Beyond the Minimum: Purposefully Designing (or Redesigning) Ground Water Sampling Schemes

Mindy Erickson, P.E.

Water Resources Science

University of Minnesota

Funding for arsenic research provided by CURA, MDH, WRC and USGS

Sampling Purposes

- Initial delineation
- Infill sampling
- Technology demonstration
- Routine compliance sampling

Compliance Sampling Problems

- “Random” variability resulting compliance problems
- “Moving” average resulting in compliance problems
- Anecdotal “evidence” driving sampling decisions

Statistics and science can both play a role.

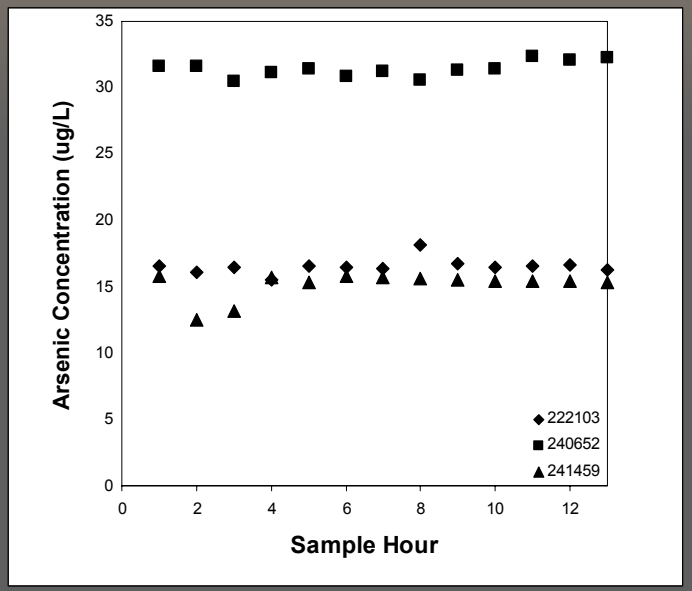
Example: As in MN Groundwater

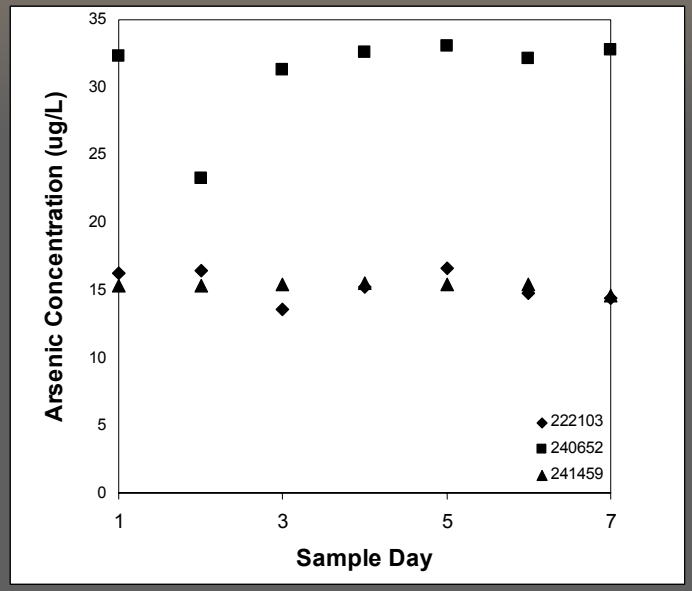
Starting January 2006 As MCL enforced at 10 ug/l

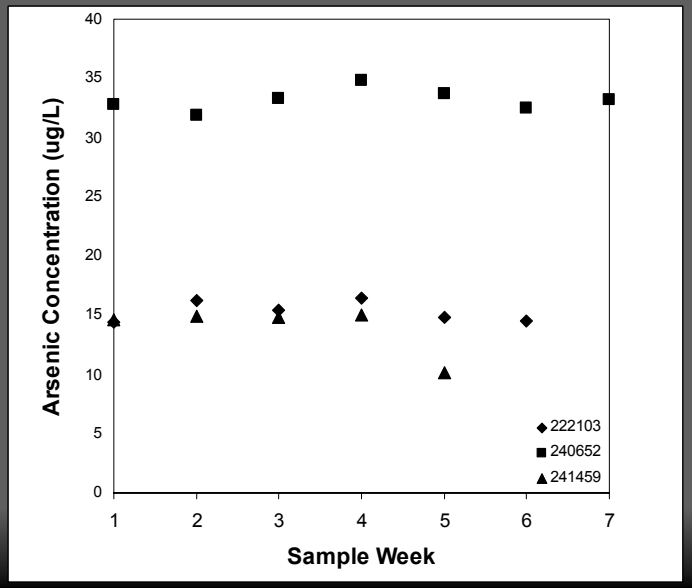
100 Minnesota public water systems affected

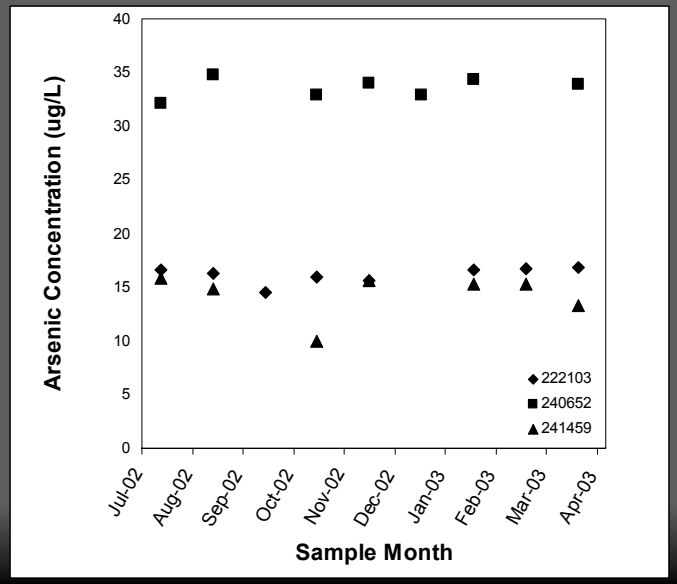
- How many samples are enough?
- Is there a pattern to arsenic variability?
  - Long time scale
  - Short time scale
- If there is a pattern, why?

Variability Sampling





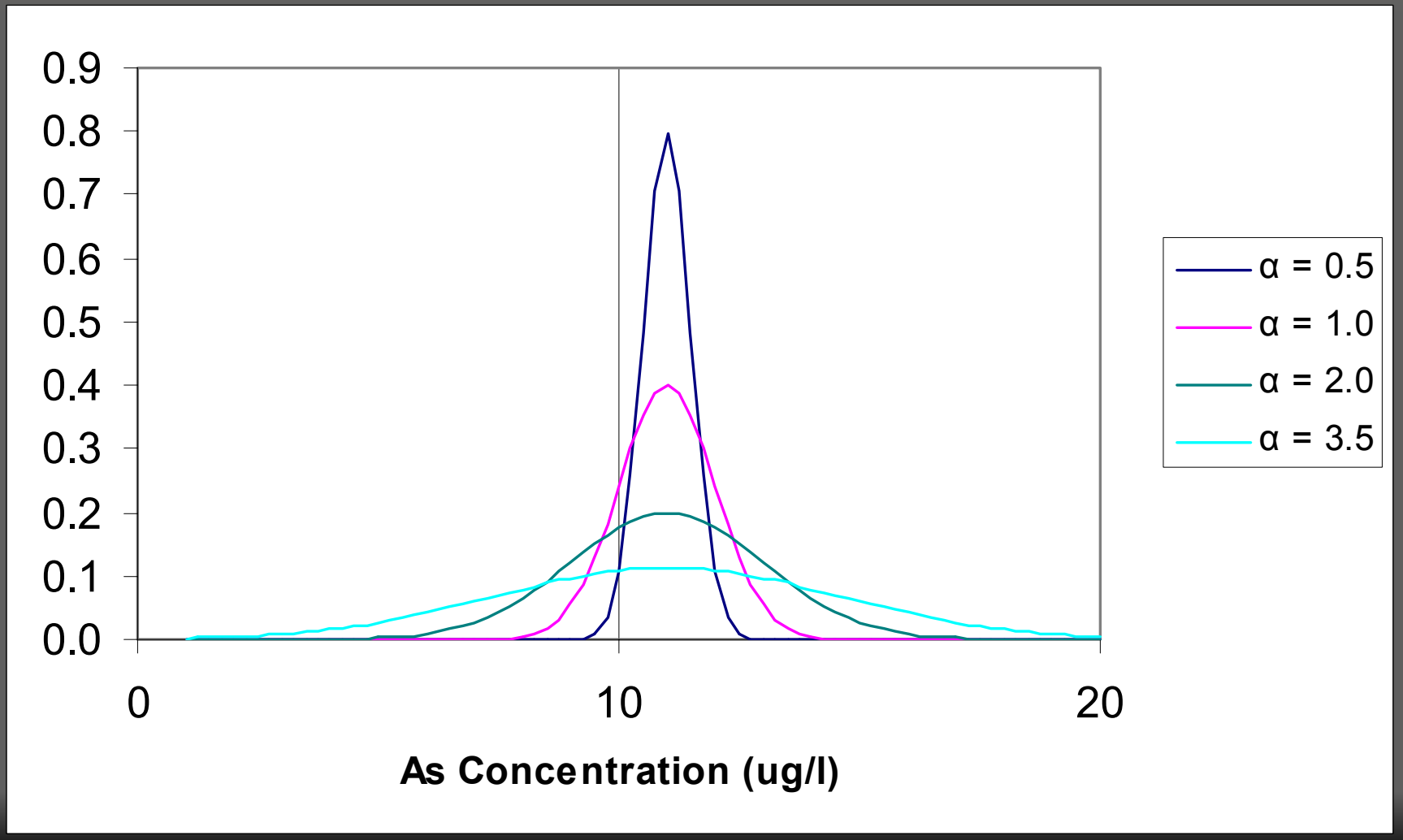




Summary Statistics

Well ID	Average Arsenic Concentration (ug/l)									
	Hourly		Daily		Weekly		Monthly		All	
	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD
222103	16.5	0.56	15.3	1.16	15.3	0.89	16.3	0.76	16.0	0.95
241459	15.2	1.02	15.3	0.33	13.9	2.07	14.0	2.13	14.7	1.53
240652	31.4	0.57	31.1	3.48	33.2	0.93	33.6	0.91	32.2	1.93

Example

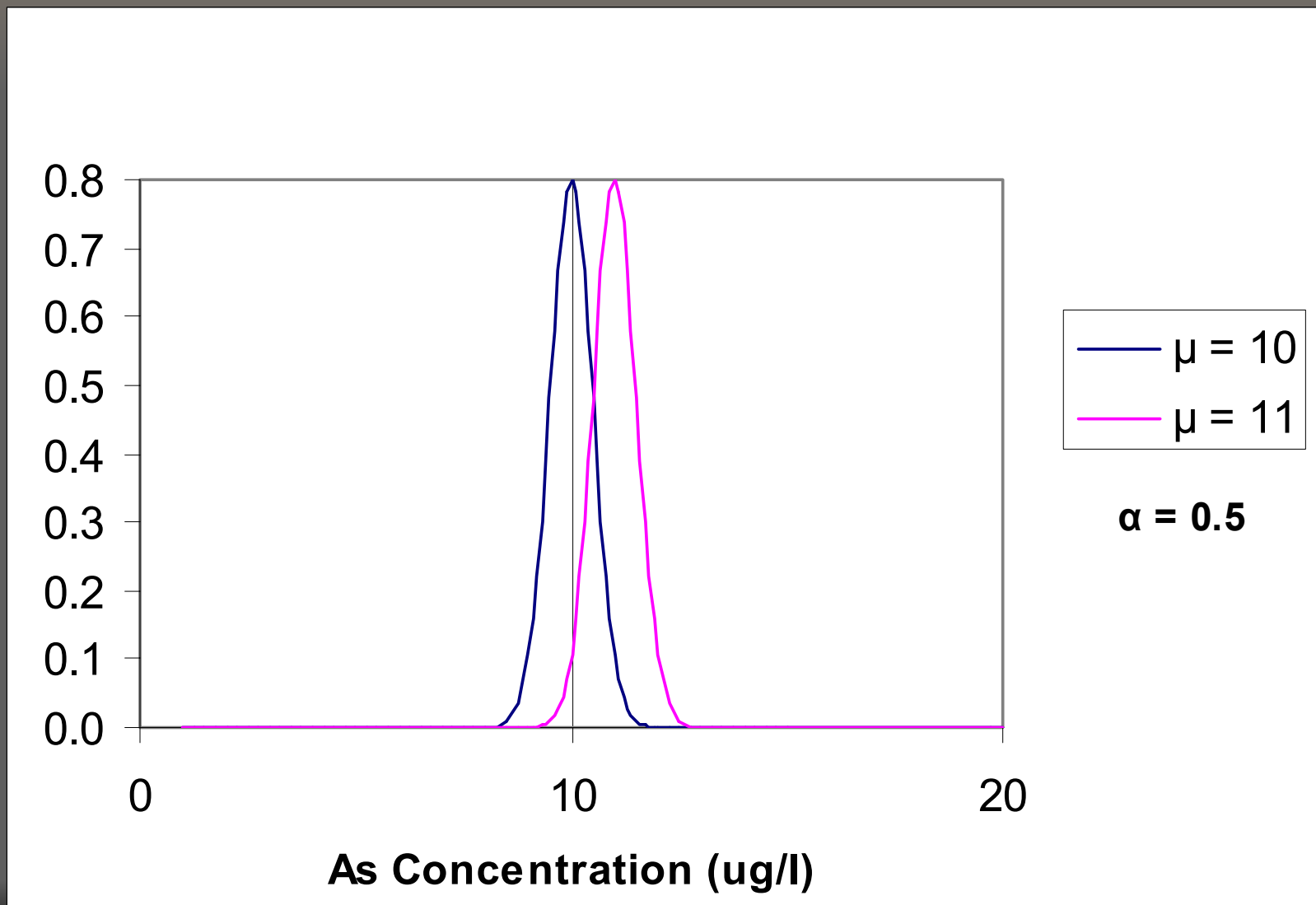

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
10
20
As Concentration (ug/l)
α = 0.5
α = 1.0
α = 2.0
α = 3.5

So What?

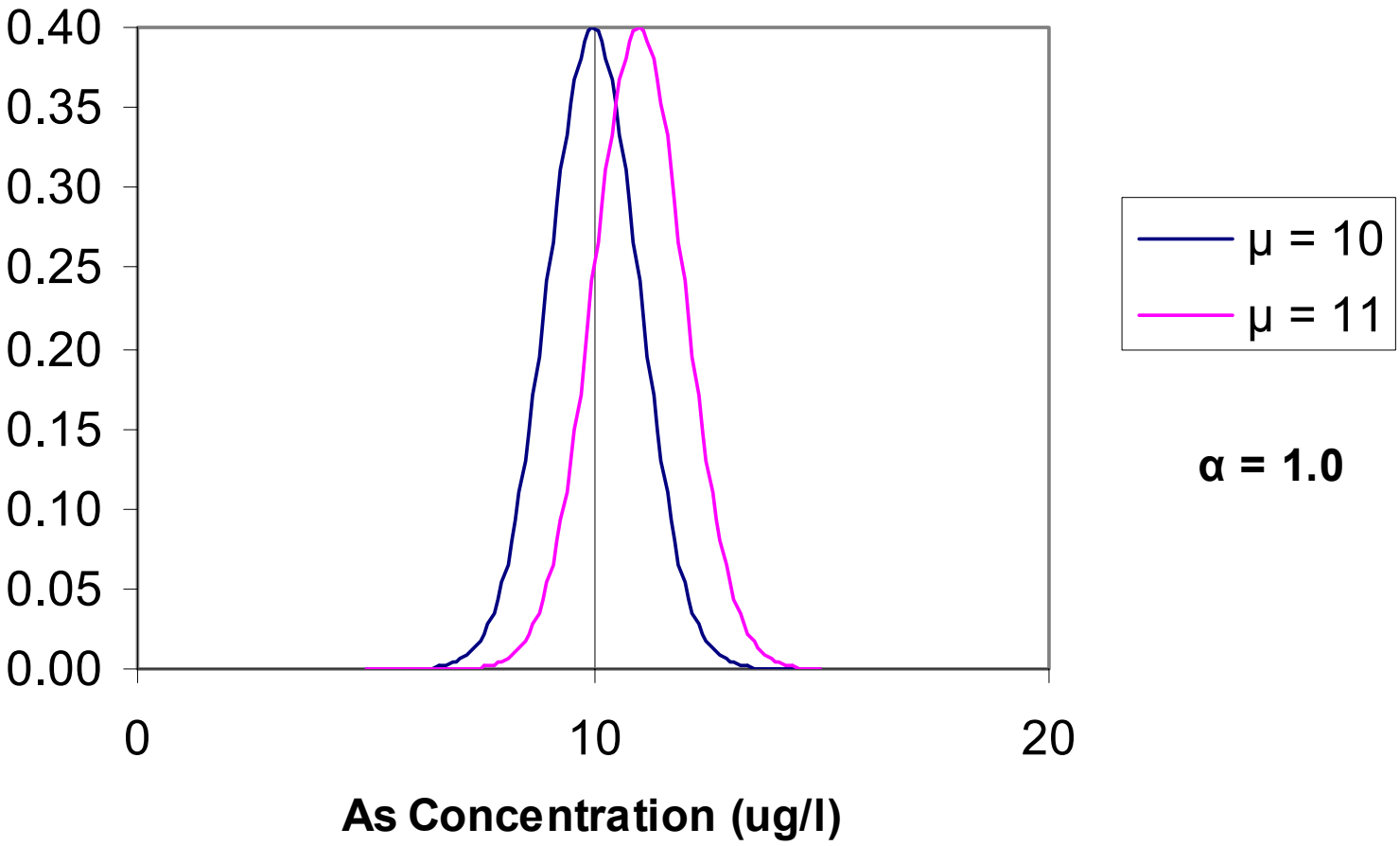
Standard Deviation	Power	Sample Size
0.5	0.755	4
	0.998	8
1	0.289	4
	0.680	8
→	0.803	10
2	0.111	4
	0.465	16
→	0.807	34
3.5	0.070	4
	0.229	20
	0.492	48
→	0.808	100

Difference in mean = 1 μg/l

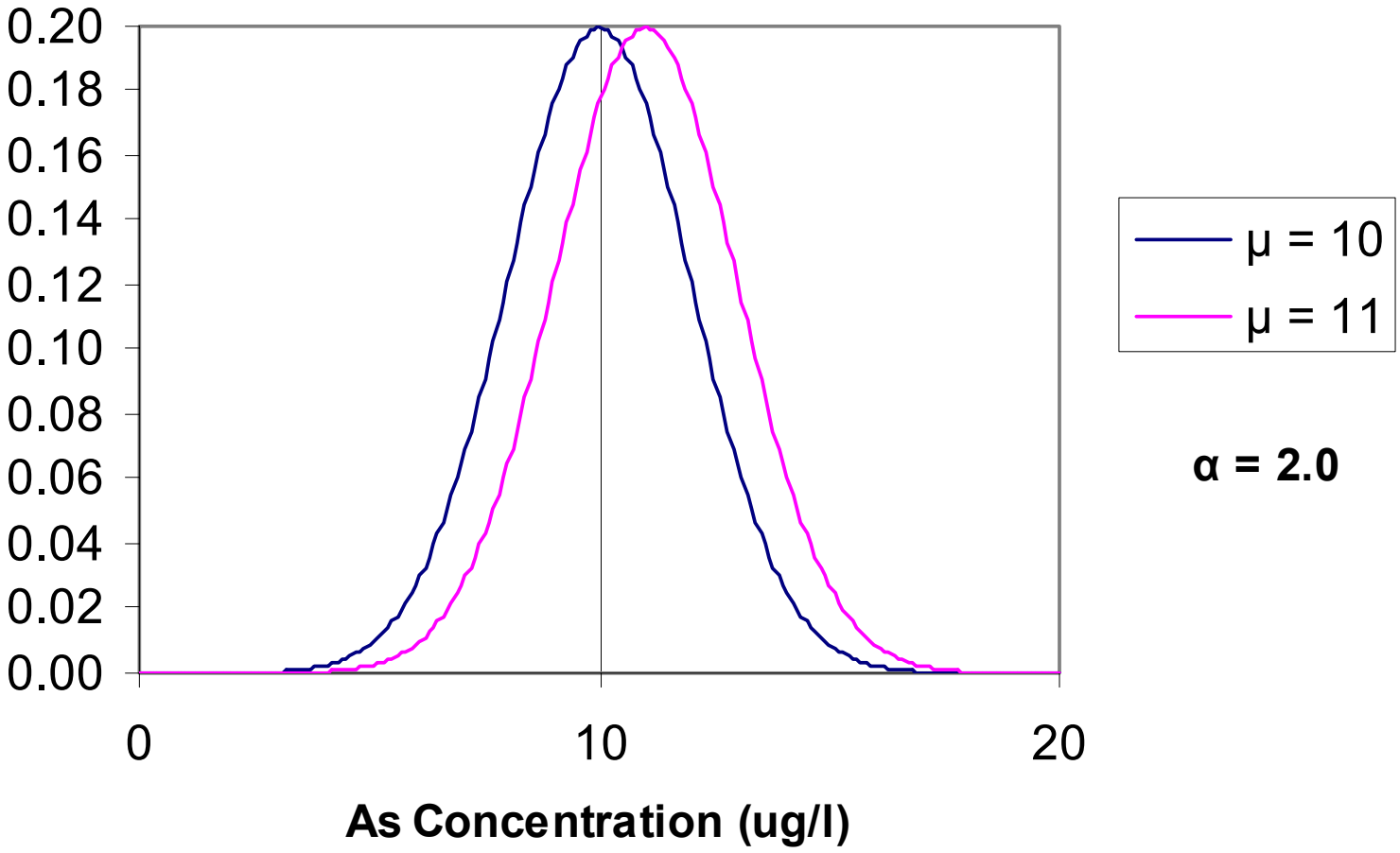
Example


0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
10
20
As Concentration (ug/l)
μ = 10
μ = 11
α = 0.5

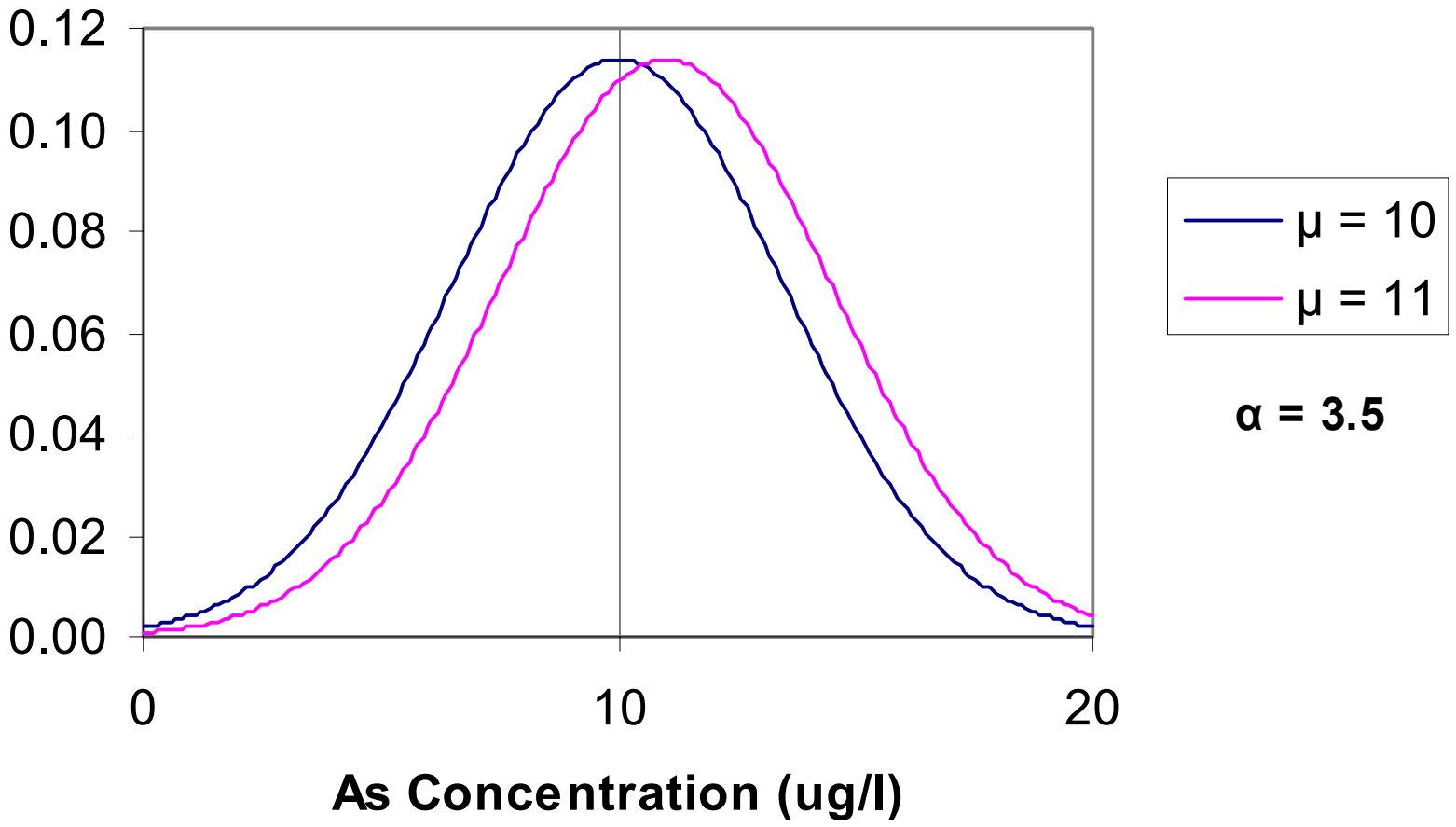
Example


0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
10
20
As Concentration (ug/l)
μ = 10
μ = 11
α = 1.0

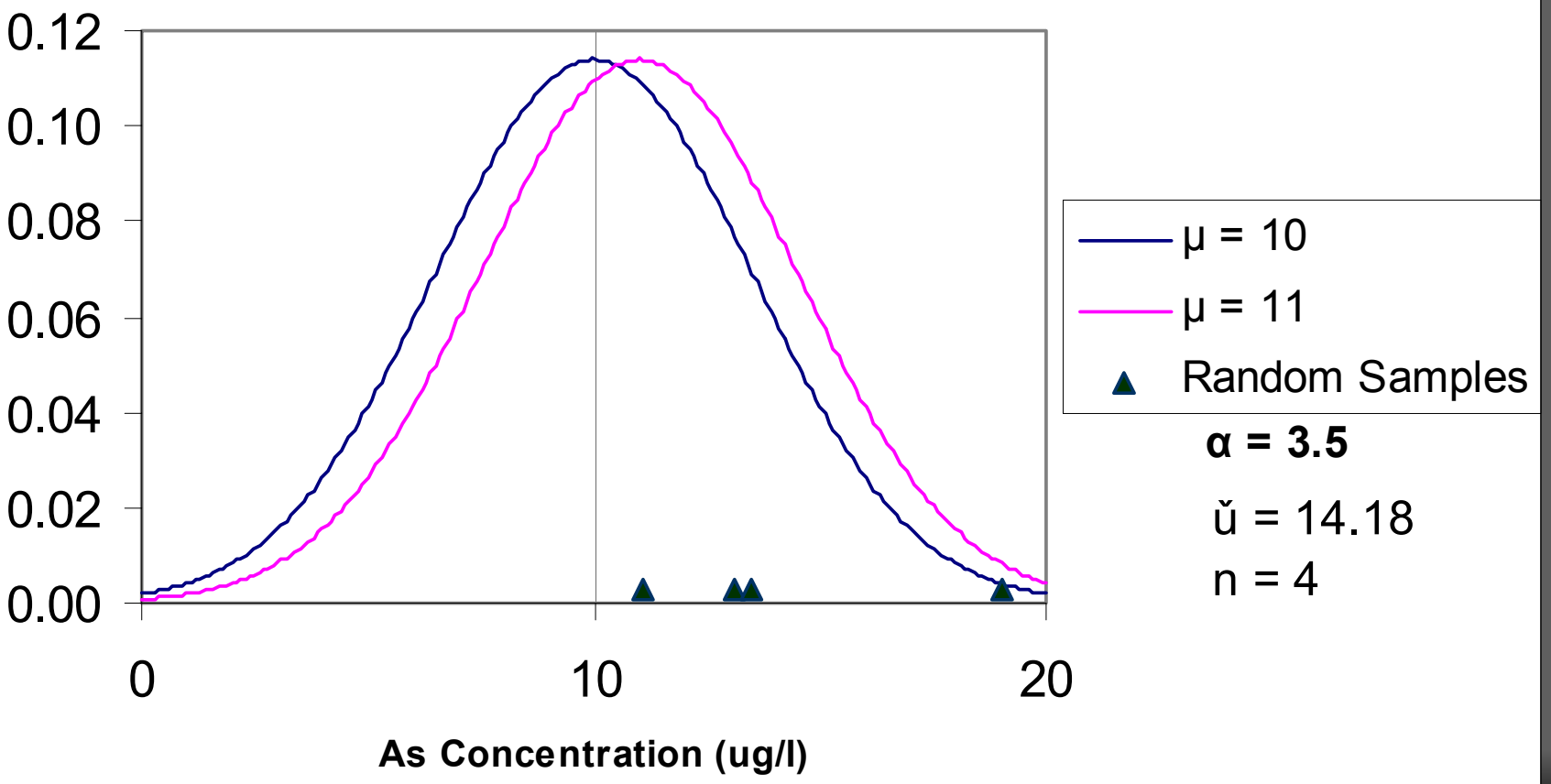
Example


0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
As Concentration (ug/l)
μ = 10
μ = 11
α = 2.0

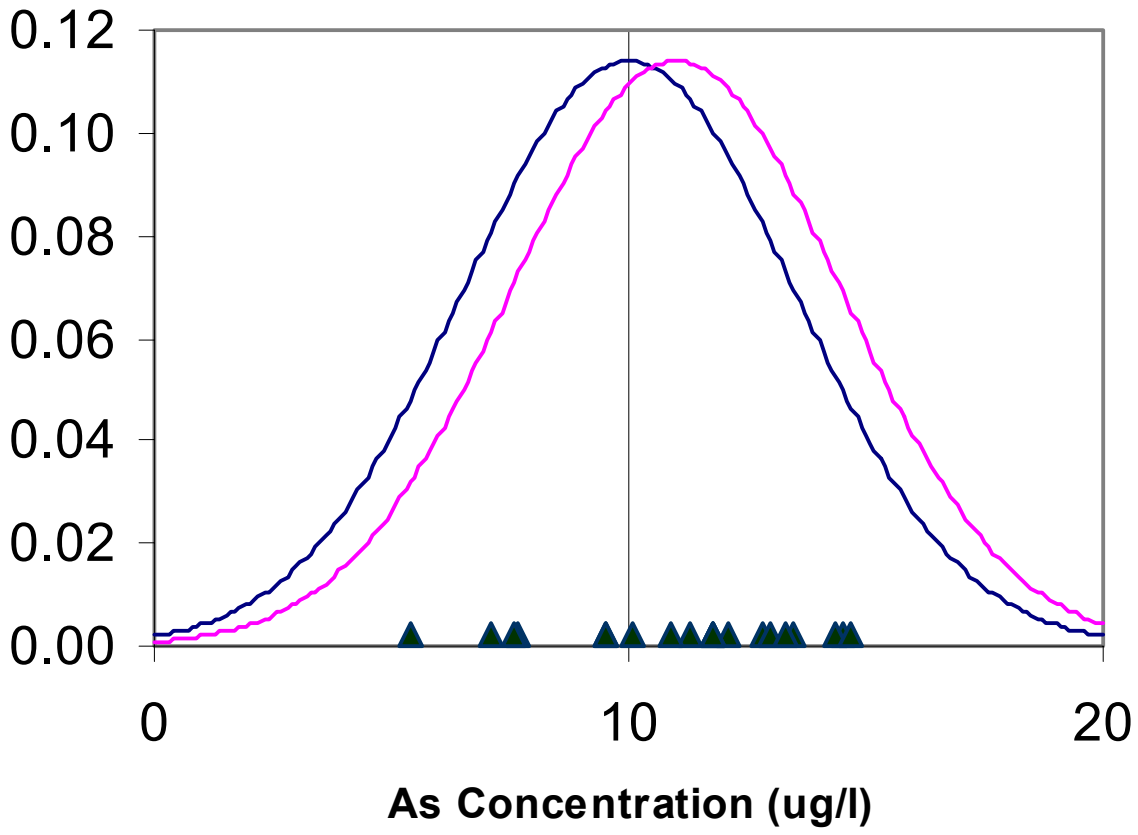
Example


0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
As Concentration (ug/l)
μ = 10
μ = 11
α = 3.5

Example


0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
10
20
As Concentration (ug/l)
μ = 10
μ = 11
Random Samples
α = 3.5
ŭ = 14.18
n = 4

Example



α = 3.5

ŭ = 11.13

n = 20

So What?

Standard Deviation	Power	Sample Size
0.5	0.755	4
	0.998	8
1	0.289	4
	0.680	8
→	0.803	10
2	0.111	4
	0.465	16
→	0.807	34
3.5	0.070	4
	0.229	20
	0.492	48
→	0.808	100

Difference in mean = 1 μg/l

Questions and Answers

- How many samples are enough?
  - It depends…
- Is there a pattern to arsenic variability?
  - Not at a long time scale (> one hour)
- What about the short time scale??

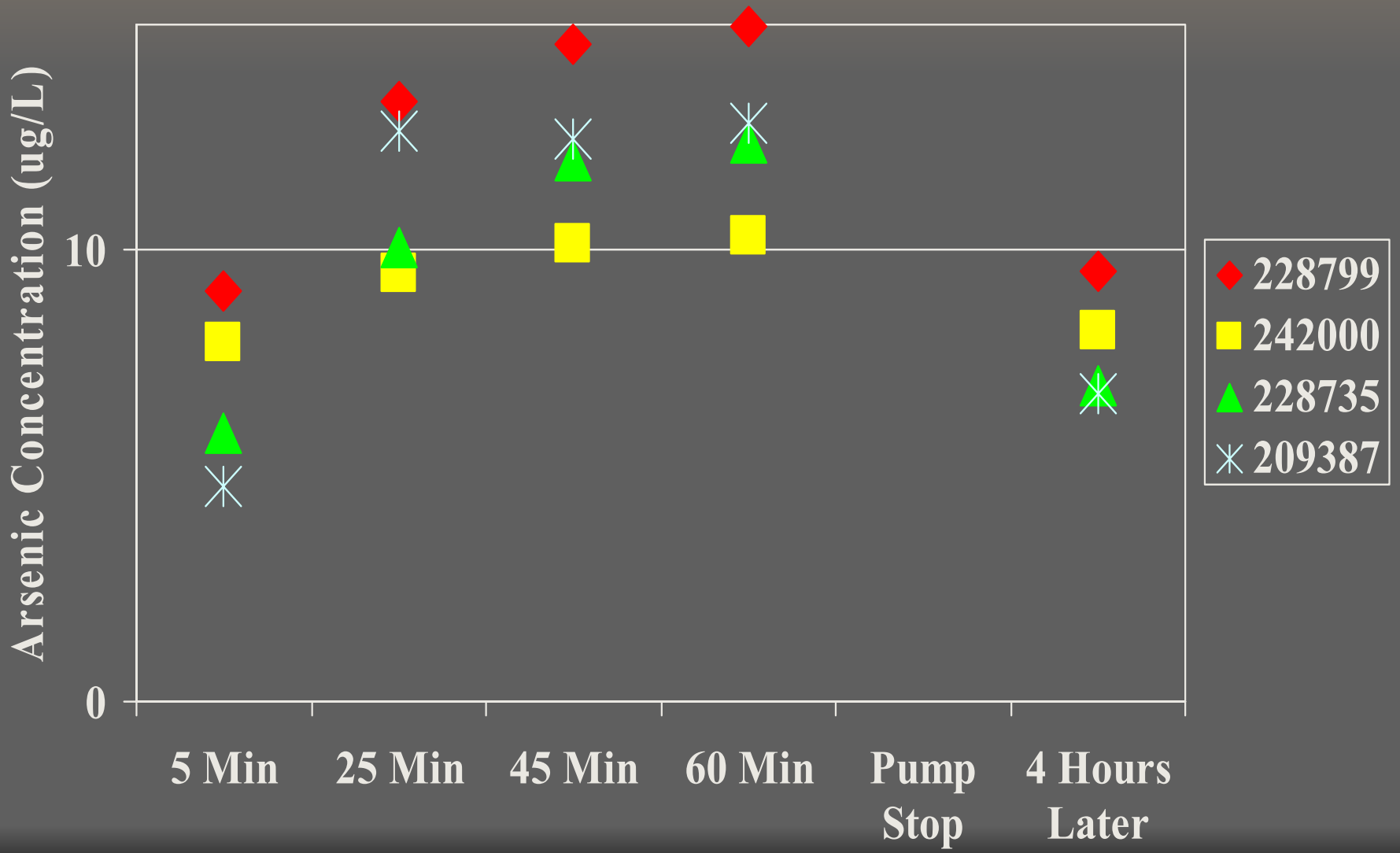
Arsenic Release Mechanisms

- Reductive Desorption
- Reductive Dissolution
- Anion Competition
- Pyrite Oxidation

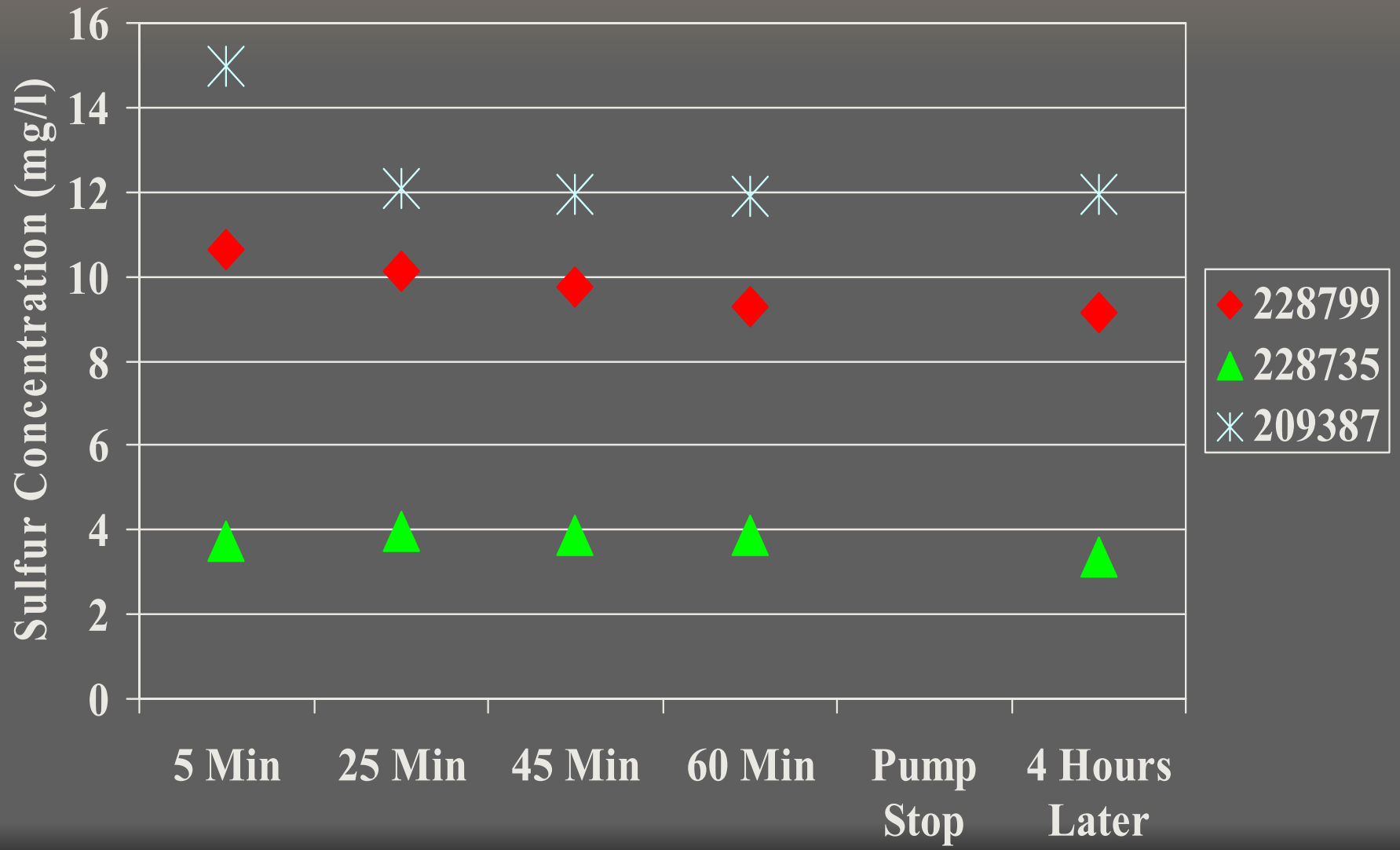
Considerations for Arsenic

- Arsenate (As^{+5} ➔ $H_2AsO_4^-$, $HAsO_4^{-2}$)
  - Oxidized form
  - Adsorbs to metal oxides
- Arsenite (As^{+3} ➔ H_3AsO_3)
  - Reduced form
  - Adsorbs to iron oxides
- Fe, S, pH, pe, competing anions may play important roles

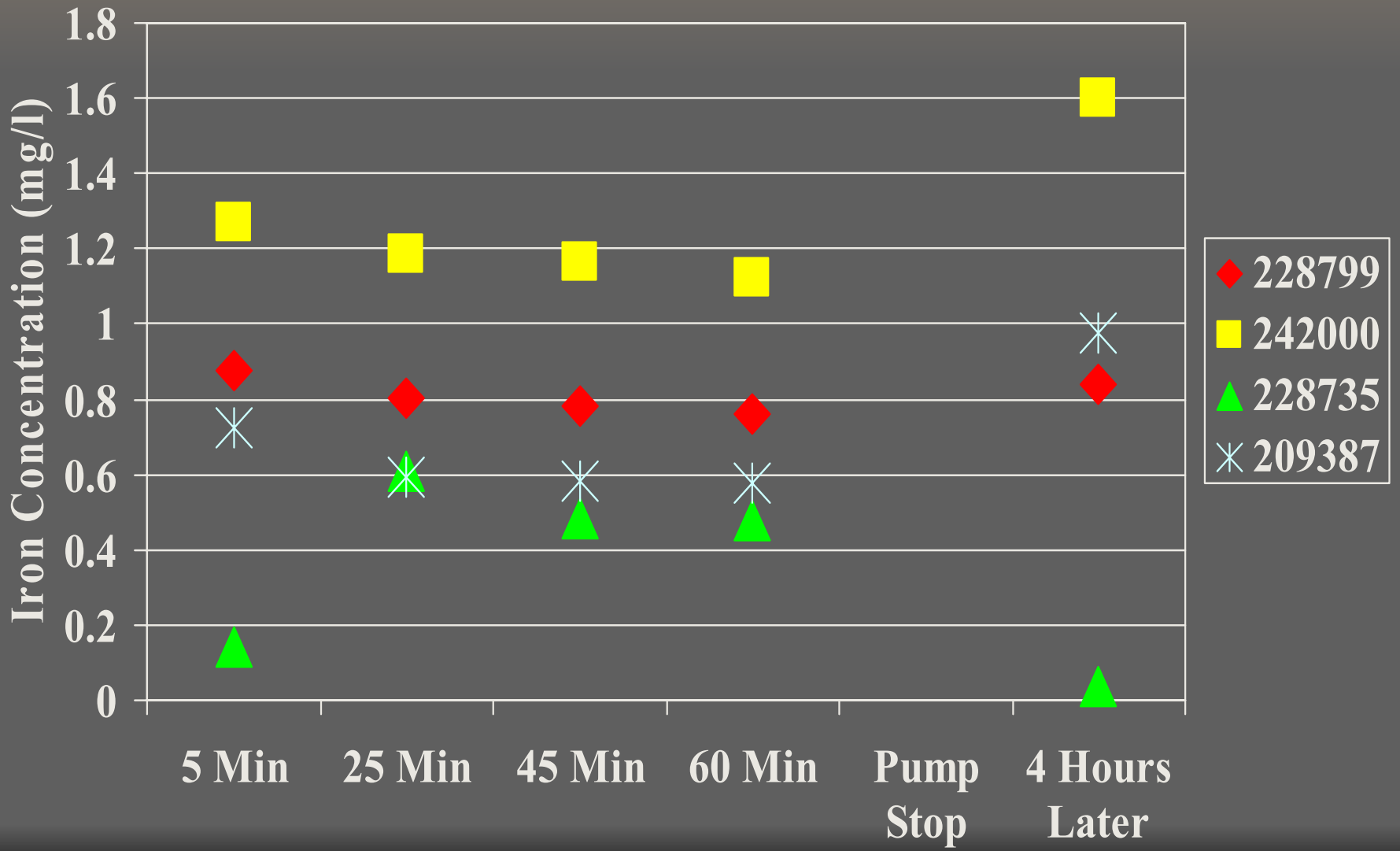
Short-Term Temporal Results



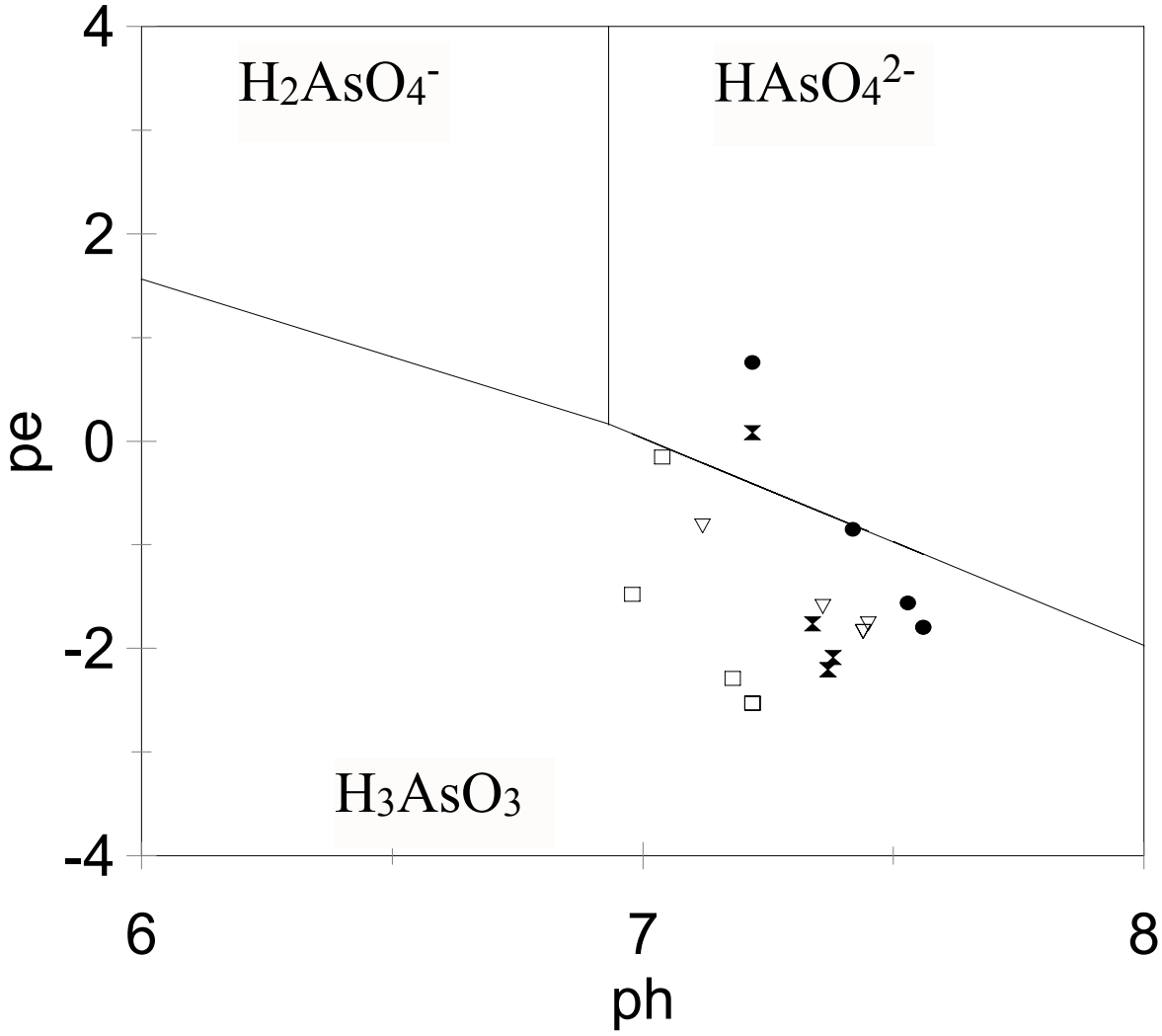
Short-Term Temporal Results



Short-Term Temporal Results



Short-Term Temporal Results



Questions and Answers

- Is there a pattern to short-term arsenic variability?
  - Sometimes…
- Why is there a pattern?
  - Reductive arsenic mobilization mechanisms

Extra Samples are Worth it When...

- The cost of being wrong is very high
- The cost of being wrong is sufficiently higher than the cost of additional sampling
- The need for better understanding is great
- The cost of extra sampling is low and the likelihood of increasing understanding is high

Important Considerations

- Identify the specific reason for collecting additional samples
- Run the numbers – cost/benefit
- Talk to the right people (technical experts, regulatory contact, client, etc.)
- Design sampling scheme to meet the need
  - More frequent samples?
  - Different analytes?
  - Different location or depth?