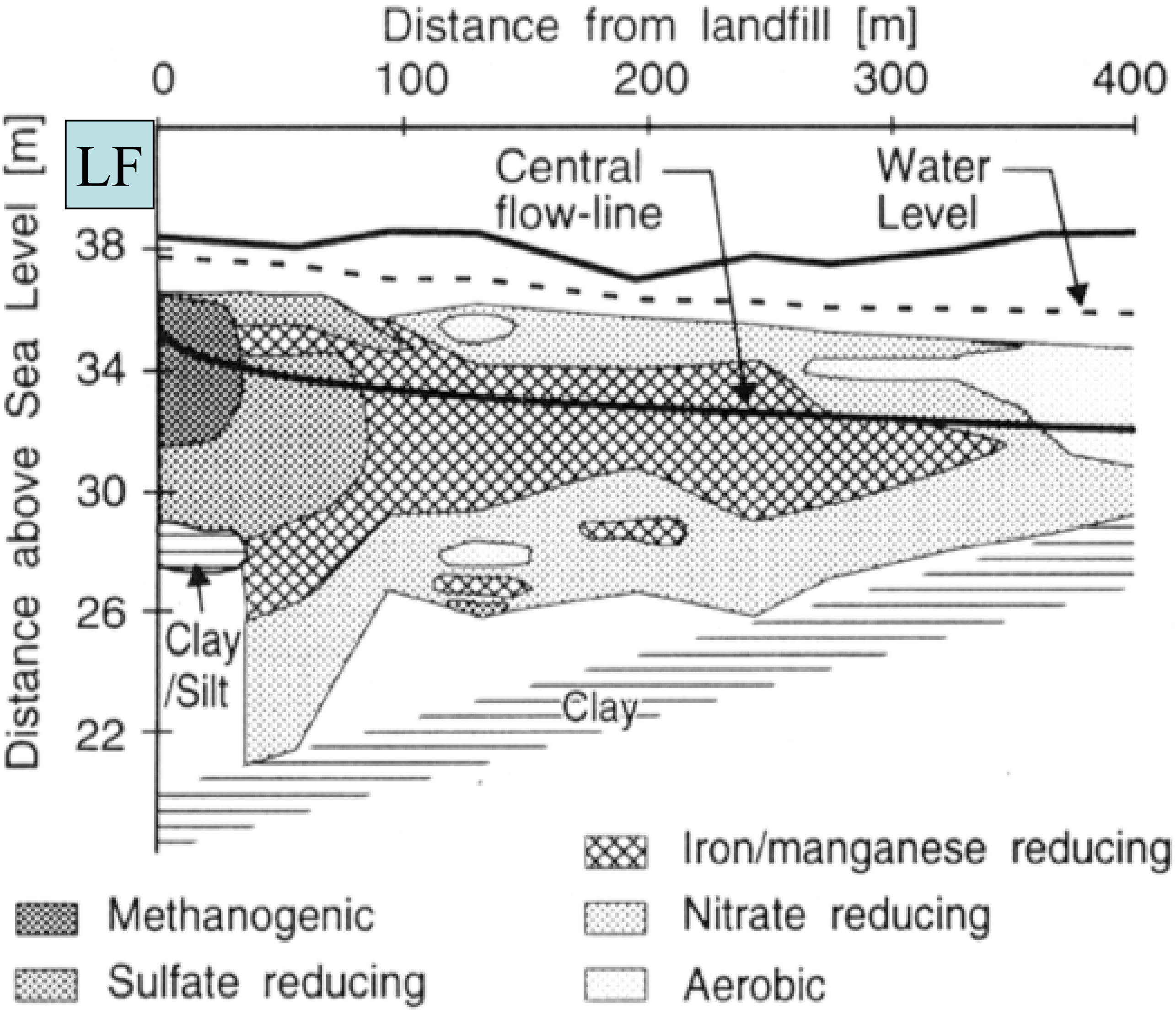
Arsenic Mobilization– Geochemical Explanation



Arsenic & Iron vs ORP – GW Near Landfills




Landfill sites
N
Winthrop LF
Coakley
LF
Central Mass. LF
NYSDEC
Region 3
Landfills
Townsend
Pepperell
Devens
Fitchburg
Shirley
Clinton
Hyde Park
Dutchess County Airport
Plattekill
Dutchess County Balefill
Fishkill
Al Turi
Town of Southeast
Black Rock Forest
Kilometers
0 25 50 100
Data Source: EPA Superfund,
NYSDEC, Rudi Hon, ESRI
02/08/2006
CIESIN



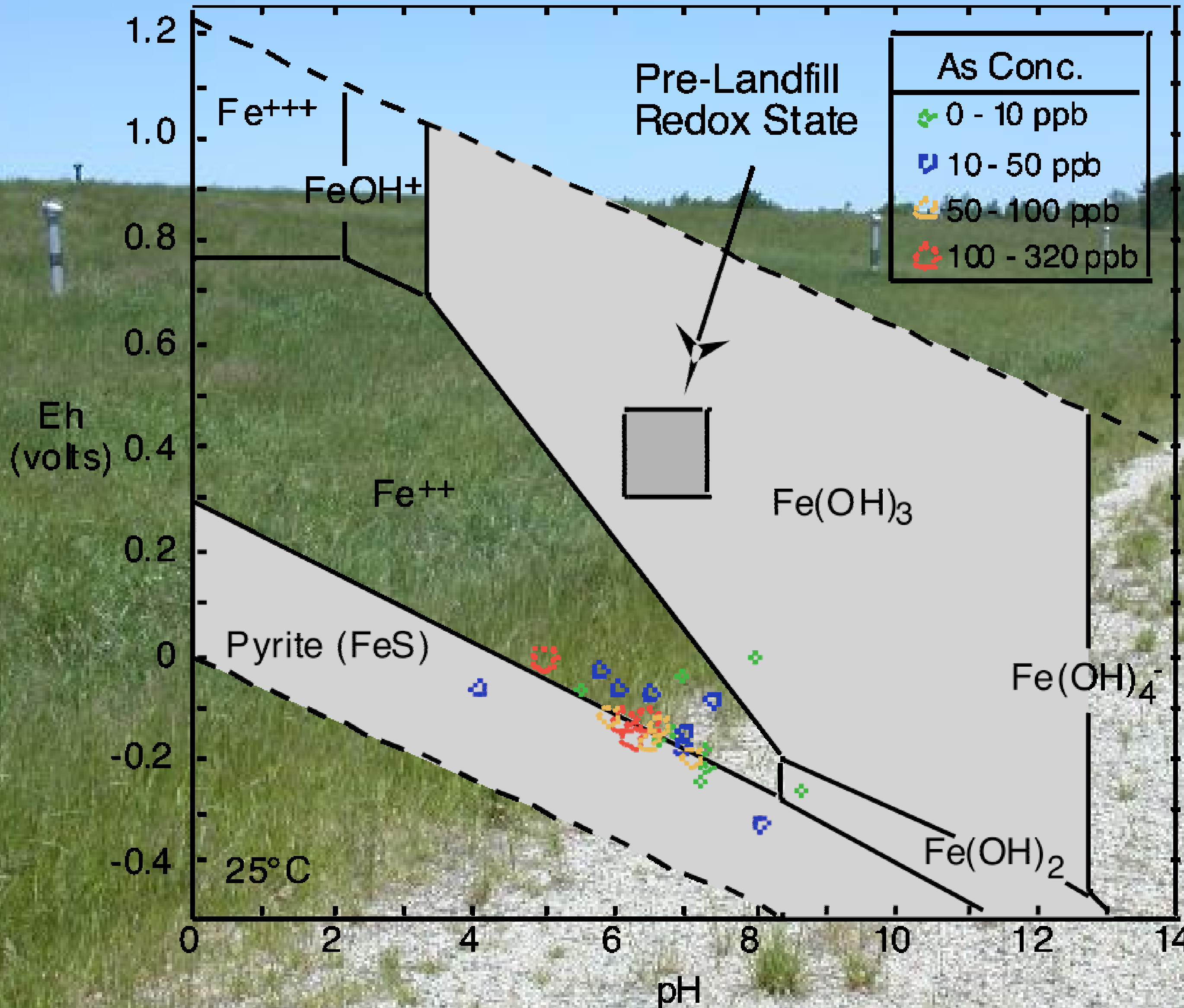
from Heron et al. 1995

Redox zonation of landfills

Baedecker & Back 1979 ;

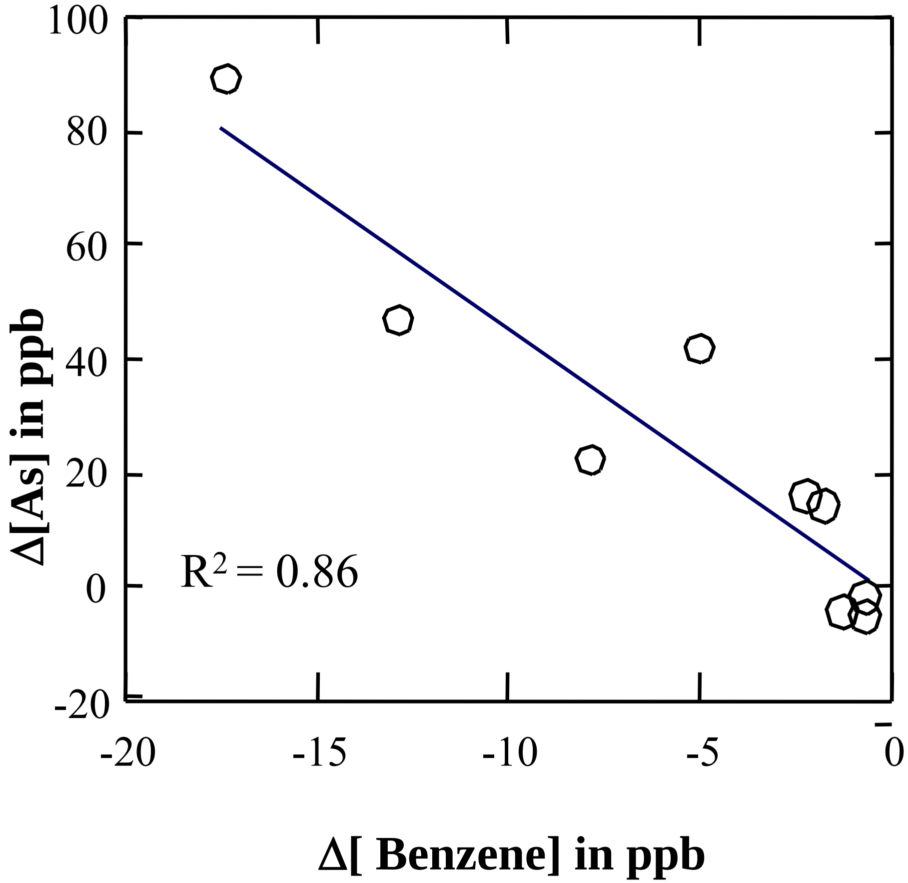
Danish landfills T.H. Christensen and colleagues (mid 1990s -

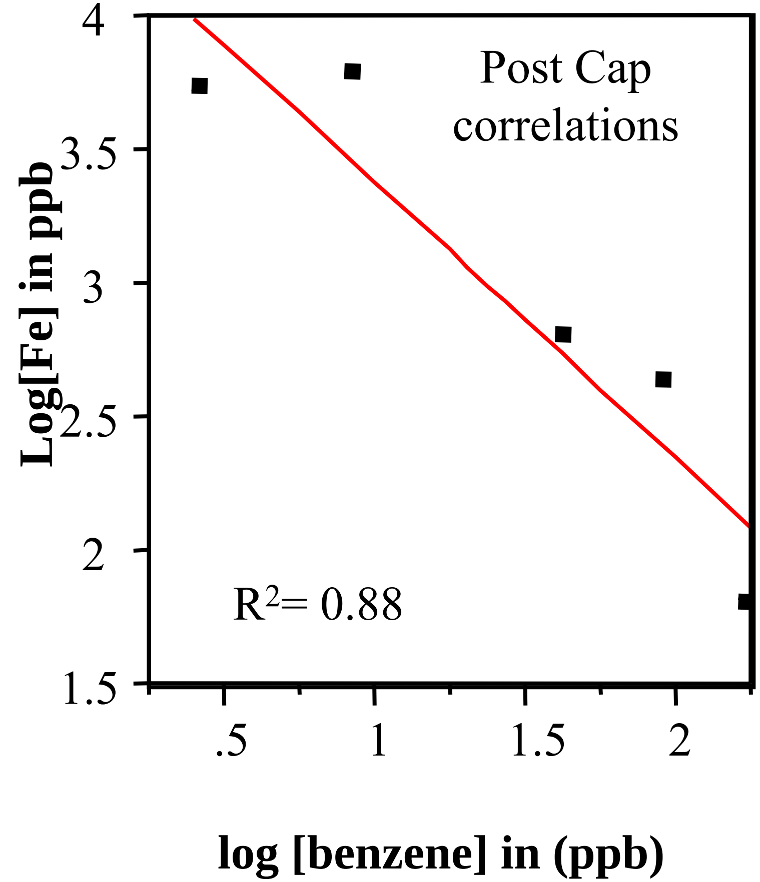
Coakley: Batch Experiments and Field Data

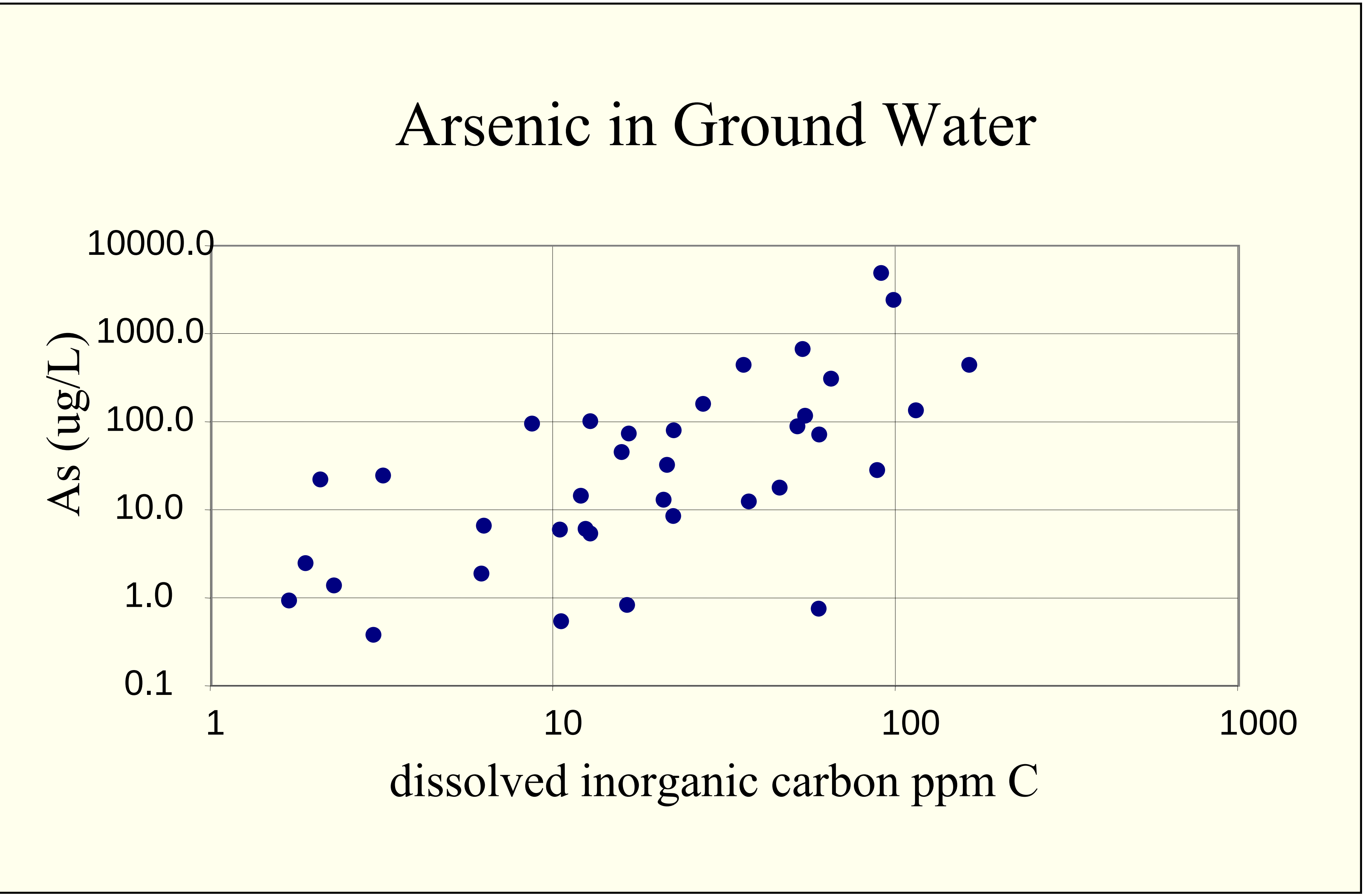


Coakley: Arsenic Mobilization & Natural Attenuation

$$30Fe(OH)_3 + C_6H_6 + 60H^+ \Rightarrow 30Fe^{2+} + 6CO_2 + 78H_2O \quad \Delta G^o = -2359.96 \text{ kJ}$$

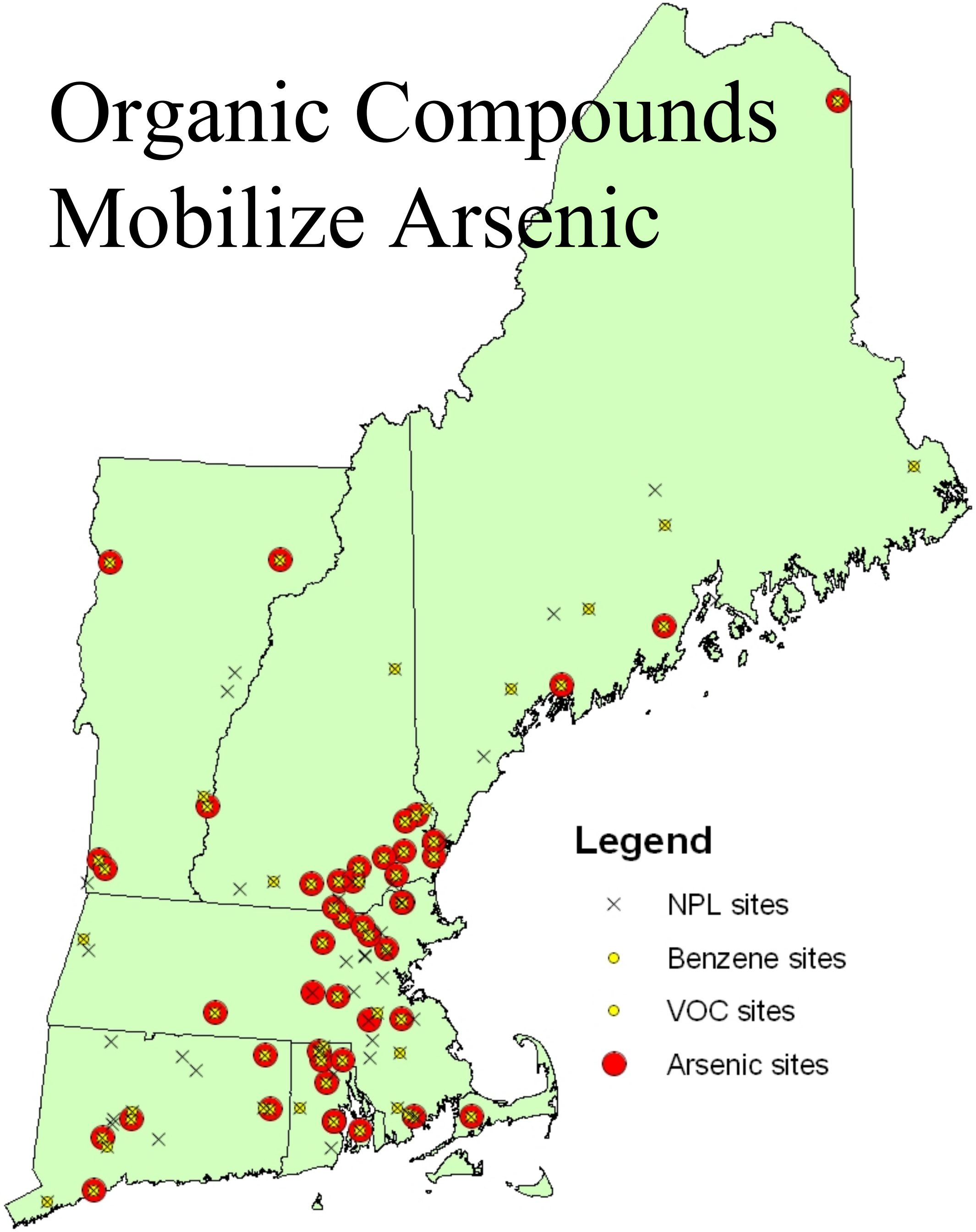






Arsenic in Ground Water
10000.0
1000.0
100.0
10.0
1.0
0.1
As (ug/L)
1
10
100
1000
dissolved inorganic carbon ppm C

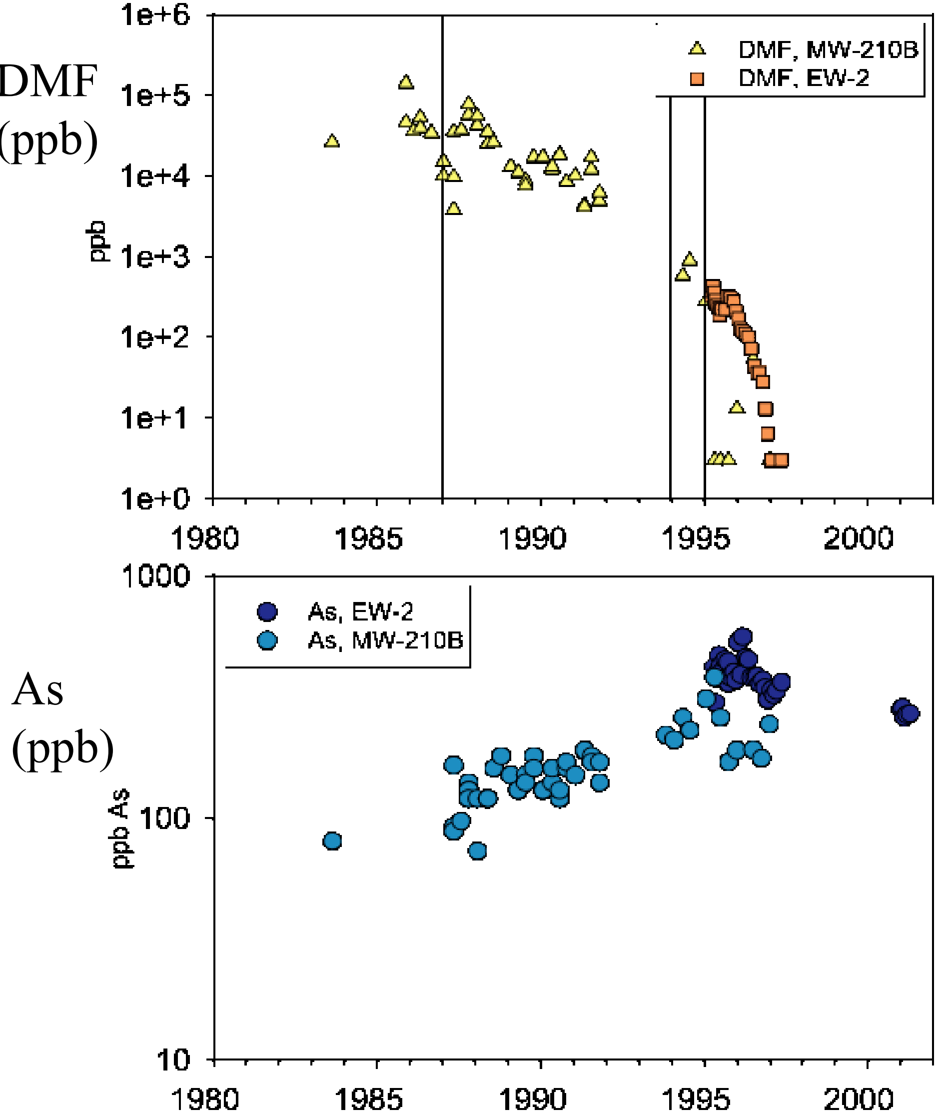
Organic Compounds Mobilize Arsenic



Superfund Sites: Arsenic and Benzene/VOC (DOC) Sites are Highly Correlated

- Northeast
  - 42 of 45 As contaminated sites are contaminated with either Benzene or VOC
- National
  - 419/555 As sites also have aromatic hydrocarbon contamination
  - That is roughly twice the random probability

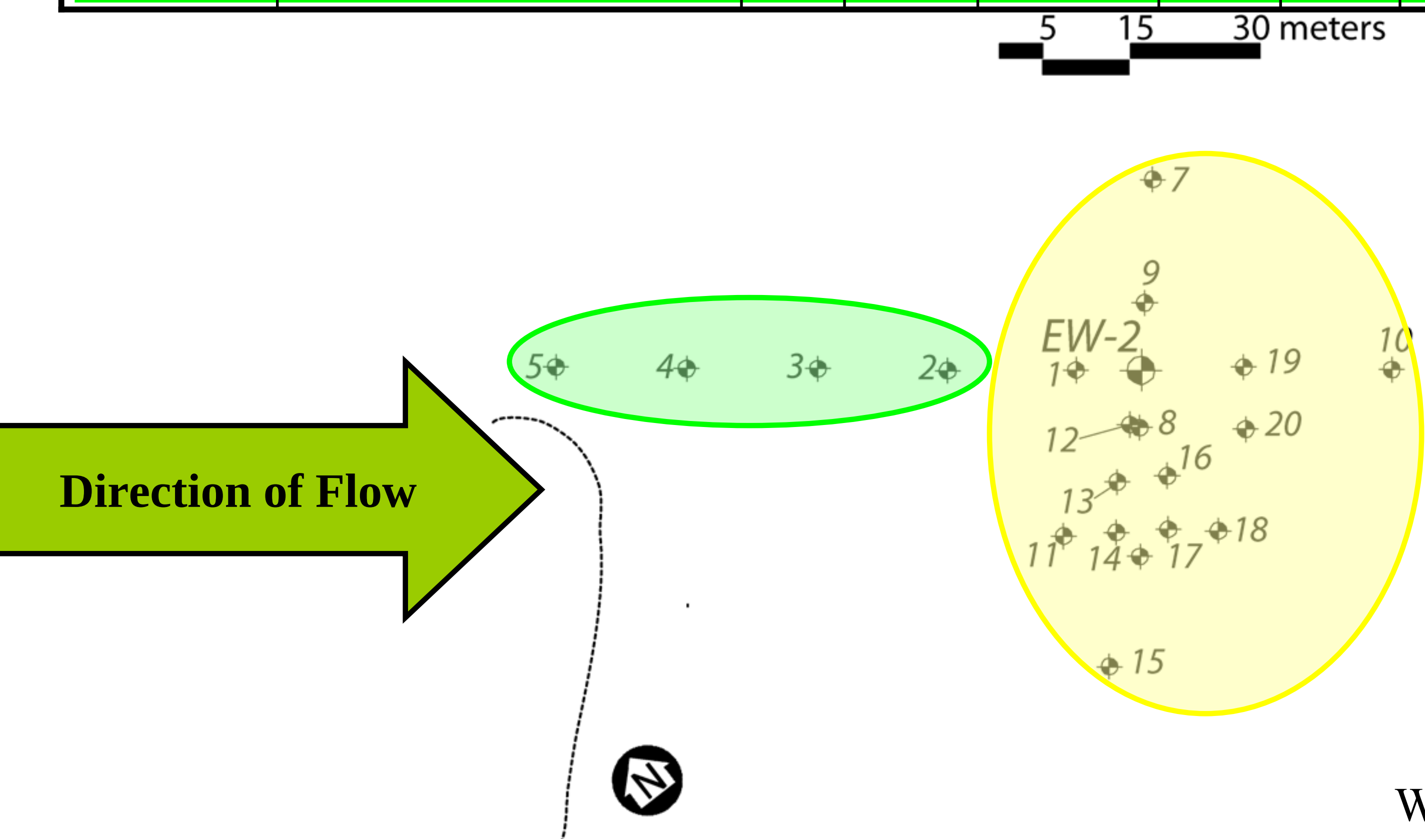
Winthrop Contamination & Remediation



1930: Dump operation begin including industrial waste
1972: Landfilling begins and serves adjacent towns
1979: Buried drums found
1982: Landfilling ceases
1987: Clay cap installed (Capping ≠ help As)
1995: SVE and P&T remediation starts
2004: Rebound experiment begins

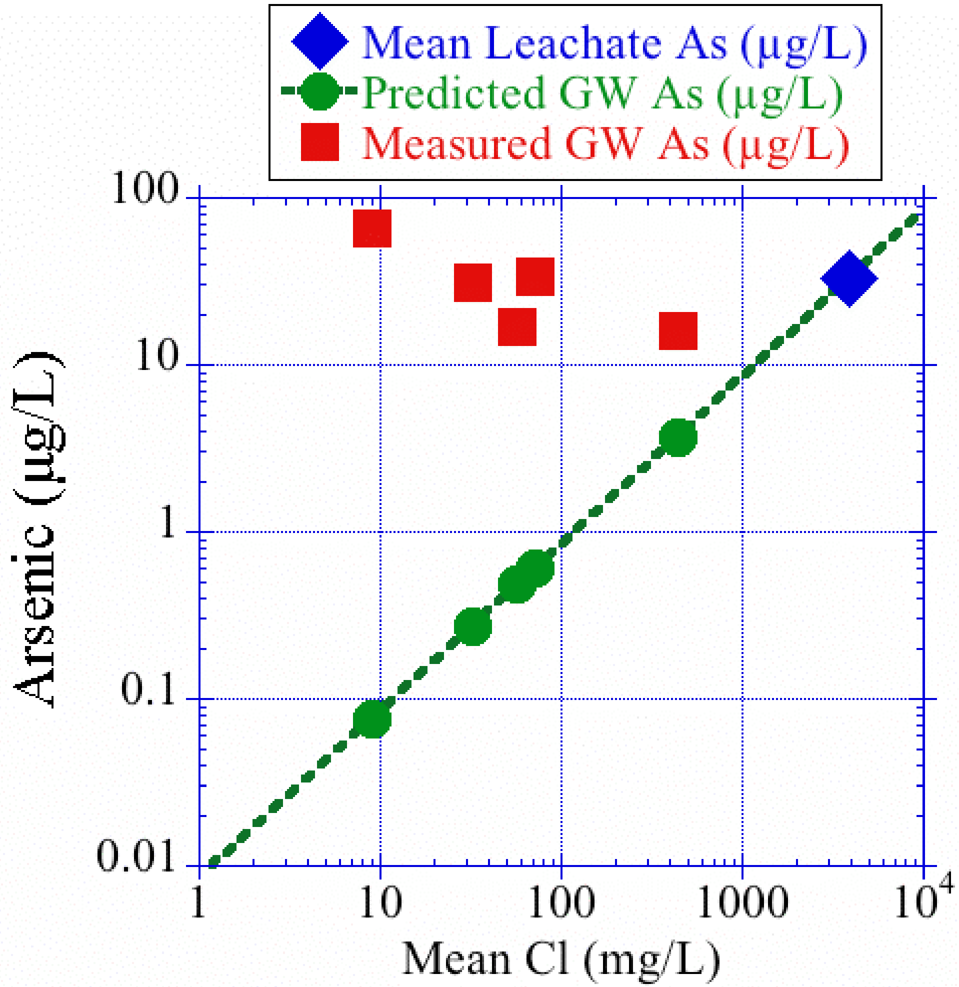
Reduction Induced by Leachate

Sed As mg kg^{-1}	Dissolved Species mean, mg L^{-1}	Cl^-	DOC	Sulfide	Fe^{2+}	Iron	COD	Water As
7 ± 1	Central Region	29 ± 6	26 ± 14	53 ± 49	24 ± 15	37 ± 9	35 ± 23	0.3 ±0.1
8 ± 2	Upgradient Region	10 ± 2	16 ± 4	5 ± 2	2 ± 4	2 ± 4	1 ± 0	0.01 ±0.005

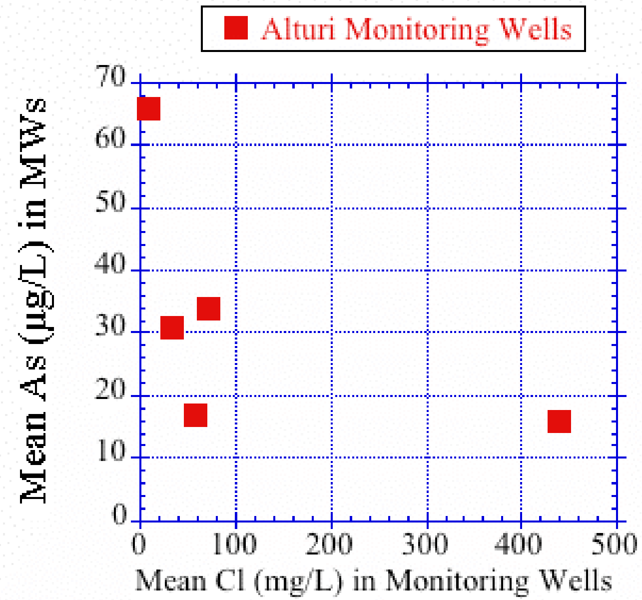


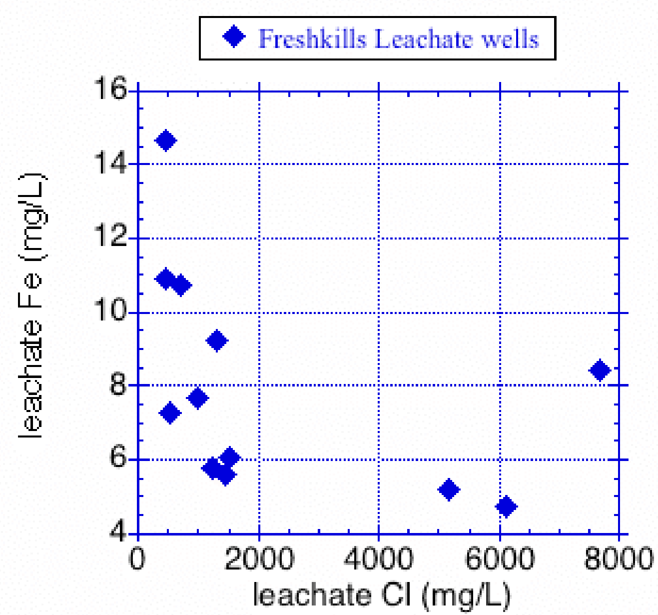
Winthrop As mobilization

- Al Turi Landfill- 129 Acres
- Sections range from unlined (older) to single layer, to modern double lining
- Leachate well characterized
- Monitoring wells in overburden (below waste)



NYSDEC, unpublished data





Freshkills Landfill
Staten Island, NY

Leachate monitoring wells
(screened in waste)

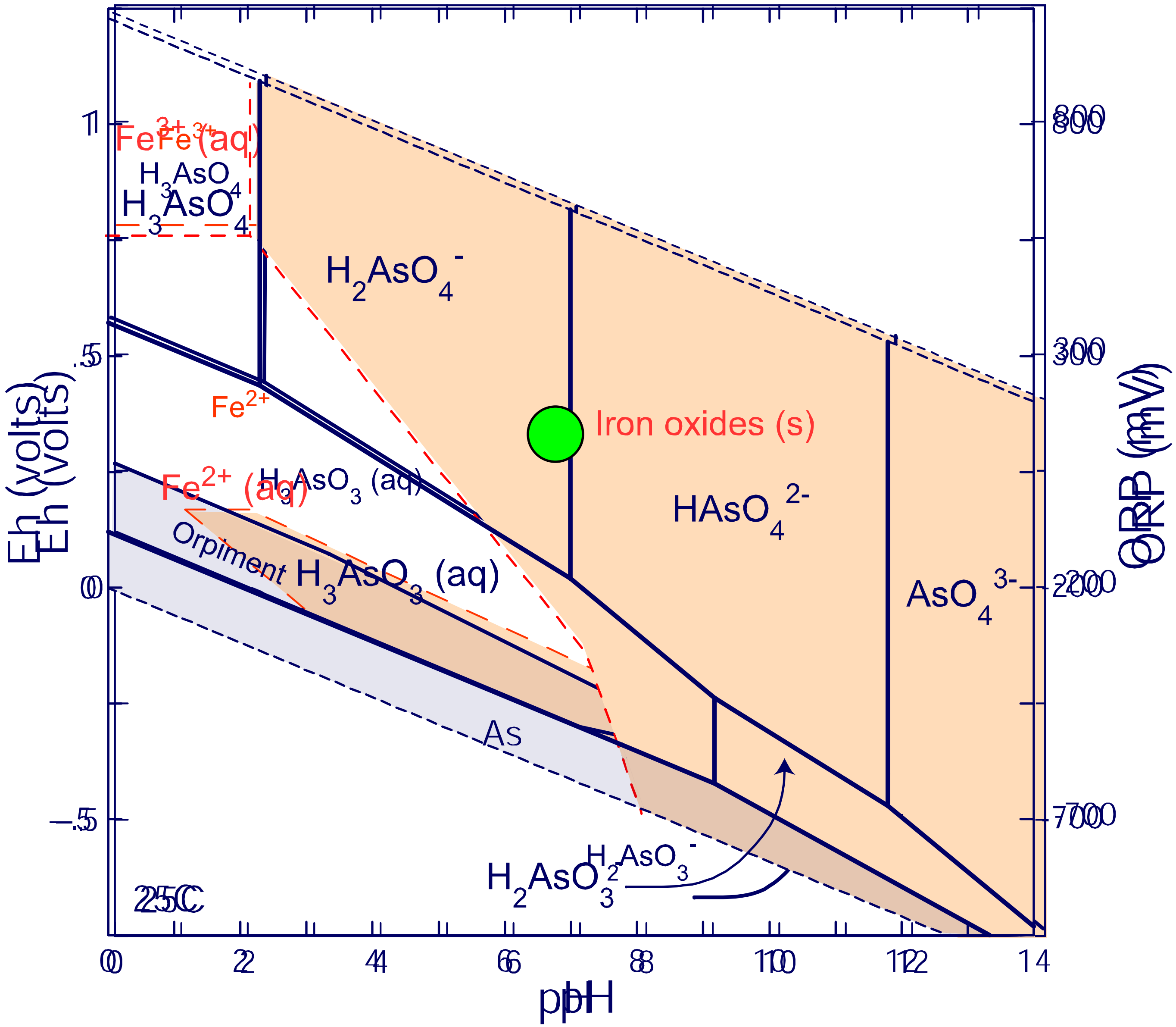
Cl is conservative tracer of
leachate strength and mixing

Sources for Fe
- acid solubilization
- redox mobilization

Sinks for Fe, Mn
- sulfide formation
- carbonate precipitation
- ion exchange

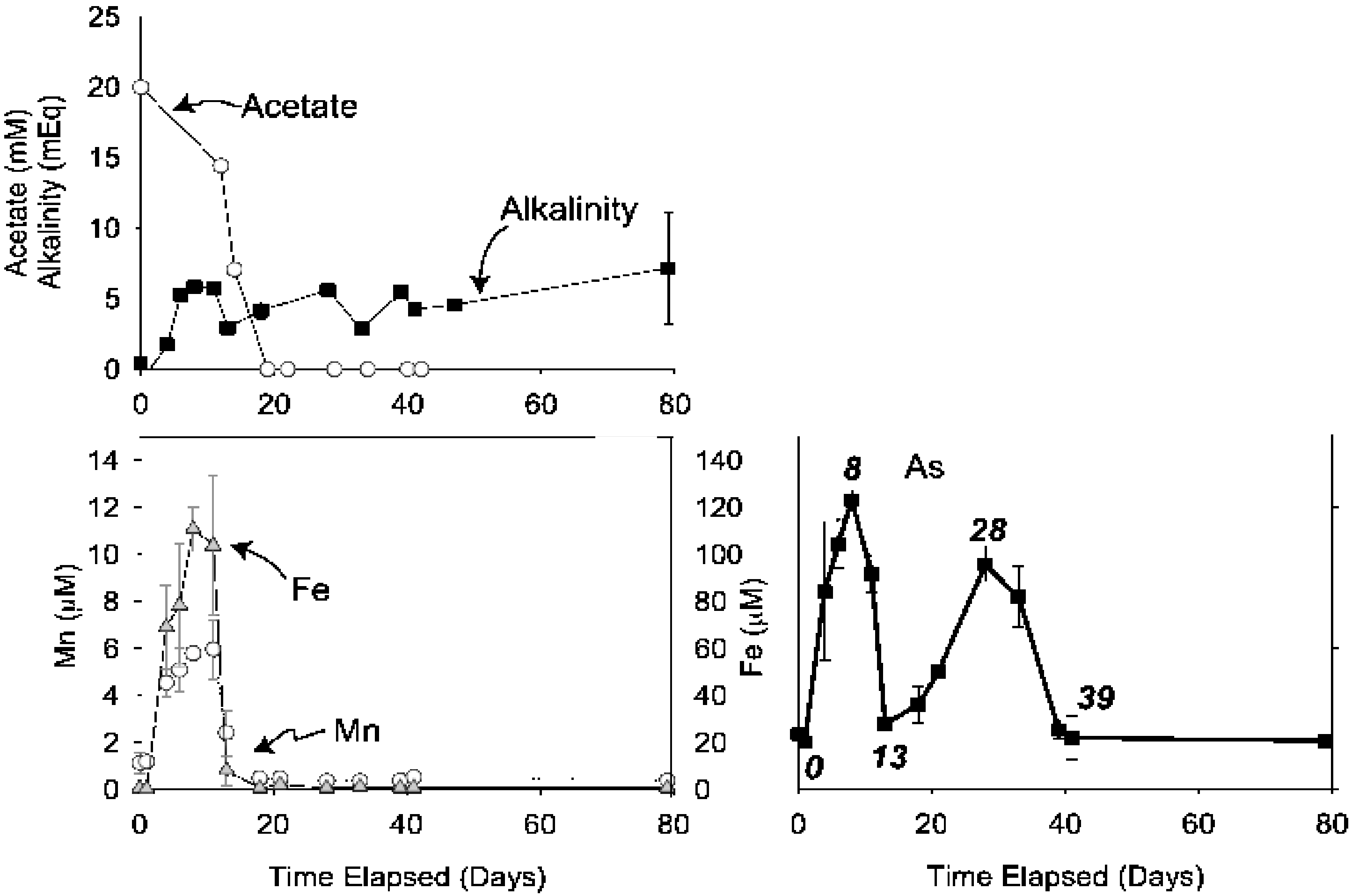
Data from Walsh 1996

As Immobilization via Reduction

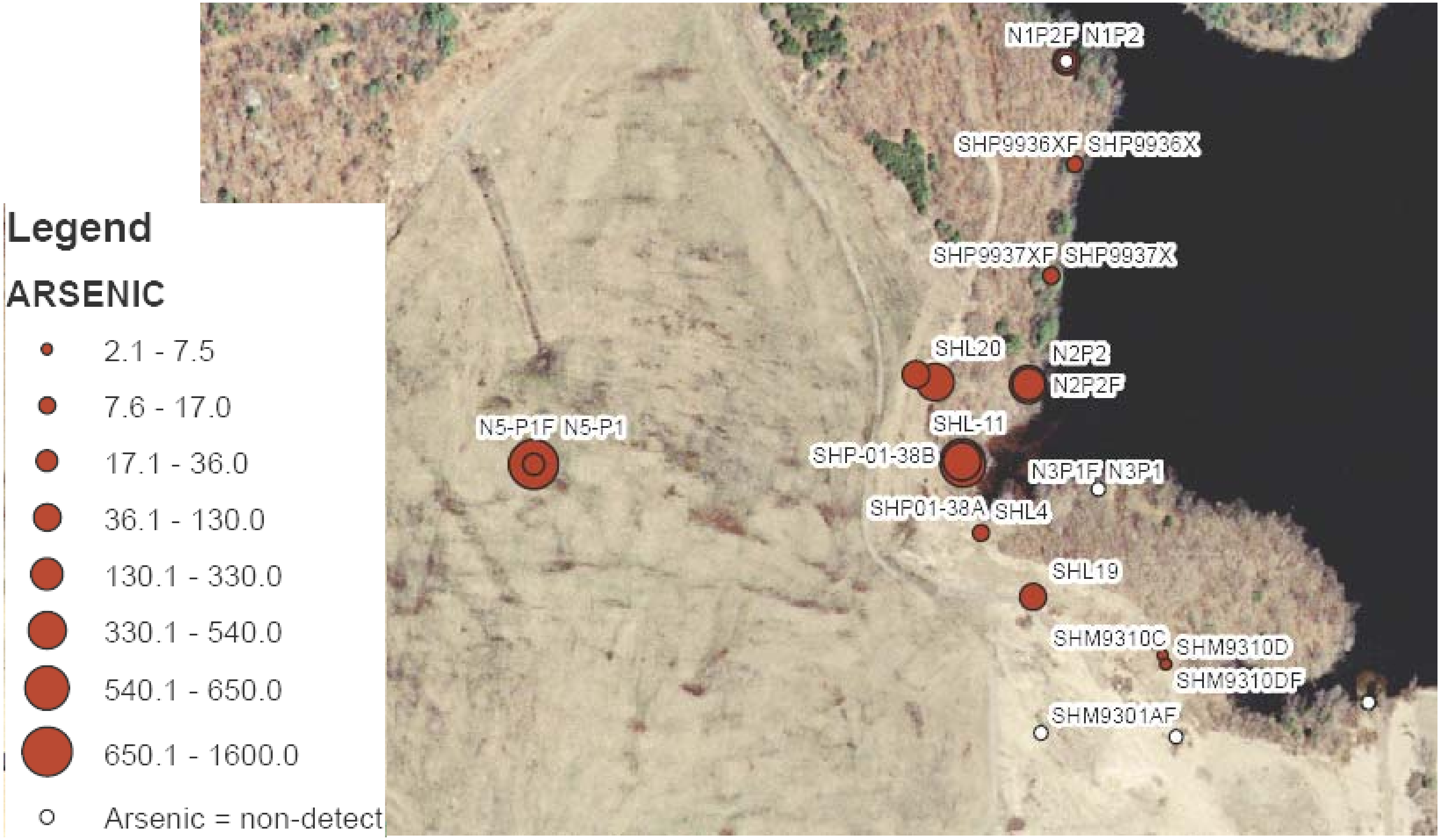


Arsenic remediation via reduction?

Aqueous Phase

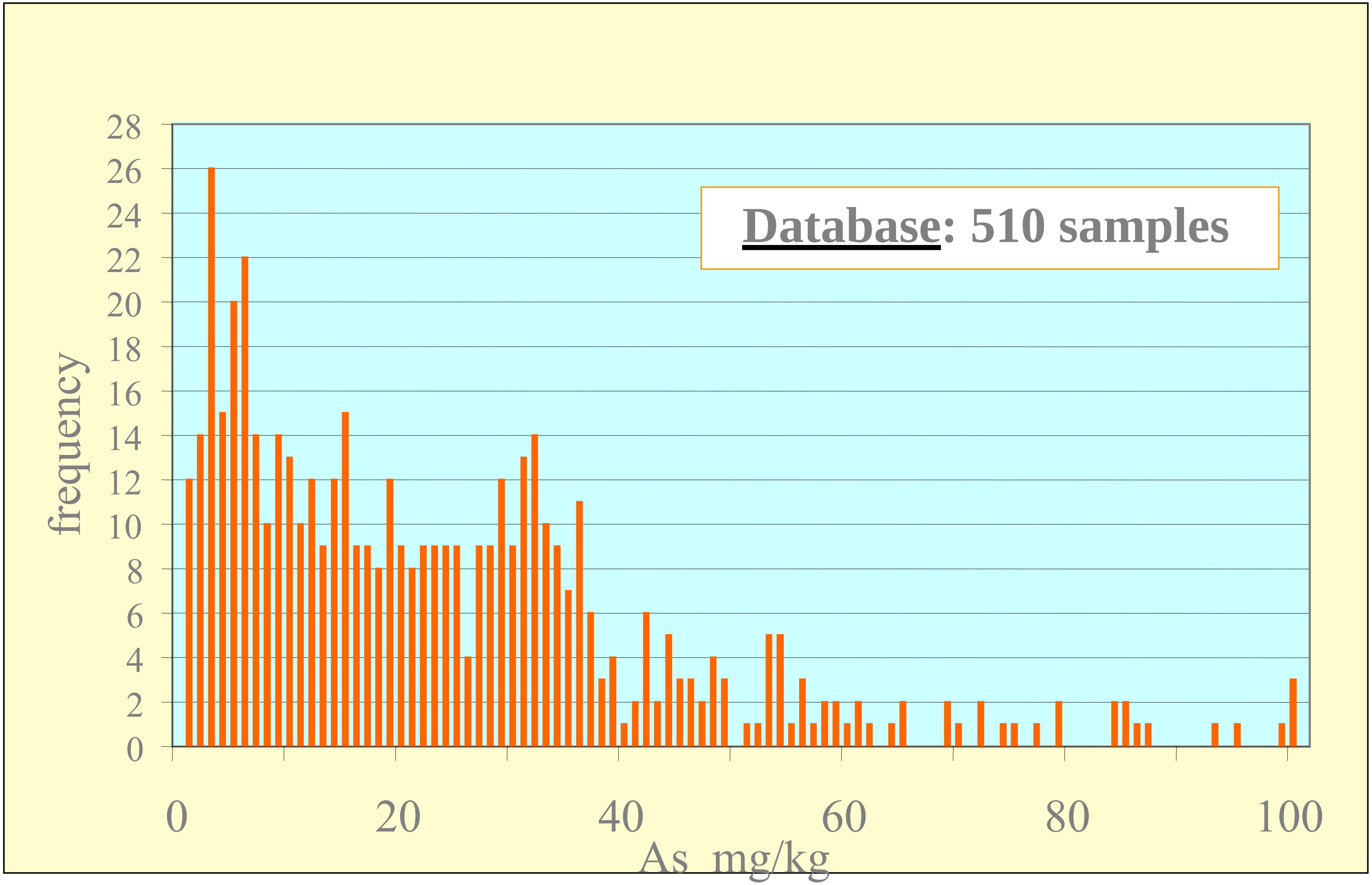


Arsenic in Ground Water (ppb) at SH Landfill
November 2004

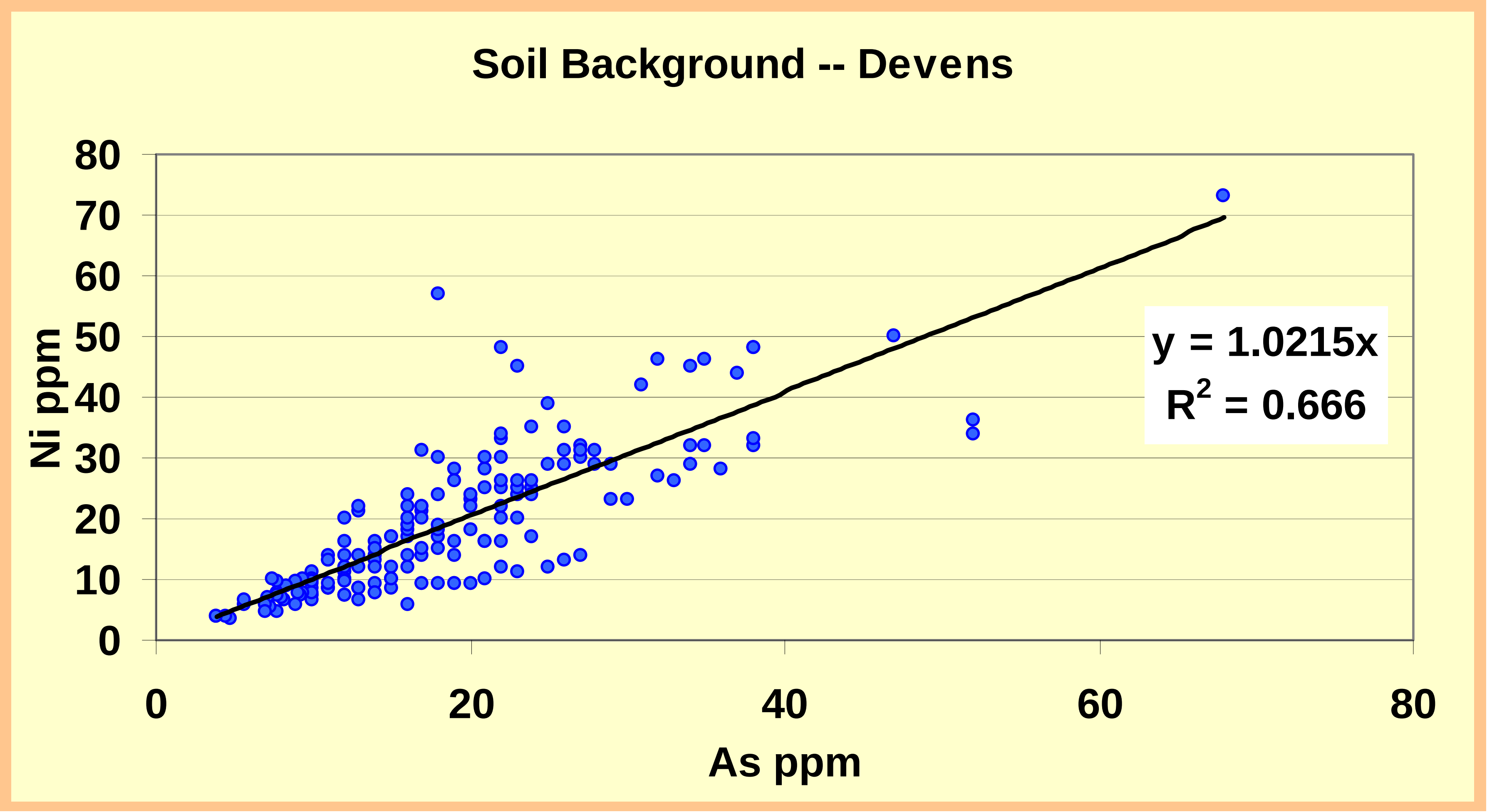


Frequency of Arsenic Levels in Soils

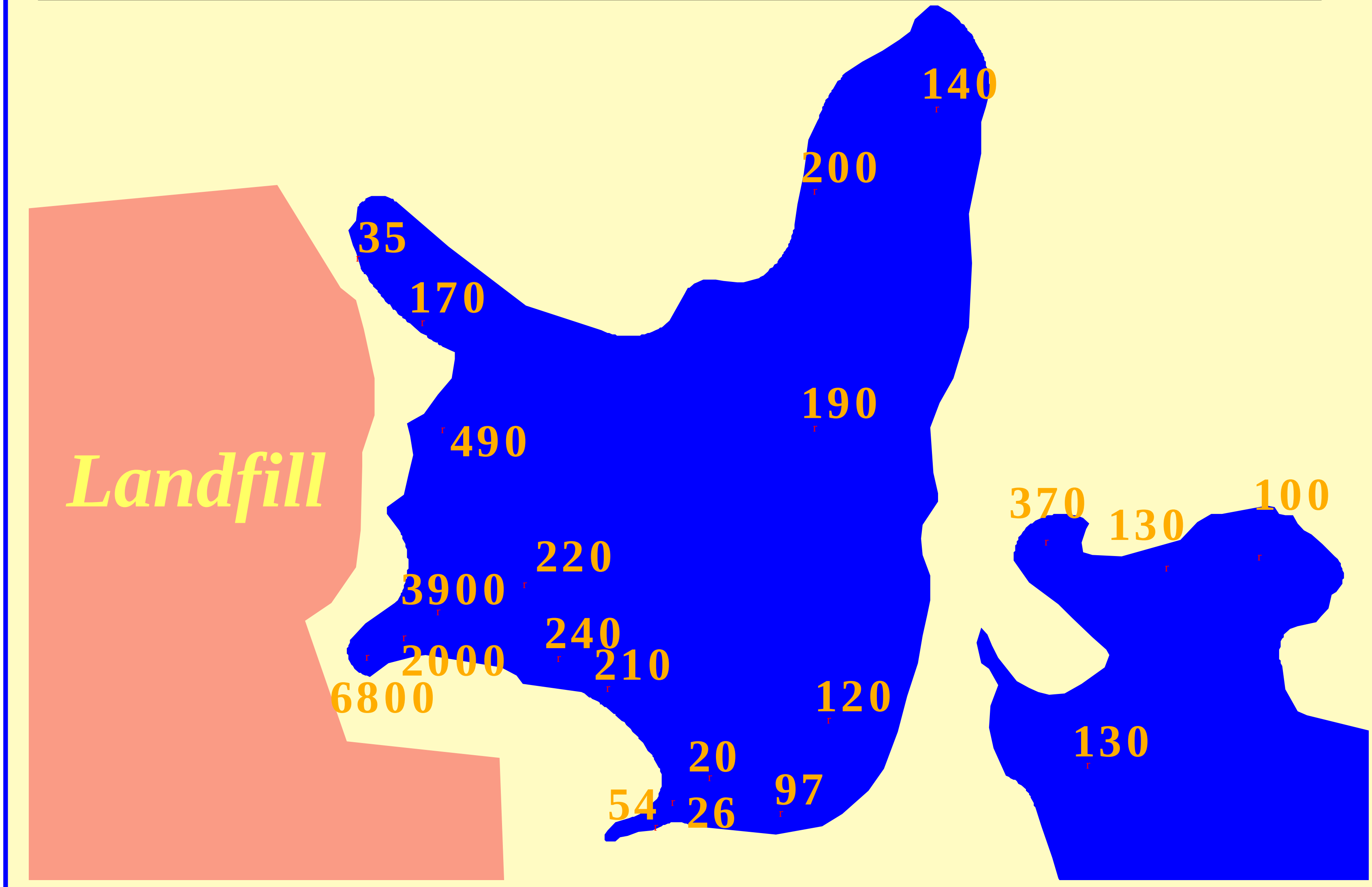
CENTRAL MASSACHUSETTS



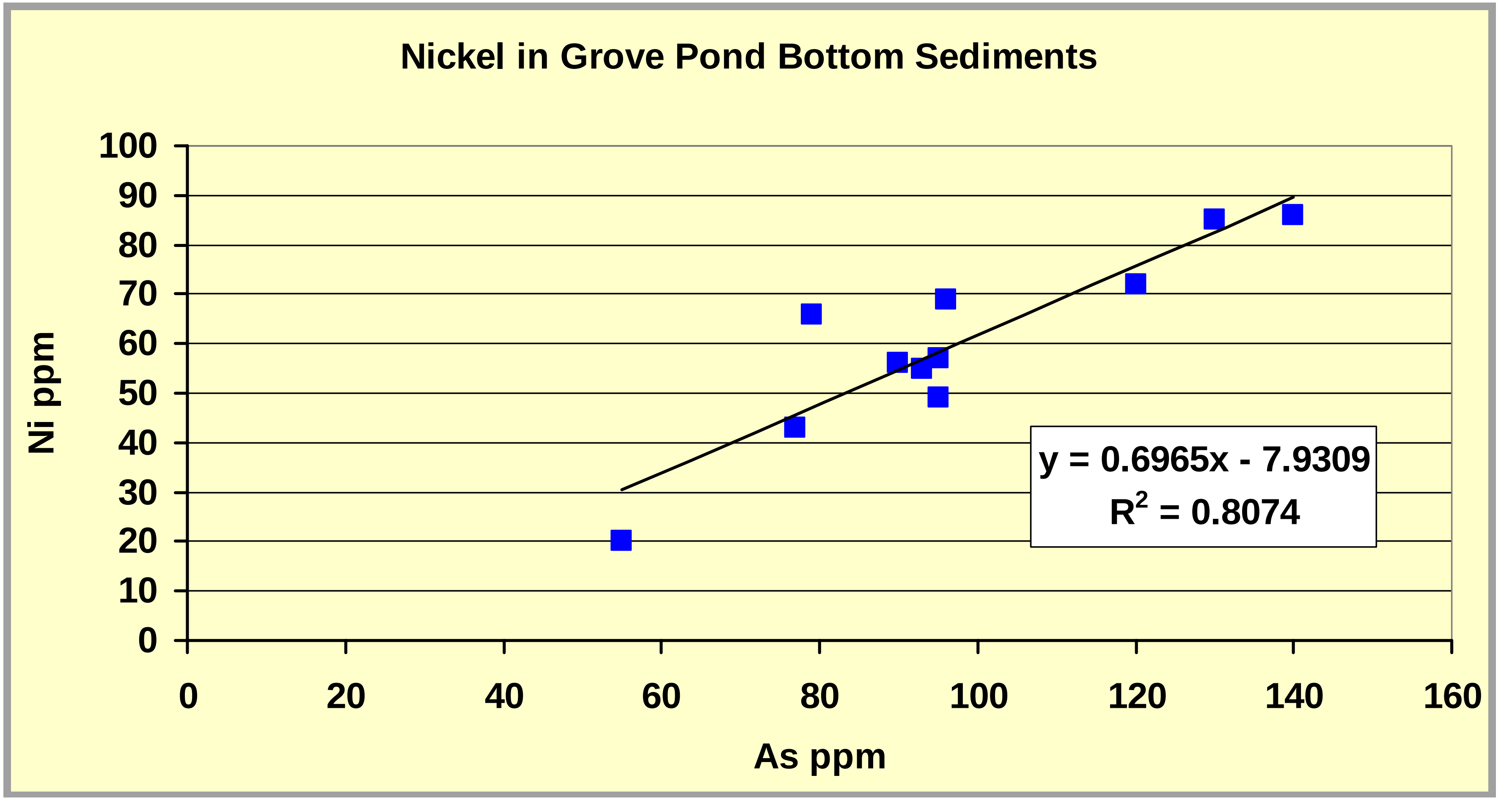
Nickel vs Arsenic in Soils -- Devens



Arsenic in Bottom Sediments mg/Kg



Grove Pond Bottom Sediments



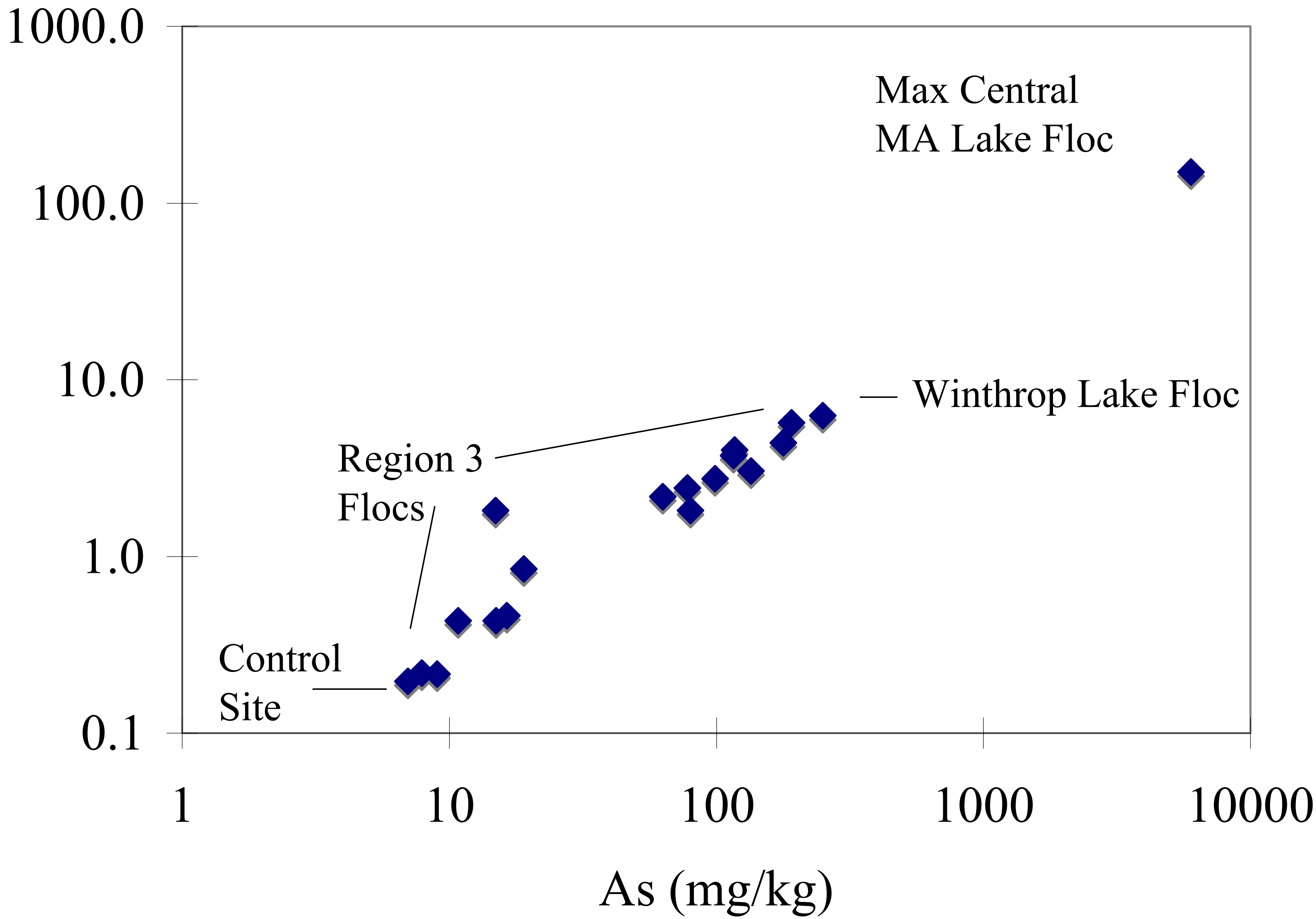
Iron Flocs as integrating triage tool

- Seeps near old landfills easy to locate (color)
- Relatively easy to collect and analyze (compared to installing wells)

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

5 µm pore size

absorbant pad for thin films

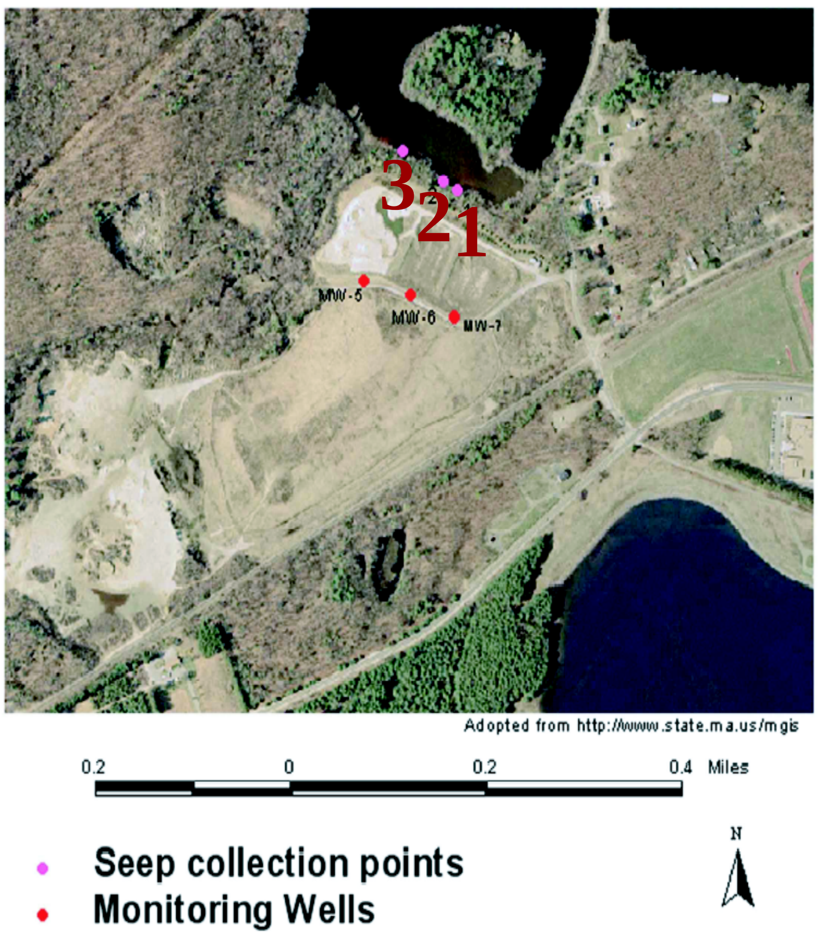


Central MA data from Hon R. 20003 GSA *Abstracts with Programs*, Vol. 35. No. 6 September 20003, p. 48.

CLINTON LANDFILL DATA

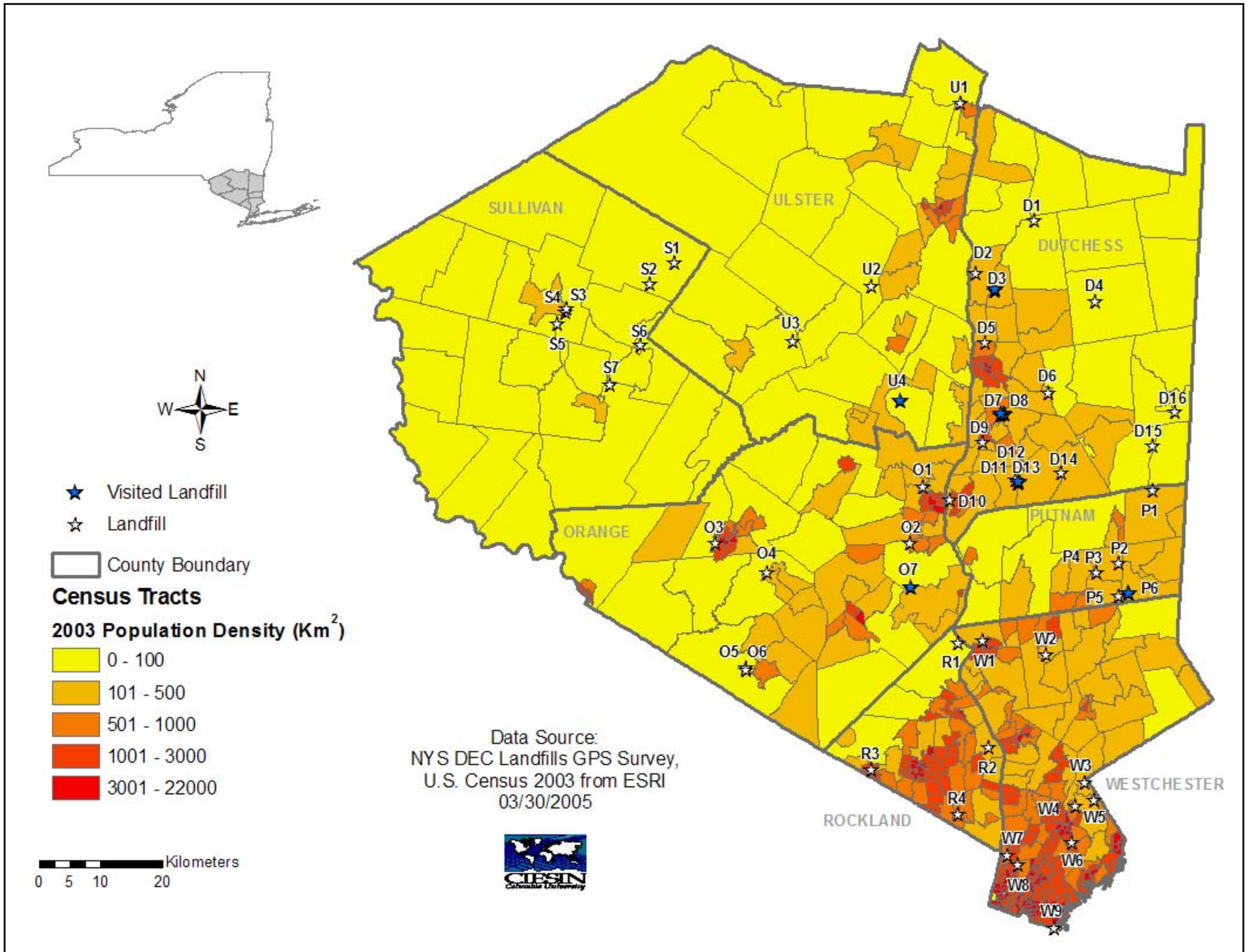
South Meadows Pond Seep Samples

Clinton Sampling Points



Site	Unfiltered Total Arsenic	Unfiltered Total Iron	Unfiltered Total Manganese
Seep 1	600 µg/L	75,000 µg/L	8,200 µg/L
Seep 2	71 µg/L	30,000 µg/L	1,700 µg/L
Seep 3	4,100 µg/L	120,000 µg/L	6,700 µg/L
Monitoring Well	Dissolved As		
MW6	429 µg/L		
MW7	427 µg/L		
MW5	1209 µg/L		

~150 old landfills in Region 3 (2M people) => thousands nationwide



NYSDEC Region 3 landfill locations (open stars) 47 of ~150 inactive landfills are shown with census track population densities. Seven landfill sites (filled stars) have been sampled for Fe floc chemistry by state personnel and Columbia SBRP researches in 2004-2005.

Implications for iron residuals

- Field and laboratory data consistent with
  - –widespread impacts of landfill organics on Fe, Mn, As
  - –groundwater [As] range from 10s to 1000s of μg/L higher levels in Central MA w/ higher soil [As]
  - –publications that indicate TCLP not an appropriate test for Arsenic leachability for arsenic bearing iron residuals
  - – Predict large mobilization of As from ABRs, will this lead to high [As]?
  - –sulfide and carbonate precipitation, limiting dissolved [As]?, complicated by thioarsenites

Implications (continued)

- Any liner failures could result in future assessments needing to separate out two sources (leachate As & induced mobilization of As)
- As toxicity to methanogens @ As(III) > 300 ppb?
  - Spatial separation of methanogenesis and iron mobilization suggests that field data from Central MA monitoring wells (not in waste) not necessarily applicable to laboratory results of As toxicity of methanogens at As > 300 ppb

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The End