Speciation, Fate, and Cycling of Arsenic in Subsurface Environments

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UNIVERSITY OF CALIFORNIA
UCMERCED

Z=33

As

Atomic wt. 74.922

Mechanistic understanding of arsenic speciation can help predict its behavior in subsurface environments

- Can we use geochemical scenarios to categorize potential As mobilization?
- How do we optimize kinetics of biogeochemical processes to enhance natural As attenuation?

Geochemical Parameters:

-- Amount of labile iron

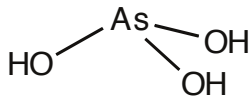
-- Amount of sulfur available for reduction/oxidation

-- pH & Eh (local and gradients)

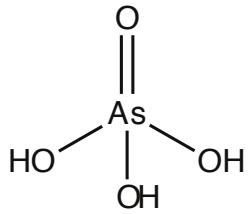
-- Role of nitrogen species?

Arsenic Speciation in the Environment

Inorganic Arsenic



Arsenious acid or
Arsenite ($As^{III}(OH)_3$)
$pK_{a_{1,2,3}}$ = 9.23, 12.13, 13.40

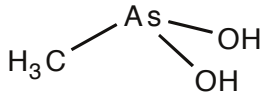


Arsenic acid or
Arsenate ($H_3As^{V}O_4$)
$pK_{a_{1,2,3}}$ = 2.20, 6.97, 11.53

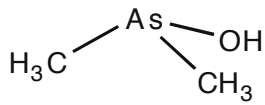
Arsenic Minerals

Orpiment (As_2S_3)
Realgar (As_4S_4)
Arsenopyrite (FeAsS)
Scorodite ($FeAs^{V}O_4.2H_2O$)
Oxides, Arsenites, Arsenates

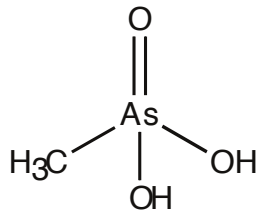
Methylated Arsenic Compounds



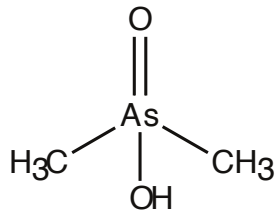
Monomethylarsonous
acid or MMAs(III)
($As(OH)_2CH_3$)



Dimethylarsinous
acid or DMAs(III)
($As(OH)(CH_3)_2$)

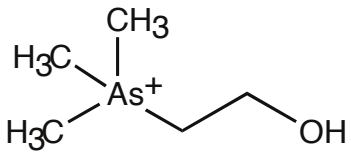


Monomethylarsonic
acid or MMAs(V)
($AsO(OH)_2CH_3$)

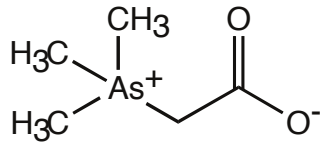


Dimethylarsinic
acid or DMAs(V)
($AsO(OH)(CH_3)_2$)

Organoarsenic Compounds

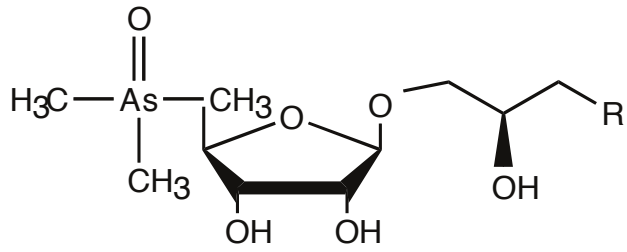


Arsenocholine
($(CH_3)_3As^+CH_2CH_2OH$)



Arsenobetaine
($(CH_3)_3As^+CH_2COO^-$)

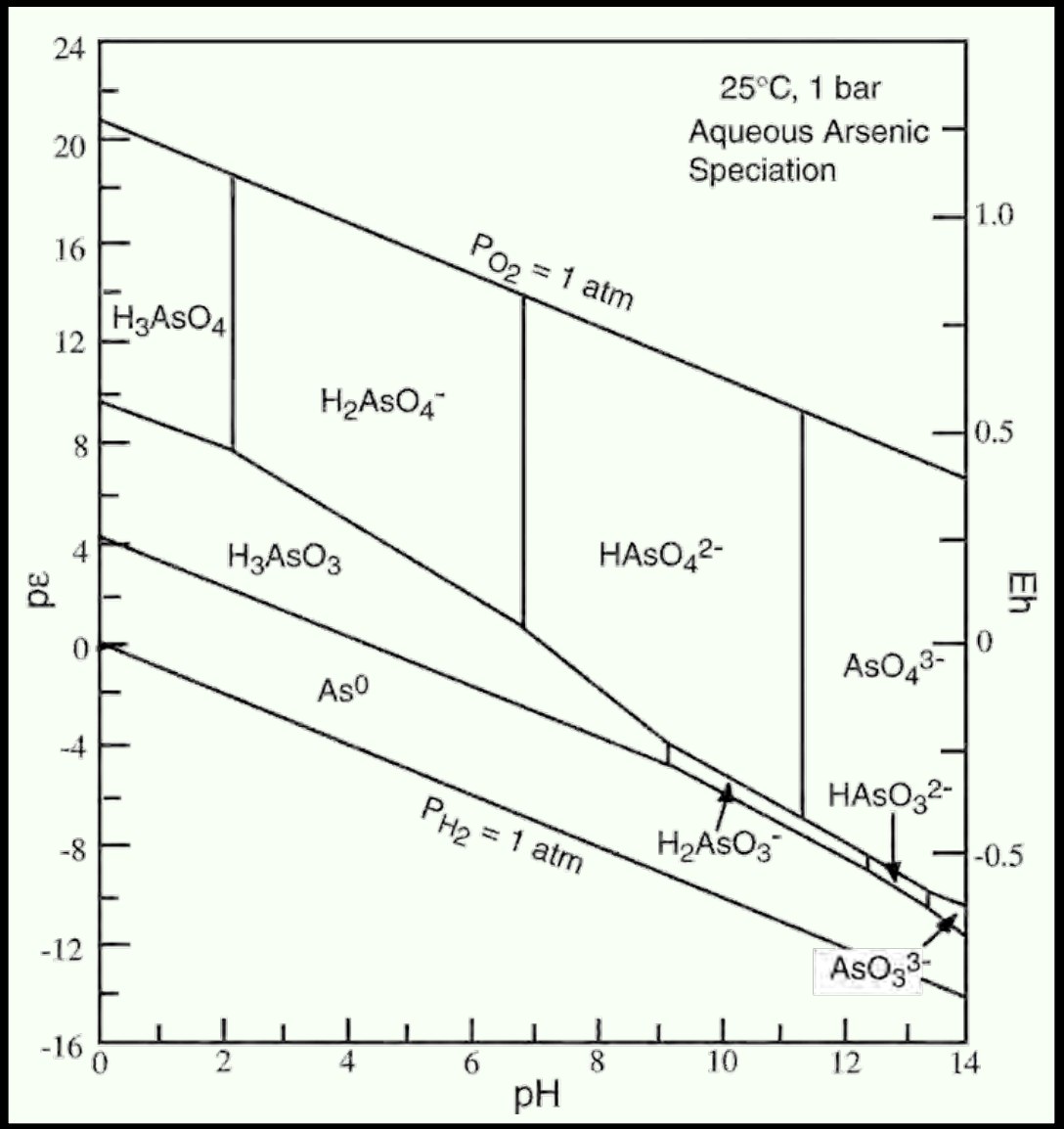
Organoarsenic Lipids



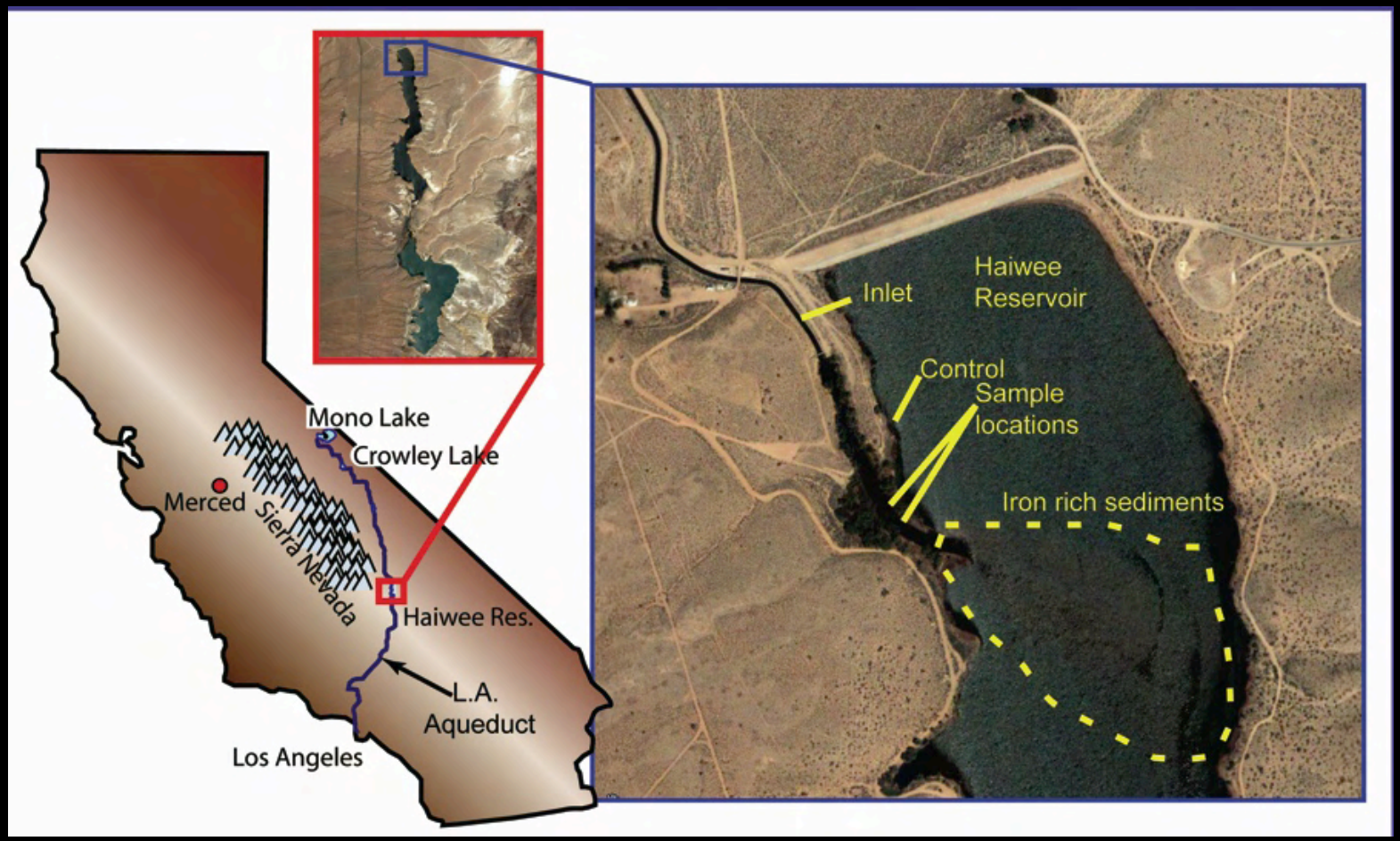
R = OH
R = $OP(O)(O^-)OCH_2CH(OH)CH_2OH$
R = SO_3^-
R = OSO_3^-

Arsenic Speciation & Partitioning: Tied to Major Element Chemistry

- Precipitation important for sulfides and sulfates
- Adsorption: Strongly associates with Iron hydroxides/oxides; competitive sorbates?
- Organic carbon and microbial activity
- Microbial coupling/ competition with Nitrogen species?



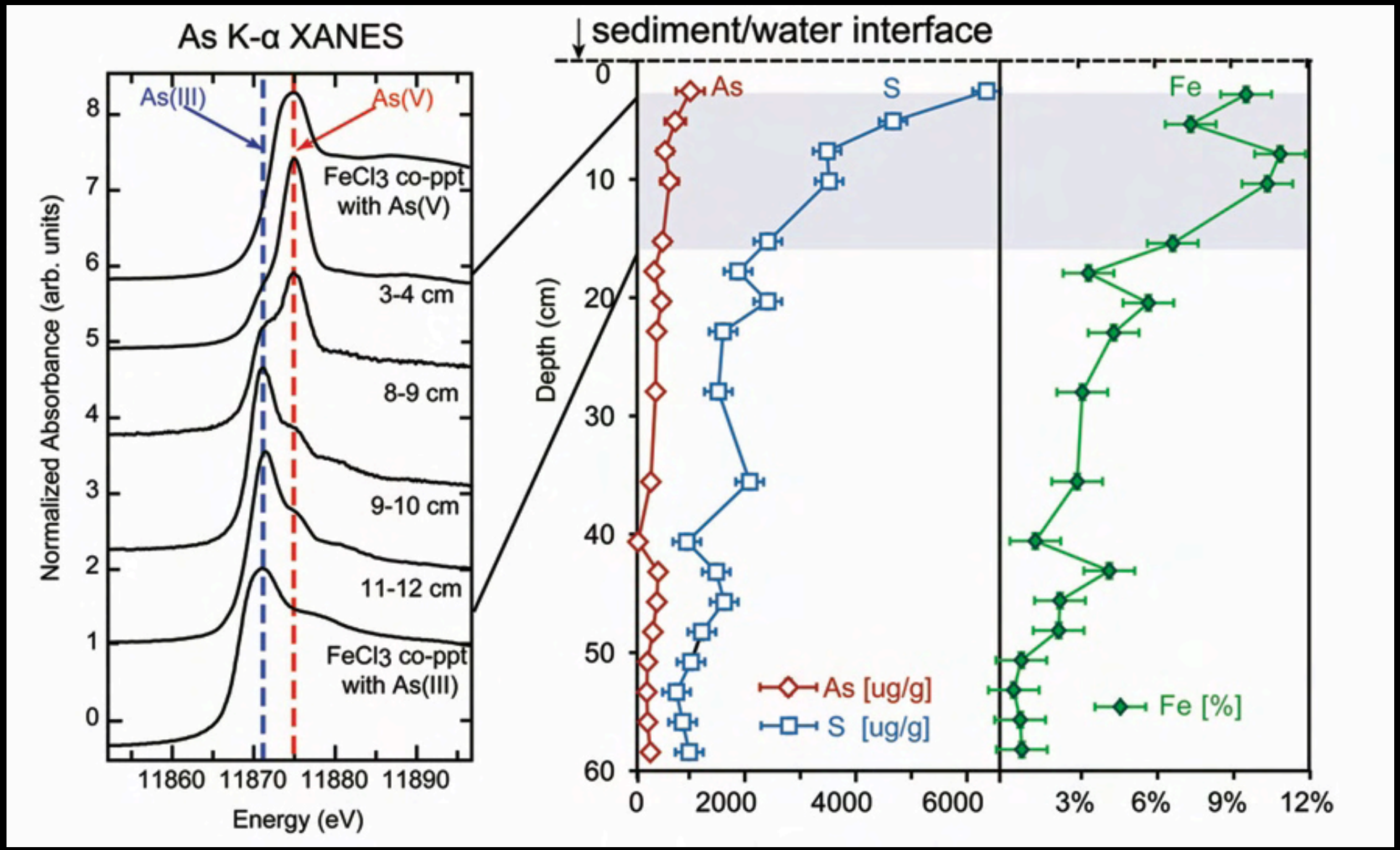
Haiwee Reservoir, Owens Valley



- Aqueduct water dosed with $FeCl_3$ to remove As
- Deposition of high Fe, low S sediments with sorbed As(V)

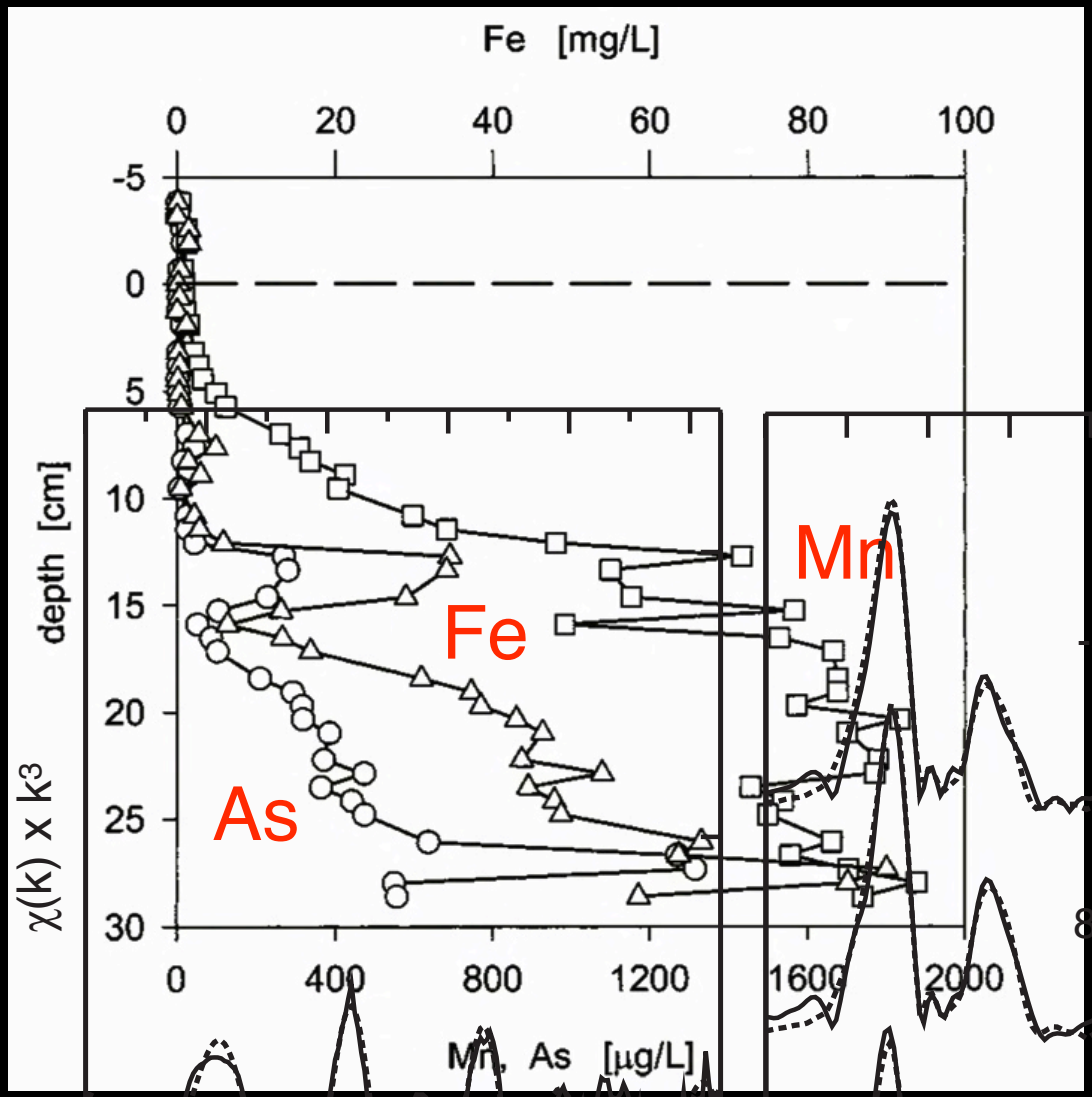
Haiwee Reservoir, Owens Valley

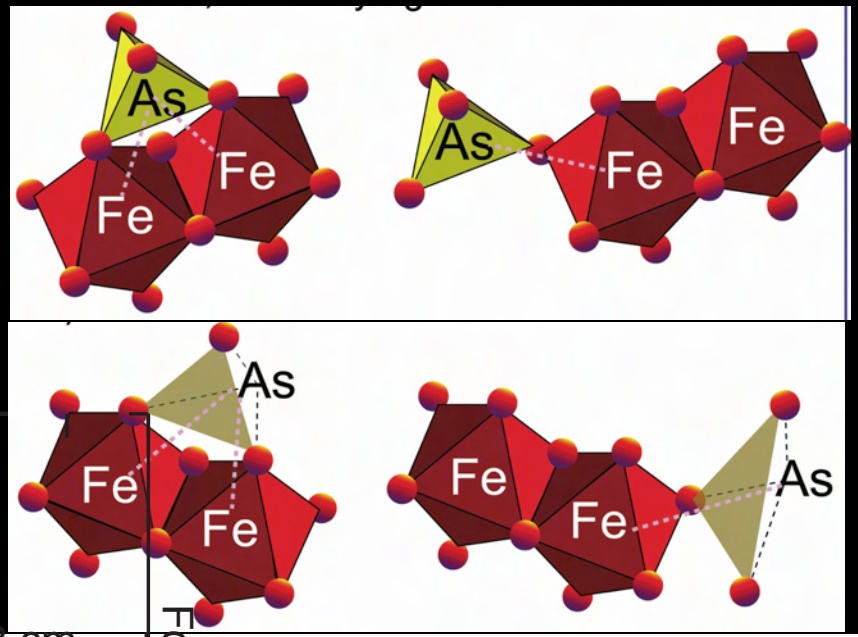
Haiwee Reservoir: Core Sediments



Porewater Concentrations

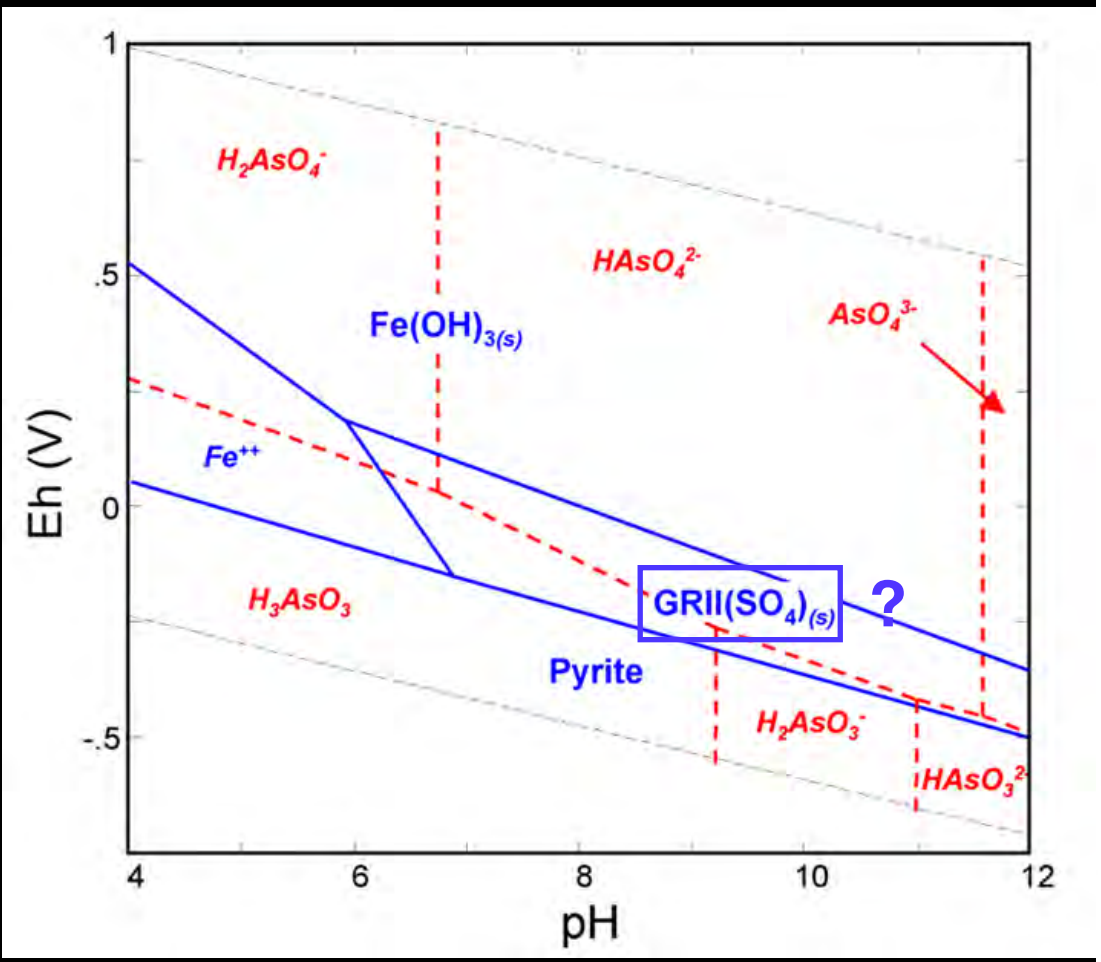
Sediment As & Fe Speciation

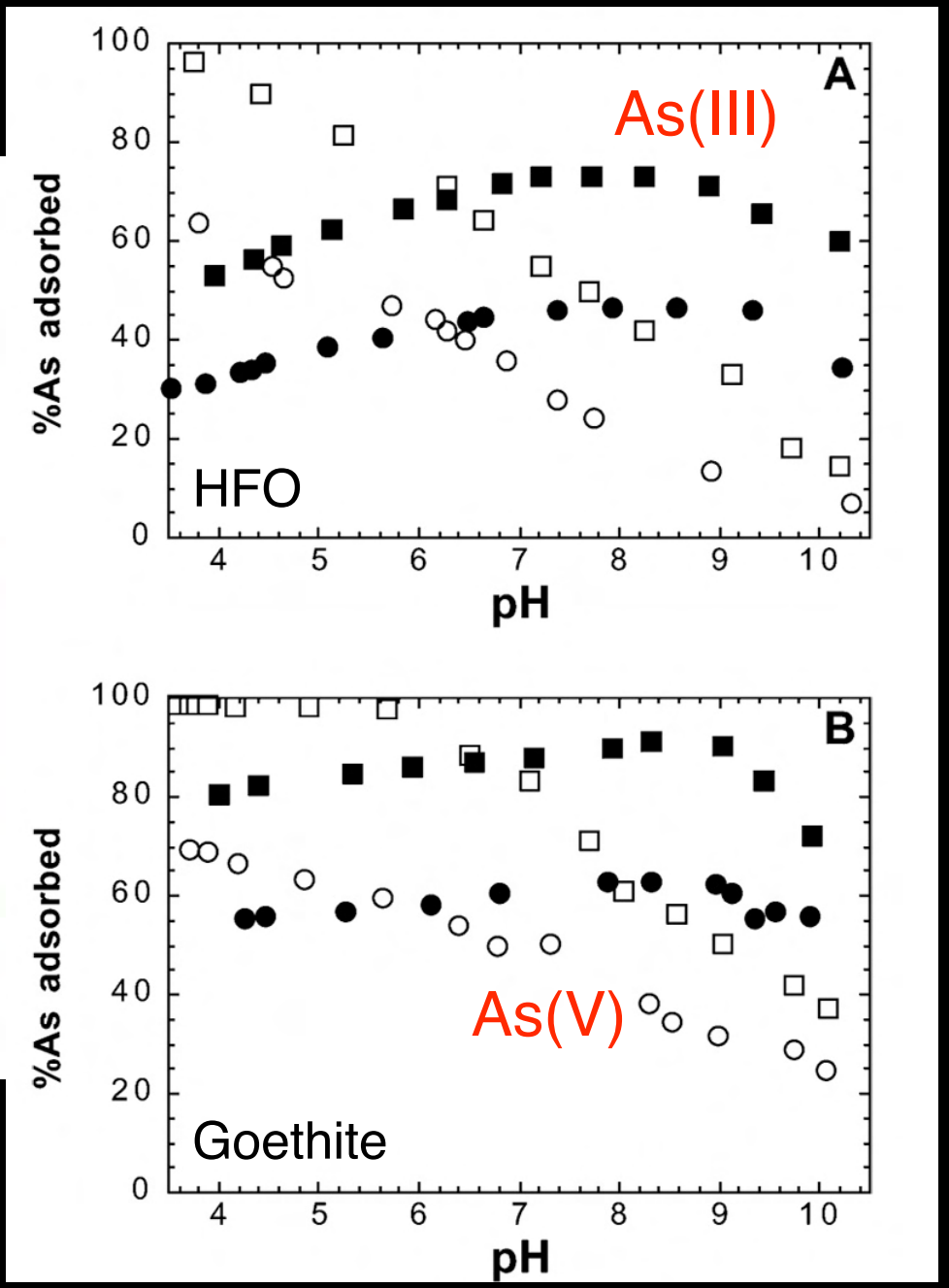




Kneebone et al. (2002) ES&T 36, 381-386

High Iron, low Sulfur, Carbon System

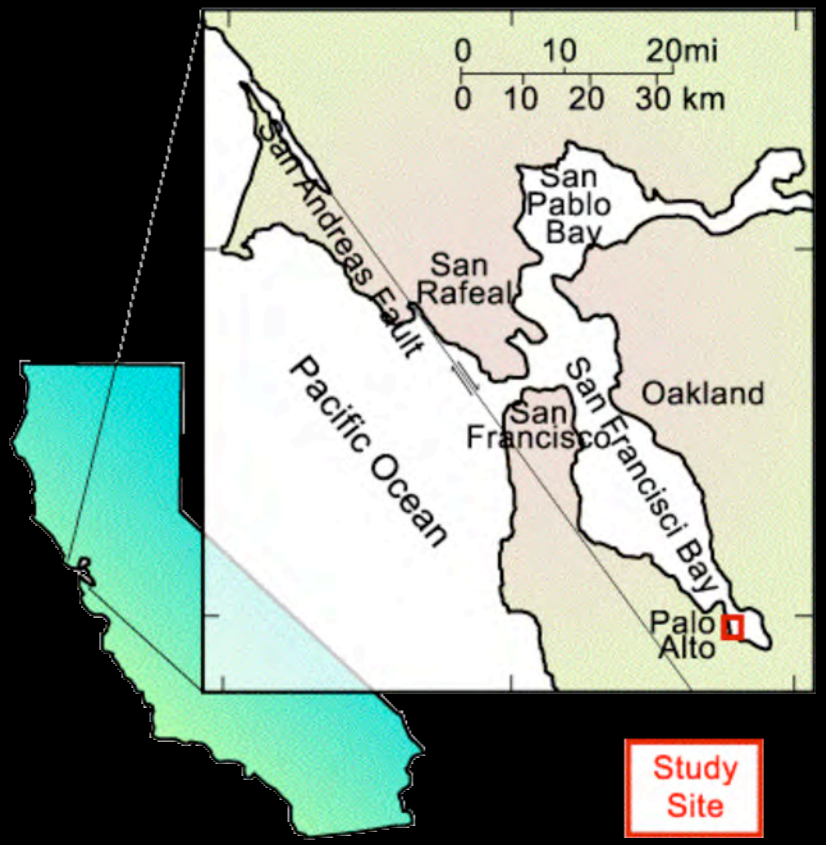




Dixit & Hering (2003) ES&T 37, 4182-4189

High Iron, low Sulfur, Carbon System

- Reductive dissolution of sorbent $Fe(OH)_3$ releases As
- Low potential for Sulfur reduction -- no removal by sulfides
- Reduction of As(V) to As(III) -- may remain sorbed
- As(III) sorption depends on pH, competitive sorbates, available sorbents



Bay Road Site
East Palo Alto CA.

- Tidal influence
- Sulfate reducing

Natural Arsenic Attenuation

Bay Road Site, East Palo Alto (CA, USA):

Subsurface plume below former sodium arsenite herbicide & pesticide manufacturing facility (1926-71)

Contaminant Plume:

[As$_T$] in Groundwater

Up to 100 mg l^{-1}

[As$_T$] in Sediments

Up to 1000 mg kg^{-1}

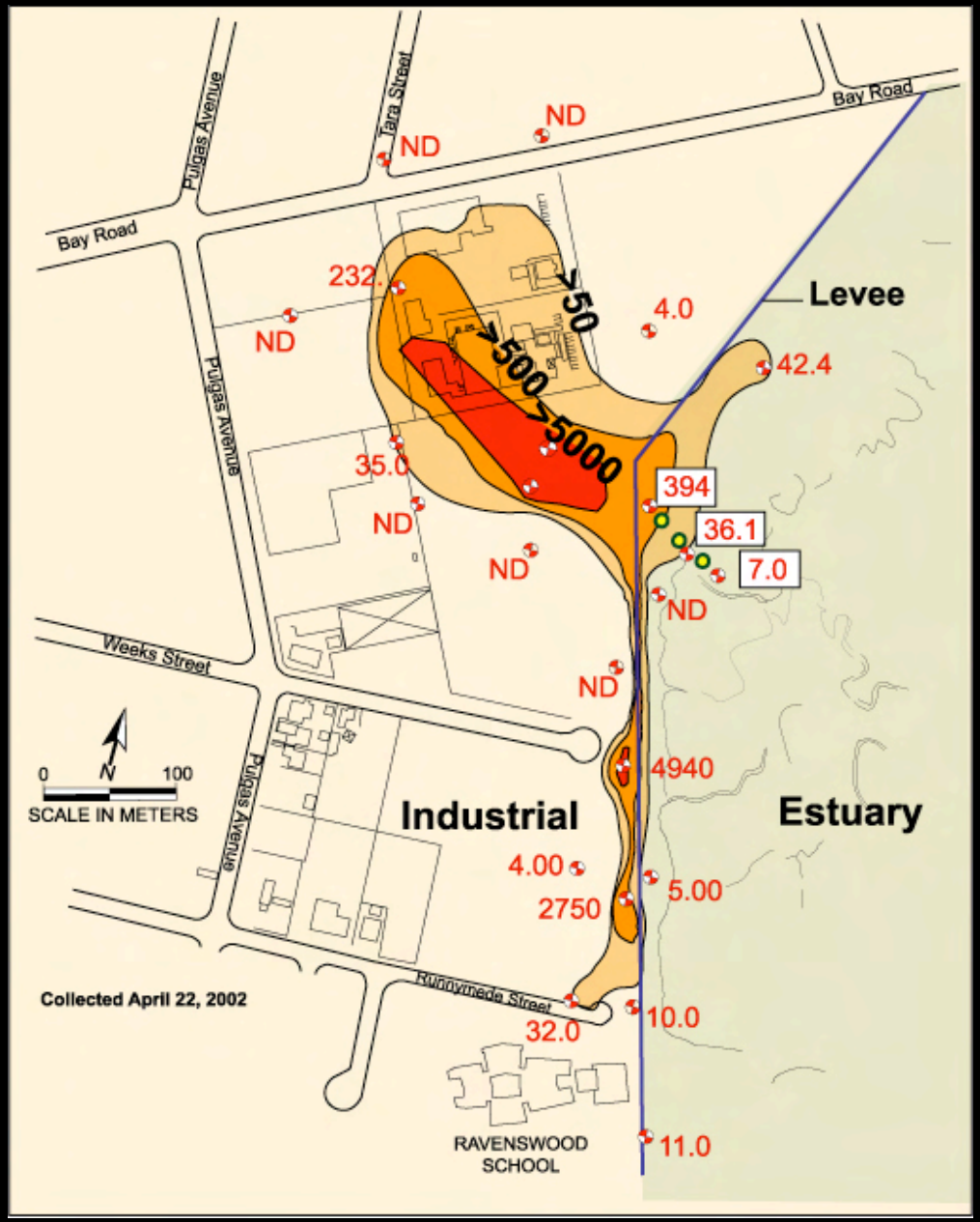
Down-gradient of Plume:

[As$_T$] in Groundwater

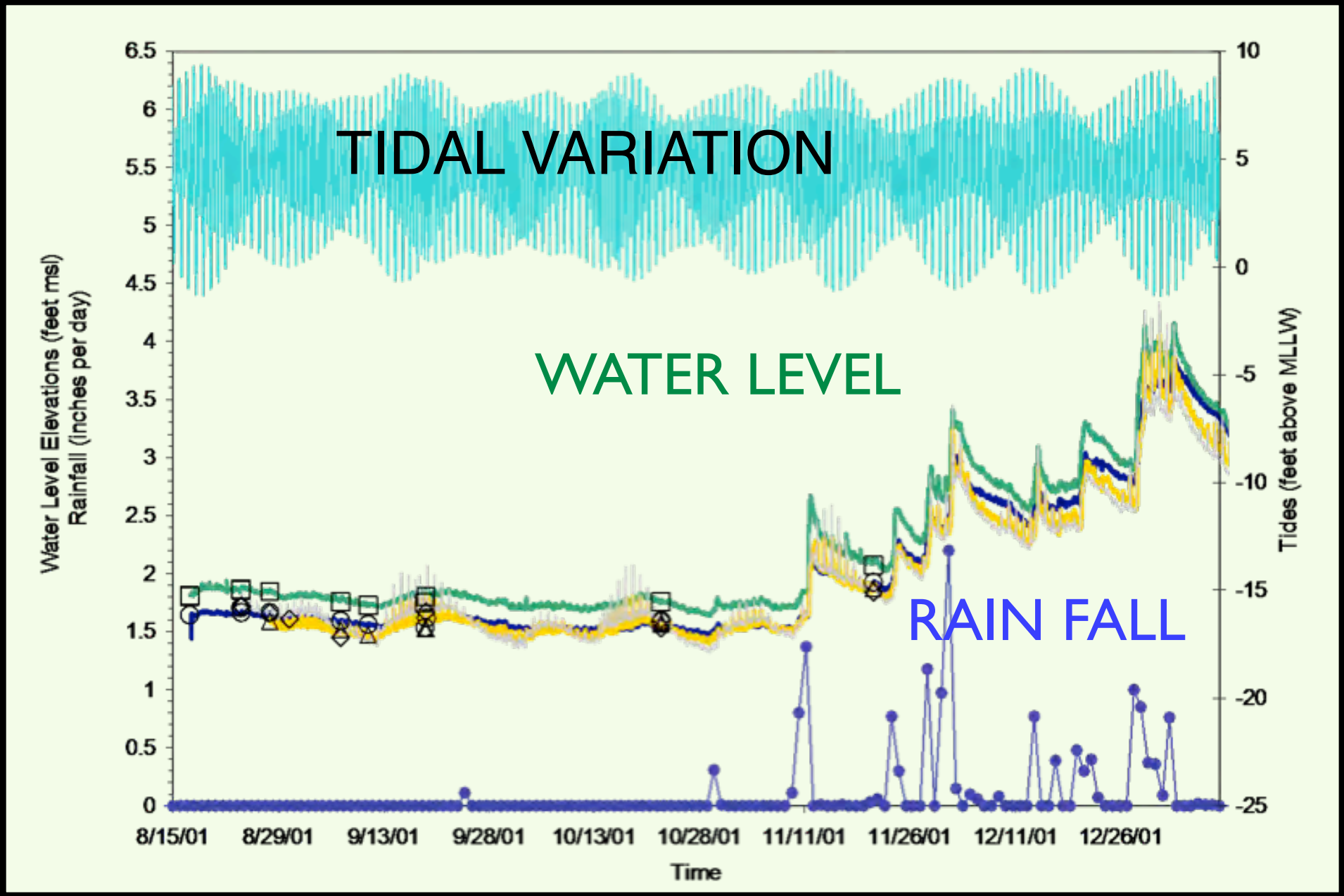
<0.01 mg l^{-1}

[As$_T$] in Sediments

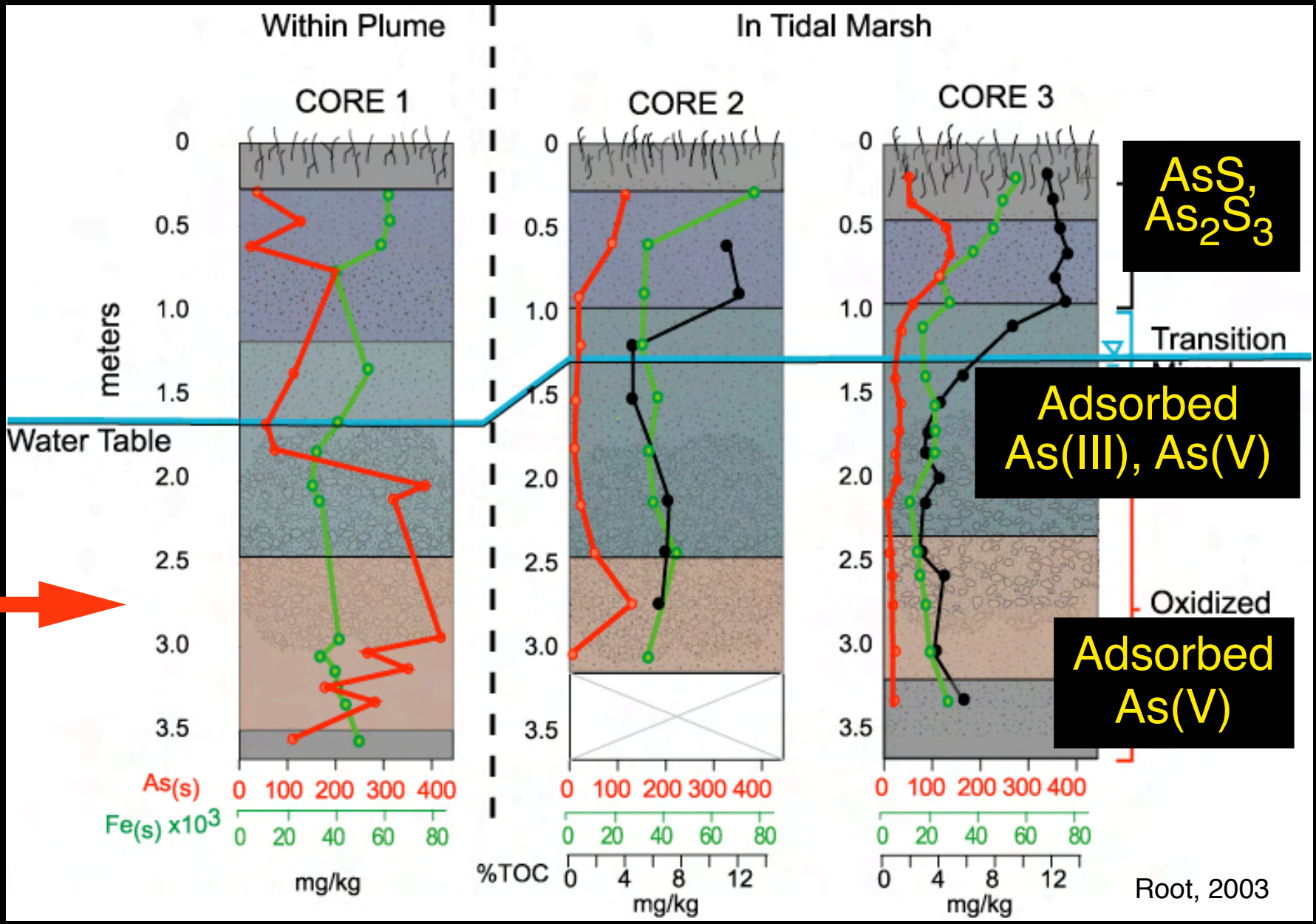
Natural Background



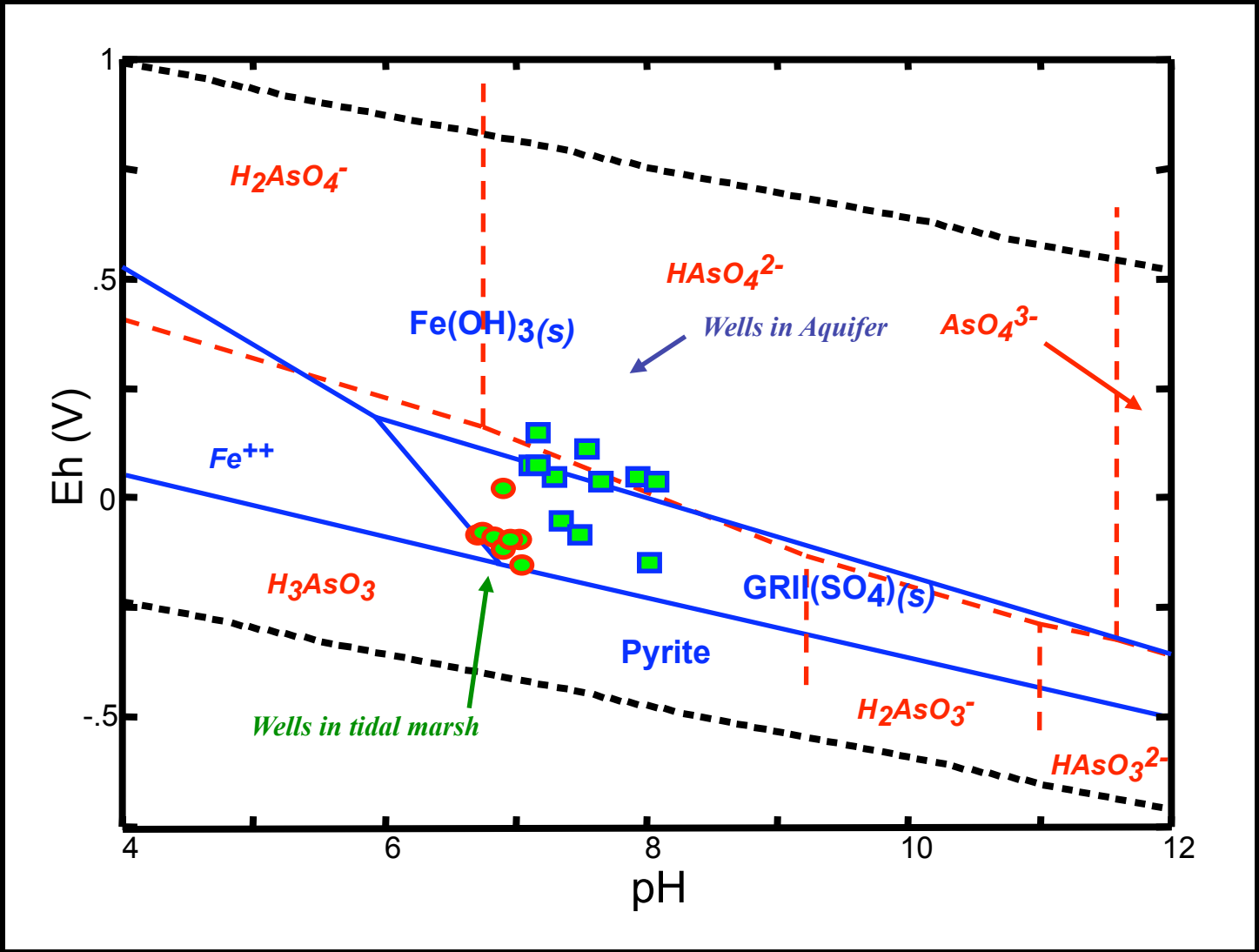
Seasonal variation in well water level compared to tidal variation and rainfall (8/15/01-1/15/02)



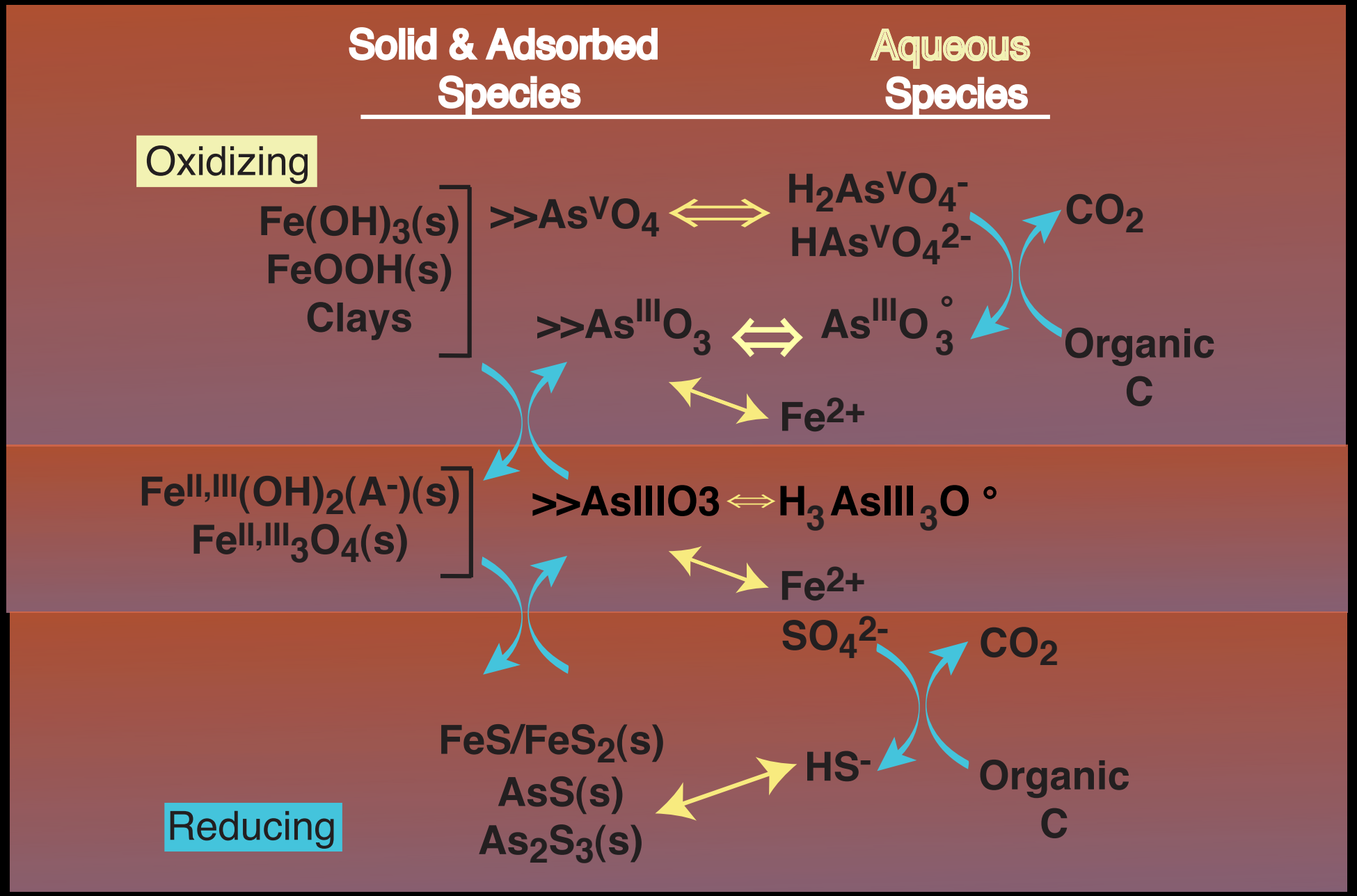
Sediment Arsenic, Iron, & Organic Carbon



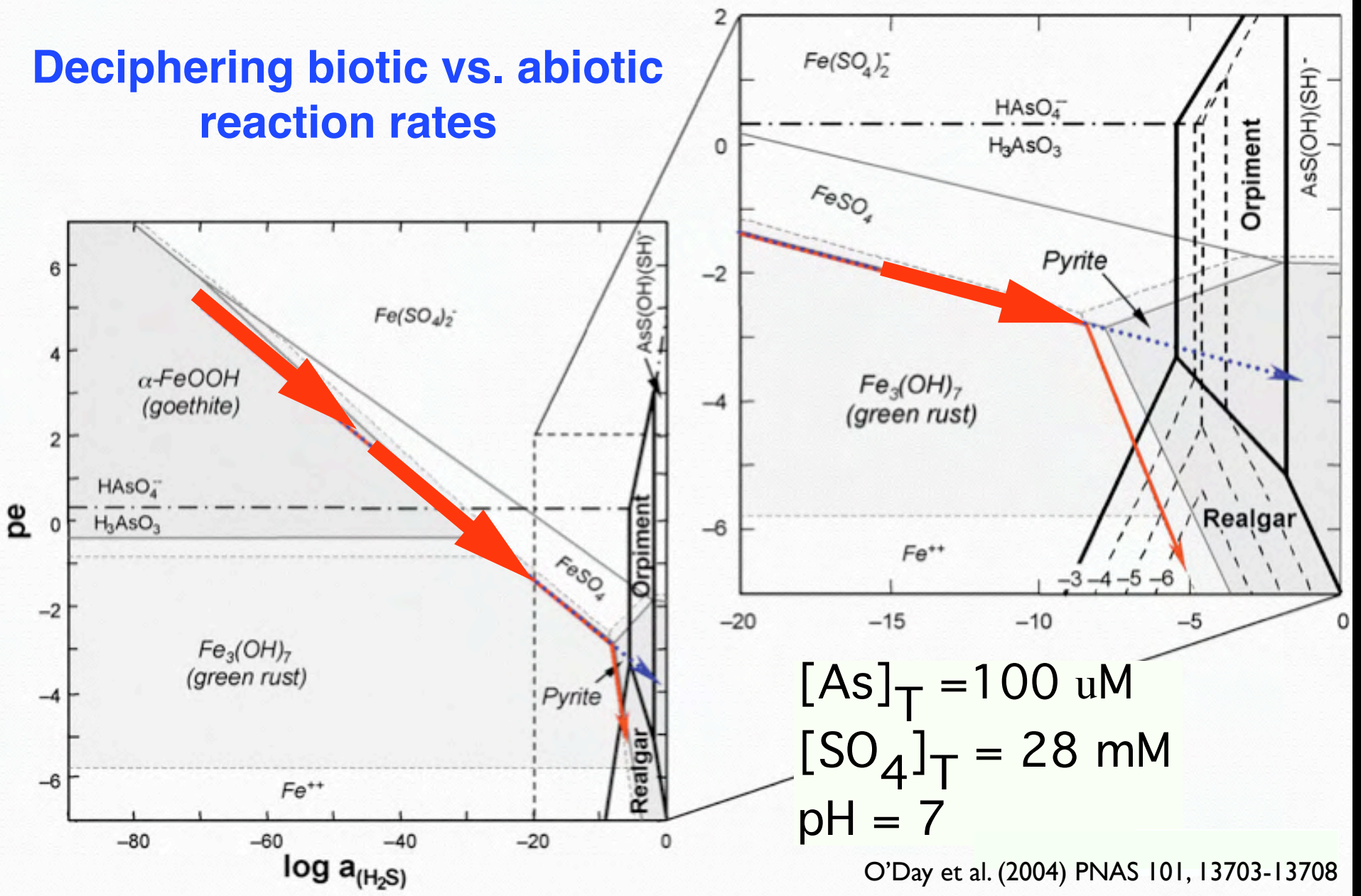
As-Fe-S Speciation



Green Rust: GRII: $Fe^{II}_6Fe^{III}_2(OH)_{16}(SO_4)\cdot 4H_2O$


Solid & Adsorbed Species
Aqueous Species
Oxidizing
Fe(OH)3(s)
FeOOH(s)
Clays
>>AsVO4
H2AsVO4-
HAsVO42-
CO2
>>AsIIIO3
AsIIIO3°
Organic C
Fe2+
FeII,III(OH)2(A-)(s)
FeII,III3O4(s)
>>AsIIIO3
H3AsIII3O°
Fe2+
SO42-
CO2
FeS/FeS2(s)
AsS(s)
As2S3(s)
HS-
Organic C
Reducing

Deciphering biotic vs. abiotic reaction rates



$[As]_T$ =100 uM

$[SO_4]_T$ = 28 mM

pH = 7

O'Day et al. (2004) PNAS 101, 13703-13708

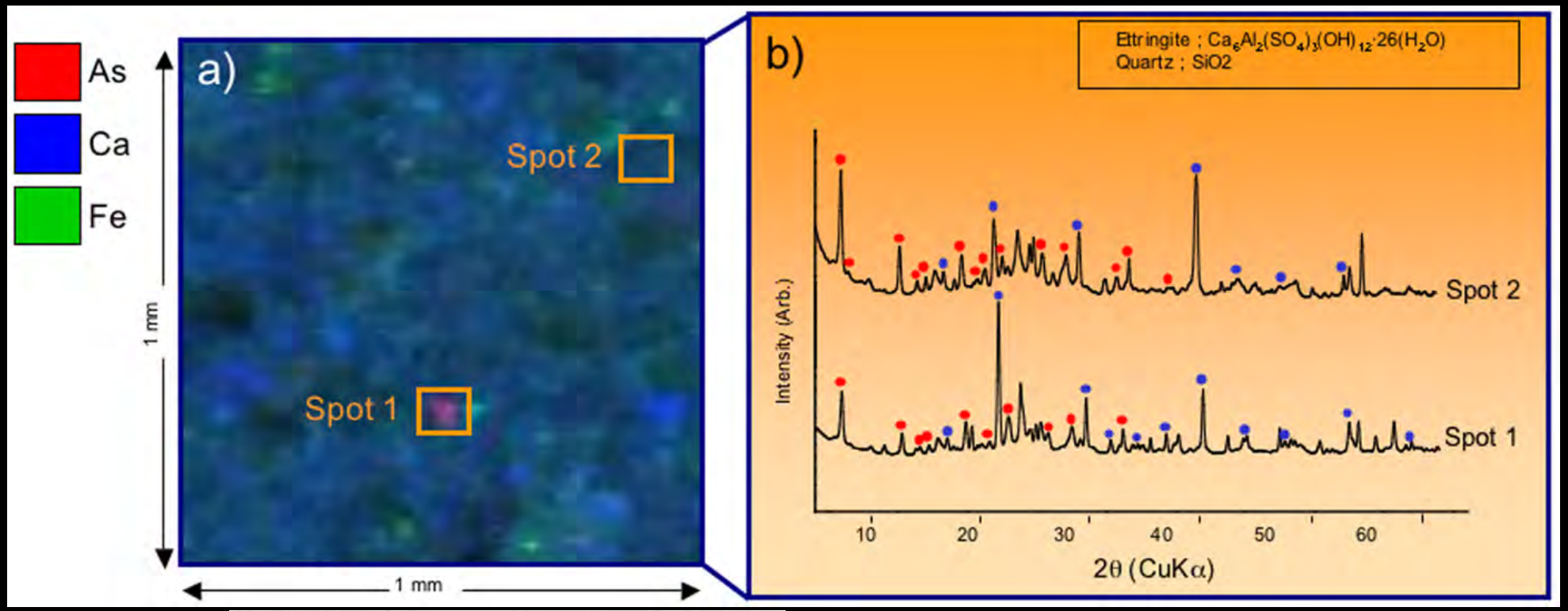
Soil Amendments for As Stabilization
Bay Road Site

Amendments:
Ferrous sulfate (3% w/w)
Portland Cement (Type V, 10% w/w)

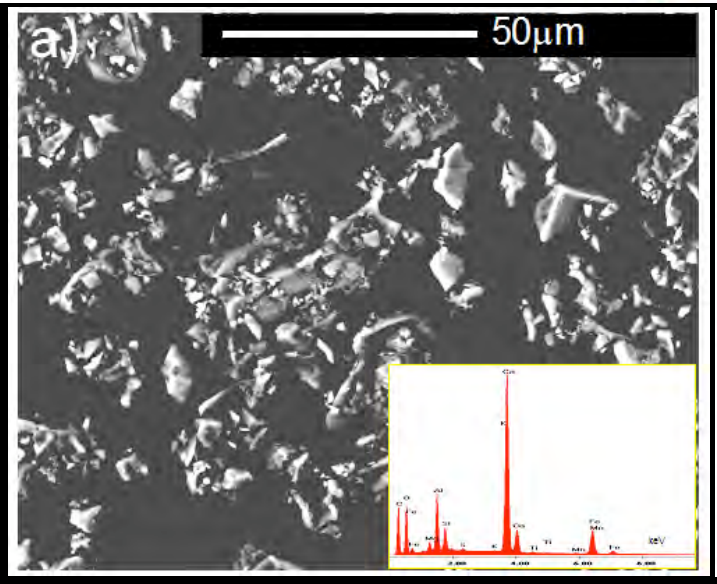
As Concentrations:
500-5000 mg/kg

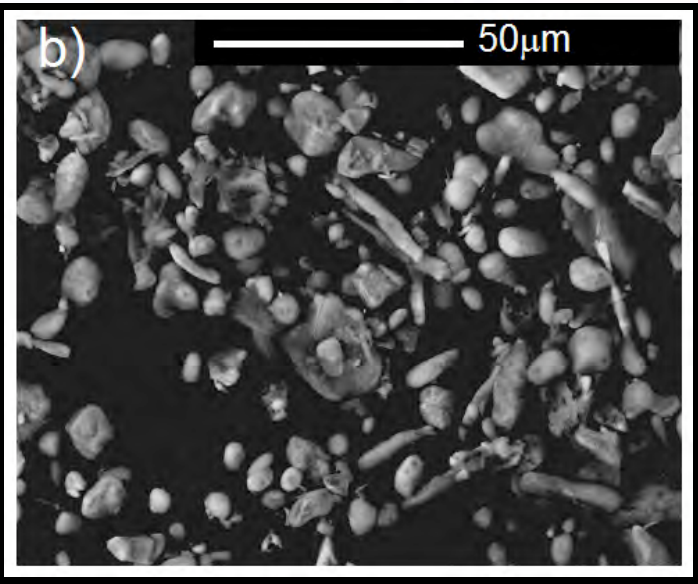
Treatments:
1992, 1996, 2000
1-9 m depth
surface capped

Microfocused Synchrotron XRD: Bay Road Field Samples



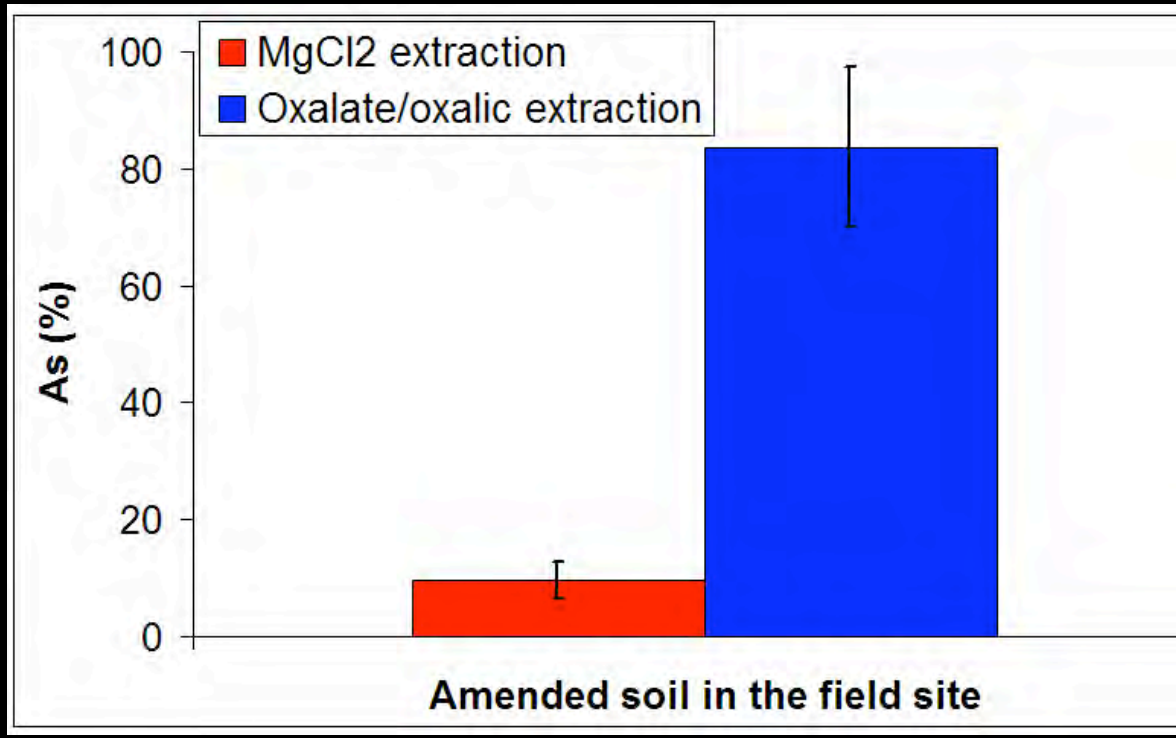
SEM

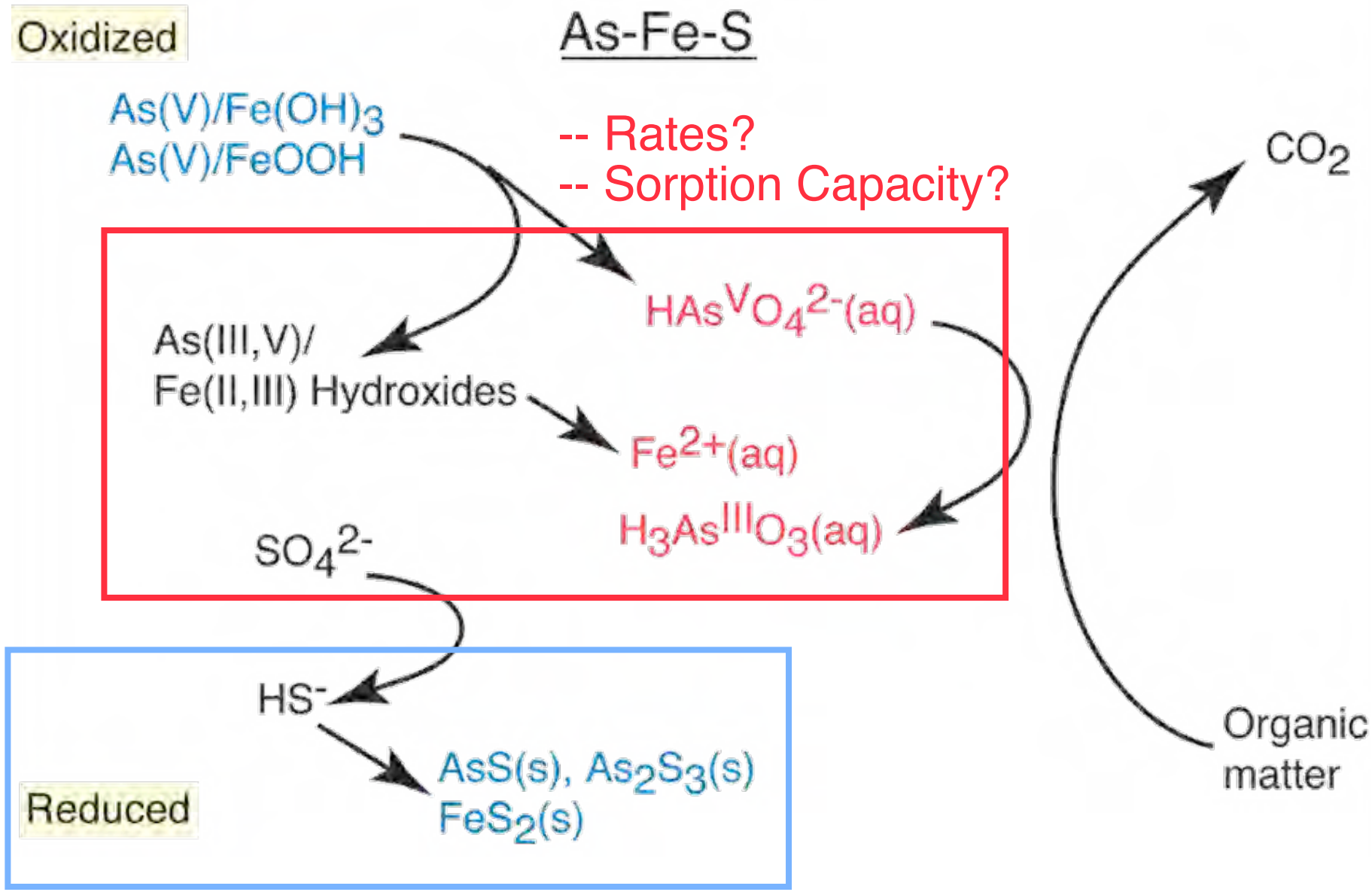




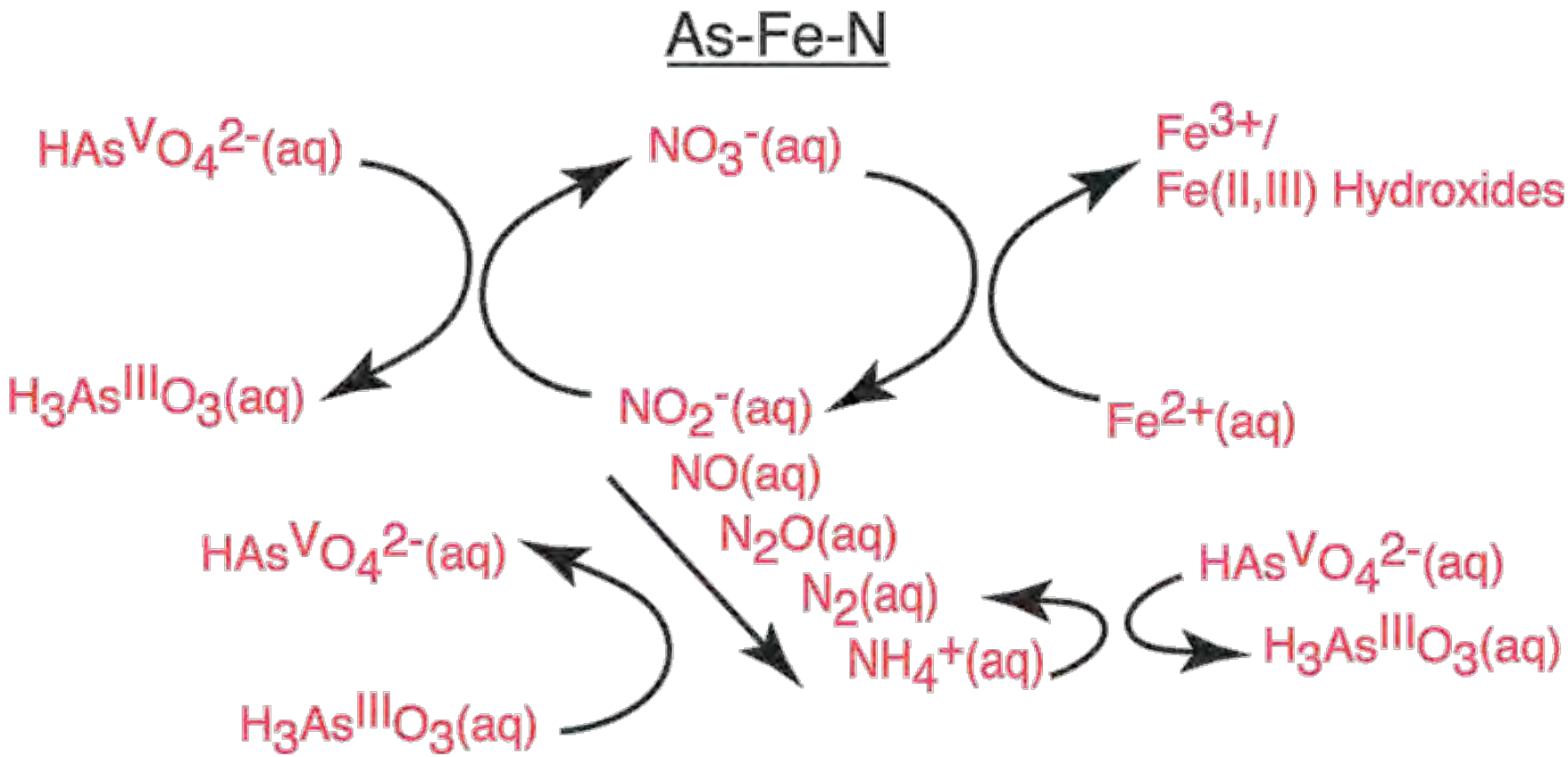
Soil Amendments for As Stabilization

- Arsenate incorporated into crystalline sulfate phases
- No evidence for reduction to As(III) after 10+ years
- High pH stabilized
- Aging process relatively rapid -- weeks? (experiments in progress)





-- Limited by rate of sulfate reduction


As-Fe-N
$HAs^{V}O_4^{2-}(aq)$
$NO_3^-(aq)$
Fe^{3+}/
Fe(II,III) Hydroxides
$H_3As^{III}O_3(aq)$
$NO_2^-(aq)$
$Fe^{2+}(aq)$
NO(aq)
$N_2O(aq)$
$HAs^{V}O_4^{2-}(aq)$
$N_2(aq)$
$HAs^{V}O_4^{2-}(aq)$
$NH_4^+(aq)$
$H_3As^{III}O_3(aq)$
$H_3As^{III}O_3(aq)$

Z=33

As

Atomic wt. 74.922

Assessing the Potential for Arsenic Mobilization

- Rates of reductive dissolution of Fe(III) and Fe(II,III) (hydr)oxides and potential release of sorbed As
- pH-dependent desorption and competitive effects (phosphate, sulfate, silica)
- Rates of sulfate reduction and production of As-bearing sulfides; rates of re-oxidation
- Influence of N species on As-Fe-S redox rates
- Cost/benefit of amendment stabilization
- Validation of reactive transport models: accurate coupling of biogeochemical and hydrologic processes