Geochemical Investigation of Naturally Occurring Arsenic in Upper Midwest Ground Water

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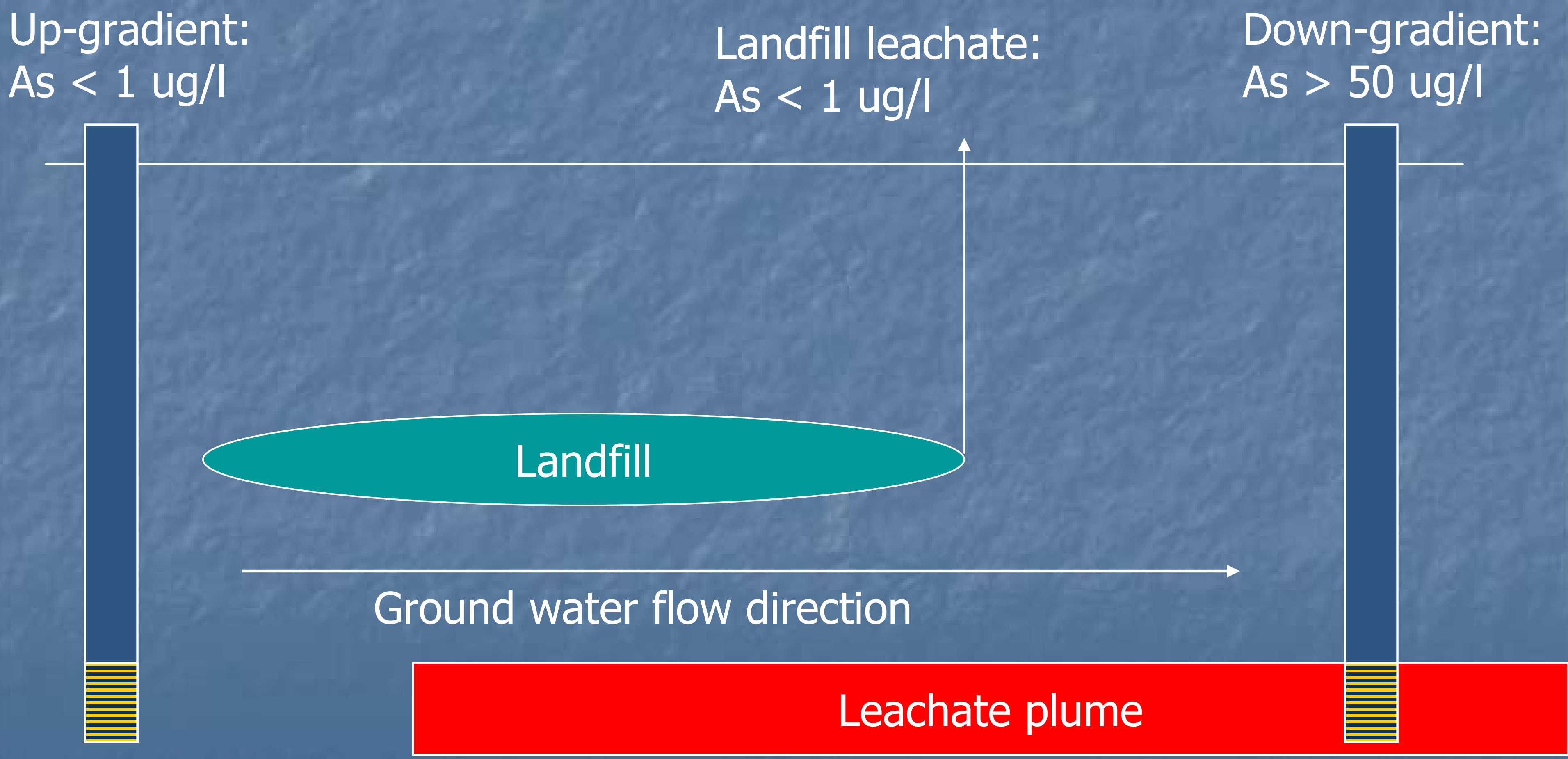
Source vs. Geochemistry



Source vs. Geochemistry

- Source
  - Localized human action
  - High concentration, localized contaminant source
  - Define and remove contaminant source
- Geochemistry
  - Often unrelated to human activity
  - Widespread presence, often no high concentration contaminant source
  - Understand and avoid geochemical conditions that mobilize contaminant

Arsenic Occurrence

- Arsenic naturally in rock and sediment at 1 to 100s mg/kg
- Crustal average is 1.8 mg/kg
- At 1.8 mg/kg, solubilization of 0.09% yields 10 ug/L arsenic in water
- Certain geochemical conditions mobilize arsenic into ground water
- Previous study proposed link between Des Moines lobe till and elevated arsenic

Arsenic Release

$$f = (As_{aq} * n)/(M*D*(1-n)*1000)$$

$$f = 0.09\% \quad (1.62\ ug/Kg)$$

f = fraction of arsenic released

D = specific gravity (e.g. 2.6 g/cm^3)

n = porosity (e.g. 0.3)

M = sediment arsenic concentration (e.g. 1.8 mg/kg)

As_{aq} = aqueous arsenic concentration (e.g. 10 ug/l)

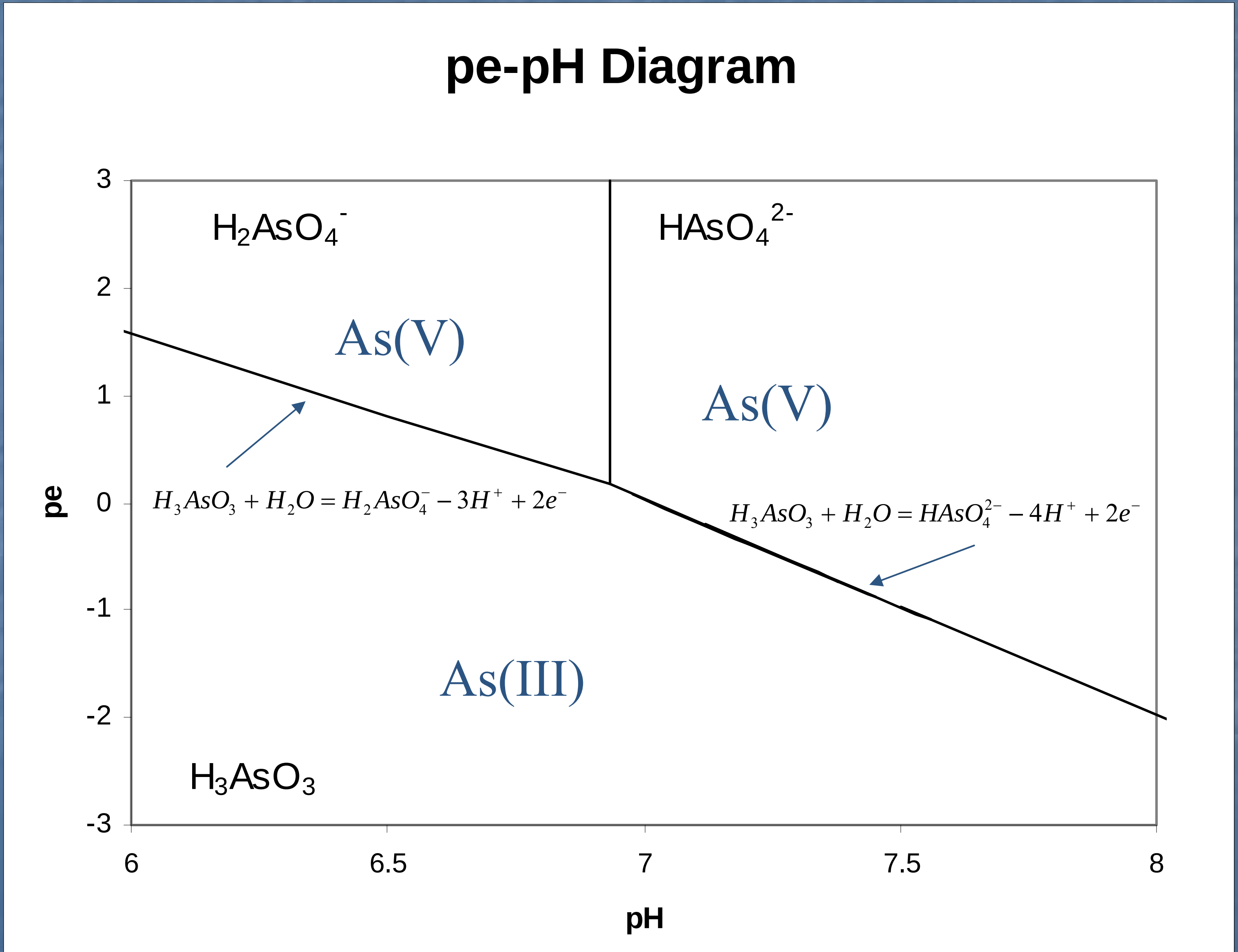
Arsenic Species

- Arsenate (As V → $H_2AsO_4^-$, $HAsO_4^{-2}$)
  - Oxidized form
  - Adsorbs to various metal oxides
- Arsenite (As III → H_3AsO_3)
  - Reduced form
  - Adsorbs to iron oxides

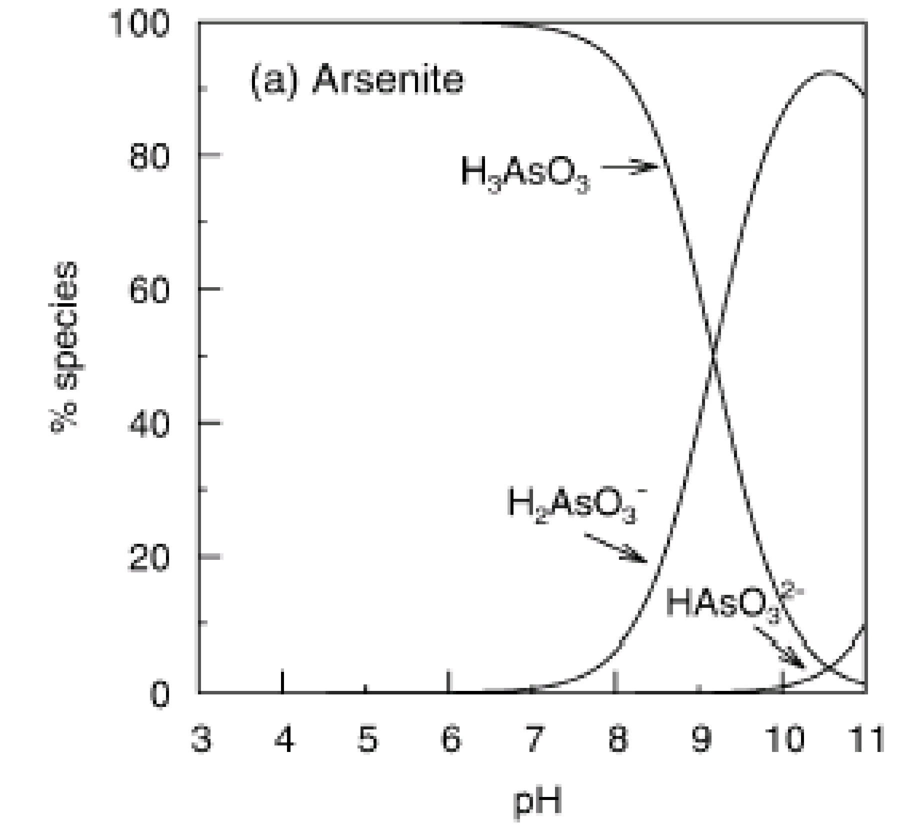
Arsenic Speciation

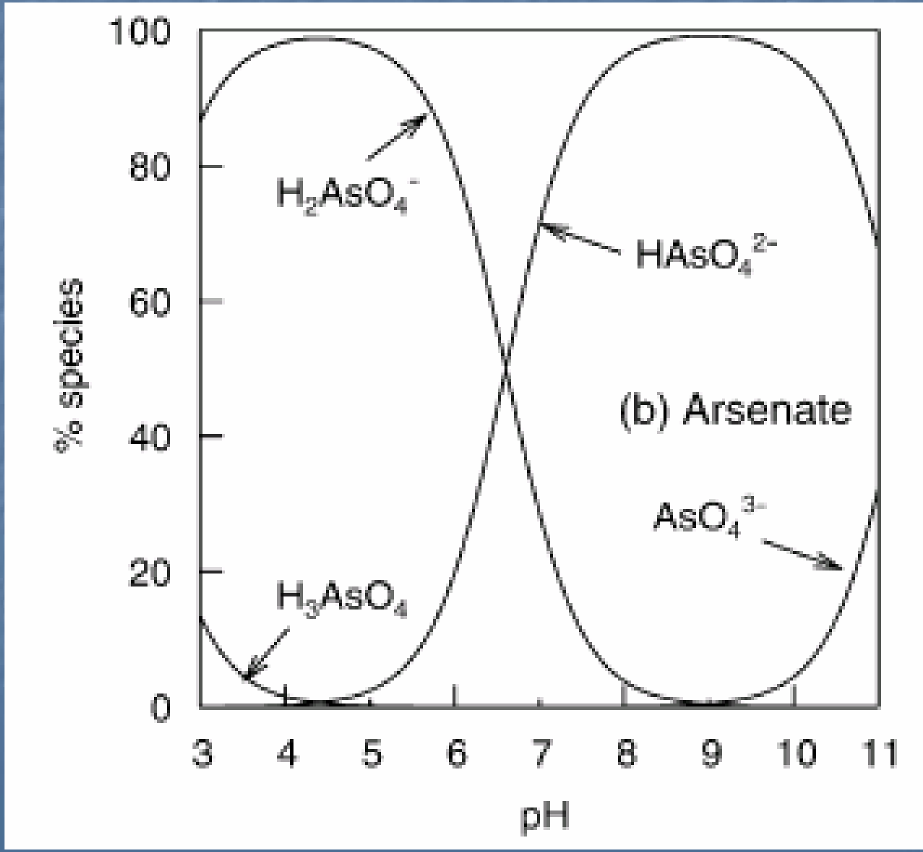
Description	Reaction	log K
As(V)/As(III) Couples	$H_3AsO_3 + H_2O = HAsO_4^{2-} - 4H^+ + 2e^-$ $H_3AsO_3 + H_2O = H_2AsO_4^- - 3H^+ + 2e^-$	-28.63 -21.13
As(III) Dissociation	$H_3AsO_3 = H_2AsO_3^- + H^+$	-9.29
As(V) Dissociation	$H_3AsO_4 = H_2AsO_4^- + H^+$ $H_2AsO_4^- = HAsO_4^{2-} + H^+$ $HAsO_4^{2-} = AsO_4^{3-} + H^+$	-2.24 -6.94 -12.19

Arsenic Speciation



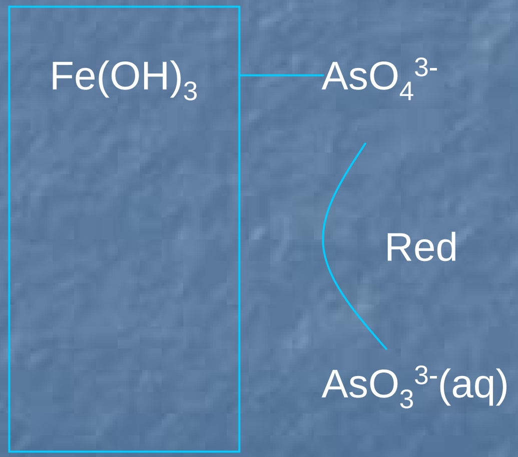
Arsenic Speciation



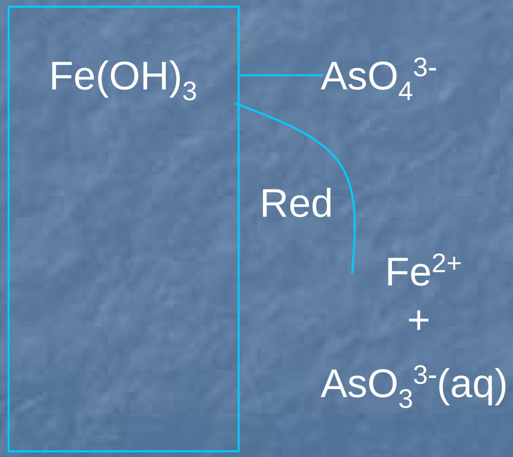


Reductive Arsenic Release Mechanisms

Reductive Desorption
(As V → As III Reduction)

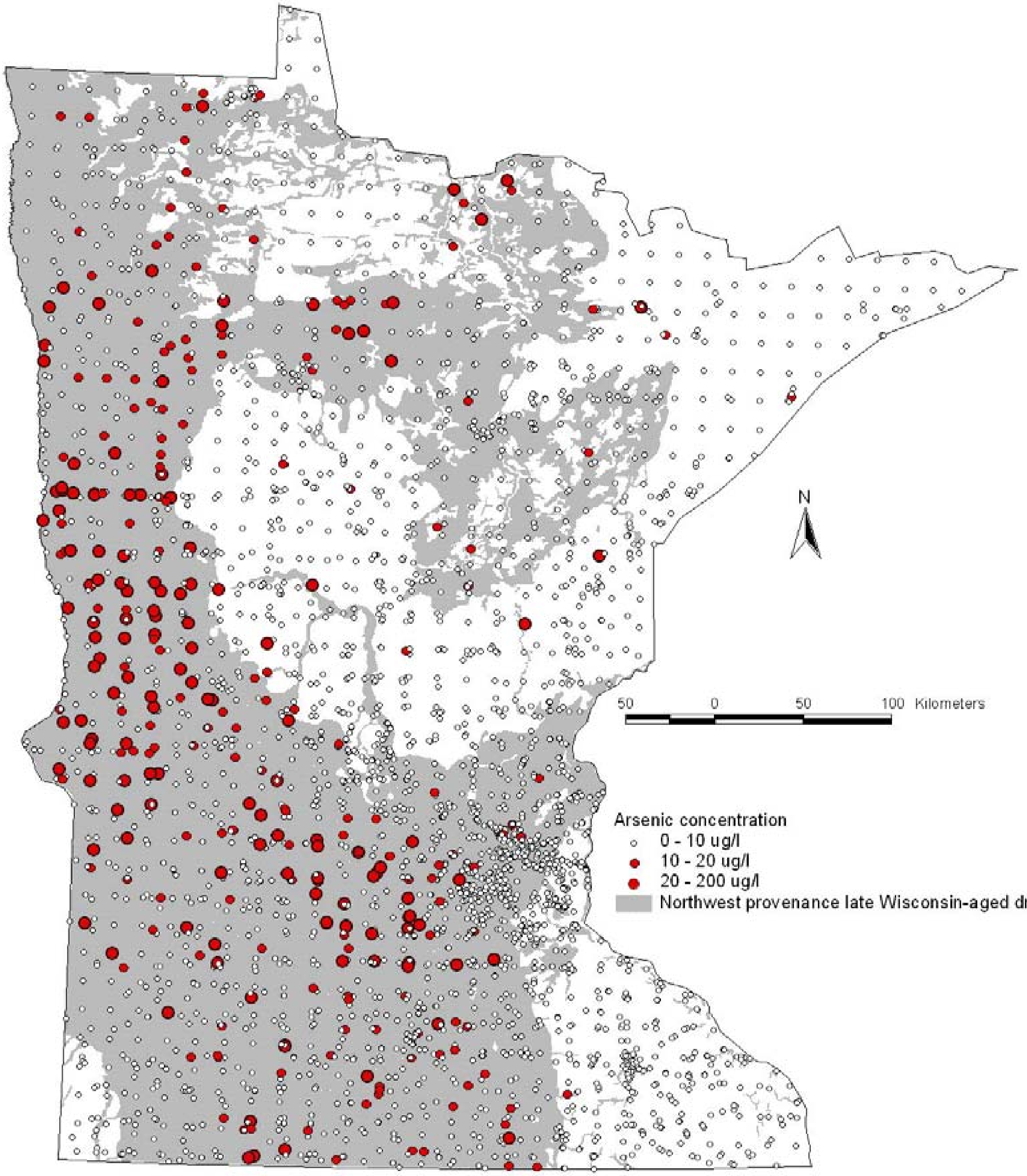


Reductive Dissolution
(Fe III → Fe II Reduction)



Potential Upper Midwest Arsenic Mobilization Mechanisms

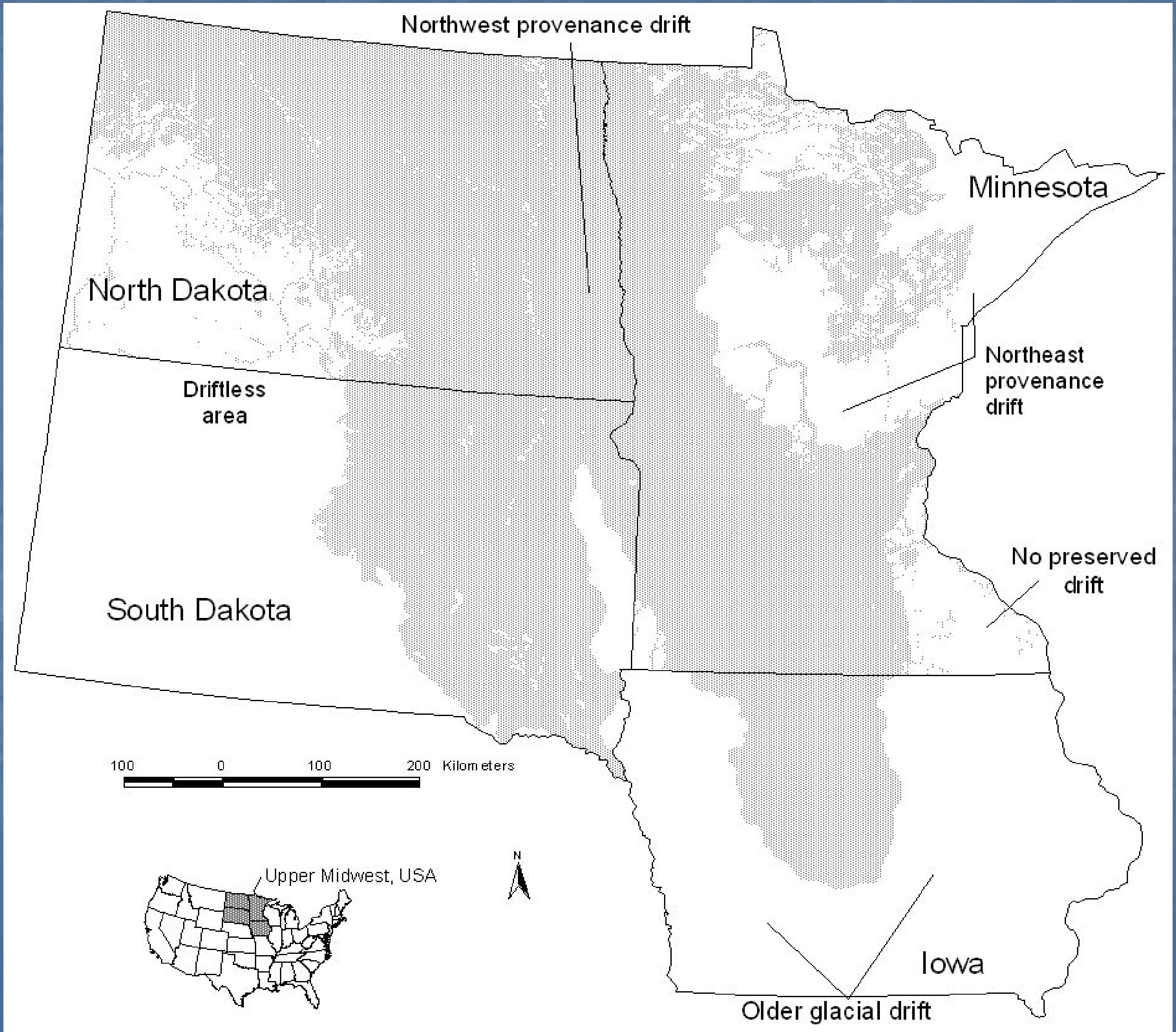
- Waste disposal
- Mining
- Aquifer acidification
- High pH desorption
- Reductive Desorption
- Reductive Dissolution
- Anion Competition
- Mineral Oxidation (often pyrite)

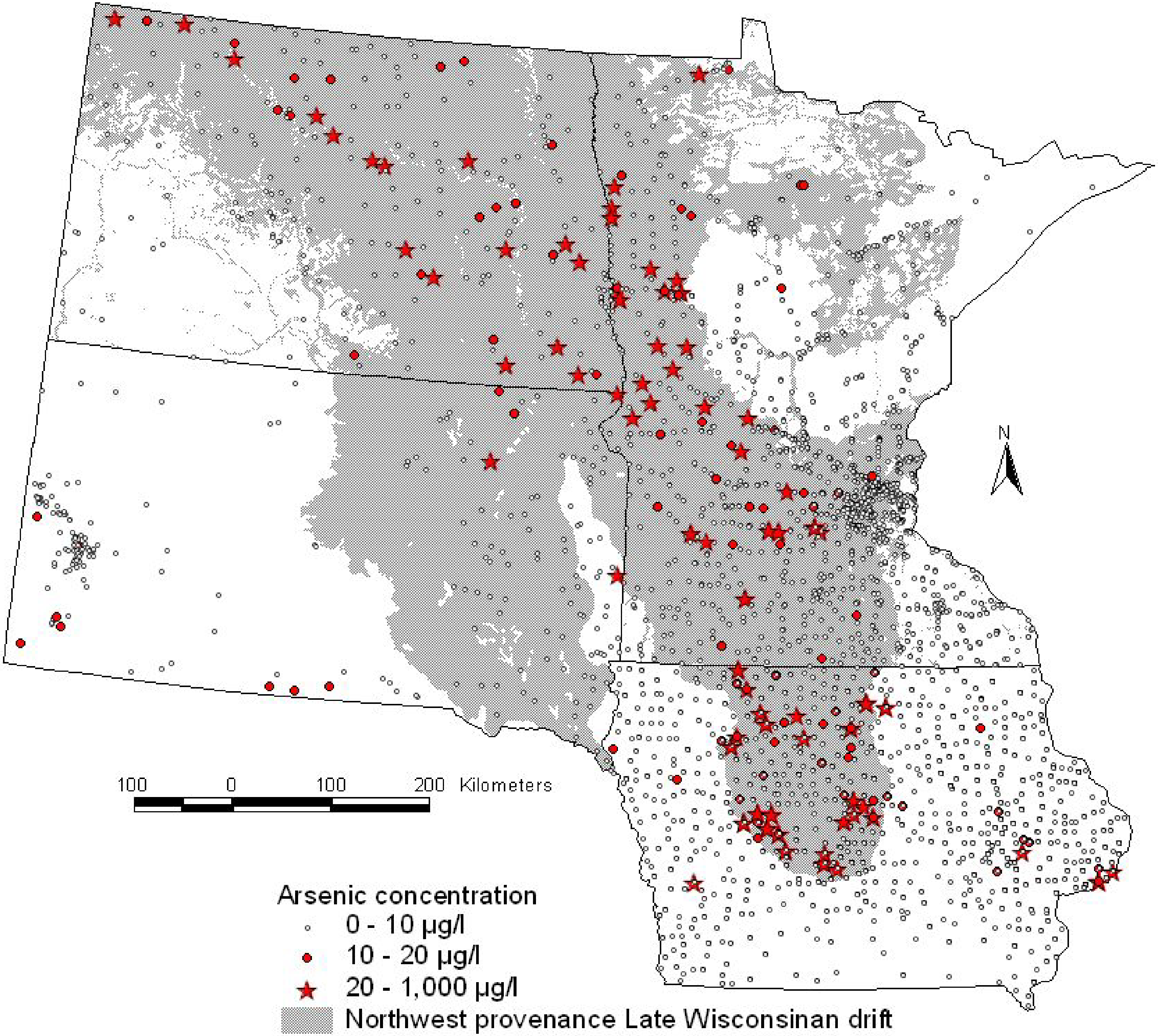

N
50 0 50 100 Kilometers
Arsenic concentration
0 - 10 ug/l
10 - 20 ug/l
20 - 200 ug/l
Northwest provenance late Wisconsin-aged drift

Generalized Geologic Setting

- Heterogeneous glacial sediments overlying bedrock
- Late Wisconsinan (16,000 to 12,000 years ago)
- Northwest provenance Late Wisconsinan till
  - Distinct pebble composition – much carbonate and shale
  - Gray
  - Large fraction of fine-grained material
- Northeast provenance Late Wisconsinan till
  - Distinctly different pebble composition – basalt, red sandstone, agates
  - Red
  - Larger fraction of sand

Generalized Geologic Setting




N
100 0 100 200 Kilometers
Arsenic concentration
0 - 10 µg/l
10 - 20 µg/l
20 - 1,000 µg/l
Northwest provenance Late Wisconsinan drift

Regional Statistics

Group	Count	Count Exceeding 10 ug/l As	% Exceeding 10 ug/l As
Inside footprint	7,101	1,690	23.8%
Outside footprint	4,333	186	4.3%

Inside Footprint Statistics

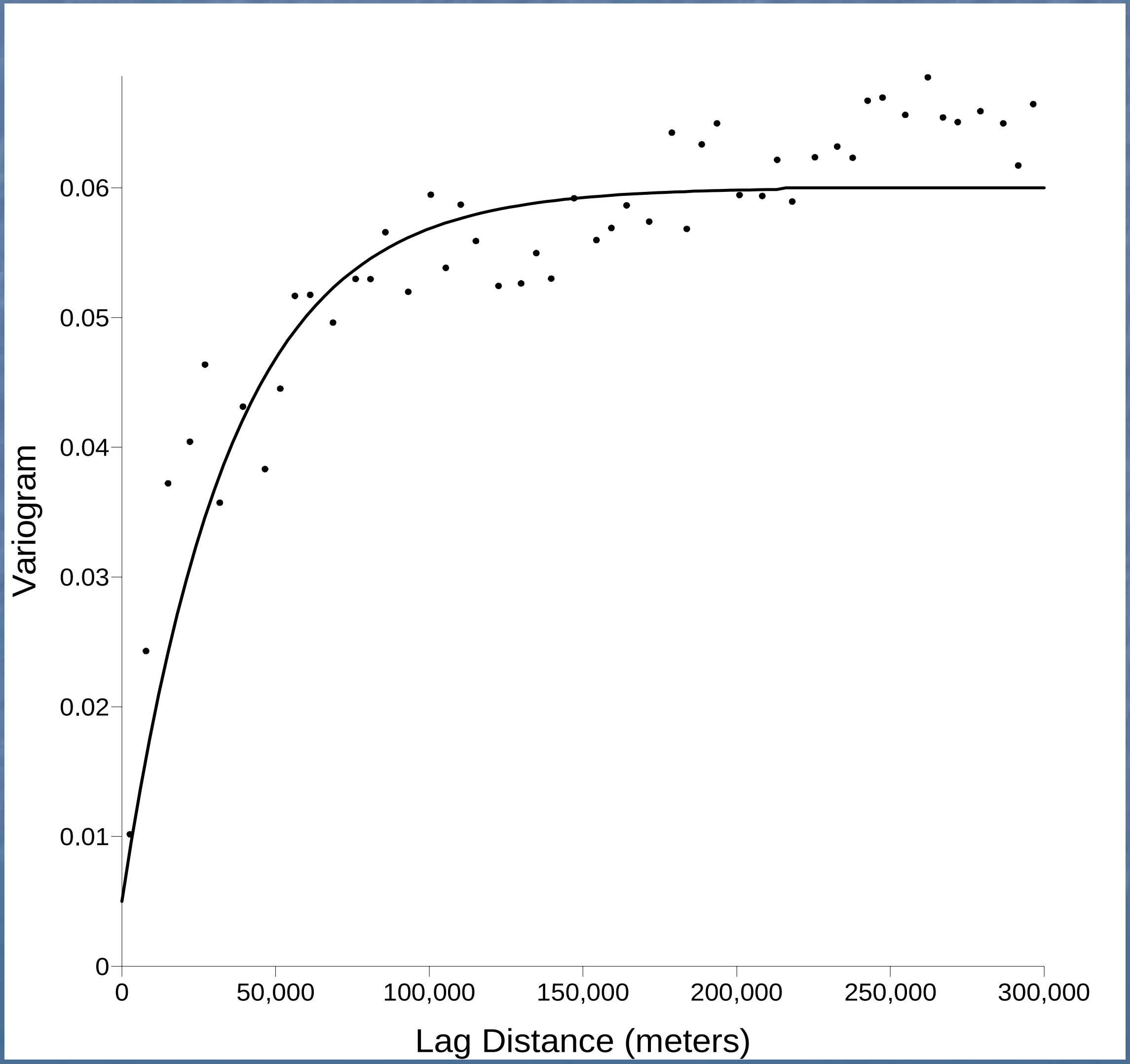
Well Type	Count	Median Depth (m)	% Exceeding 10 ug/l As
Glacial Drift	4,275	29	30.9%
Bedrock	1,174	106	7.0%
Unknown	1,652	16	17.1%

Inside Footprint Statistics

Well Type	Count	Depth Range (m)	% Wells > 10 ug/l As
Bedrock	132	800 - 186	1.5%
	263	185 - 92	3.8%
	131	**91 – 4[a]**	**22.1%**
Glacial Drift	120	157 - 65	8.5%
	236	**64 - 28**	**27.0%**
	118	28 - 7	7.4%

[a] All but 4 of these wells are more than 30 m deep.

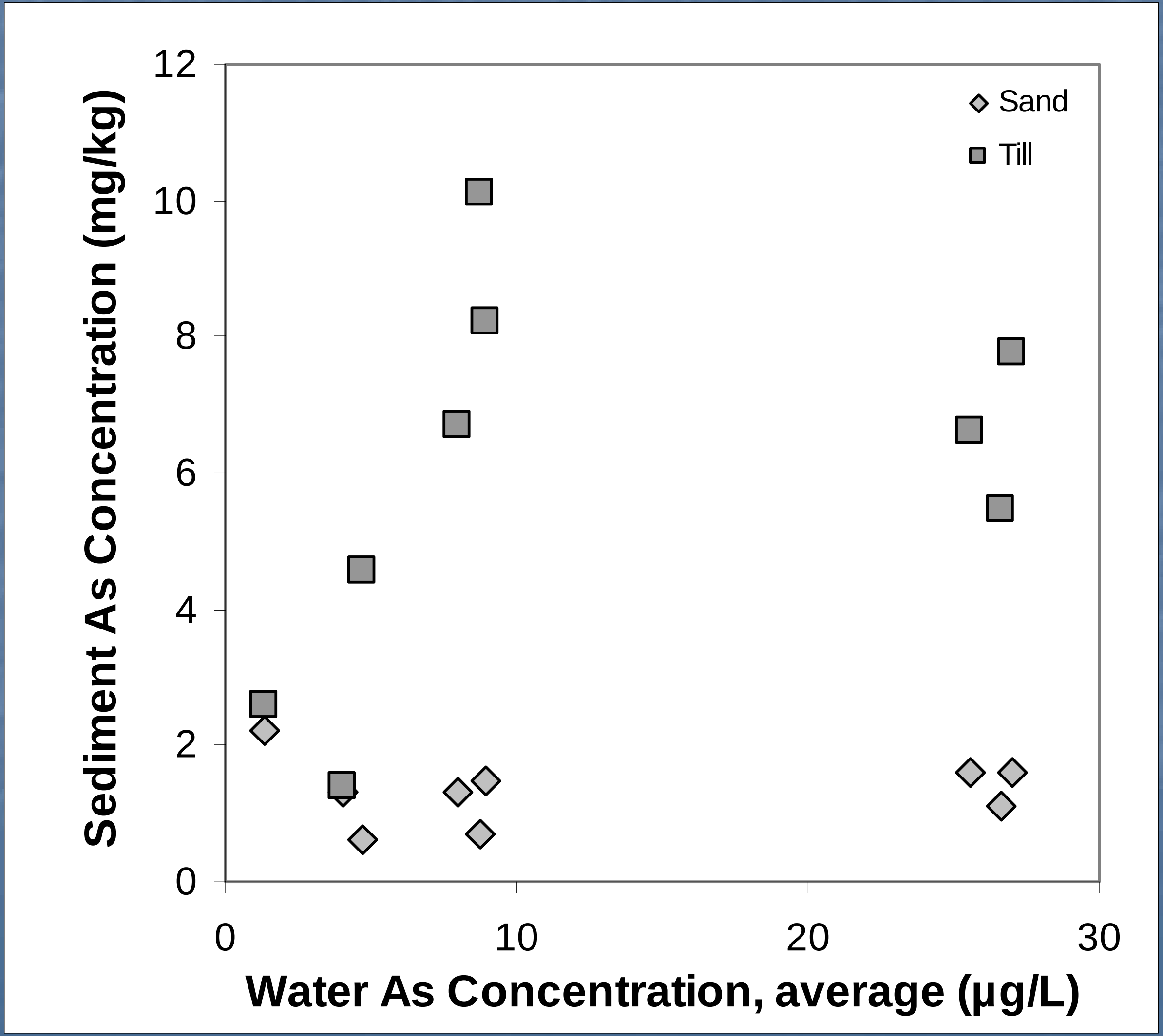
Spatial Correlation



Arsenic in Minnesota Sediment

- Northwest provenance sediment has 2 to 26 mg/kg arsenic
- Northeast provenance sediment has 1 to 17 mg/kg arsenic
- As in sediment **not** correlated to As in water

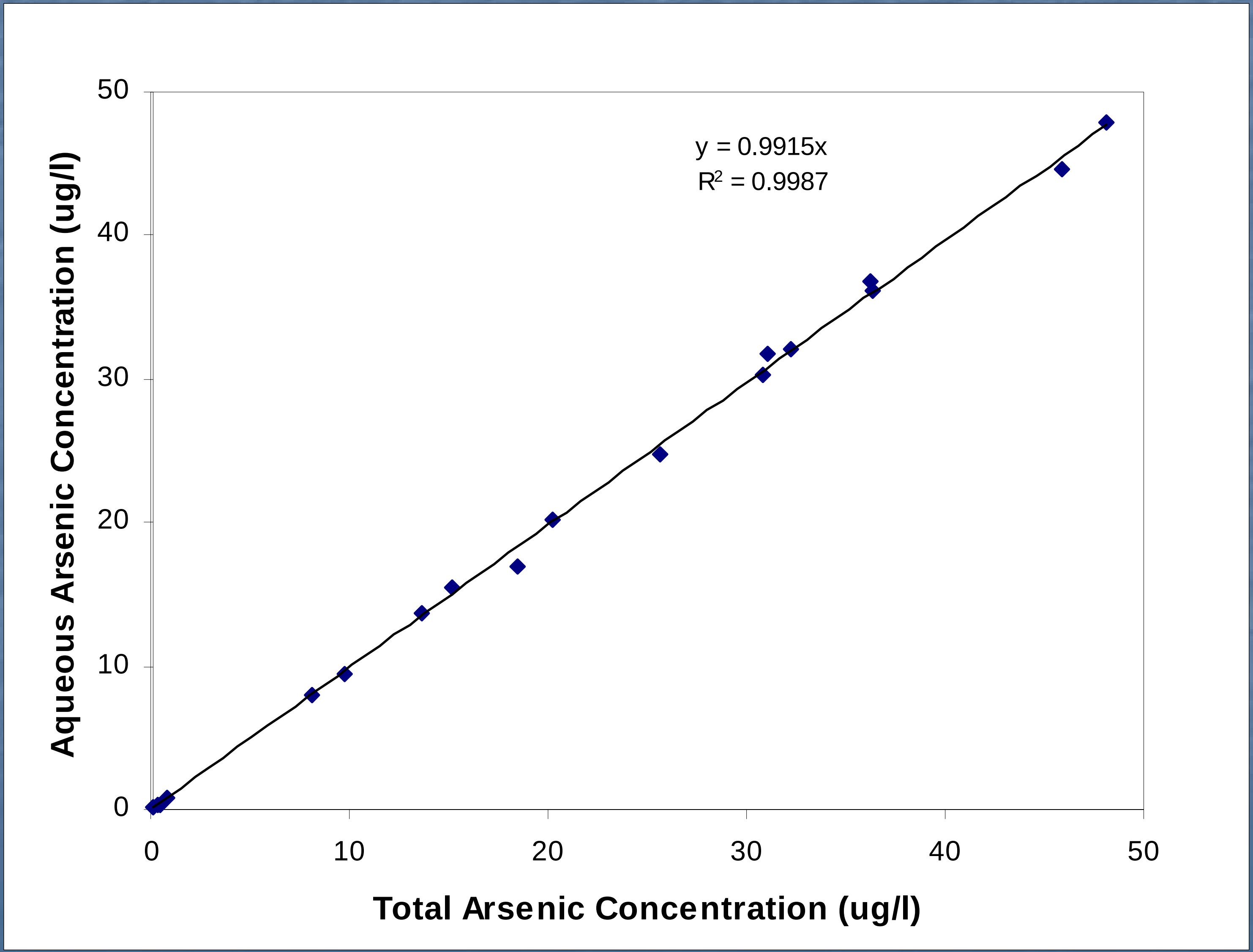
High-As Sediment ≠ High-As Water



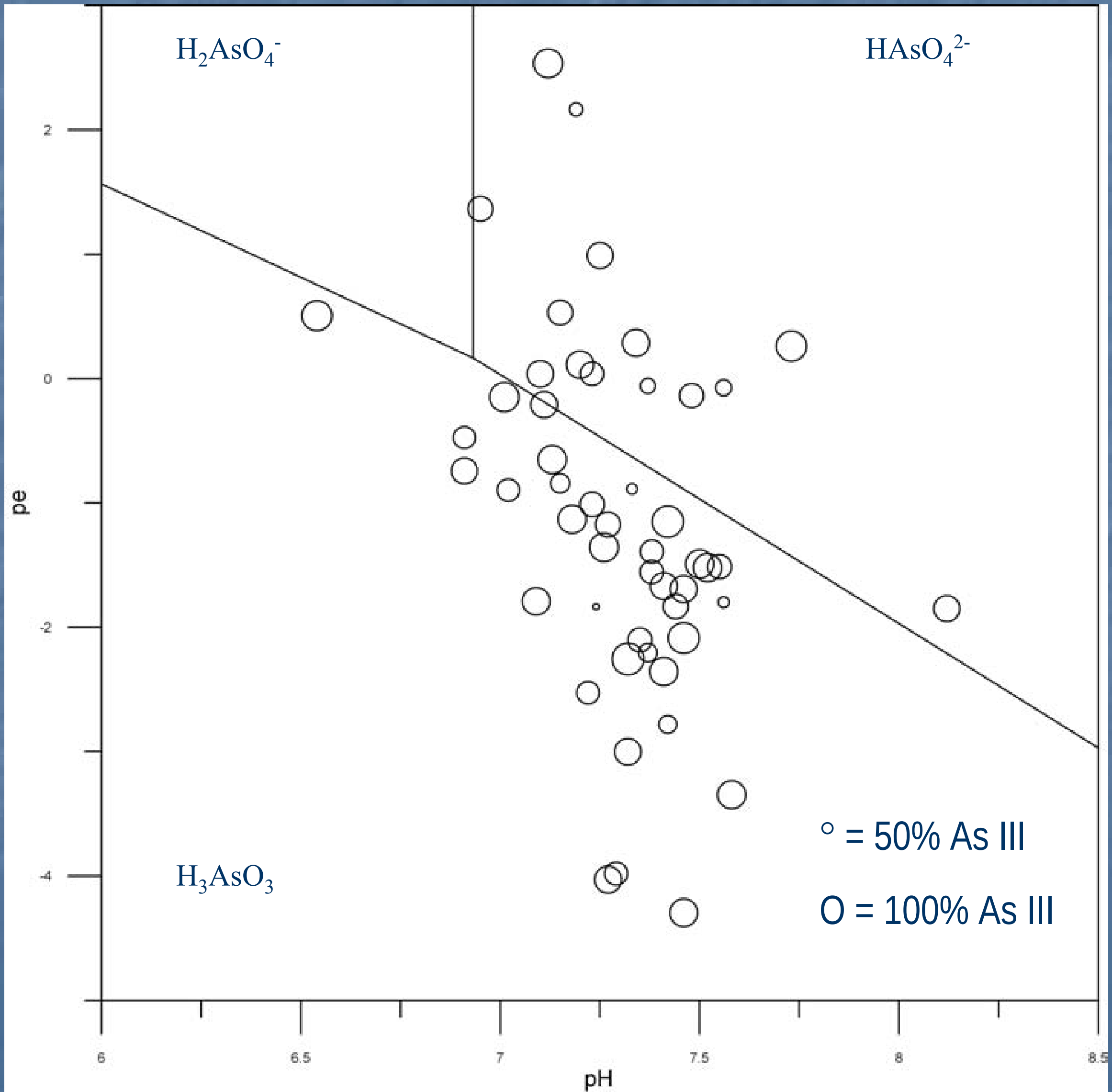
Labile Arsenic is Crucial

- At 1.8 mg/kg As, solubilizing 0.09% yields 10 ug/L As
- Total sediment As concentration **not** key factor
- Adsorbed/coprecipitated As labile
- Measured 0.4 - 0.8 mg/kg labile As
- Solubilizing 0.21% to 0.41% of measured labile sediment As yields 10 ug/l As

Total Arsenic = Aqueous Arsenic



Predominantly Reduced Arsenic



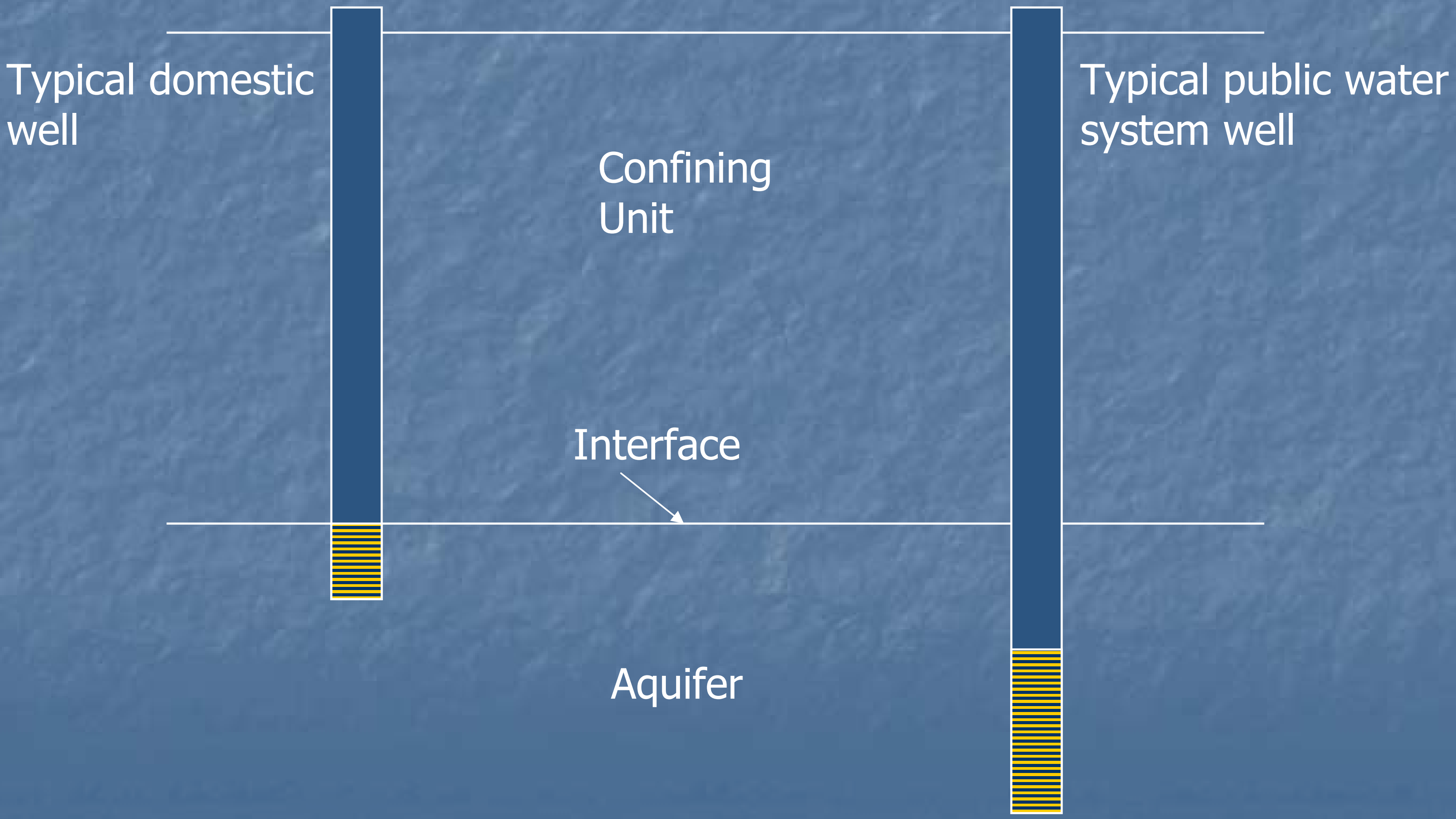
Upper Midwest Arsenic Occurrence Summary

- Northwest provenance sediment → elevated As
- Long-distance spatial correlation
- Elevated sediment As ≠ elevated water As
- Labile As present
- As III dominant, aquifers moderately reduced

Well Characteristics

PWS Wells		Other Wells		Excluding MARS	
Count	% > 10 ug/l As	Count	% > 10 ug/l As	Count	% > 10 ug/l As
1,764	**12.0%**	5,337	**27.7%**	4,511	**23.2%**

As and Well Characteristics



As and Well Characteristics

Description	Avg As (ug/l)	% As > 10	Avg Fe (ug/l)	Count
Screen ≤ 8 feet long Clay ≤ 4 feet away	20	60	2,484	224
Screen > 8 feet long Clay > 4 feet away	12	40	1,660	71
Screen sand or clay	18	53	2,117	754
Screen gravel	13	41	1,836	56

Well Characteristics
Summary and Conclusions

- PWS and domestic wells have distinctly different well construction characteristics
- PWS well construction coincidentally yields lower arsenic
  - Coarser aquifers
  - Larger aquifers
  - Longer screens
- Reductive arsenic mobilization mechanisms active at the till-aquifer interface

Results and Conclusions

- Northwest provenance Late Wisconsinan drift causes widespread elevated arsenic in ground water
- High-arsenic sediment *not necessary*
- Large areal data sets necessary to identify regional environmental problems
- Well characteristics influence arsenic concentration
- Random and systematic temporal arsenic concentration variability observed

Steps for Successful GSI

Focus on geochemistry, not “source”

- Geochemistry of contaminant
- Geochemical interactions between contaminant and other constituents
- Geochemical interactions between contaminant and its environment

Acknowledgements

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