Southern Illinois University

CARBONDALE

ILLINOIS DEPARTMENT OF NATURAL RESOURCES

# Remediation of Acid Mine Drainage using a Sulfate-reducing Bioreactor at the Tab-Simco Passive Treatment System – An Update[1]

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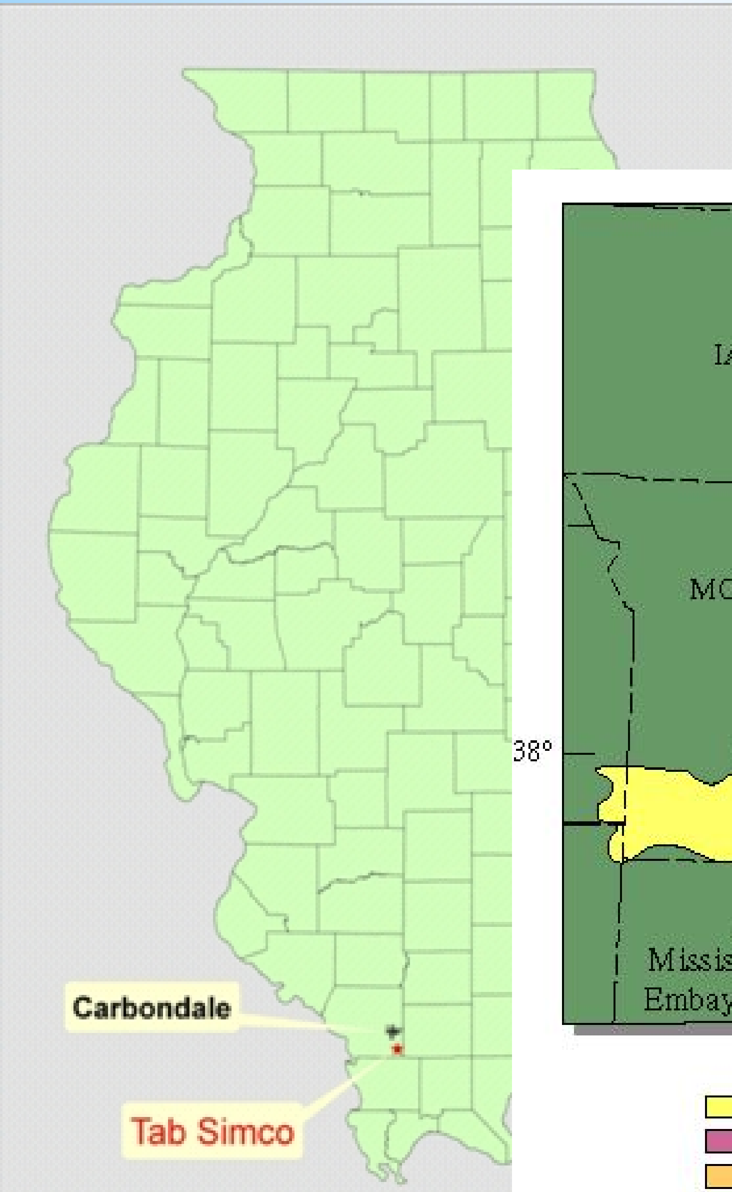
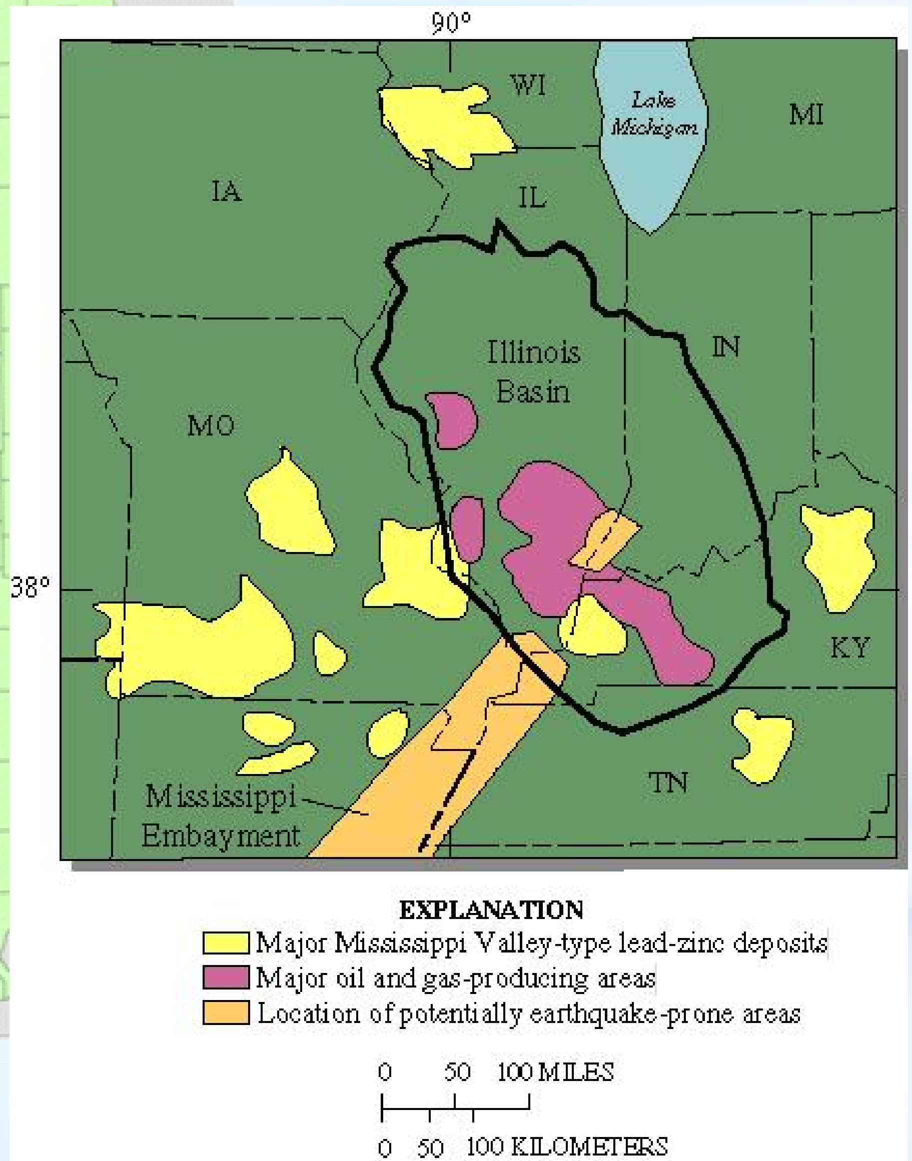
# Case Example Site Location




Tab-Simco Site Map Location.

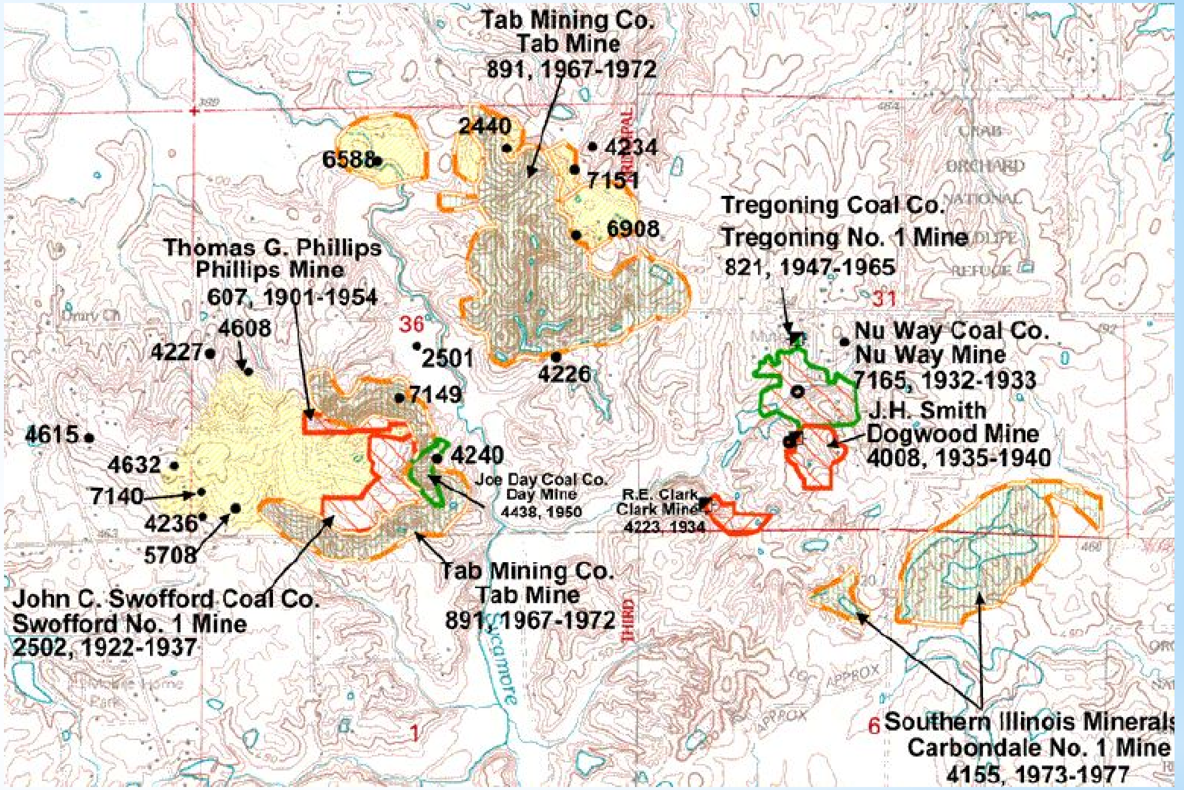



Source: U.S. Geological Survey

Tab-Simco is an abandoned coal mine located in the Illinois Basin 3.2 km southeast of Carbondale, Illinois, USA.

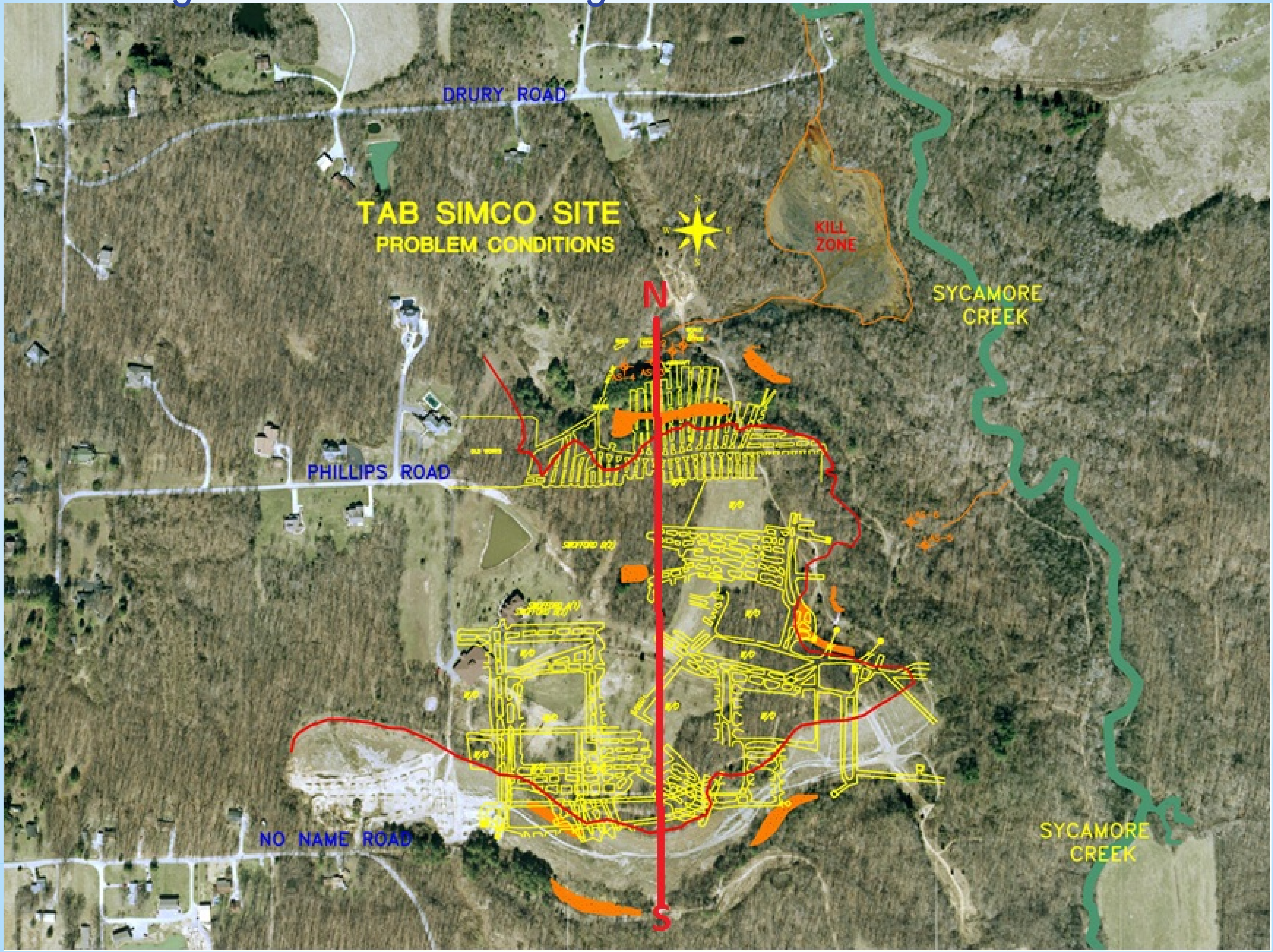
# Background: Coal Mining History

- Underground Mining: Between the 1890's and 1955 mined the 2.5 m (8.2 ft.) thick Murphysboro Coal and the overlying 0 - 1.5 m (4.9 ft) thick Mt. Rorah Coal.
- Surface Mining: Contour-type surface mining occurred 1967 - 1972 by Tab Mining Co. (Tab) and 1973 - 1977 by the Southern Illinois Minerals Co.(SIMCO).
- The horseshoe-shaped strip area removed coal from the outcrop barrier and "daylighted" some of the old underground workings.



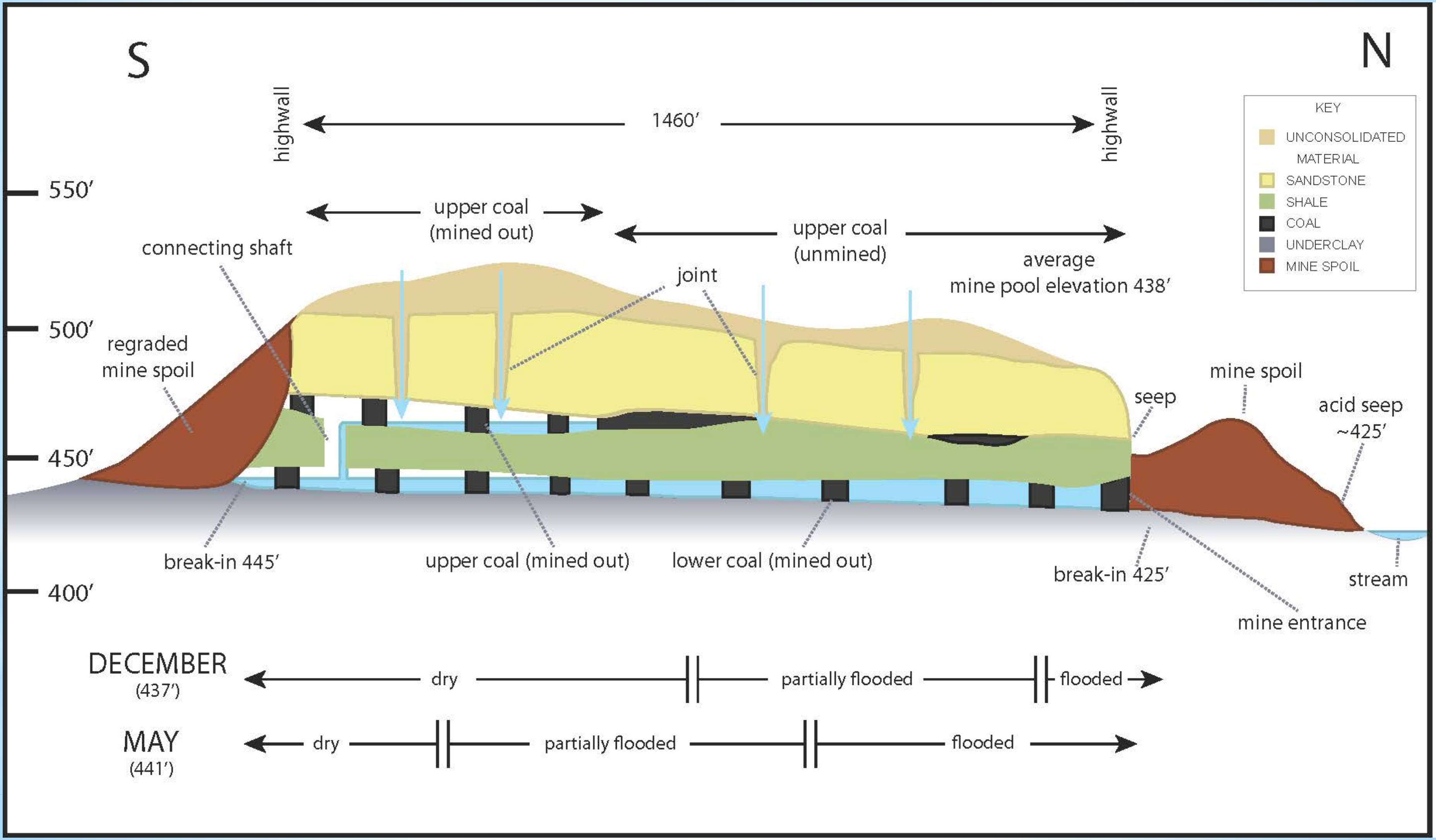

Murphysboro Seam Coal Mines

# Underground Mine Workings – Location of Cross Section




Source: J. Nawrot, SIUC, Personal Communication, 2005.

# Mine Pool and Main Acid Seep




Source: Modified from Smith, 2004.

# *Tab-Simco Problem Identification:

- *Mine Pool: The old underground workings are partially flooded with seasonal fluctuations and contains **40,000 - 77,000 $m^3$ (10.6 - 20.3 million gallons)** of acidic, metal-laden water (Smith, 2004).
- *Acid Seeps: North Seep at **1.2 LPS (19 GPM) with pH= 2.4;** total acidity = **1,816 mg/L CCE** (median values).
- *Kill Zone: **3.7-ha (9-acre)** area was devoid of vegetation and covered with acid salts.
- *Sycamore Creek: **3.2 km (2 miles)** were impacted with acidic water and metal precipitates.

# *Acid Seeps

Flow = 1.2 liters per second (19 gpm)

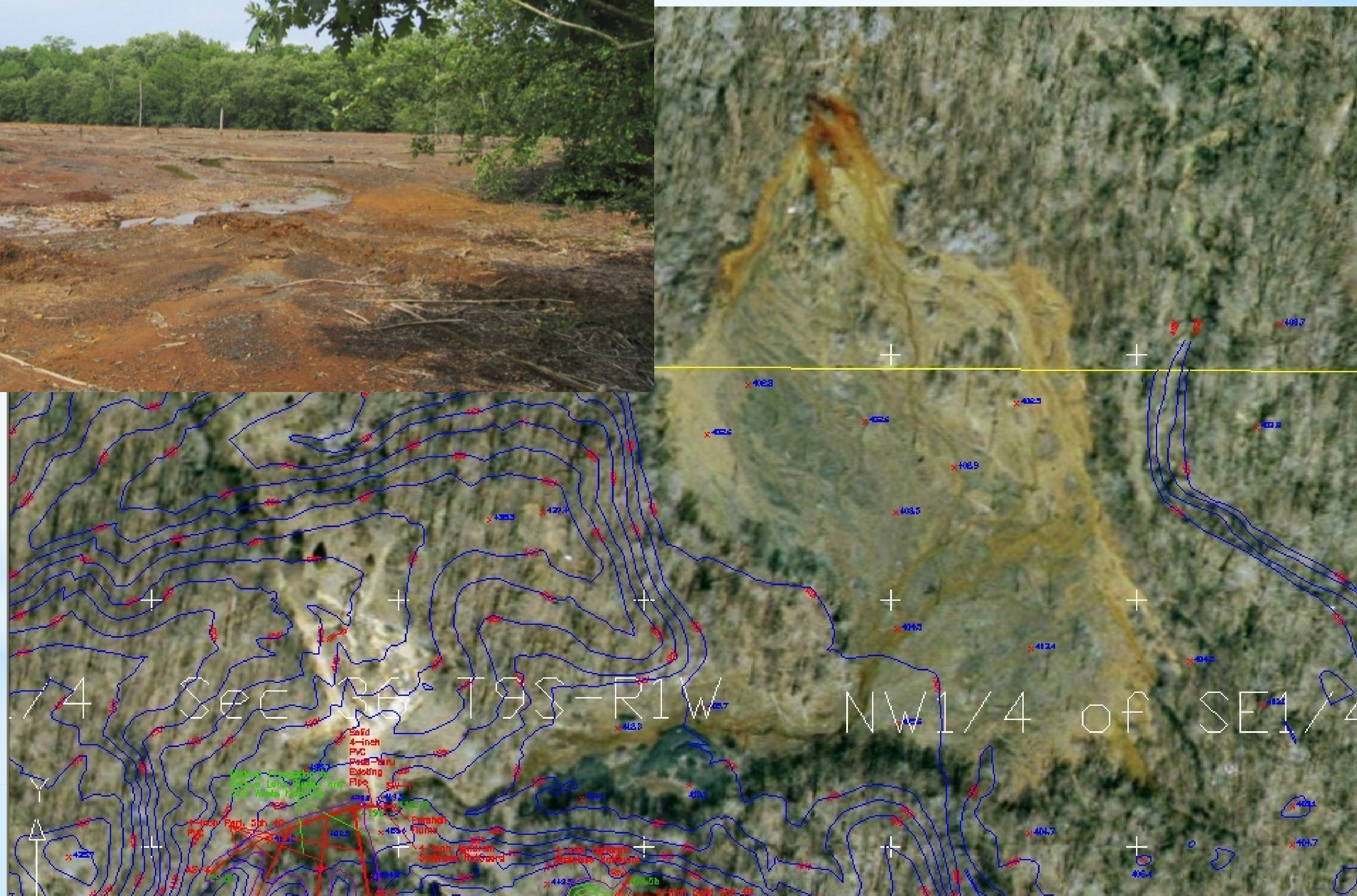
## Baseline Data:

### North Seep

| Parameter | Value* (median) | Units |
|---|---|---|
| pH | **2.40** | |
| SpCon | **3,645** | *u*S/cm |
| D. Fe. | **389.3** | mg/L |
| D. Al | **123.2** | mg/L |
| Tot. Mn | **27.9** | mg/L |
| Tot. Acidity | **1,631** | mg/L CCE |
| Sulfate | **2,188** | mg/L |

* Number of samples (n) = 8.

# Problem ID: 3.7-ha (9-acre) "Kill Zone"



# *Sycamore Creek Impacts

Sycamore Creek prior to passive treatment system construction.

**Downstream Sample Site**

| Parameter | Value* (low flow) |
|---|---|
| pH | 2.92 |
| SpCon | 2,350 |
| Tot. Fe. | 109.0 |
| Tot. Al | 56.6 |
| Tot. Mn | 28.9 |
| Tot. Acidity | 705.97 |

* October 26, 2005

# Timeline: AMD remediation at the Tab-Simco Mine

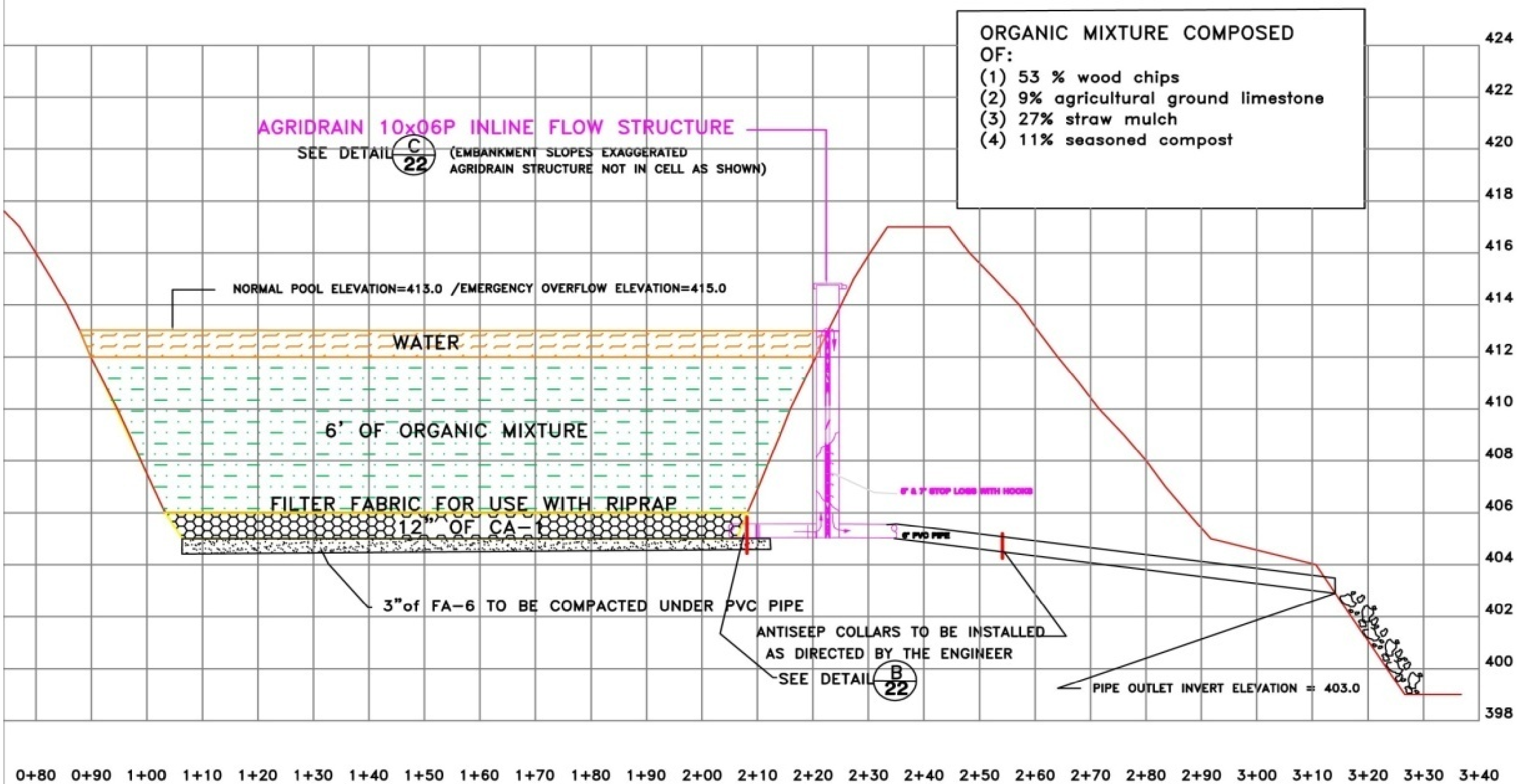
Collection of mine pool elevation data.

* 2005-2007: Site investigation and design OMM/OSM/SIUC.
* 2007: Passive treatment system designed, bid and constructed.
* 2008 - Present: Post-construction evaluation.
* 2012- 2014: Research by OSM-SIUC cooperative agreement.
* Fall 2013: Replacement of bioreactor compost.

# * Selected Solution: AMD Passive Treatment System

* Stage 1: 0.3-ha (0.75-acre) Sulfate Reducing Bioreactor – Lower sulfate, iron, and aluminum concentrations add alkalinity and increase pH.
* Stage 2: Deep Oxidation Pond – Oxidize remaining ferrous iron and store iron precipitates.
* Stage 3: Surface Flow Wetlands - Complete iron oxidation and precipitation.
* Stage 4: Open Limestone Drain – Aerate discharge and lower manganese levels.

# Tab-Simco Bioreactor Construction



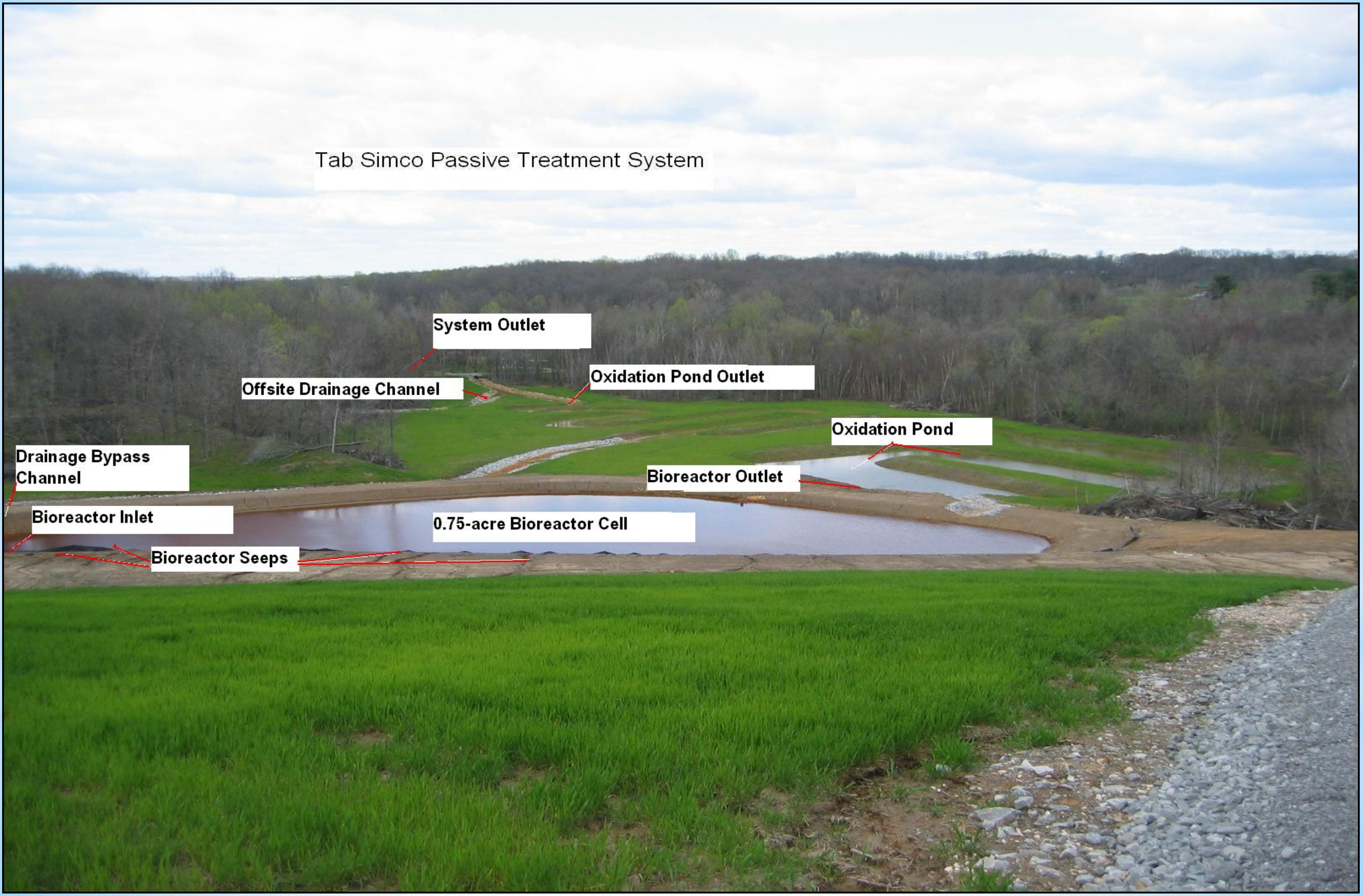

B/23 TYPICAL SECTION THROUGH ANEROBIC BIOREACTOR CELL

# *2007 Bioreactor Construction

Under Drain Construction: Rip-rap is shoreline wave erosion protection.


Compost Placement:
5,887 $m^3$ (7,700 CY)

# * Tab-Simco AMD Passive Treatment System




Overview of the Passive Treatment System looking North from the edge of the

# * Stage 1: Sulfate Reducing Bioreactor

* Reduce sulfate and iron; add bicarbonate ($HCO_3^-$) alkalinity – The principle processes are:
  * **Anaerobic microbial sulfate reduction ($CH_2O$ representing biodegradable organic compounds).**

$$2\ CH_2O + SO_4^{2-} \rightarrow H_2S + 2\ HCO_3^-$$

  * **Limestone dissolution.**

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$$

* Bicarbonate neutralizes the acidity--raising pH and increasing the precipitation of metals such as Fe and Al.

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2(aq)$$

# * Stage 1: Sulfate Reducing Bioreactor - Metal removal processes.

* Hydrogen sulfide readily dissolves in water and combines with metals (Me), such as Fe, Ni, and Zn, to form sulfide mineral precipitates MeS according to the following reaction:

$$H_2S_{(aq)} + Me^{2+} \quad MeS_{(s)} + 2\ H^+$$

* Adsorption of metals on clay minerals, metal hydroxides and organic matter within the bioreactor.
* Cation exchange reactions.

# Sequestration of Metals: Iron and Trace Metals?

Discharge of suspected Fe mono-sulfides from the bioreactor; possible reaction within pond sediment:

$$FeS^* + S \rightarrow FeS_2$$

(iron mono-sulfide) (pyrite)

*Intermediate precursors such as:

Mackinawite [$(FeNi)_{1+x}S$]

(where x = 0 - 0.11)

Greigite [$Fe(II)Fe(III)_2S_4$]

Discharge from the Tab Simco Bioreactor in 2008

# * Stage 2: Deep Oxidation Pond and Stage 3: Surface Flow Wetlands

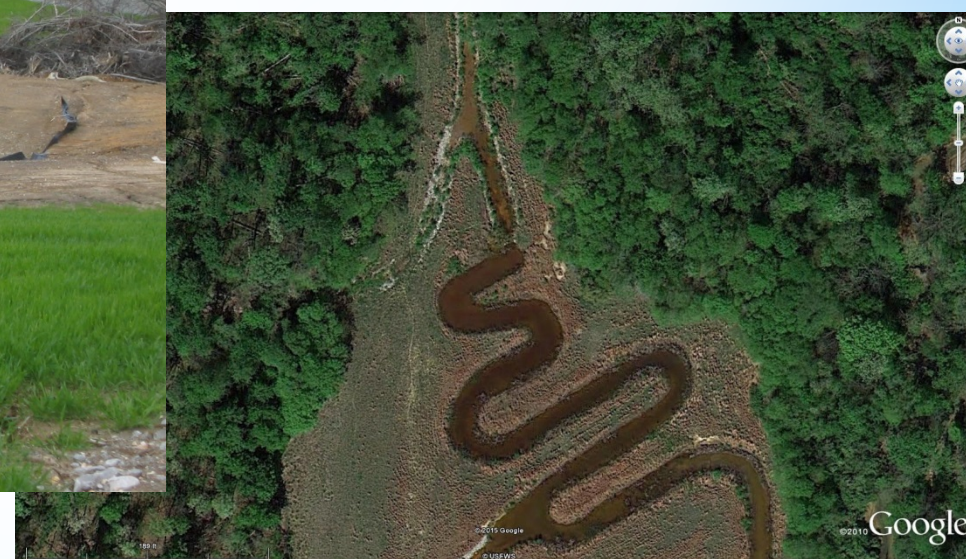
Oxidize remaining ferrous iron -- and manganese?

Store metal precipitates.

Possible Reactions:

$Fe^{+2} + 3\ H_20 \rightarrow Fe(OH)_3 + 3H^+$

$4\ Fe^{+2} + O_{2\ (aq)} + 10\ H_20 \rightarrow$
$4\ Fe(OH)_3 + 8H^+$



# Unplanned Pre-treatment: Low-pH Fe Oxidation

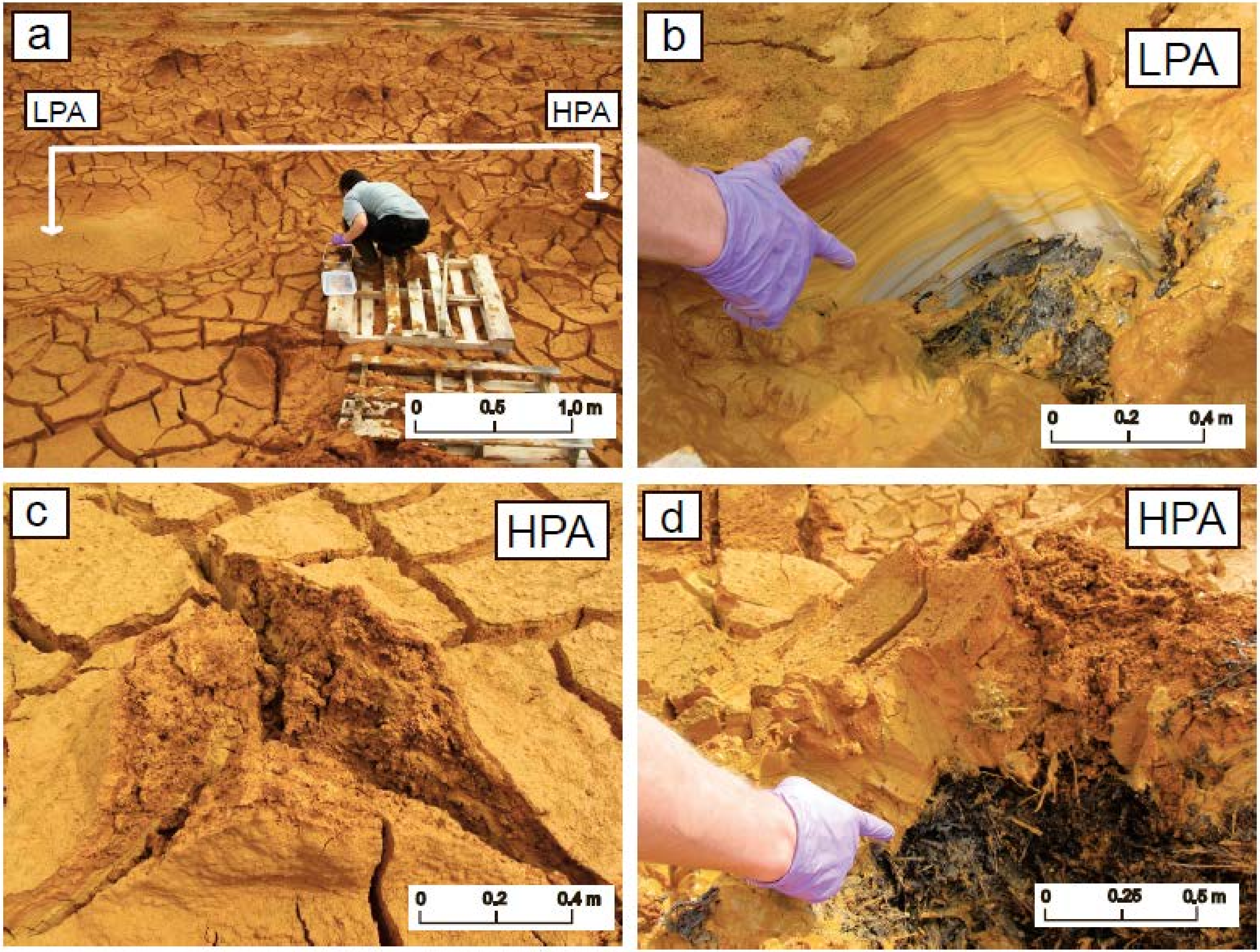
AMD Collection Drain

“Fresh-water” Bypass Channel

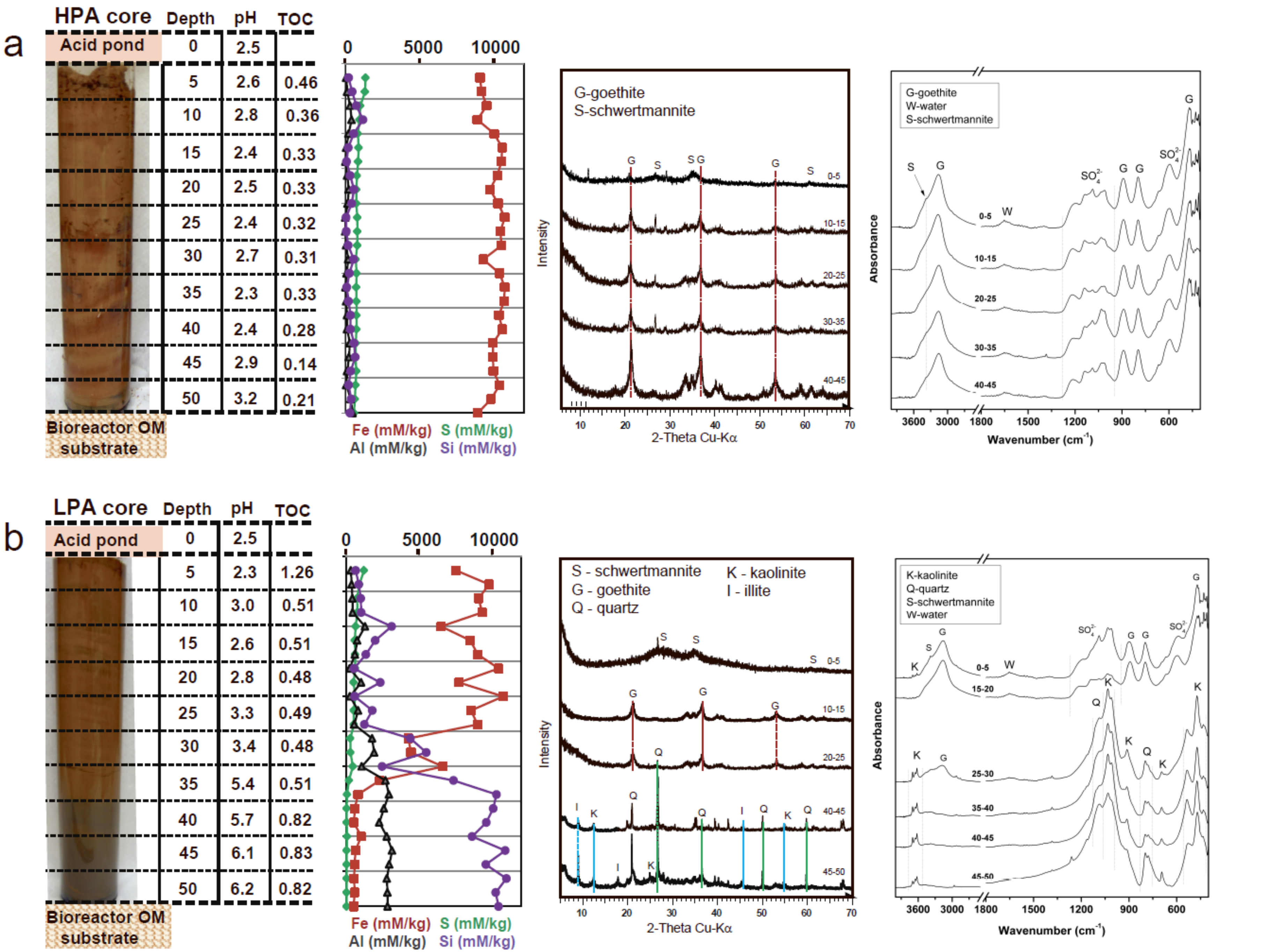
# * 2012 Failure of Bioreactor Component Treatment

2012-2013 Biopsy of iron precipitates & treatment media by SIUC researcher team.

Failure apparently due to short-circuiting of Influent AMD to under drain. Deposition of clay from erosion of adjacent highwall backfill spoil is believed to be a factor.

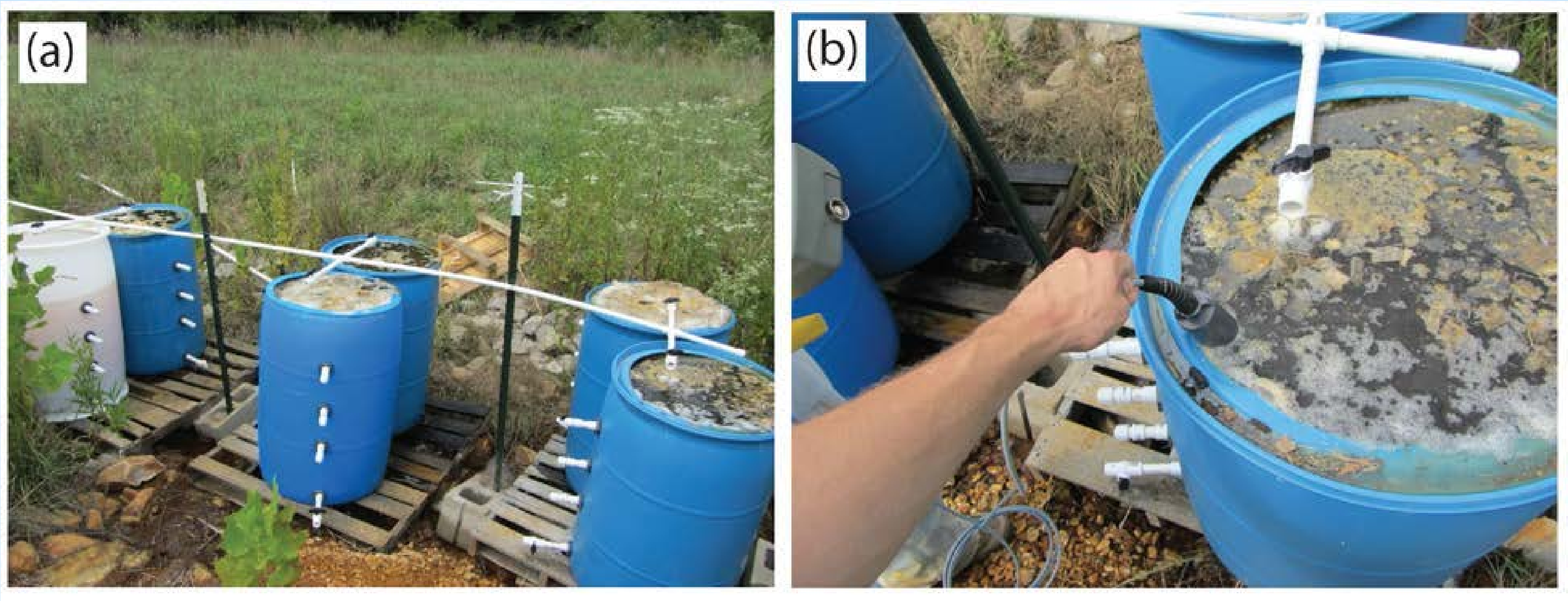



* Source: 2013 OSM-funded Applied Science Study by Dr. Lilianna Lefticariu, SIU Carbondale




Source: 2013 OSM-funded Applied Science Study by Dr. Lilianna Lefticariu, SIU Carbondale

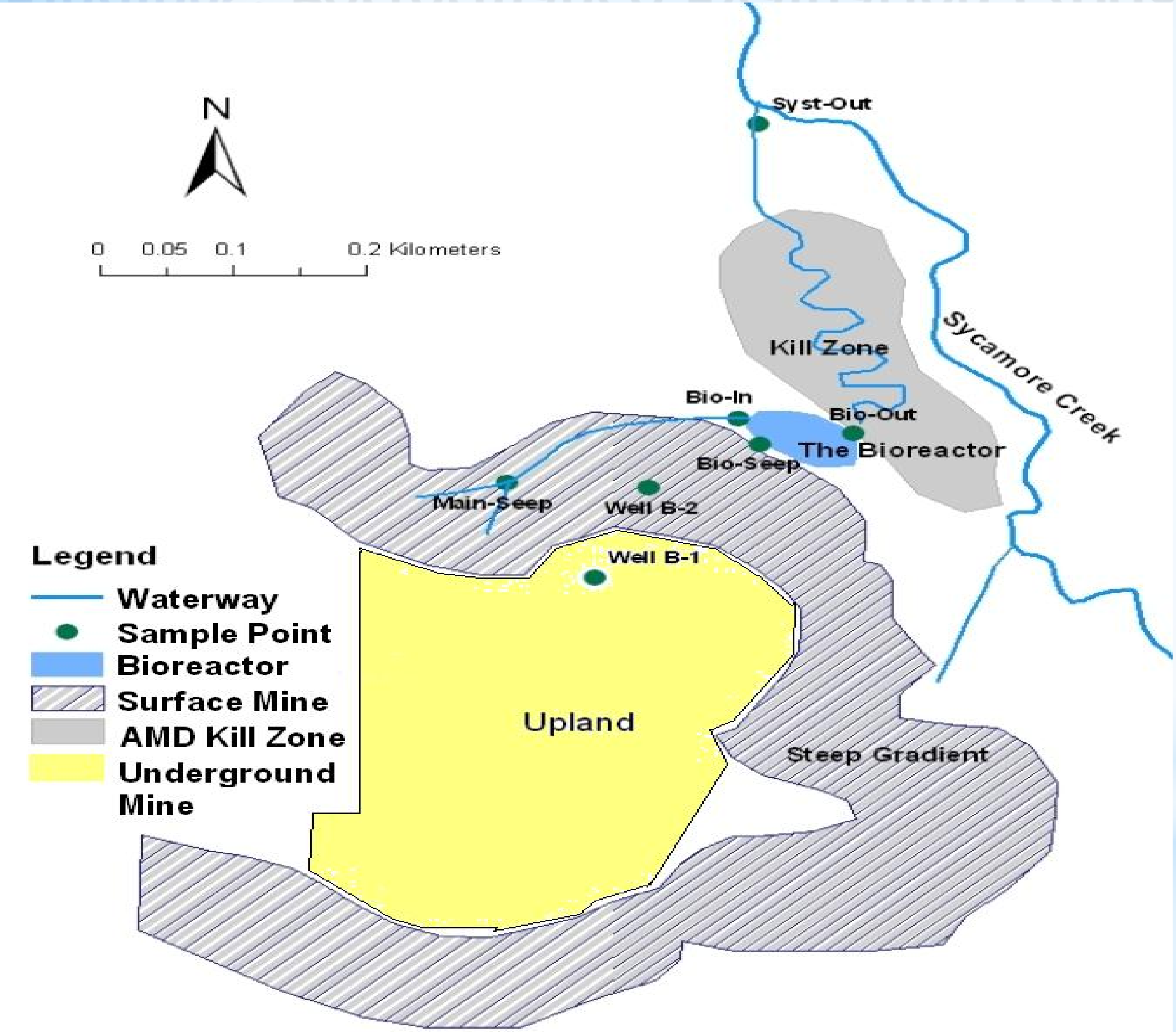
# 2013 Compost Replacement




* SIUC 2012-2013 barrel testing of compost alternatives.
* AMLRD Replacement Bioreactor Mix.
  * (1) 40% wood chips (hardwood)
  * (2) 10% sawdust (hardwood)
  * (3) 12% agricultural ground limestone
  * (4) 27% straw mulch
  * (5) 11% seasoned compost

    (by volume)

# Findings: Performance Evaluation (2008-Present)




Source: Segid (2010)

Sample locations: Tab-Simco Passive Treatment System

# **Findings:** Performance Data (Median Values) - Tab-Simco Passive Treatment System*

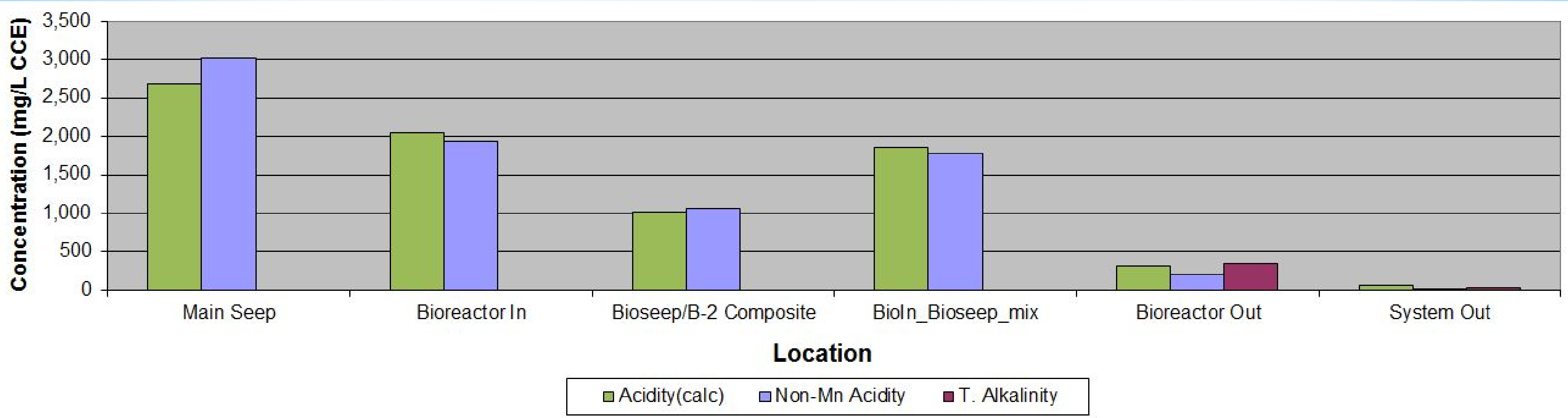
| Site ID | pH | D. Fe | D. Mn | D. Al | D. Ni | D. Zn | D. Co | Acidity | Alk. | $SO_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Main AMD Seep | 2.82 | **795.4** | 39.3 | **186.0** | 2.23 | 3.02 | 0.51 | **2,681** | 0 | **4,845** |
| Bioreactor In (BioIn) | 2.90 | **556.9** | 38.4 | 134.4 | **2.03** | 2.56 | **0.44** | **2,051** | 0 | **3,523** |
| BioSeep/ Well B2 | 3.02 | **257.7** | 35.6 | 98.2 | 1.34 | 1.84 | 0.36 | **1,020** | 0 | 2,306 |
| Bioreactor In/B2 Mix | 2.92 | **502.2** | **37.9** | 122.6 | 1.90 | **2.43** | 0.42 | **1,863** | 0 | **3,301** |
| Bioreactor Outlet (BioOut) | 6.30 | 212.1 | 33.1 | 0.36 | 0.07 | 0.10 | 0.07 | 312 | **351** | 2,254 |
| System Outlet (SysOut) | **6.14** | 6.77 | **22.2** | 0.48 | 0.22 | 0.25 | 0.07 | **65.8** | **33.3** | 1,693 |

*All values except pH are in mg/L; acidity and alkalinity (Alk.) are calcium carbonate equivalent values (CCE); acidity = calculated acidity; red = increasing values, green = decreasing values; n = 10 - 60.

# Tab-Simco Case Study: Observations

* Sources of alkalinity
  * Sulfate reduction or carbonate dissolution?
  * Long-term trends.
* Sulfate reduction
  * Comparison with published data and design criteria.
  * Long-term trends.
* Implications of the use of bioreactors for the lowering of TDS where $SO_4$ is a major component.
* Metal removal within bioreactor-based passive systems.
  * Is this pain or pleasure?
  * Long-term trends.
* Sequestration of trace metals.

# Sources of Alkalinity: Changes in Acidity and Alkalinity



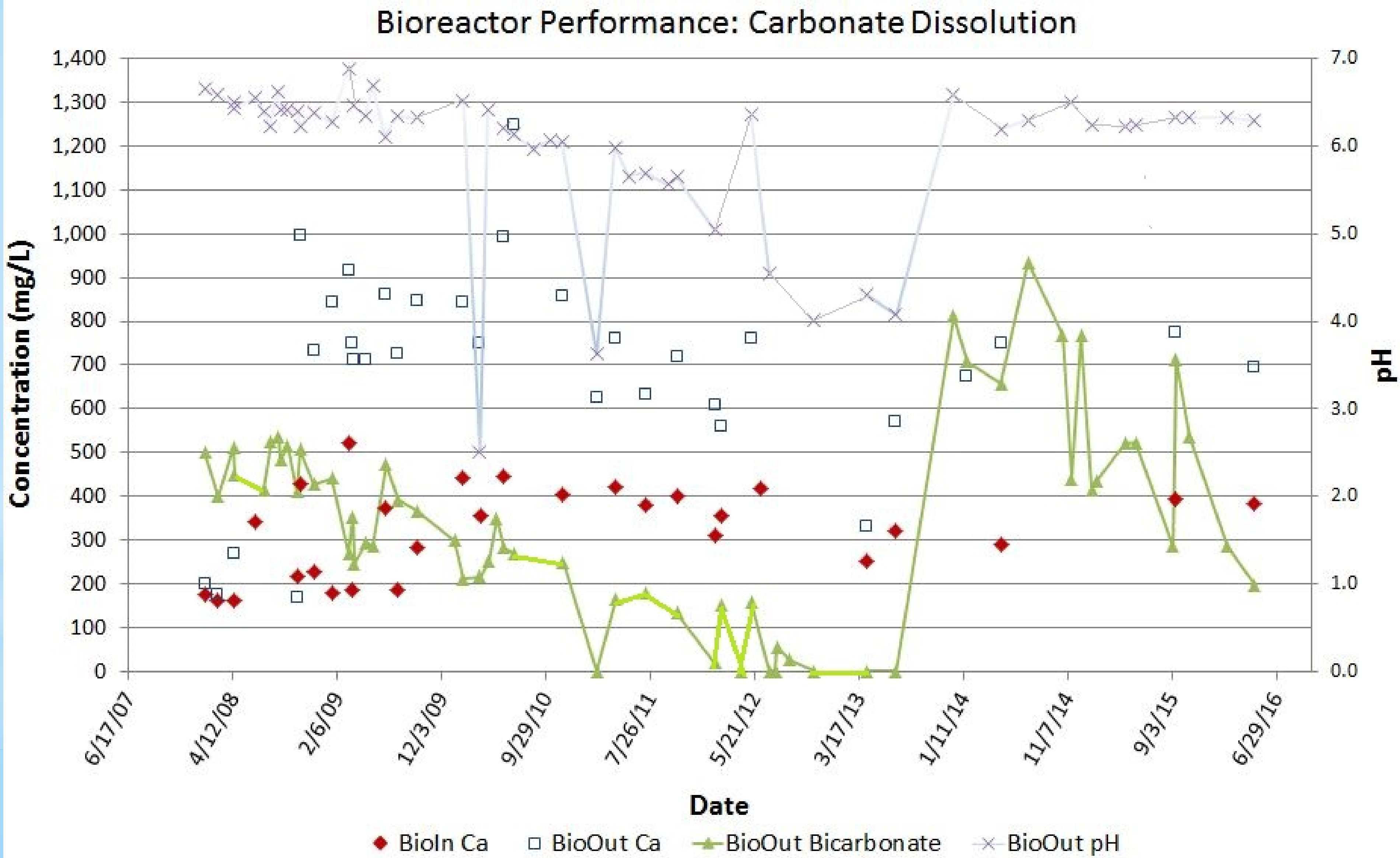

Acidity has dropped from a median **1,863** to **65.8** mg/L CCE, a **96.5%** improvement.

The inlet acidity is sequestered as metal sulfides and neutralized by a median bicarbonate alkalinity of **351** mg/L CCE in the bioreactor discharge.

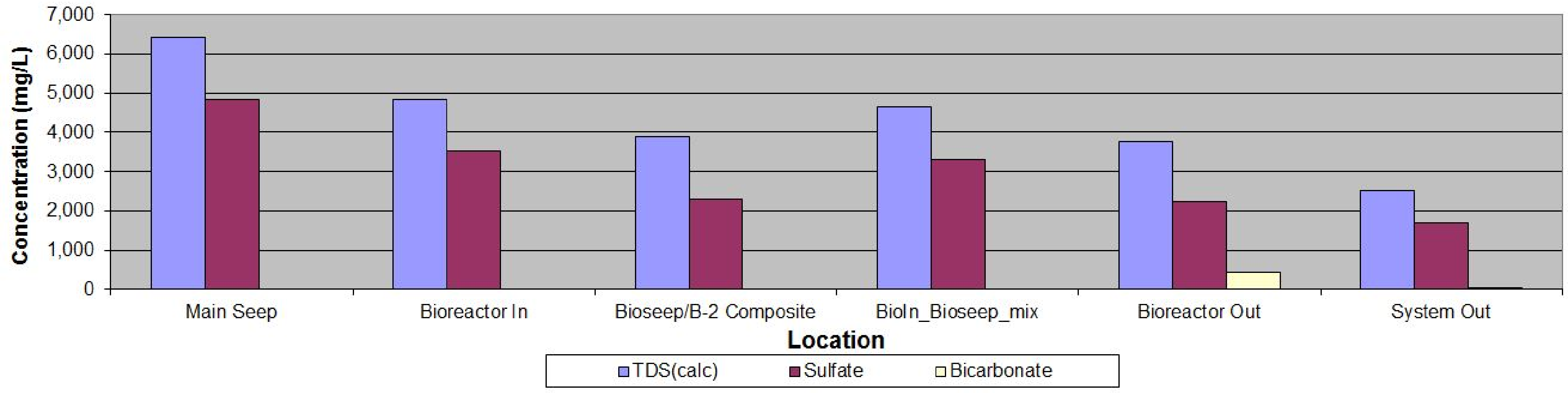
Nearly all of the alkalinity generated by the bioreactor is used up in the oxidation structures -- discharges a Net Non-Mn acidity = **22.5** mg/L CCE.

(based on median values)

# * Sources of Alkalinity: Dissolution of Limestone and Sulfate Reduction



# Sulfate Reduction: Changes in TDS, Sulfate and Bicarbonate values within the Treatment System



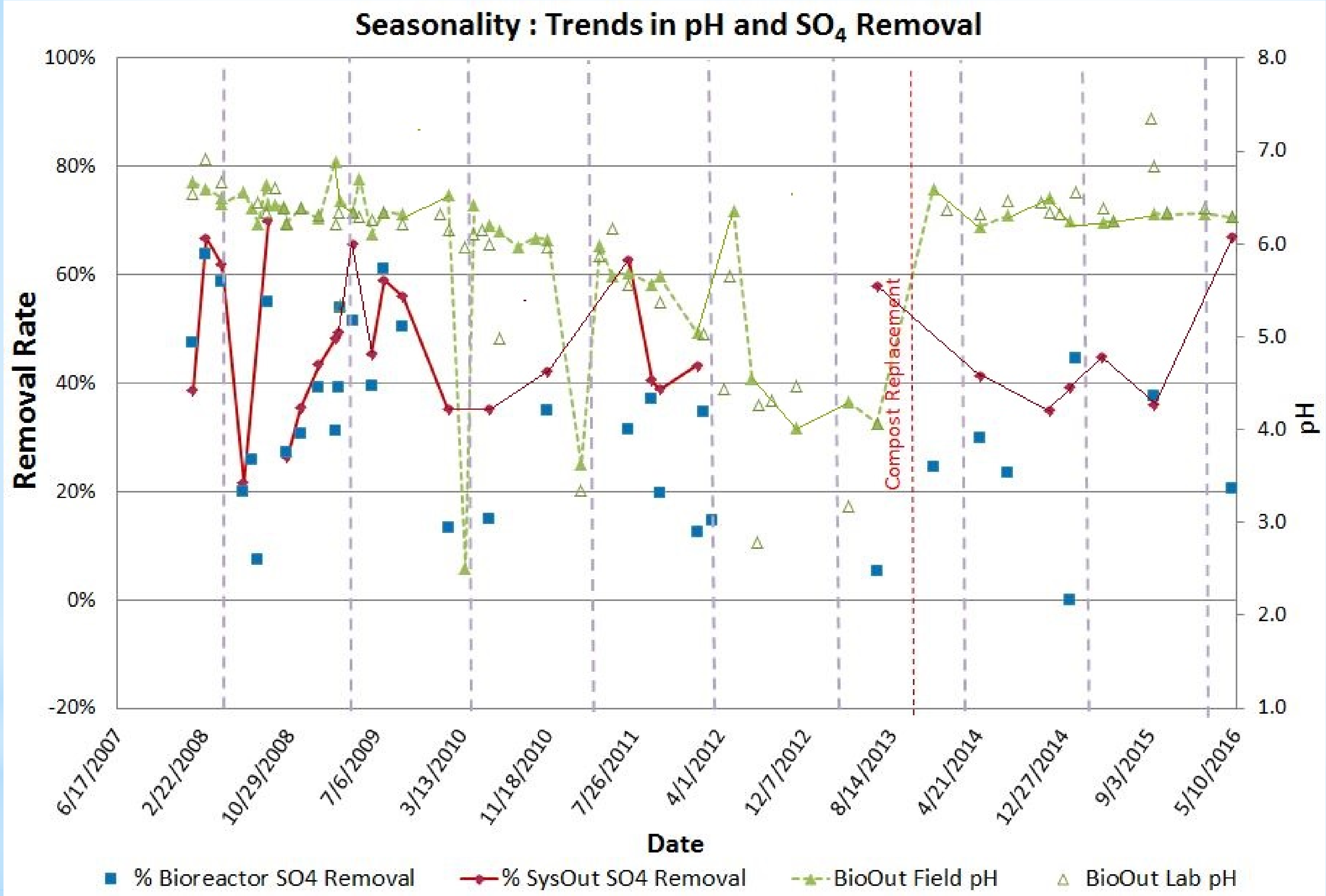

The inlet acidity is sequestered as metal sulfides and neutralized by a median bicarbonate alkalinity of **351** mg/L CCE in the bioreactor discharge. Nearly all of this alkalinity generated by the bioreactor is used up in the oxidation structures.

Considerable sulfate reduction occurs within the oxidation ponds!

**32%** of the $SO_4$ is removed by the bioreactor cell (2008-Present).

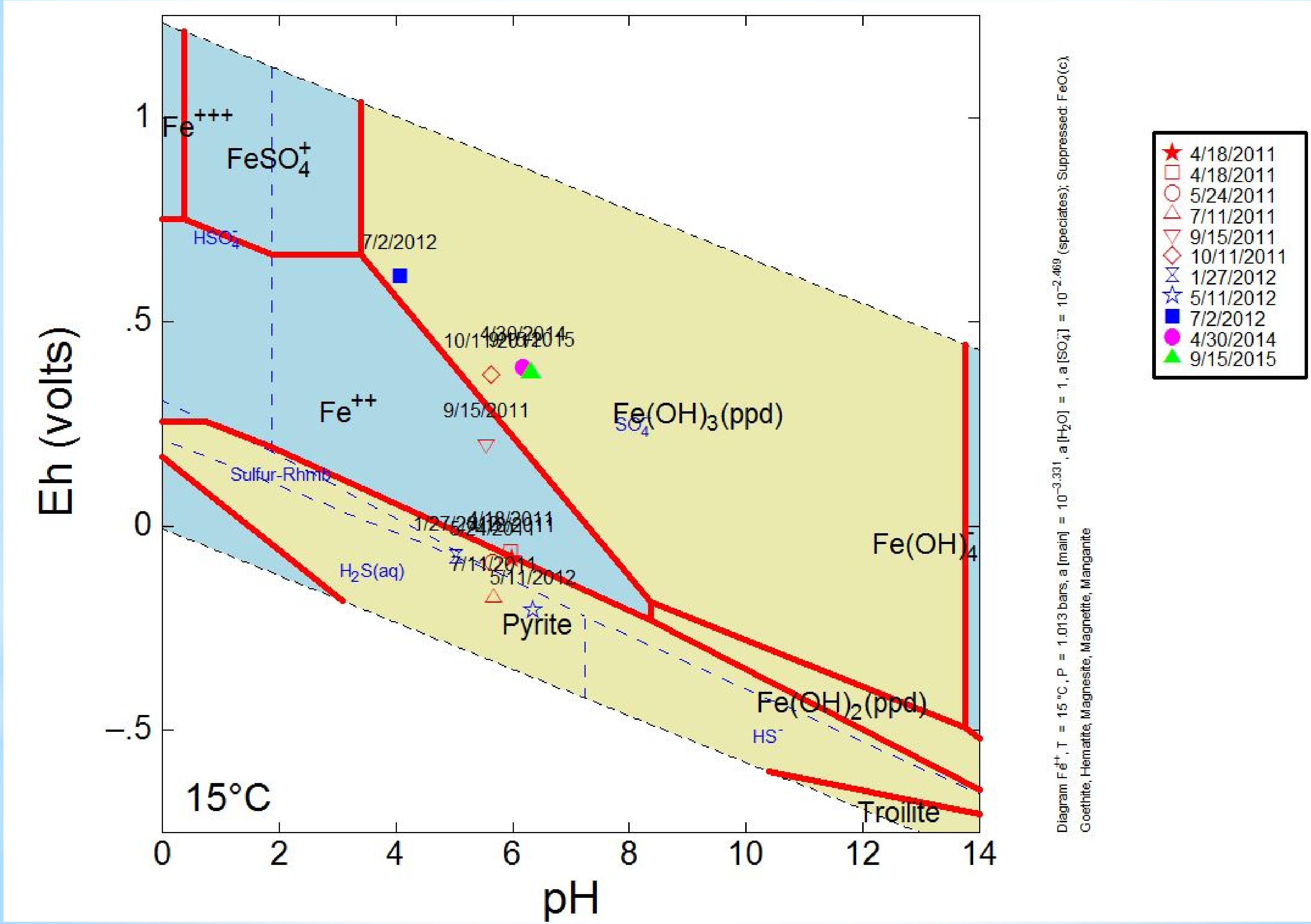
**49%** of the $SO_4$ is removed by the entire system (2008-Present).

# * $SO_4$ Removal Trends: System Discharge




Additional sulfate reduction may be occurring within the oxidation pond.

# $SO_4$ Removal: Eh-pH diagram of Bioreactor Discharge




Fe hydroxide precipitate was stable in some bioreactor-treated water .

# Sulfate Reduction: Median Loading and Removal Rates

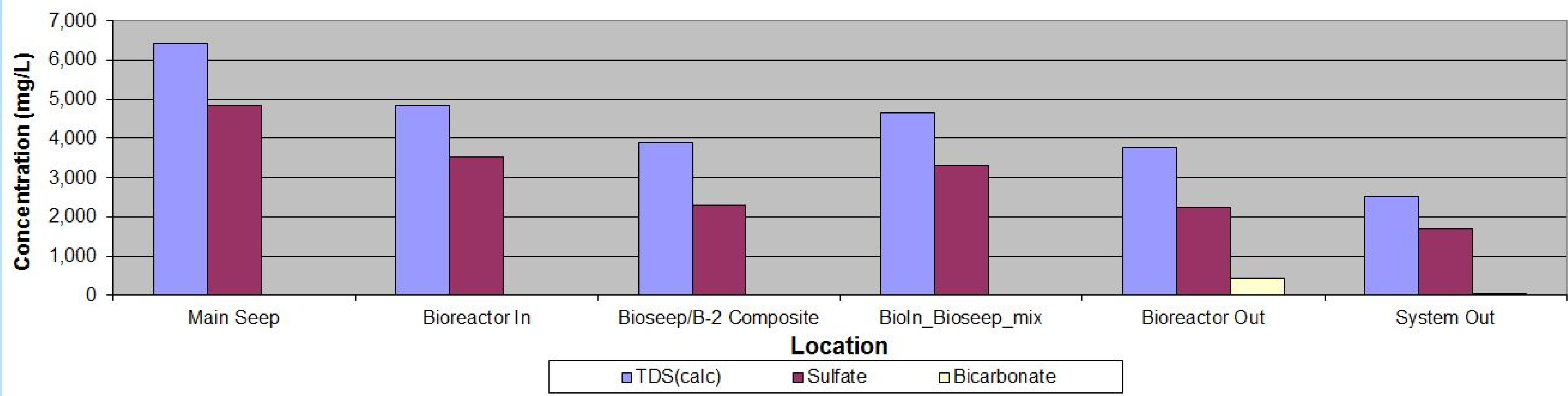
| Site ID | D. Fe | D. Al | D. Mn | D. Ni | D. Zn | Cumulative Metals | $SO_4$ |
|---|---|---|---|---|---|---|---|
| Bioreactor Loading* Rate (moles/$m^3$/day) | 0.214 | 0.110 | 0.0164 | 0.0008 | 0.0009 | 0.326 | 0.817 |
| Bioreactor Removal Rate (moles/$m^3$/day) | 0.162 | 0.110 | 0.0007 | 0.0008 | 0.0001 | 0.276 | 0.259 |
| Removal (%) | 75.9 | 99.7 | 12.7 | 96.3 | 95.9 | 84.1 | 31.7 |
| Oxidation Cell Load Rate (moles/$m^3$/day) | 0.052 | $3.2 \times 10^{-4}$ | 0.0143 | $2.8 \times 10^{-5}$ | $3.6 \times 10^{-5}$ | 0.066 | 0.558 |
| Oxy. Cell Removal Rate (moles/$m^3$/day) | 0.049 | $1.1 \times 10^{-4}$ | 0.0047 | $-6.1 \times 10^{-5}$ | $-5.5 \times 10^{-5}$ | 0.053 | 0.139 |
| Cumulative Removal (%) | 98.7 | 99.6 | 41.5 | 88.4 | 89.7 | 96.2 | 48.7 |

*Bioreactor Inlet and B2 mix.

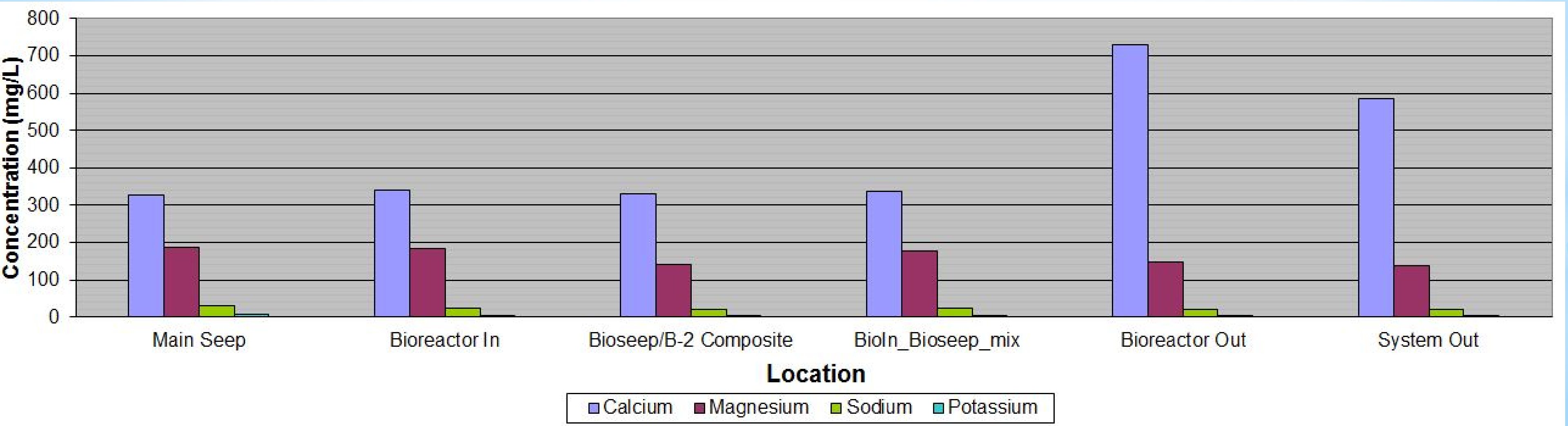
# Sulfate Reduction: Comparison of Sulfate Removal Rates

* McCauley *et al*.(2009) reported an average sulfate removal rate of **0.308** moles/m$^3$/day in bench tests.
* Gusek (2002, 2005) suggested a removal rate of **0.30** moles/m$^3$/day as a design criterion.
* Tab-Simco system is **0.259** moles/m$^3$/day, a value lower than the optimal rates. Detrimental factors include:
  * **Undersized system due to site constraints.**
  * **Lower than optimum inlet pH (2.9).**
  * **High metal loading (Fe = 502 mg/L, Al = 123 mg/L).**
  * **Variable inlet flow rate (2 - 63 GPM)**
  * **Variable inlet chemistry (seasonal metal and sulfate changes).**

# Implications of the use of bioreactors for the lowering of TDS: $SO_4$ Reduction Partially Offset by > Calcium

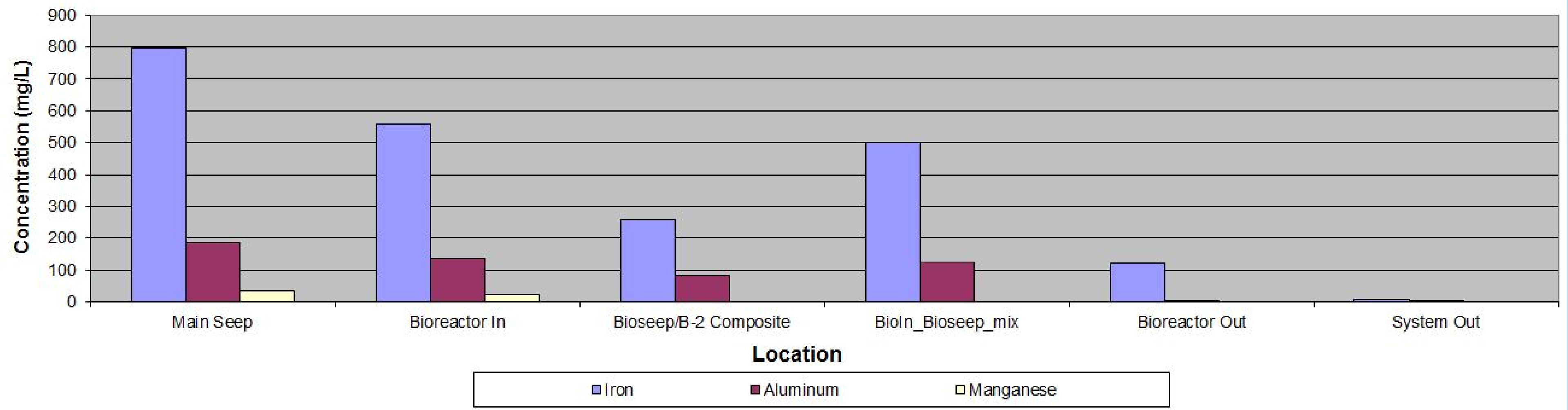



Tab-Simco: 49% of the sulfate is removed by the bioreactor-based system.




Tab-Simco: Ca is increased from 160 mg/L to 730 mg/L (BioOut), declining to 587 mg/L at the system discharge by dilution.

# Metal Removal: Changes in Iron, Aluminum and Manganese Values



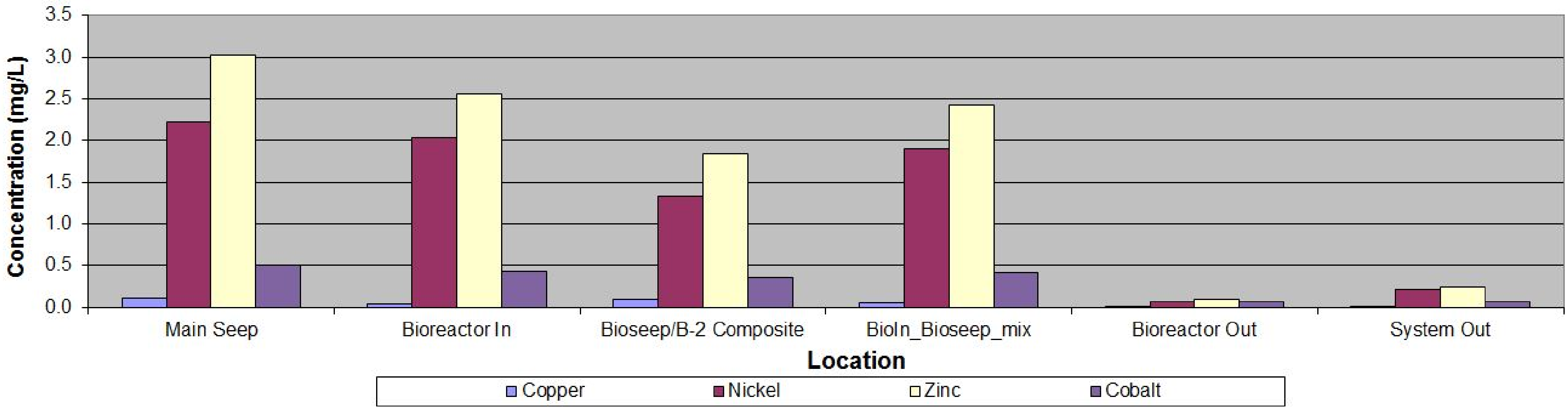

The bioreactor inlet AMD is a blend of the bioreactor Inlet AMD (BioIn) and seepage directly into the bioreactor cell (BioSeep/Well B-2). The median dissolved iron of **502** mg/L in the bioreactor inlet declines to **63.9** mg/L in the bioreactor discharge.

**75.9%** of the Fe is removed by the bioreactor cell (2008-Present).

**98.7%** of the Fe is removed by the entire system (2008-Present).

**99.6%** of Al and **41.5%** of Mn is removed by the system (2008-Present).

# Metal Removal: Changes in Trace Metal Values within the Treatment System




The bioreactor inlet AMD (BioIn/BioSeep blend) contains measureable amounts of trace metals Ni and Zn with lesser amounts of Cu and Co. The median dissolved zinc declines from **2.43** mg/L the bioreactor inlet to **0.1** mg/L in the bioreactor discharge (BioOut).

**96.3%** of the Ni is removed by the bioreactor cell (2008-Present).

**95.9%** of the Zn is removed by the entire system (2008-Present).

# Metal Removal: Median Loading and Removal Rates

| Site ID | D. Fe | D. Al | D. Mn | D. Ni | D. Zn | Cumulative Metals | $SO_4$ |
|---|---|---|---|---|---|---|---|
| Bioreactor Loading* Rate (moles/m$^3$/day) | 0.214 | 0.110 | 0.0164 | 0.0008 | 0.0009 | 0.326 | 0.817 |
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| Removal (%) | 75.9 | 99.7 | 12.7 | 96.3 | 95.9 | 84.1 | 31.7 |
| Oxidation Cell Load Rate (moles/m$^3$/day) | 0.052 | $3.2x10^{-4}$ | 0.0143 | $2.8x10^{-5}$ | $3.6x10^{-5}$ | 0.066 | 0.558 |
| Oxy. Cell Removal Rate (moles/m$^3$/day) | 0.049 | $1.1x10^{-4}$ | 0.0047 | $-6.1x10^{-5}$ | $-5.5x10^{-5}$ | 0.053 | 0.139 |
| Cumulative Removal (%) | 98.7 | 99.6 | 41.5 | 88.4 | 89.7 | 96.2 | 48.7 |

*Bioreactor Inlet and B2 mix.

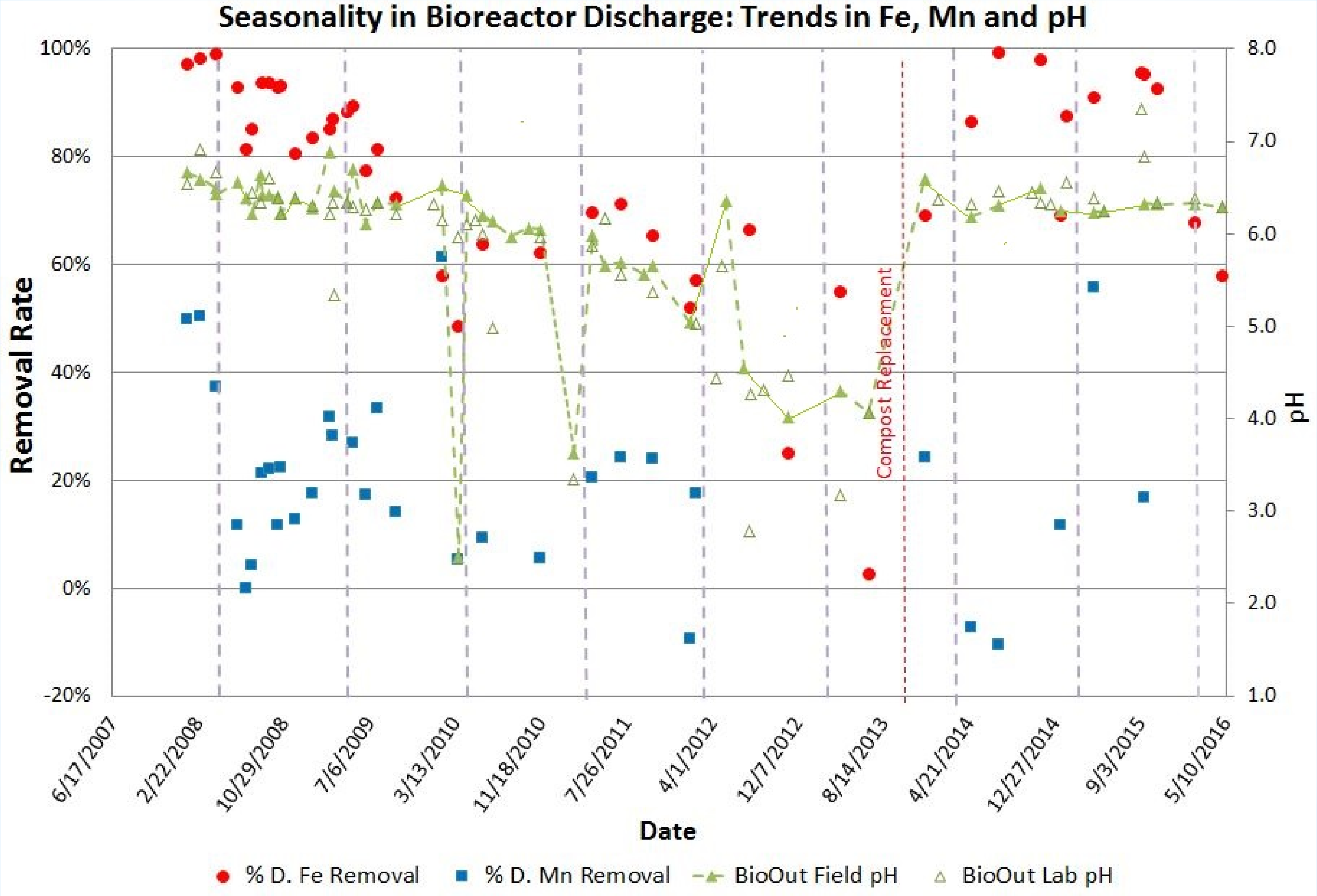
# Metal Removal: Comparison of Metal Removal Rates

- Consider Reaction: $H_2S_{(aq)} + Me^{2+} \quad MeS_{(s)} + 2\ H^+$

  Suggests that for every mole of sulfate removed one mole of metals are also removed!

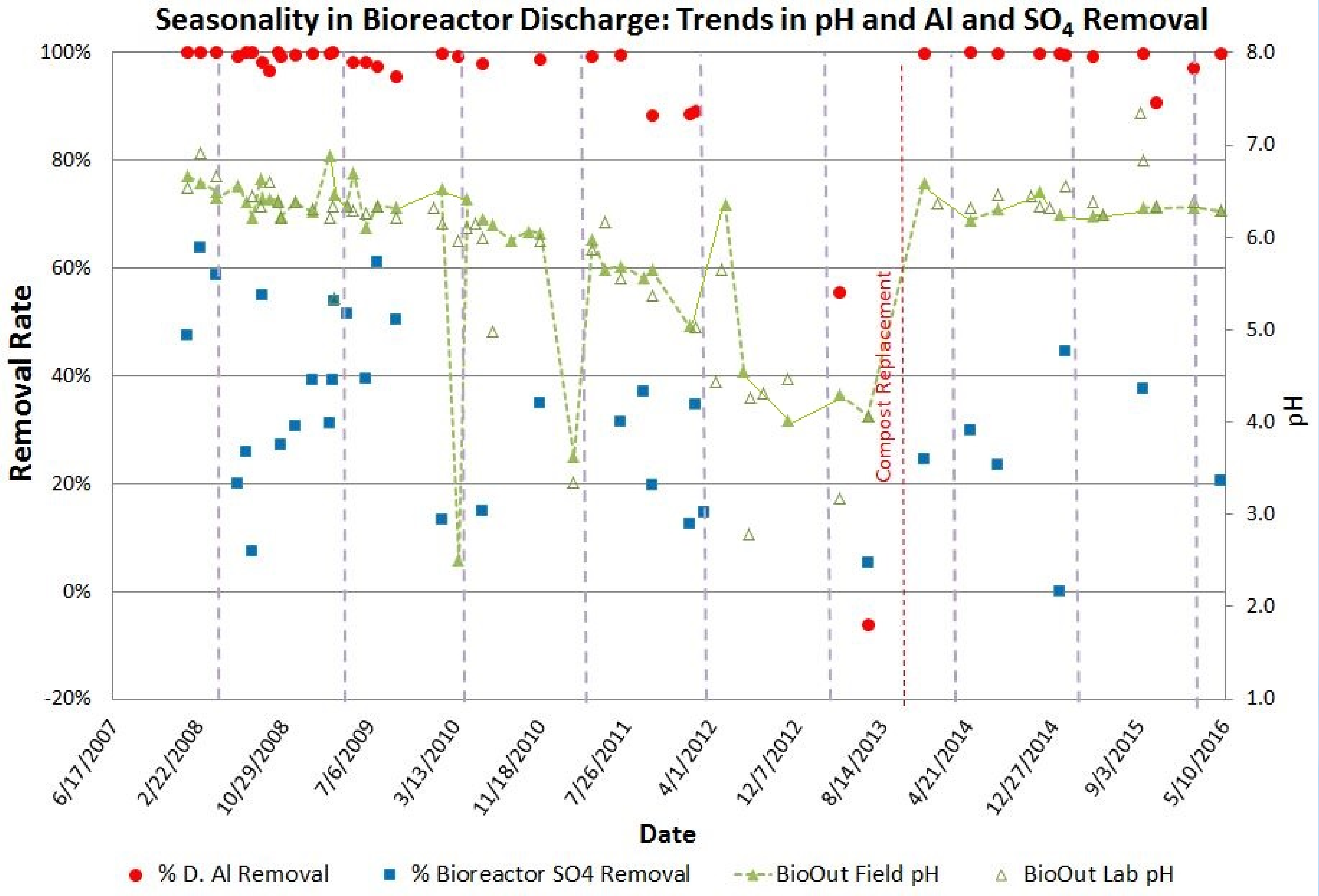
- The cumulative metal load of **0.276** moles/m$^3$/day is higher than sulfate a removal rate of **0.259** moles/m$^3$/day.
- A 2003 study of a metal mine site by URS recommended a lower cumulative heavy metal flux value of only **0.150** moles/m$^3$/day.

# Metal Removal: Bioreactor Fe and Mn Removal Trends



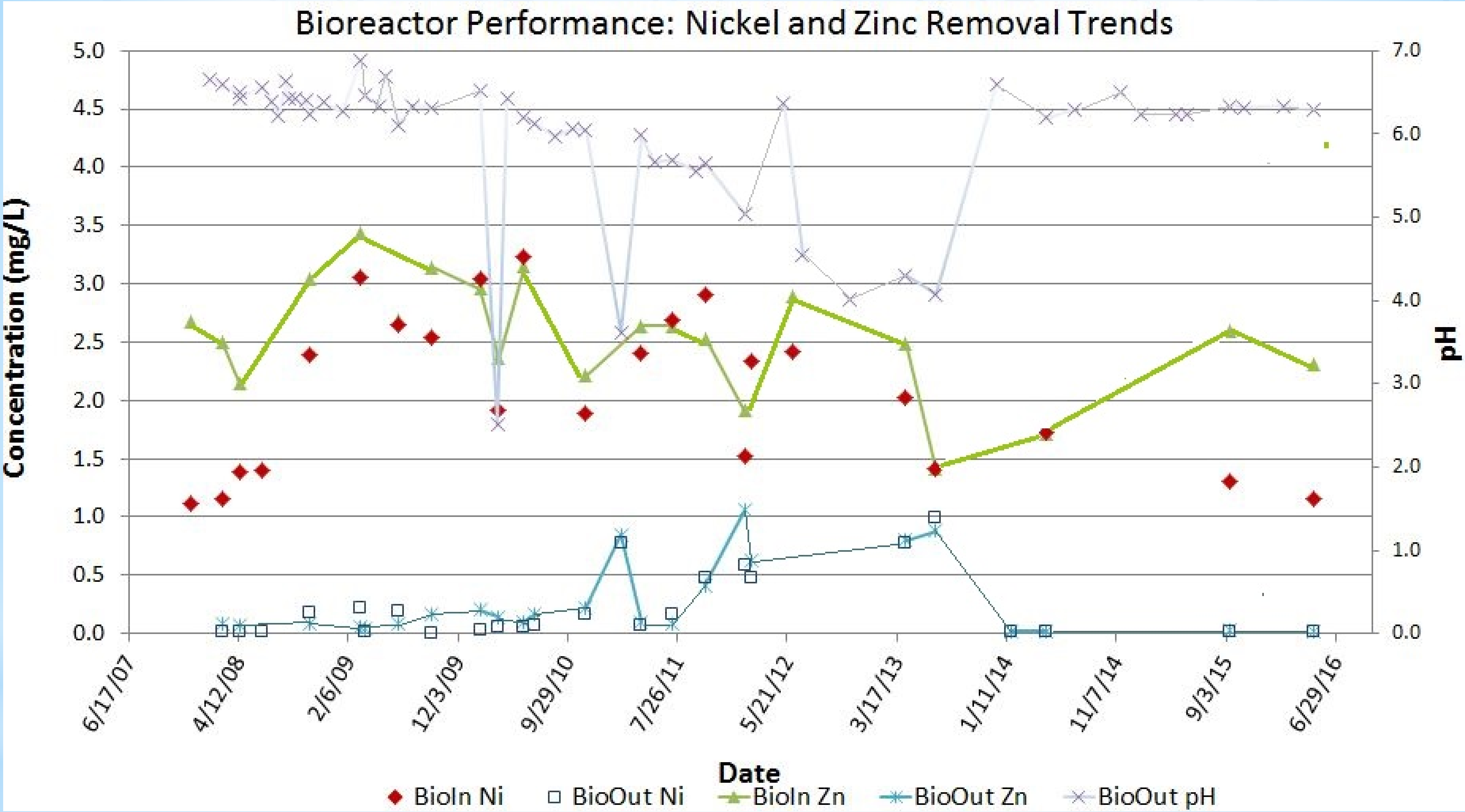

Percent iron and manganese removal declined in late 2009, but rebounded some in 2010 only to decrease again in 2011 prompting replacement of the treatment media.

# **Metal Removal:** Spatial Trends in Al Removal




Percent sulfate removal declined in 2009, but rebounded some in 2010 only to decrease again in 2011 prompting replacement of the treatment media.

# Sequestration of Trace Metals: Spatial Trends in Removal




Ni and Zn are the principle trace metals in the Inlet AMD; the concentrations of both metals are gradually declining with time. Both metal are removed to a low level except during low pH periods between 2009-2013.

# Tab-Simco Case Study: Lessons Learned

* Low-pH iron oxidation in the inlet AMD:
  * Lowered metal and sulfate loading into bioreactor.
  * Metal hydroxides and oxysulfates accumulated rapidly on the compost surface (~ 2 inches/yr.).
* Seasonality:
  * Lower $SO_4$ and metal removal in high flow periods (wet season).
  * Delayed response to winter cold temperatures?
* Design criteria:
  * Expect less performance with > metal and sulfate loading and < pH.
* Sedimentation:
  * Clay washed into bioreactor cell and may have contributed to premature failure.
* Unanticipated AMD seepage:
  * AMD entering bypass channel impacts final discharge water quality.

# * Acknowledgements

* Larry Lewis (Ret.) with the AMLRD, Illinois Department of Natural Resources was the principle design engineer of the system, Dr. Philip A. Smith (Ret.), provided historical information.

* Dan Hause (Ret.) with the Reclamation Division of the Indiana Department of Natural Resources and Vinod Patel, Illinois Department of Natural Resources assisted in the system design.

* SIUC graduate students Yosief Segid and Evan Walters conducted geochemistry research; Dr. Kelly Bender and graduate students Andrew Burns and Charles Pugh of SIUC conducted supporting biochemistry research; Jack Nawrot (Ret.) assisted AMLRD with site studies.

* Ron Kiser, Greg Tanner and Mike Tarlton, with the with the AMLR Division, Illinois Department of Natural Resources and assisted in project management and construction monitoring.

* Nick Grant and Joy Schieferstein, Office of Surface Mining, Mid-Continent Region assisted in the evaluation of the biologic impact of the system on Sycamore Creek.

* Landowners Mike Page and Carla and Treg Brown provided access to the property and allowed facility construction.

# The End: Questions?

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