Arsenic in Groundwater Investigations – Eastern Slate Belt (ESB): Nash and Halifax Counties, North Carolina

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Overview of the Piedmont Aquifer System (courtesy of Pippin and Reid, 2005)

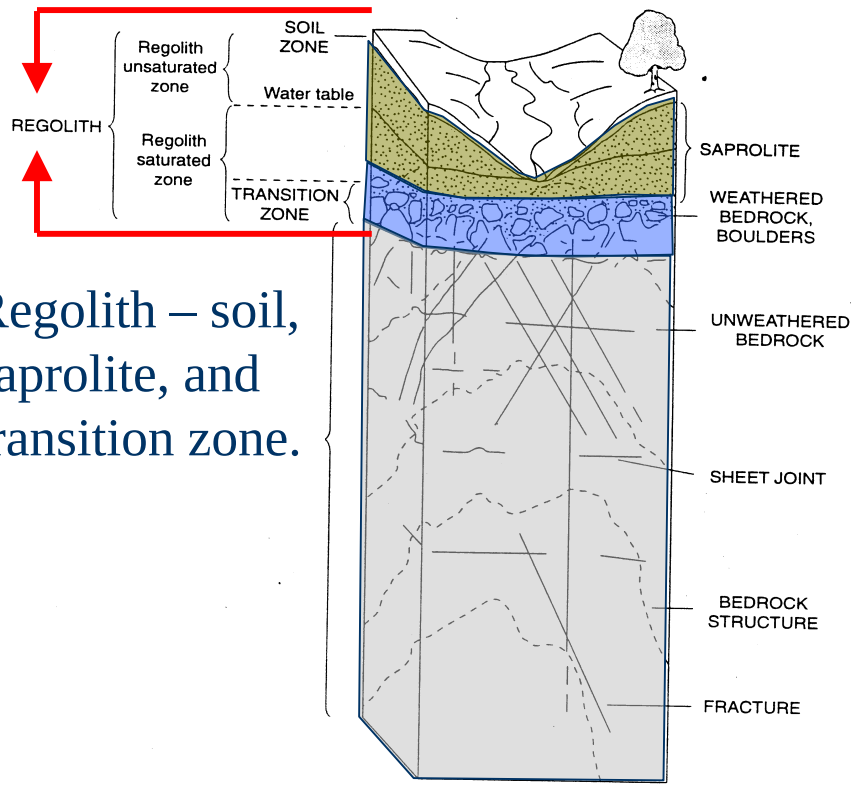


Figure 2. Principal components of the ground-water system in the Piedmont physiographic province of North Carolina (from Harned and Daniel, 1992).

Regolith – soil, saprolite, and transition zone.

Saprolite – Highly weathered parent material, often bears relict features such as primary rock textures.

Transition Zone – Weathering zone between saprolite and bedrock, generally more transmissive than the overlying saprolite zone.

Fractured Bedrock – Igneous or metamorphic rocks. Groundwater is transmitted to discharge areas or wells *via* fracture network. Highly transmissive, but little storage. Connectivity to overlying regolith determines available water.

Introduction

- Arsenic (As) is a known carcinogen
- Toxic to organs (intestines, kidneys, skin, lungs, bladder)
- Arsenic most toxic in reduced form (As +3)
- North Carolina developing As standards for groundwater
- Carolina Slate Belt Study (Reid, Pippin)
- Eastern Slate Belt (ESB) data gaps
- ESB geology
- “Initial Look”

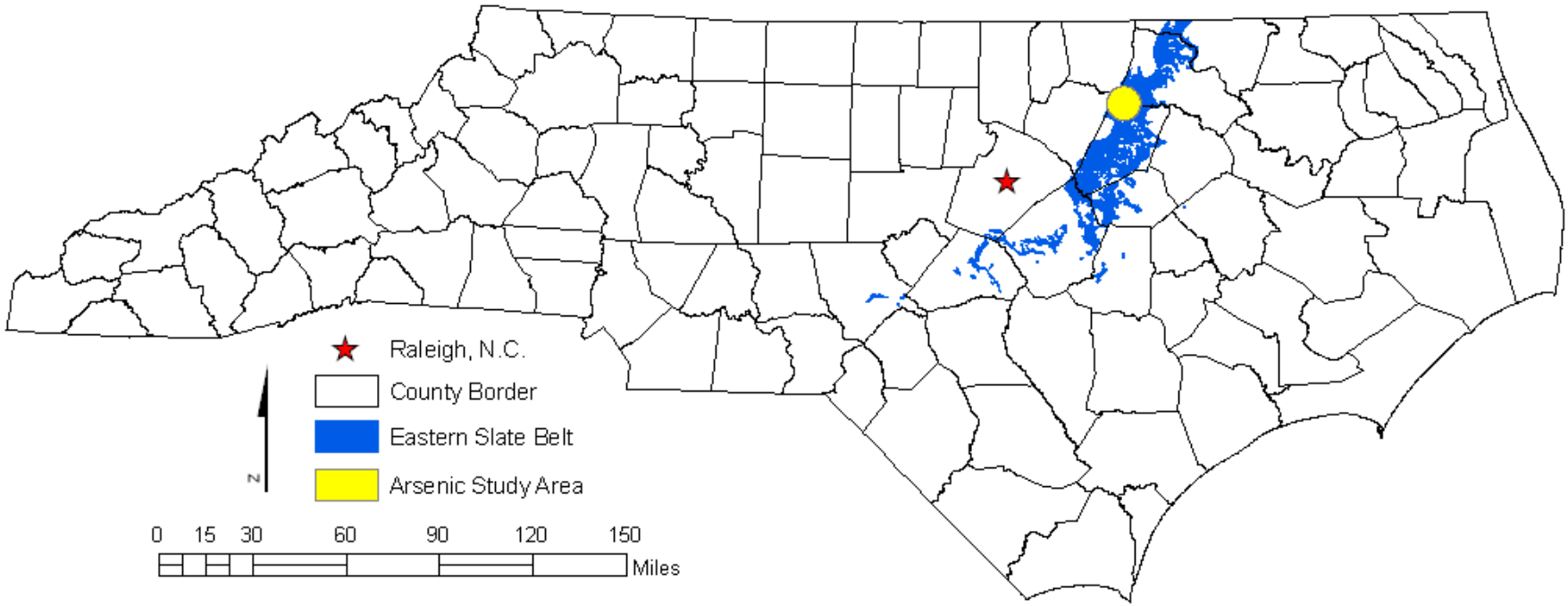
Arsenic standards

	US EPA (Max. Contam. Level)	North Carolina (health-based std)
Groundwater	10 ppb (MCL)	50 ppb (prev. 10 ppb) (revision pending)
Drinking Water	10 ppb (MCL)	10 ppb
Public Health	10 ppb (MCL) (treat-ability based)	0.02 ppb (Env. Comm. Proposed std.)

Scope and objectives

- First foray into the Eastern Slate Belt (ESB)
- Objective: determine if arsenic is present in ESB groundwater
- Collaborative project (continuing) between the NC Geological Survey and the NC Division of Water Quality
- Roughly one year initial study
- Cost maintenance!
- Basinwide Quality Planning and resolution with natural conditions

Location map



- Felsic, mafic, intermediate meta-volcanics
- Meta-mudstone, meta-argillite
- Quartz diorite

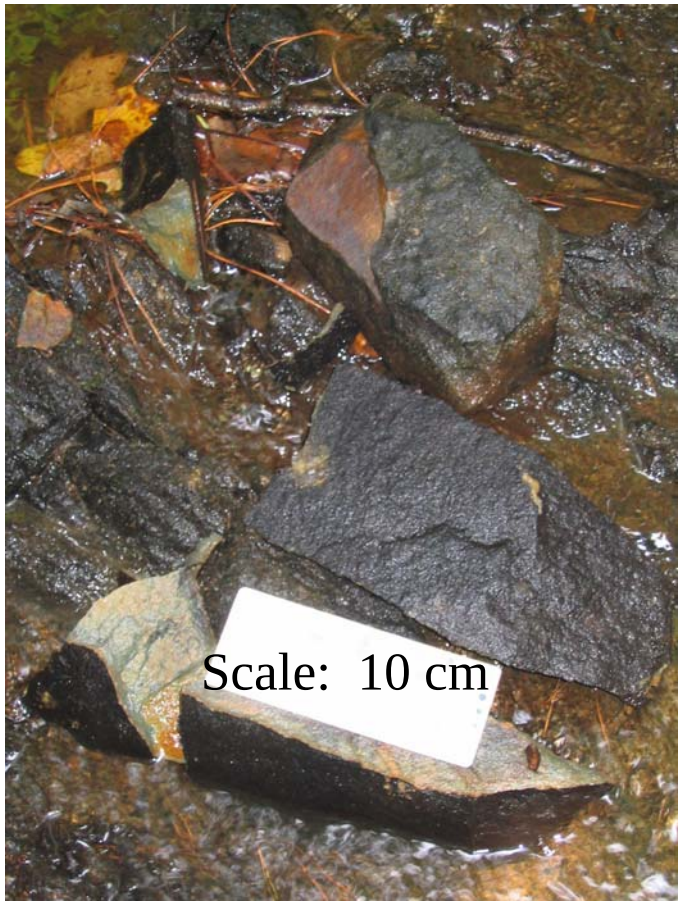
Site Selection Methods

- Old gold mines (gold/sulfide minerals occurrence)
- Ore dump sampling
- Biased sampling for As and sulfides

Site Selection:
Ore Dump Results

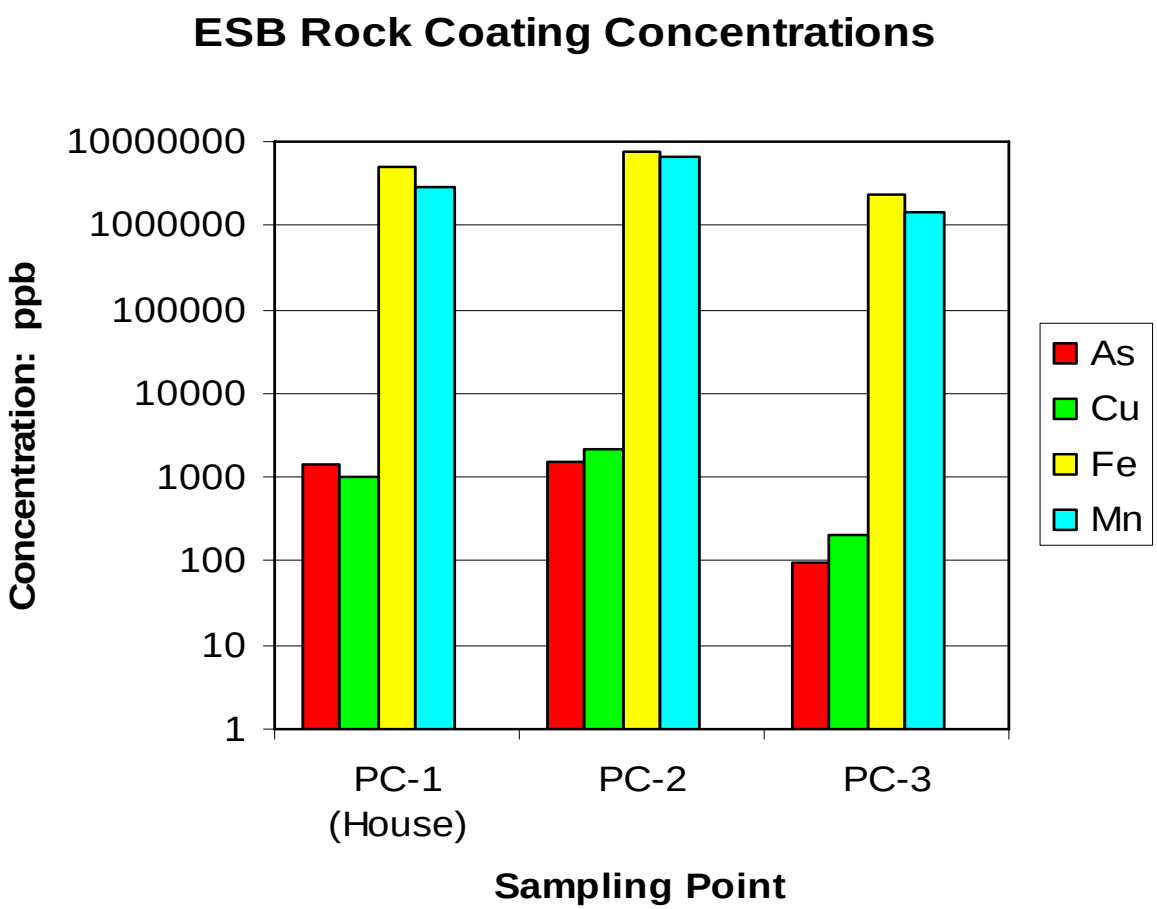
Rock Sample	Arsenic (ppm) (ICP)	Arsenic (ppm) (HAS)	Iron (ppm) (ICP)	Manganese (ppm) (ICP)
House-1 (Powell's Ck)	Not Detected	6.2	5.6	163
House-2 (Powell's Ck)	3.0	5.4	4.18	260
House-4 (Powell's Ck)	11.0	25.7	7.53	1140
House-5 (Powell's Ck)	Not Detected	1.8	7.01	1570

Site Selection Methods (continued)



Stream rock coating sampling

Site Selection: Rock Coating Results



- Not area-normalized
- "First look" results

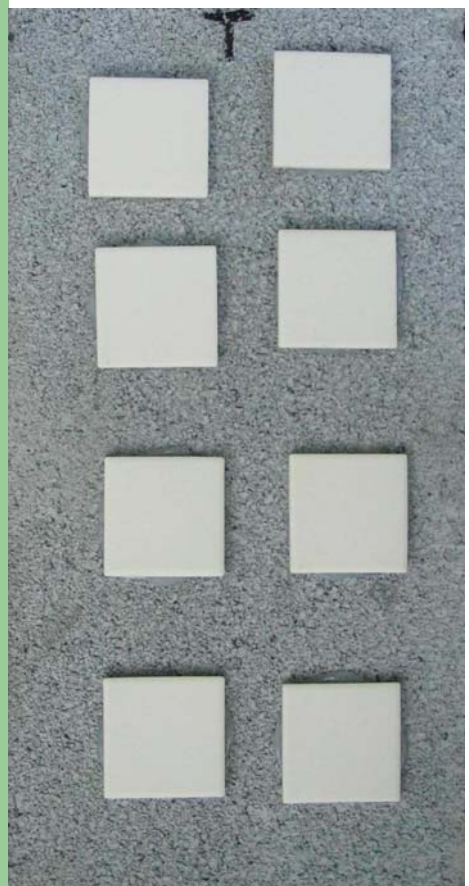
Site Selection Methods (continued)

- 1st and 2nd order streams
- Small basins – 2, 6, and 8 km^2
- "Natural" drainage basins
- Baseflow conditions
- No expected anthropomorphic contamination
- Overland flow minimal

Study Methods (~ seasonally)

- Stream conditions
  - pH, Eh, temperature
- Filtered water sampling

Study Methods (continued)

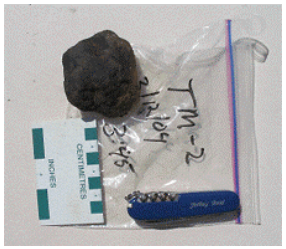


- Acid-cleaned ceramic tiles (~ 32.5 cm^2)
- Silicone caulked to cement block
- Placement into stream for oxide collection
- Induce Eh change

Study Methods (continued)

Tiles after deployment

Laboratory methods

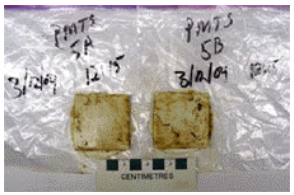


Coated 'boulder'

Nitric – hydrochloride extraction on heat plate

Mn-Fe coating extraction

(Left) Filtered and brought
Up to volume ➔
ICP analysis



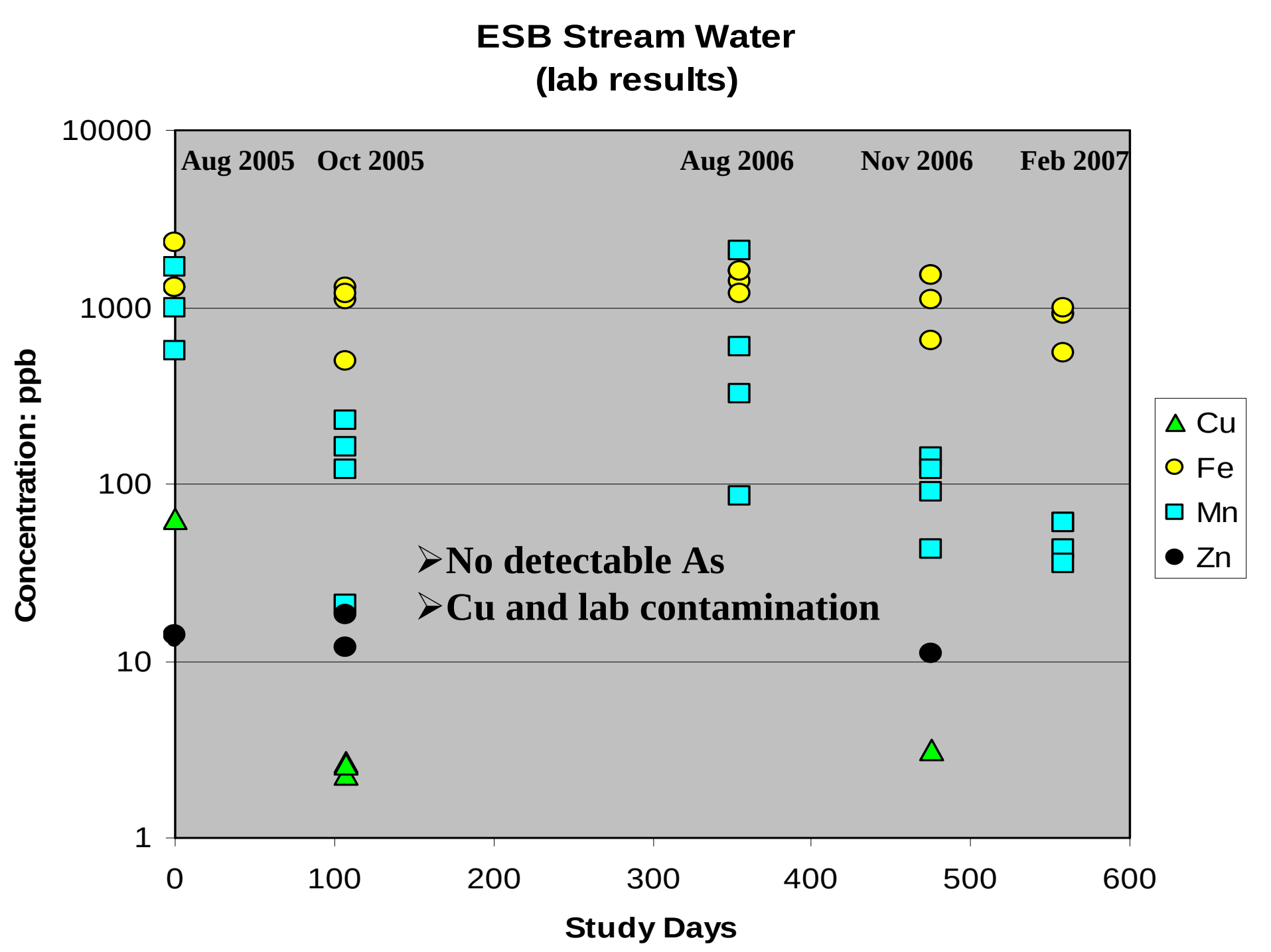
Coated streak plate
- one month

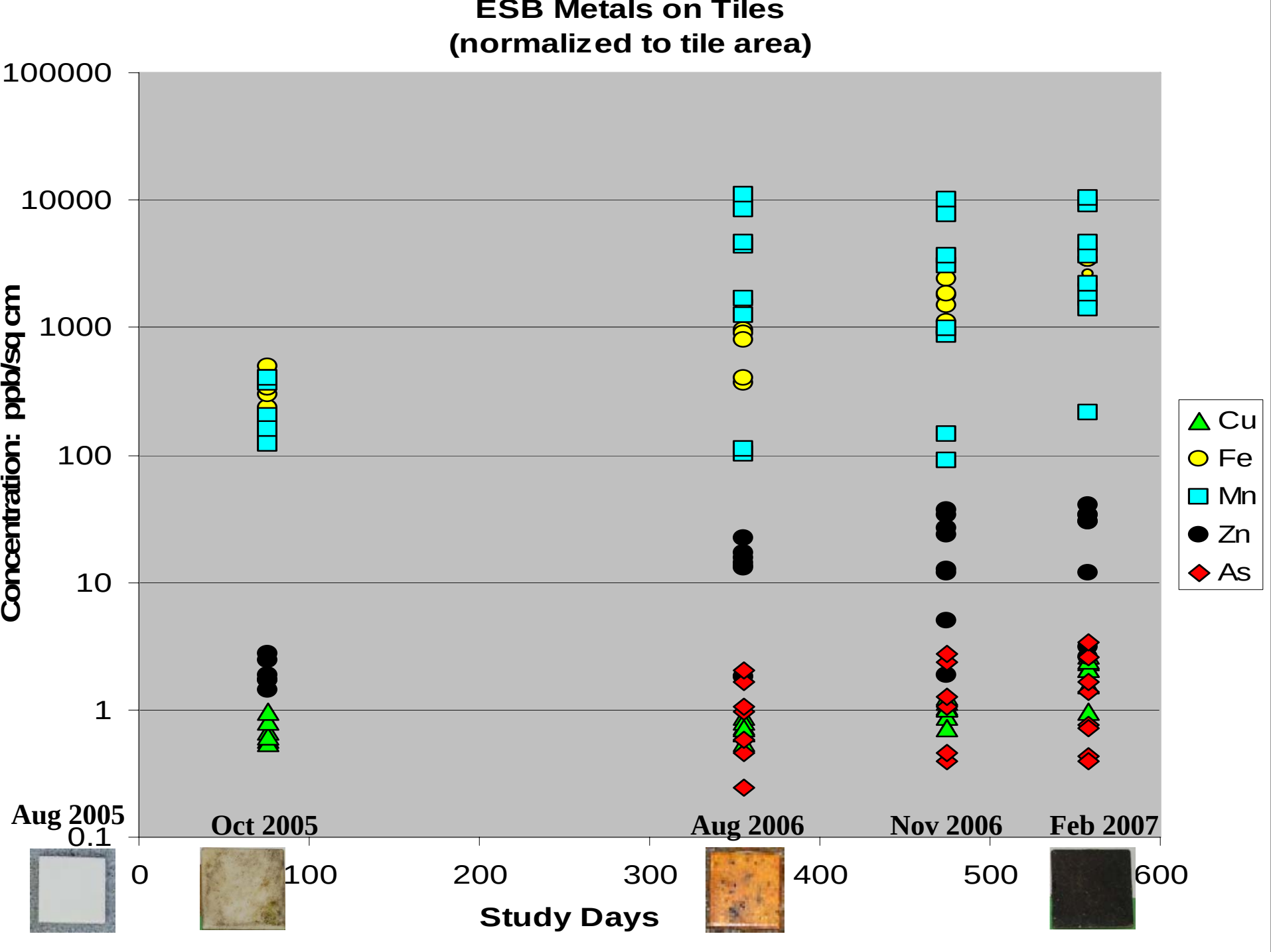
Coated streak plate
- one year

Process flow

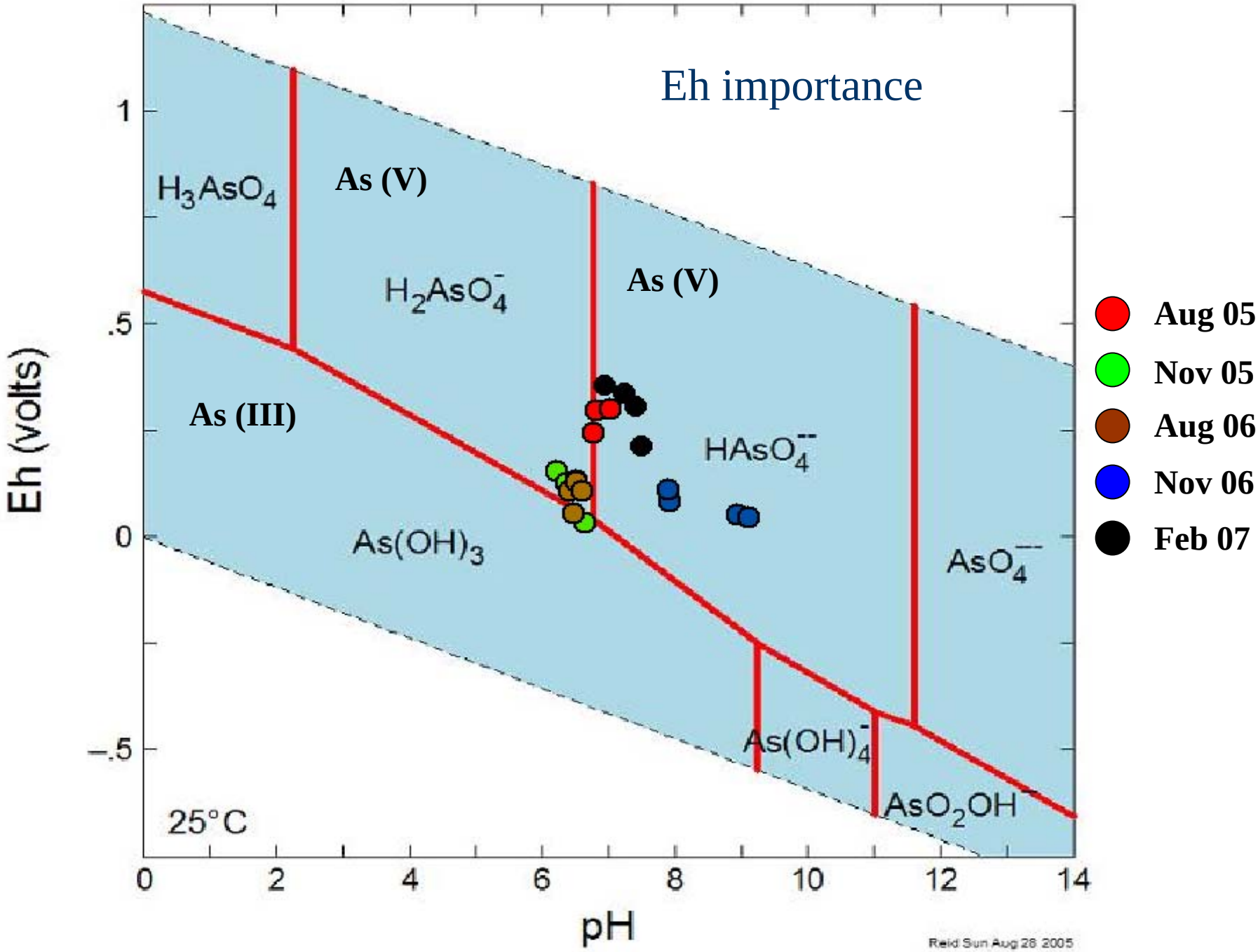
Post extraction –
streak plate (left)
- 'boulder' (above)

Analysis for
As, Cu, Fe,
Mn, Pb, Zn

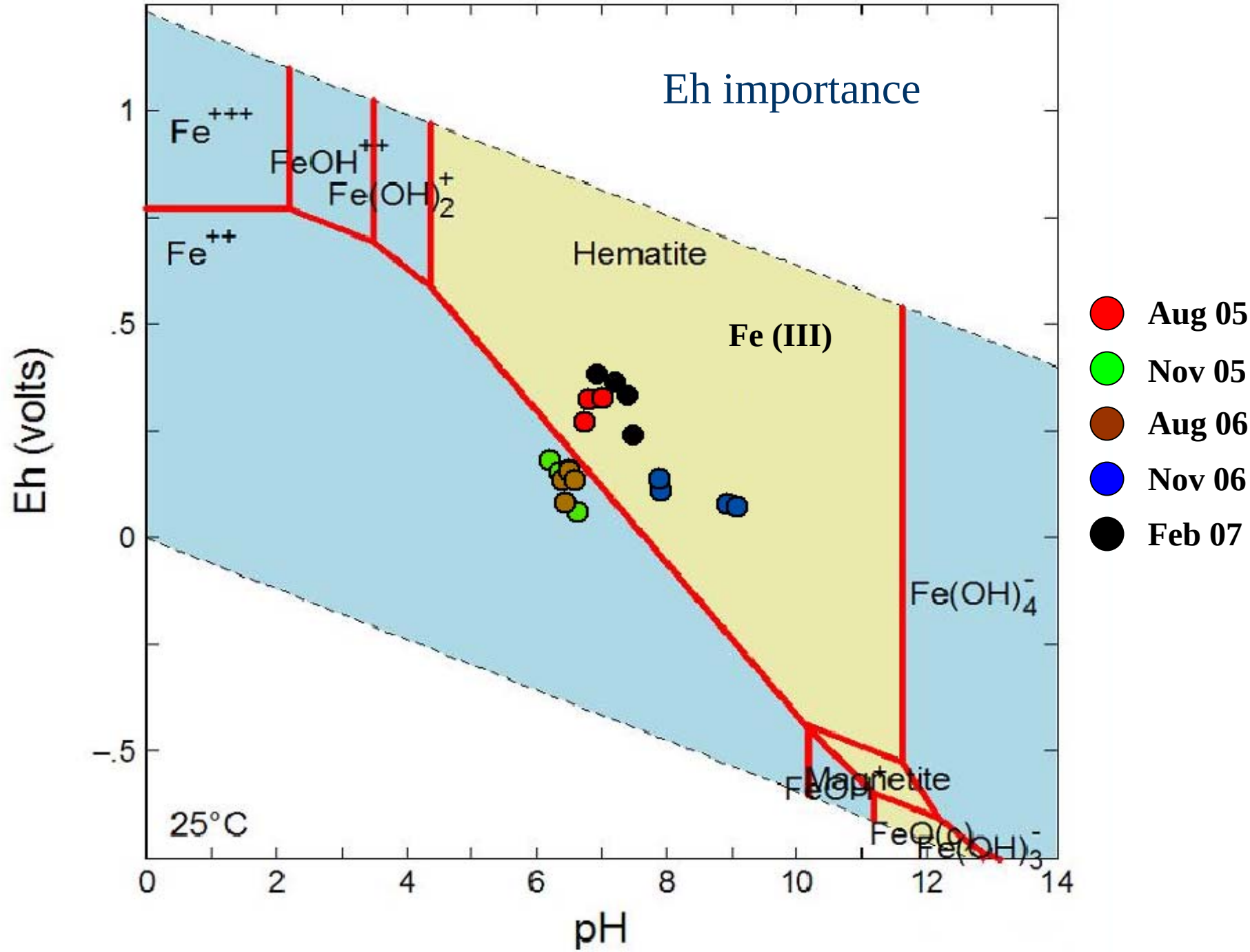

ESB Stream Water
(lab results)
10000
1000
100
10
1
Aug 2005
Oct 2005
Aug 2006
Nov 2006
Feb 2007
➢No detectable As
➢Cu and lab contamination
Concentration: ppb
0
100
200
300
400
500
600
Study Days
Cu
Fe
Mn
Zn


ESB Metals on Tiles
(normalized to tile area)
Concentration: ppb/sq cm
100000
10000
1000
100
10
1
0.1
Aug 2005
Oct 2005
Aug 2006
Nov 2006
Feb 2007
0
100
200
300
400
500
600
Study Days
Cu
Fe
Mn
Zn
As

Eh importance



- Aug 05
- Nov 05
- Aug 06
- Nov 06
- Feb 07

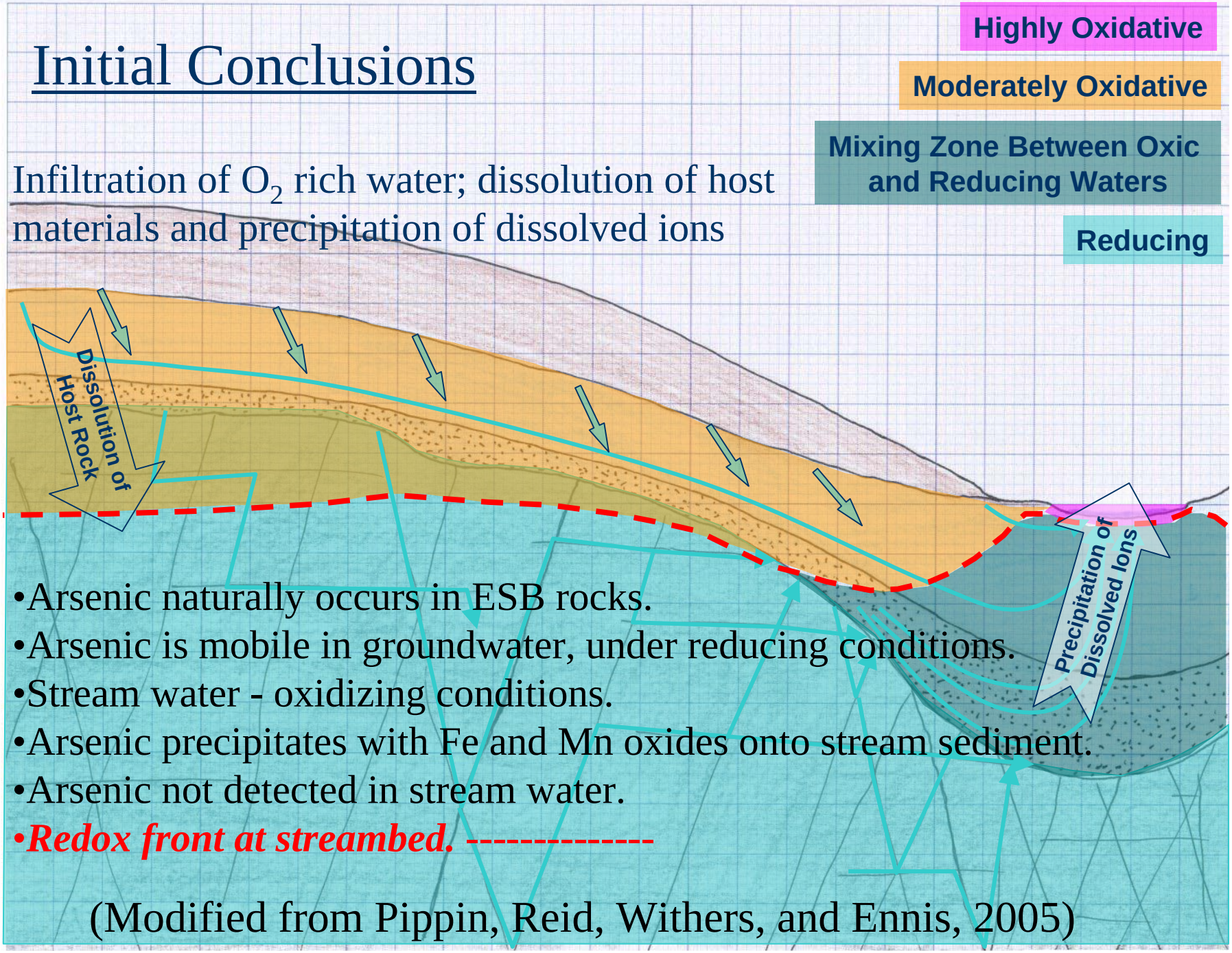

Eh importance
Fe+++
FeOH++
Fe(OH)2+
Fe++
Hematite
Fe (III)
Fe(OH)4-
Magnetite
FeO(c)
Fe(OH)3-
25°C
Eh (volts)
pH
1
.5
0
−.5
0
2
4
6
8
10
12
14
Aug 05
Nov 05
Aug 06
Nov 06
Feb 07

Initial Conclusions

- Arsenic is present in Eastern Slate Belt (ESB) rocks
- Arsenic is present in ESB stream sediment coatings
- Arsenic is not found above detection limits in ESB stream water
- Unglazed streak plates accumulate arsenic and provide insight into arsenic precipitation onto stream sediment
- Analysis of tile and rock coatings is a cost-effective method for determining arsenic occurrence
- Eh more important than pH
- ESB stream water has minor concentrations of base metals (iron, manganese) compared to rock and tile coatings

Initial Conclusions

Infiltration of O_2 rich water; dissolution of host materials and precipitation of dissolved ions



- Arsenic naturally occurs in ESB rocks.
- Arsenic is mobile in groundwater, under reducing conditions.
- Stream water - oxidizing conditions.
- Arsenic precipitates with Fe and Mn oxides onto stream sediment.
- Arsenic not detected in stream water.
- ***Redox front at streambed.*** ----------

(Modified from Pippin, Reid, Withers, and Ennis, 2005)

Future Plans

- Groundwater Sampling
  - Monitoring Wells
  - Residential Supply Wells
- Rock Coring & Sampling
- Impact on Benthic Biota and Basinwide Studies
- Notification of local population & well testing recommendations

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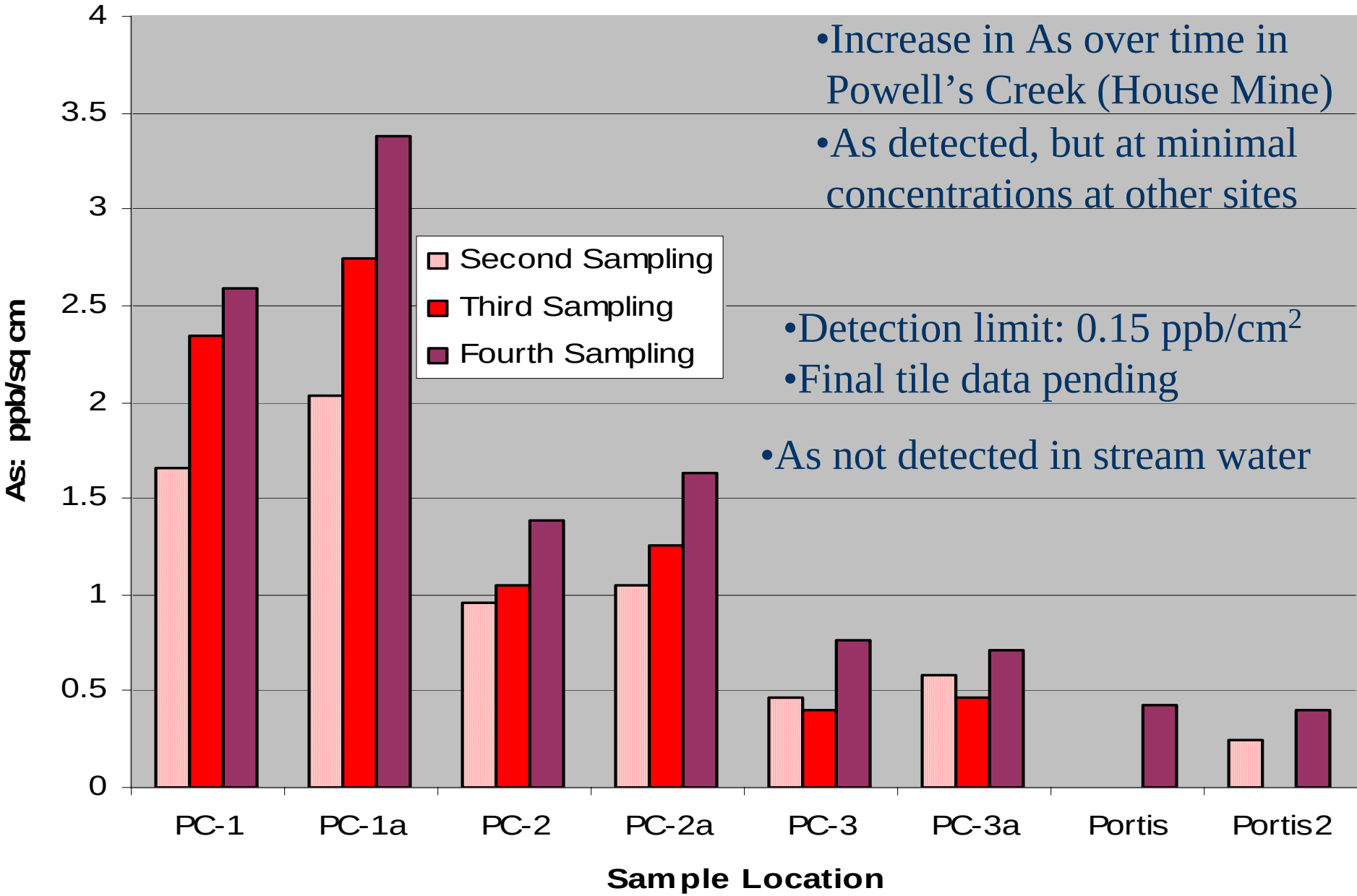
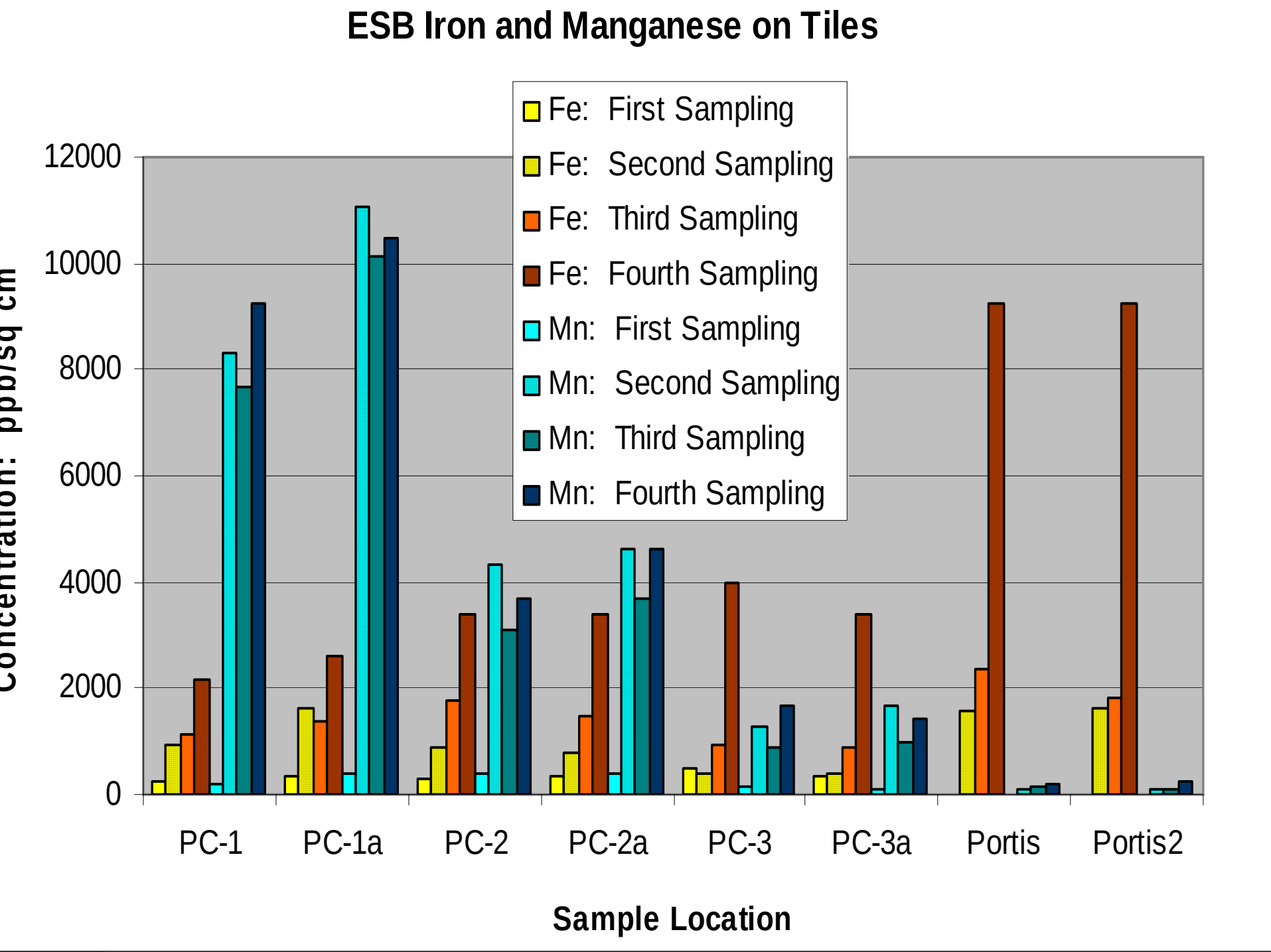
Supplementary data

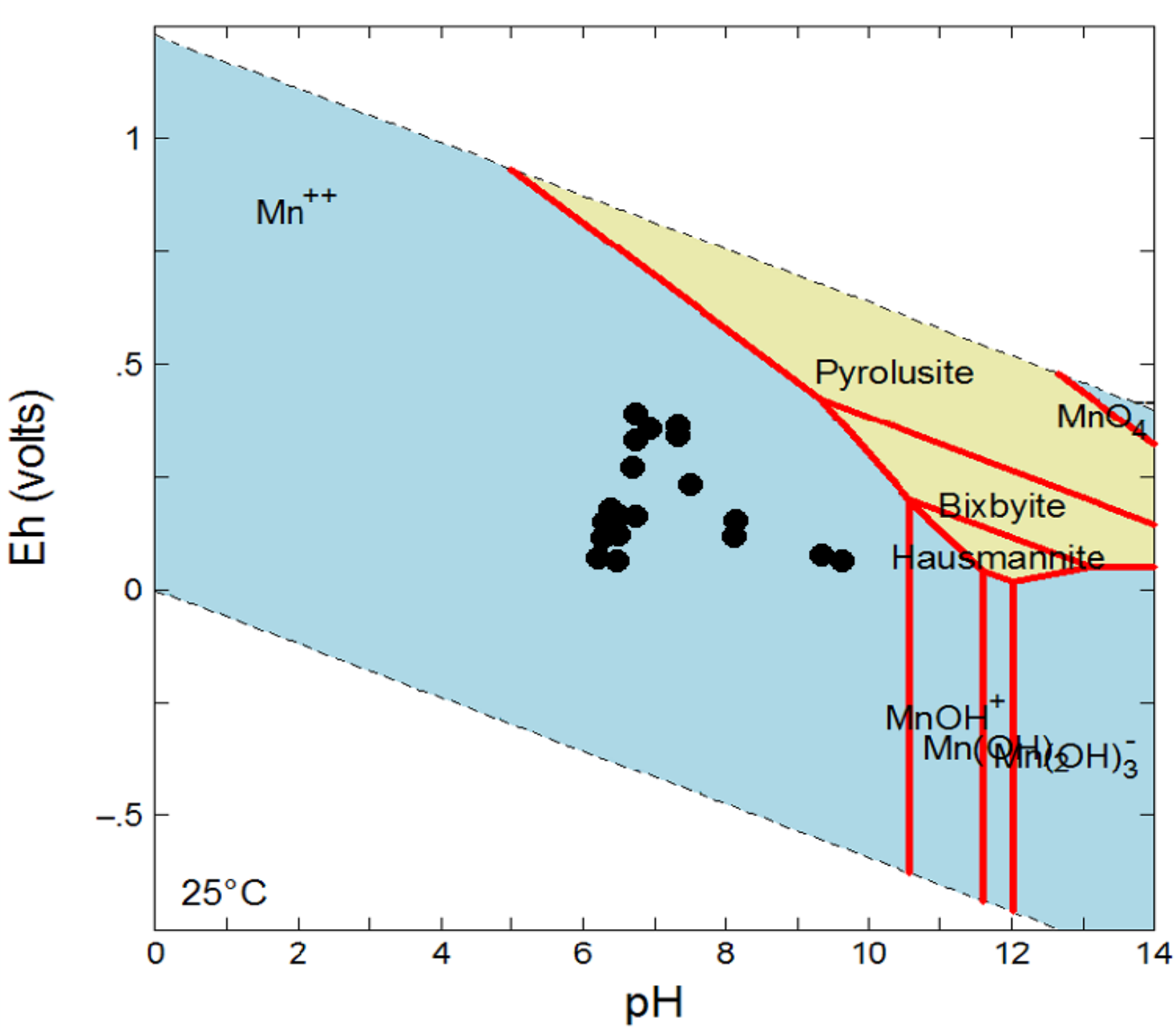
- As tile plots
- Mn and Fe tile plots
- Mn phase diagram
- Eh and pH plots

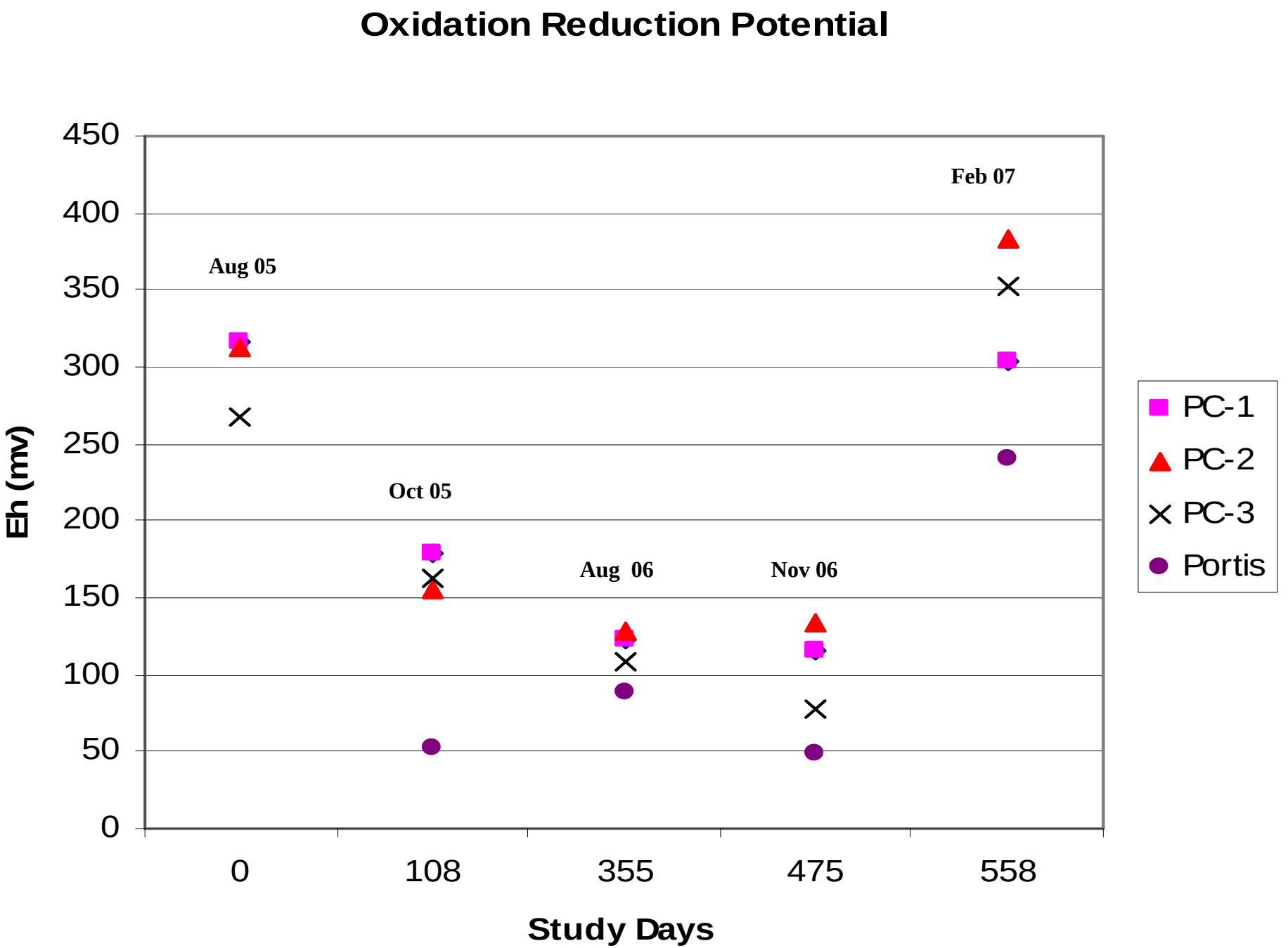
ESB Arsenic Accumulation on Tiles

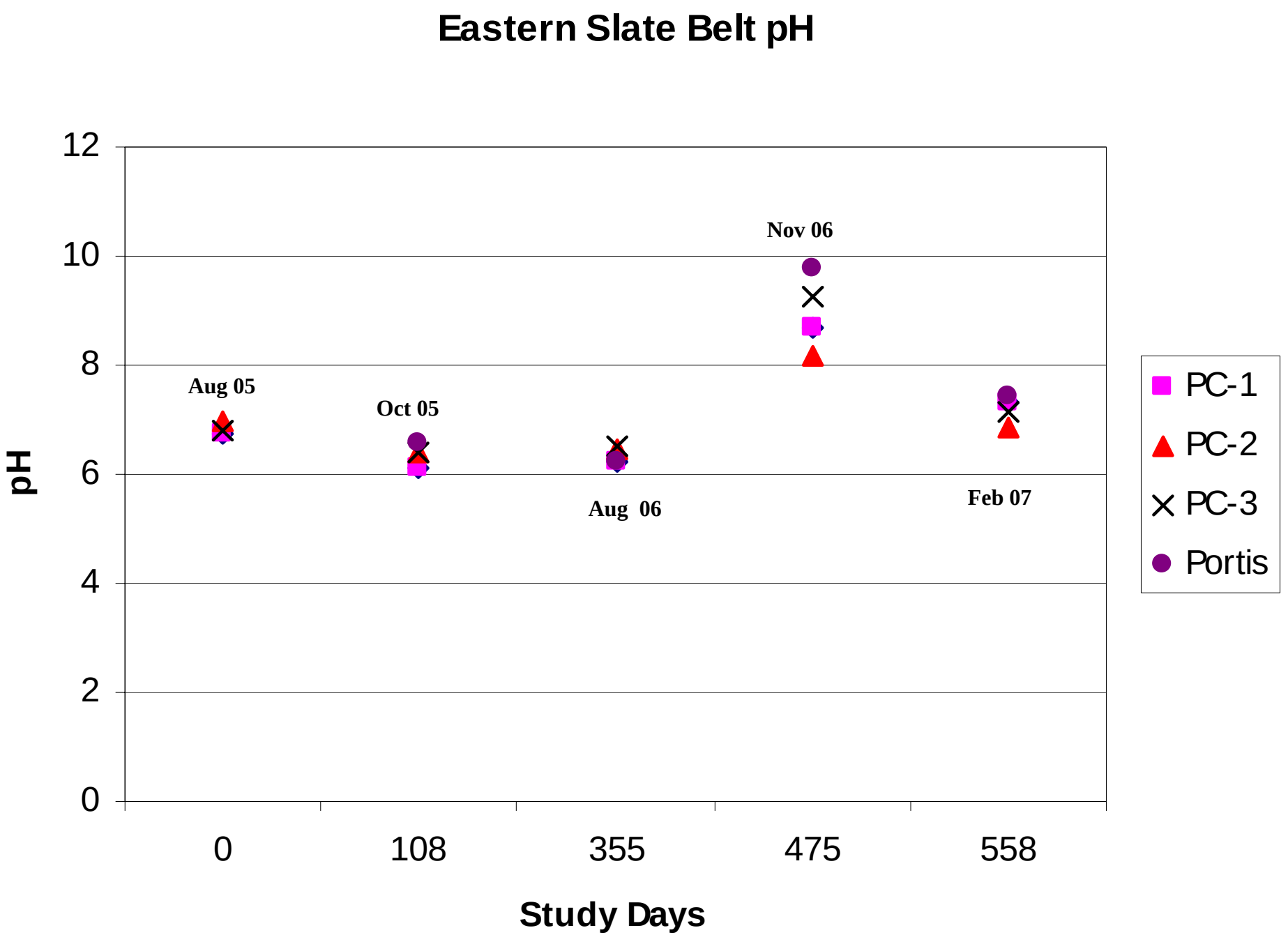


- Increase in As over time in Powell's Creek (House Mine)
- As detected, but at minimal concentrations at other sites
- Detection limit: 0.15 ppb/cm^2
- Final tile data pending
- As not detected in stream water


ESB Iron and Manganese on Tiles
Fe: First Sampling
Fe: Second Sampling
Fe: Third Sampling
Fe: Fourth Sampling
Mn: First Sampling
Mn: Second Sampling
Mn: Third Sampling
Mn: Fourth Sampling
12000
10000
8000
6000
4000
2000
0
Concentration: ppb/sq cm
PC-1
PC-1a
PC-2
PC-2a
PC-3
PC-3a
Portis
Portis2
Sample Location


Mn++
Pyrolusite
MnO4
Bixbyite
Hausmannite
MnOH+
Mn(OH)2
Mn2(OH)3-
25°C
Eh (volts)
pH
1
.5
0
–.5
0
2
4
6
8
10
12
14


Oxidation Reduction Potential
Eh (mv)
450
400
350
300
250
200
150
100
50
0
Aug 05
Oct 05
Aug 06
Nov 06
Feb 07
0
108
355
475
558
Study Days
PC-1
PC-2
PC-3
Portis


Eastern Slate Belt pH
12
10
8
6
4
2
0
pH
Aug 05
Oct 05
Aug 06
Nov 06
Feb 07
0
108
355
475
558
Study Days
PC-1
PC-2
PC-3
Portis