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Geochemical Conceptual Site Models Validated by Speciation Data to Support *In Situ* Treatment Strategies for Metals

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Imagine the result

Geochemical Conceptual Site Models

- An accurate conceptual site model (CSM) is integral to selection of an appropriate remedy
- For many sites, geochemical characterization is a critical part of developing an accurate CSM
- Geochemical conceptual site models (GCSM)
  - Interactions between aqueous and solid phases
  - Controls on contaminant mobility
  - Often require use of advanced analytical tools / methods

Metals Speciation

- Speciation: Identification / quantification of chemical forms of an element

- Chemical form of a metal determines
  - Solubility
  - Mobility
  - Bioavailability
  - Toxicity

Lead in soil: 5,000 ppm vs. 500 ppm

PbS (galena), Ksp=$10^{-28.1}$
$PbCO_3$ (cerussite), Ksp=$10^{-13.13}$
(D'Amore et al. 2005)

- Metal contaminated sites are often characterized / regulated based on total metal concentrations
  - Does not provide insight into human / ecological risk, or remedial strategy

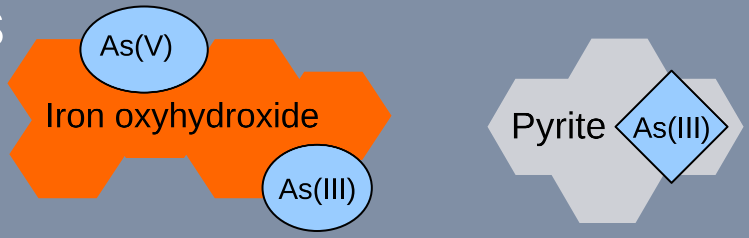
Arsenic Geochemistry

- GCSMs for two arsenic-impacted sites
  - Speciation data were critical to understanding fate and transport, and developing cost-effective remedial strategies

Oxidizing	Reducing
As(V) – arsenate	As(III) – arsenite
$H_2AsO_4^-$ and $HAsO_4^{2-}$ dominant under most GW pH conditions	H_3AsO_3 dominant under most GW pH conditions
Adsorbs to iron oxides, aluminum oxides, clay minerals	Generally less strongly adsorbed, more mobile

Arsenic Geochemistry

- Sequestration of arsenic from GW by adsorption / co-precipitation, particularly iron oxide surfaces and iron sulfide minerals



- Adsorbs to surface of mineral or occupies a lattice site in crystal structure

- Iron oxides have been shown to be the most important mineral component in determining a soil's capacity to adsorb As(V) and As(III)

(Manning and Suarez, 2000)

Characterization / Speciation Methods: Multiple Lines of Evidence

Analysis	Purpose
Groundwater analyses	Redox conditions, presence / extent of arsenic
Total metals digestion	Total arsenic content in source material and soil
TOC	Organic matter, indicator of sorptive capacity of soil
AGP / ANP	Acid-generating potential and capacity for attenuation, potential for acid rock drainage
Leach tests	Arsenic leachability under acidic, neutral, and basic pH conditions
Sequential selective extractions	Distribution of arsenic among various solid phases in soil (potentially available vs. immobilized)
XRD	Major mineral components (at least 1-5% by weight)
SIMS	Arsenic association with trace mineral phases

Example 1:
Baseline Characterization for Arsenic

- Tailings from historical mining and ore processing
- New mining operations planned
- Evaluated historical mine wastes to determine necessity for an engineered remedy
- Developed GCSM to describe baseline conditions and potential arsenic mobility

Example 1:
Initial Characterization Results

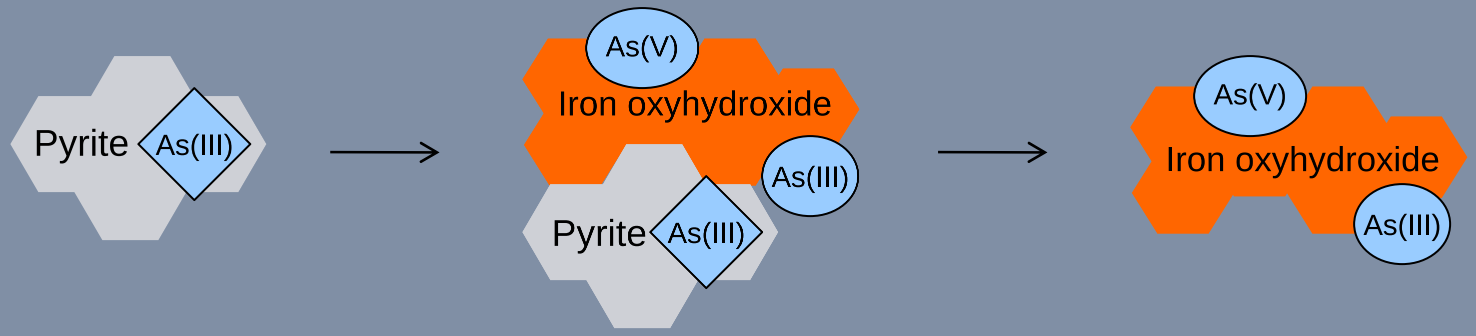
- Total metals digestion
  - Elevated arsenic in host rock, processed rock, and tailings
- Leach tests and AGP / ANP
  - Extremely low arsenic leachability and ARD potential
- GW analysis
  - Elevated arsenic, TDS, and pH
- SIMS analysis
  - Additional mineralogical testing to identify arsenic speciation

Example 1: Arsenic Association with Mineral Phases

- Host Rock
  - Arsenopyrite (FeAsS), pyrite and marcasite (FeS_2)
  - Alunite ($KAl_3(SO_4)_2(OH)_6$)
- Processed Rock
  - Goethite (FeO(OH)) and jarosite ($KFe_3(SO_4)_2(OH)_6$)
- Historical Tailings
  - Goethite and hematite (Fe_2O_3)
- Total arsenic content is consistent in all samples

Example 1:
Arsenic Mobility

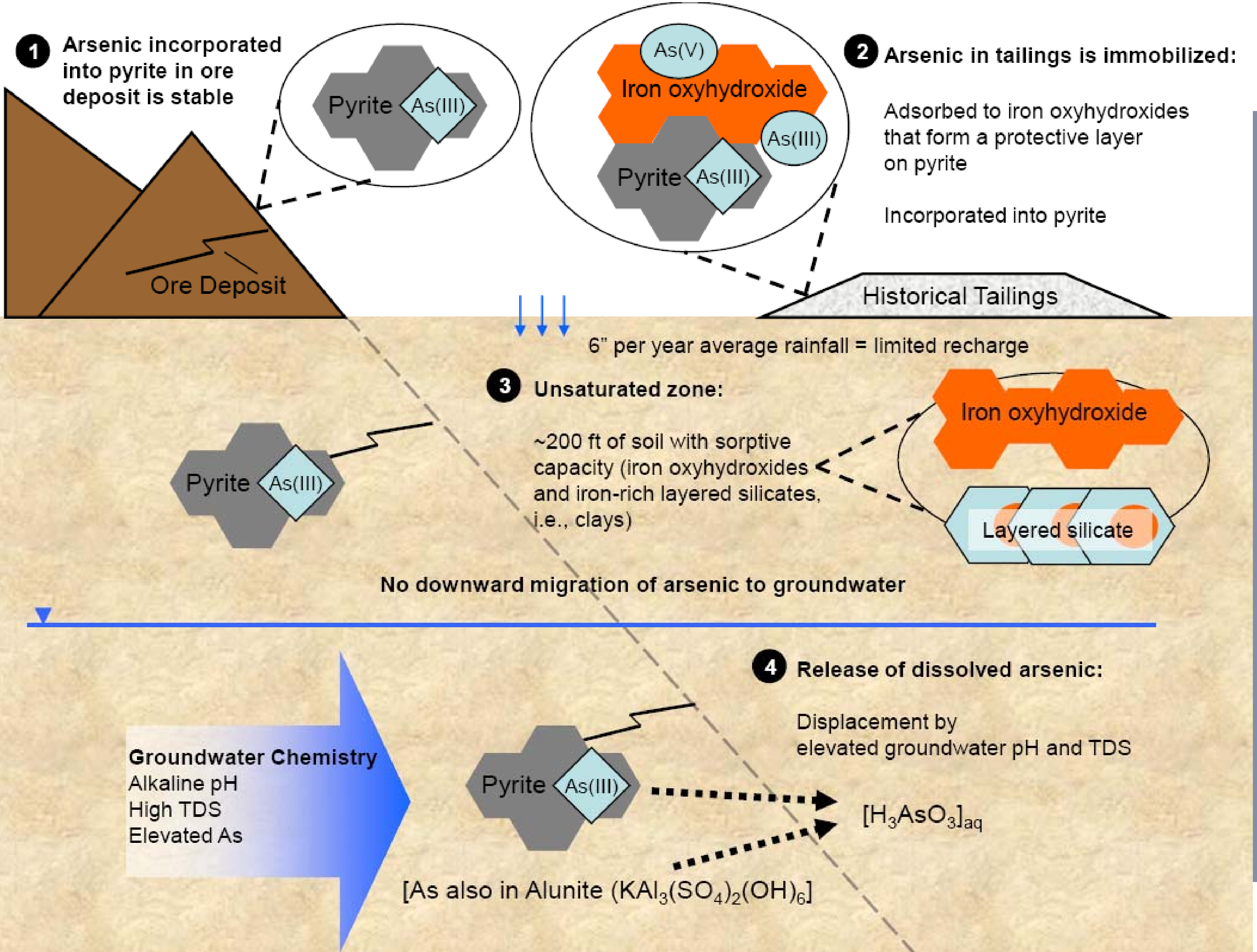
- Iron sulfide minerals are oxidized during processing
- Arsenic is redistributed from reduced to oxidized minerals
- Leach tests: minimal soluble arsenic at pH 5, 7, and 10.5
  - Exception is host rock sample at pH 10.5 (alunite)
- Arsenic in tailings is stable / immobile



Example 1:
Arsenic in Groundwater

- Arsenic from historical tailings does not influence GW
- Elevated TDS and pH in GW mobilize arsenic from mineralized zones at depth
  - Desorption of arsenic due to competition for sorption sites
  - Dissolution of arsenic from labile mineral phases
- High background levels well documented in the region
- Engineered remedy for historical tailings is not necessary

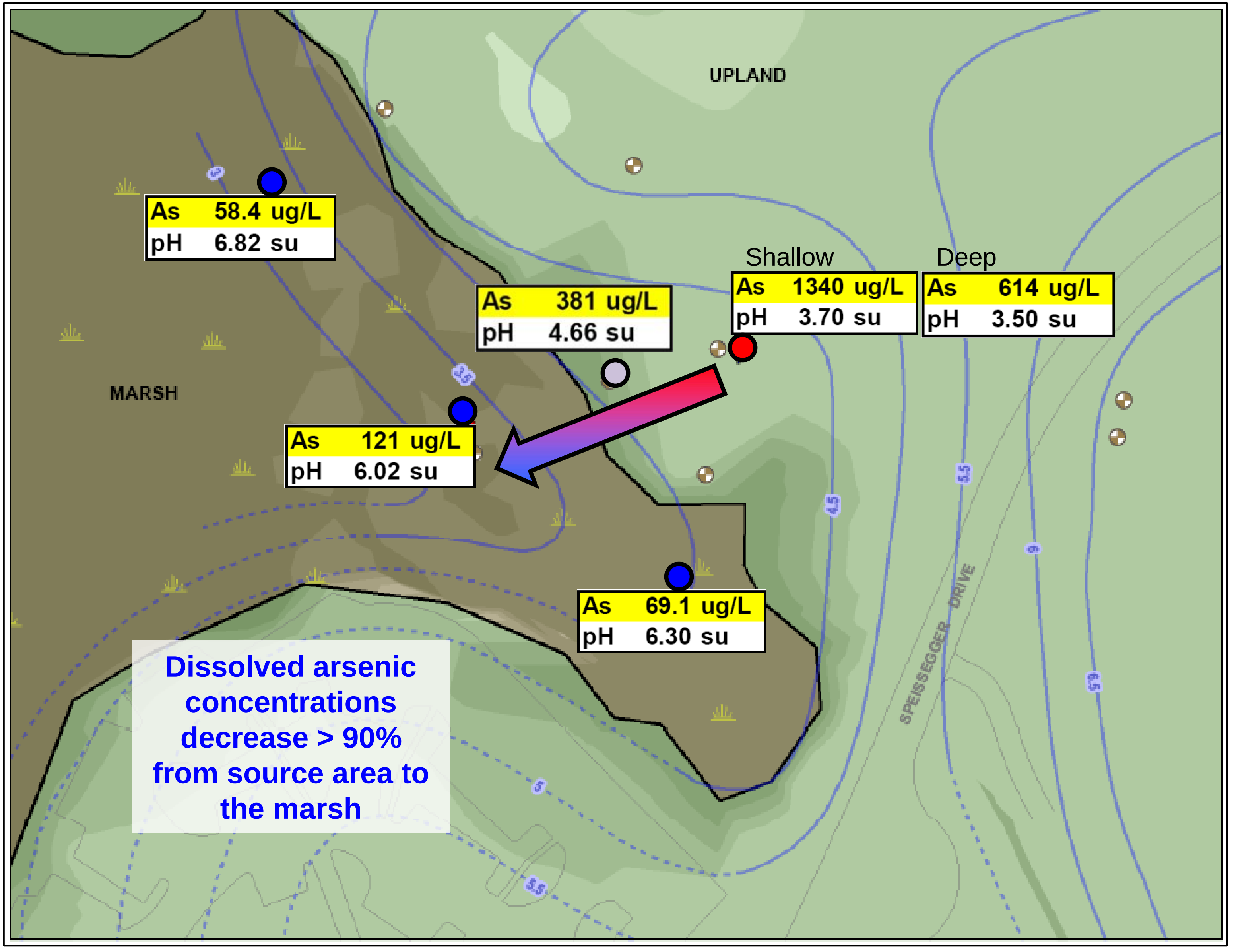
Example 1: GCSM for Arsenic Behavior



Example 2:
Identification of Natural Mechanisms for Arsenic Sequestration

- Slag and roasted pyrite material at a former phosphate fertilizer facility
- Arsenic in GW flowing toward marsh
- Regulatory agency favored a GW pump-and-treat remedy
- Developed GCSM to identify controls on arsenic transport that could be enhanced *in situ*

Example 2: Arsenic in Groundwater



Example 2:
Sequential Selective Extractions for Arsenic Speciation

Available

Extraction Step	Fraction Characterized
1:1 water	water soluble
$MgCl_2$	weakly adsorbed / exchangeable
NaOH	organic matter
AOD	amorphous iron oxides
CBD	crystalline iron oxides
HNO_3	sulfide minerals
Method 3052	recalcitrant sulfides and organic matter

Recalcitrant

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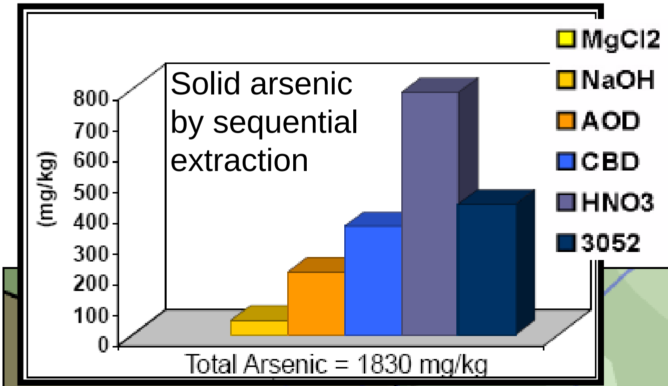
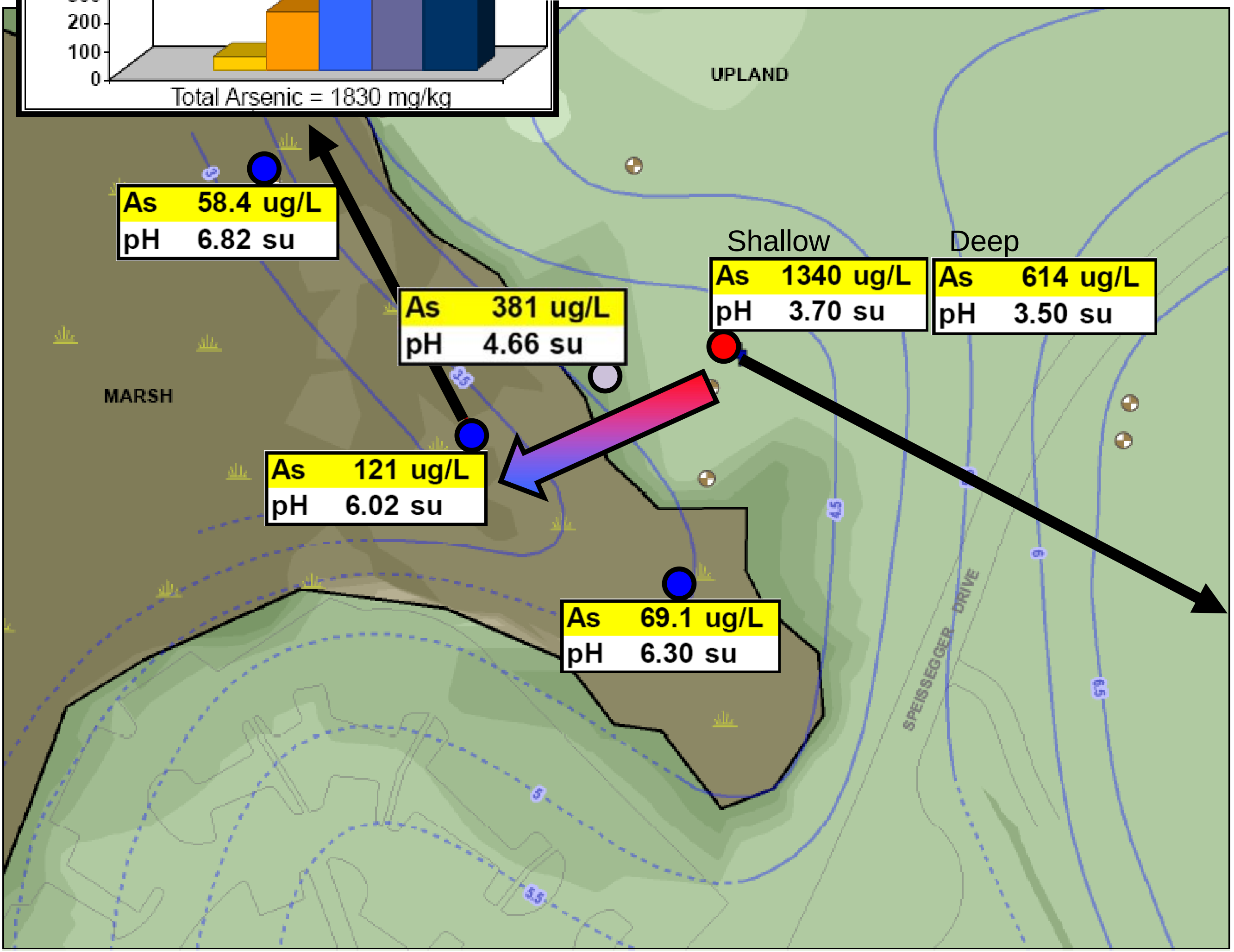
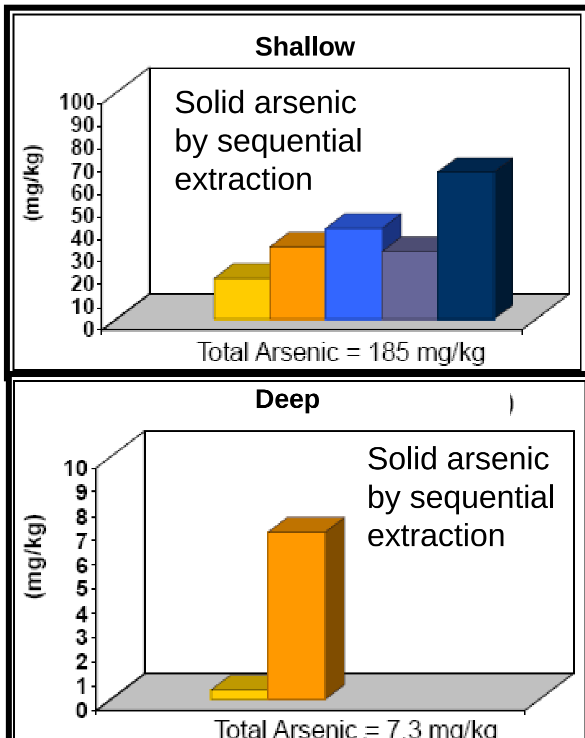
Example 2: Natural Sequestration of Arsenic



Solid phase arsenic in marsh associated with sulfide minerals, highly stable in reducing conditions at neutral pH.



Solid phase arsenic concentrations in source area decrease with depth and shift to iron oxide co-precipitates.



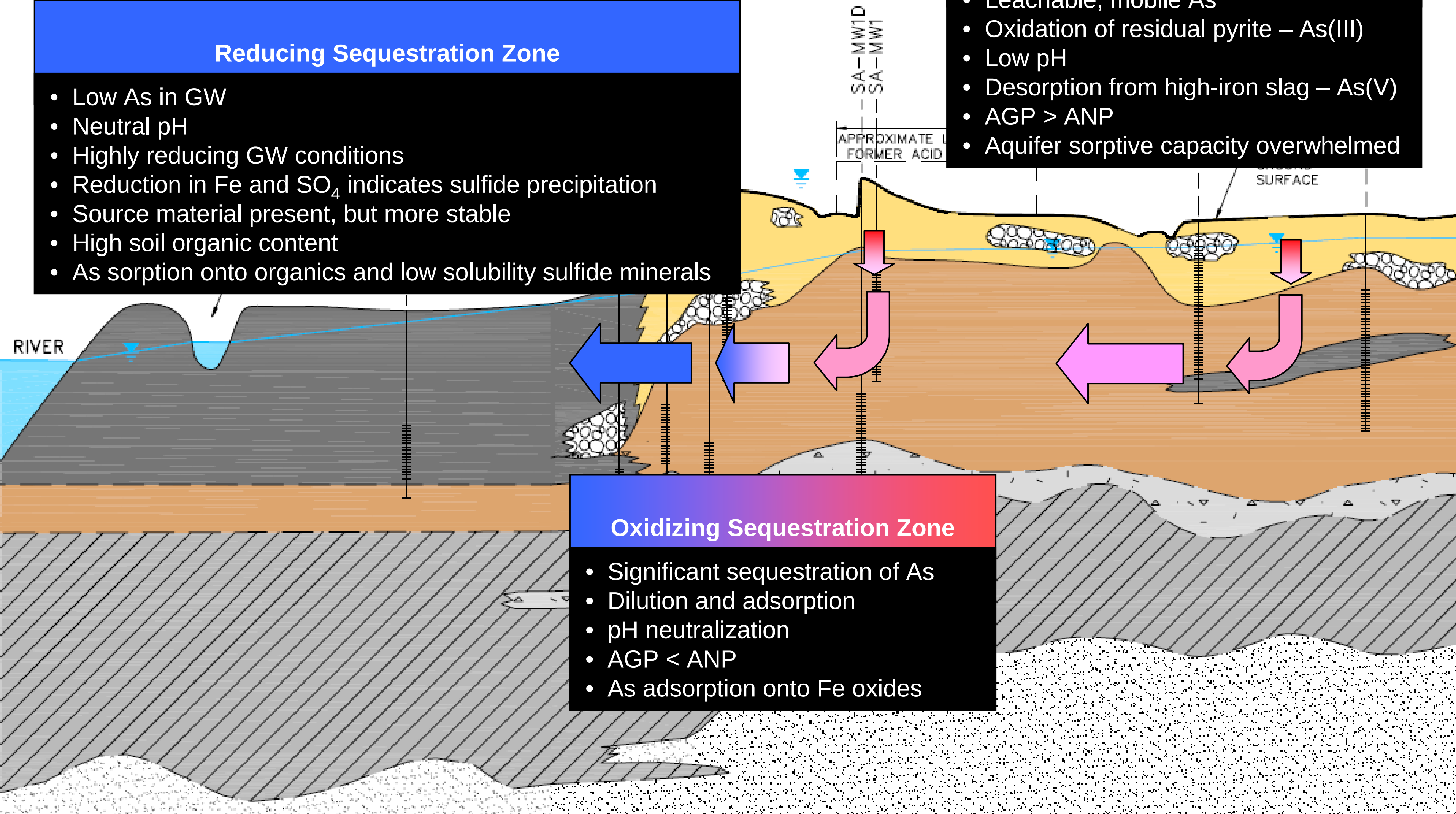
Example 2:
Mineral Identification

- XRD analysis
  - Confirmatory speciation technique
  - Verified chemical extraction results

- Iron oxides (e.g.,hematite, Fe_2O_3) and carbonate minerals (e.g.,calcite, $CaCO_3$) throughout the site

- Sulfide minerals (pyrite, FeS_2) in the marsh

Example 2: GCSM for Arsenic Behavior



Reducing Sequestration Zone

- Low As in GW
- Neutral pH
- Highly reducing GW conditions
- Reduction in Fe and SO_4 indicates sulfide precipitation
- Source material present, but more stable
- High soil organic content
- As sorption onto organics and low solubility sulfide minerals

Sources

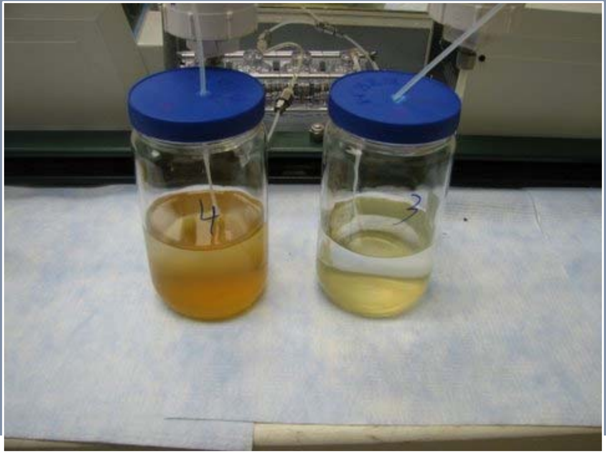
- Leachable, mobile As
- Oxidation of residual pyrite – As(III)
- Low pH
- Desorption from high-iron slag – As(V)
- AGP > ANP
- Aquifer sorptive capacity overwhelmed

Oxidizing Sequestration Zone

- Significant sequestration of As
- Dilution and adsorption
- pH neutralization
- AGP < ANP
- As adsorption onto Fe oxides

Example 2:
In Situ Approach to Augment Natural Sequestration Mechanisms

- Enhance natural capacity to immobilize arsenic
- Cost-effective and sustainable alternative to GW pump-and-treat
- Source removal + proprietary soil amendments:
  - Stabilize arsenic and reduce leachability in the vadose zone
  - Reduce arsenic concentrations in GW and neutralize / buffer the aquifer pH



Conclusions

- Examples demonstrate that accurate GCSMs based on speciation data are valuable for:
  - Understanding geochemical controls on mobility
  - Implementing cost-effective and sustainable remedies

- A comprehensive GCSM can require several analytical methods
  - Consider costs and appropriateness of the information obtained relative to the project goals
  - Methods discussed are not specific to arsenic, applicable to other metals

Acknowledgements

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