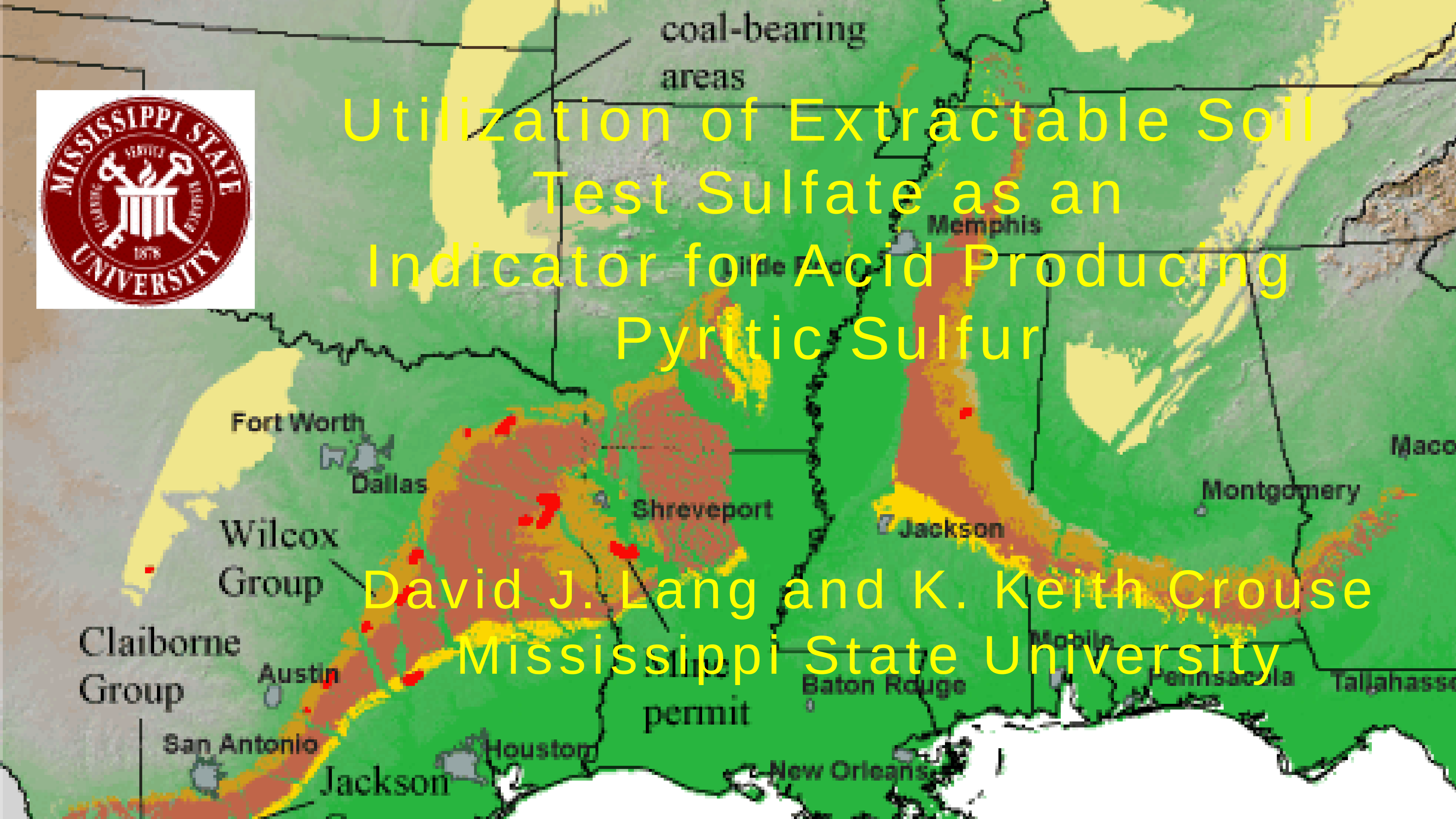
Utilization of Extractable Soil Test Sulfate as an Indicator for Acid Producing Pyritic Sulfur

David J. Lang and K. Keith Crouse
Mississippi State University



Thionic Fluvisols (acid sulfate soils)

Worldwide about 24 Mi. ha (~ 0.2 %) are found, mostly in SE Asia; often influenced by tide.

Thionic Fluvisols are found in the coastal lowlands of:

a. SE Asien (Vietnam, Indonesia, Thailand)

b. W-Africa: Senegal, Gambia, Sierra Leone

c. NE-coast of S-America (Venezuela, Guyana)

If acidification is not kept under control, the "reclaimed" land may degrade completely - even mangroves will not survive. Acid drainage water from this wasteland may endanger downstream fish stocks.

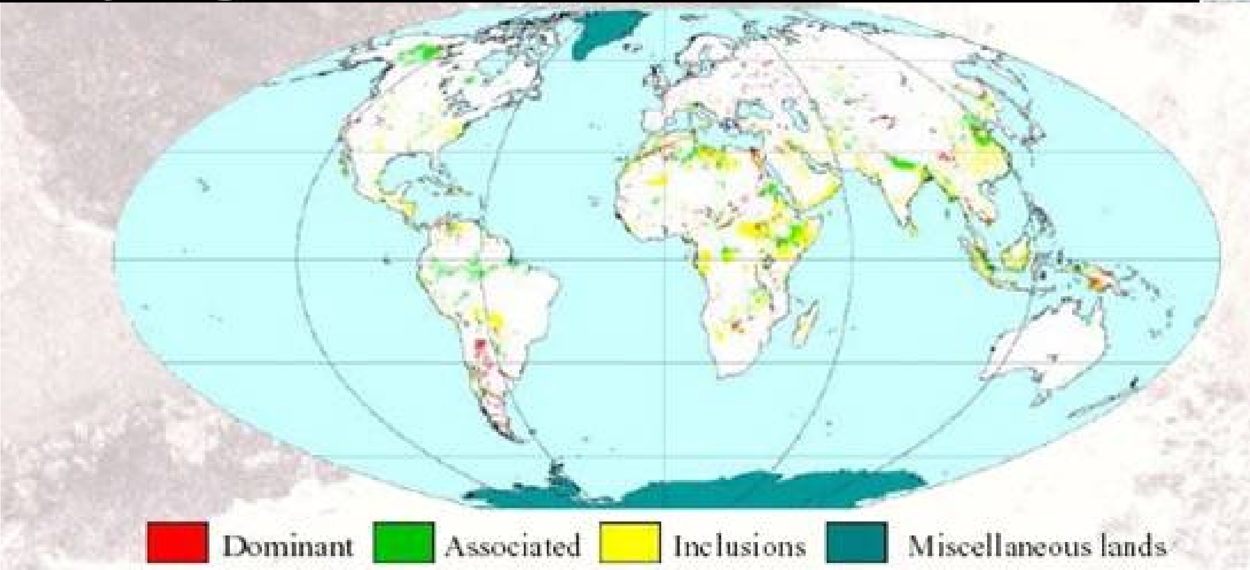
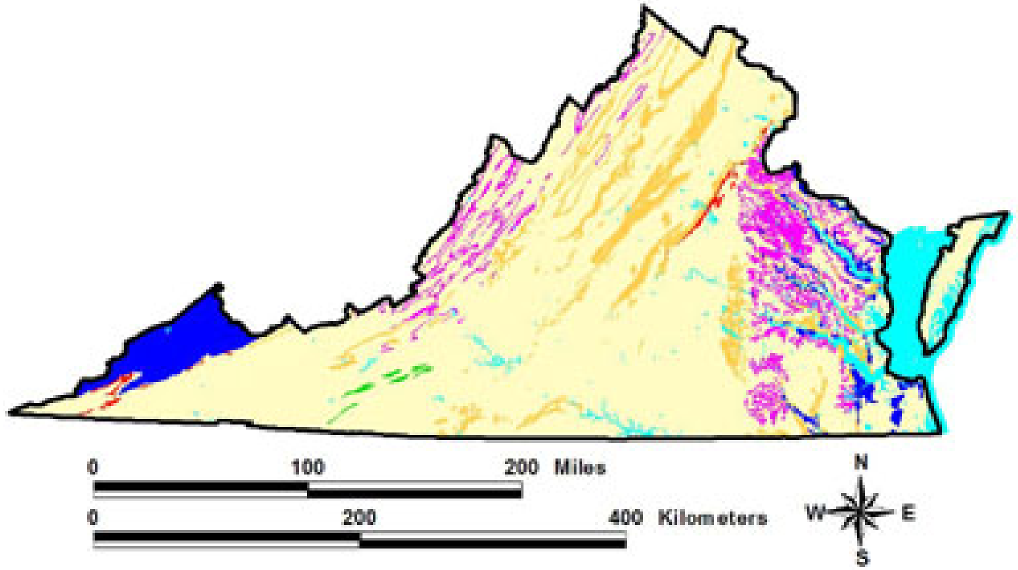


Figure 1. Fluvisols worldwide.

Virginia State Sulfide Hazard Risk Map



Estimated acid-producing rpotential of sulfide bearing materials in Virginia

- Low-mod risk: PPA < 10 Mg CaCO3/1000 Mg and %S < 0.5
- Mod risk: PPA < 10 Mg CaCO3/1000 Mg and %S > 0.5
- Mod-high risk: PPA 10 - 60 Mg CaCO3/1000 Mg
- High risk: over 10% of samples have PPA > 60 Mg CaCO3/1000 Mg
- No documented risk
- Sulfides documented in literature: risk unkown
- water

Documented acid-producing sulfidic formations in Virginia

- Coastal Plain: Tabb formation
  Appalachian Plateau: Wise, Kanawha, Norton, New River, Lee and Pocahontas Formations
- Blue Ridge: Ashe Formation of the Lynchburg Group
- Coastal Plain: Chesapeake Group and Lower Tertiary deposits
  Valley and Ridge: Marcellus shale, Millboro shale, and Needmore Formation
- Piedmont: Quantico Formation
  Valley and Ridge: Chattanooga Shale

Information provided in this document is based on detailed field and laboratory analyses completed by Zenah W. Orndorff, W. Lee Daniels, and personnel from Crop and Soil Environmental Sciences at Virginia Tech, as well as information provided by the Geologic Map of Virginia (Rader and Evans, 1993) and the Digital Representation of the 1993 Geologic Map of Virginia (VDMR, 2003).

Grey reduced sulfidic materials are commonly encountered during active construction in the Fredericksburg/Stafford area of Virginia. These materials will usually acidify over time to pH less than 3.5 unless large amounts of lime are added and incorporated.

http://www.landrehab.org/acid_sulfate_soils
Dr. Lee Daniels

Victoria
Australia
Road
Guidelines

Figure 1: Concrete bridge pier damaged by acidic runoff from ASS.

Figure 2: Scalded ground.

vicroads.vic.gov.au

Figure 3: Iron staining of surface water ponding on ASS.

Figure 4: Iron staining of groundwater discharge.

pH and Total Sulfur (S) are Initial Assessments

- Stage A: Preliminary Hazard Assessment

  - A pH of *in situ* soil or oxidised soil less than 5 indicates the presence of ASS. pH < 5

- Stage B: Detailed Soil Site Assessment
  - %S (% sulfur) if less than 0.03 %S, ASS are not present and the proposed road construction activities can proceed without restriction.
    - Pyritic Sulfur $Fe2_S$ = 53.45 % Sulfur 0.03 %S = 0.0561% Pyrite

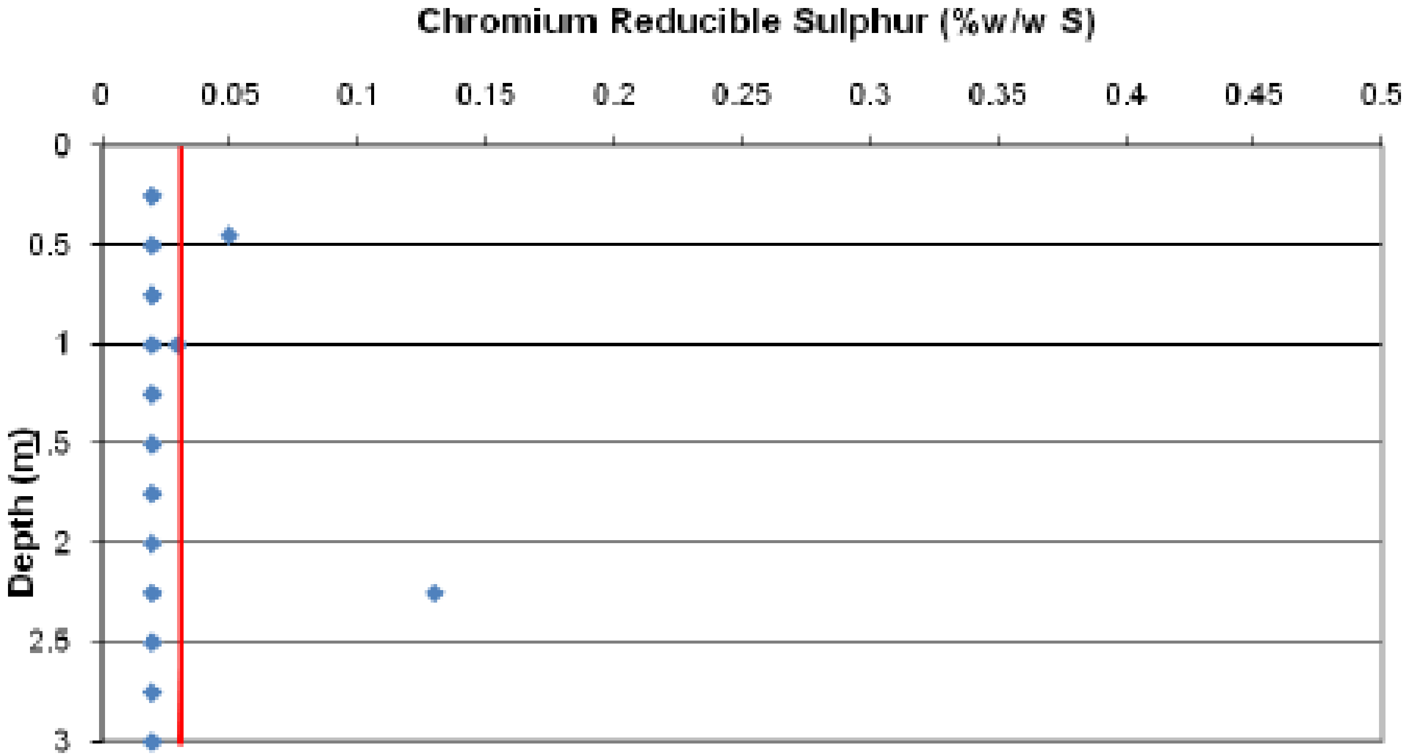
  - If the net acidity is 0.03 %S or greater, ASS are present.
    - (0.0561 % Pyrite)

  - Sulfur (S) and Acid Base Accounting Procedures are $$$$

https://www.vicroads.vic.gov.au/searchresultpage?q=acid%20sulfate%20soil

Of the 108 samples 'field' tested, 35 were analysed for PASS using the S_{CR} method. The sulphur (% w/w S) concentrations exceeding the DEC action criteria of 0.03 % w/w S are shown in **Figure 4.2**.

Figure 4.2 – PASS Distribution along a Section of the Proposed Infrastructure Corridor



The red line on Figure 4.1 represents the DEC action criteria of 0.03% w/w Sulphur

There were a number of results with concentrations less than the limit of reporting (LOR) of 0.02 % w/w S. These points are overlaid in the 0.02 column suggesting fewer than 35 samples were analysed. However, this is not the case.

Figure 3.1 – Acid Sulphate Soils Risk Map

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only. Final image will be inserted as a PDF page at appropriate resolution and qualit

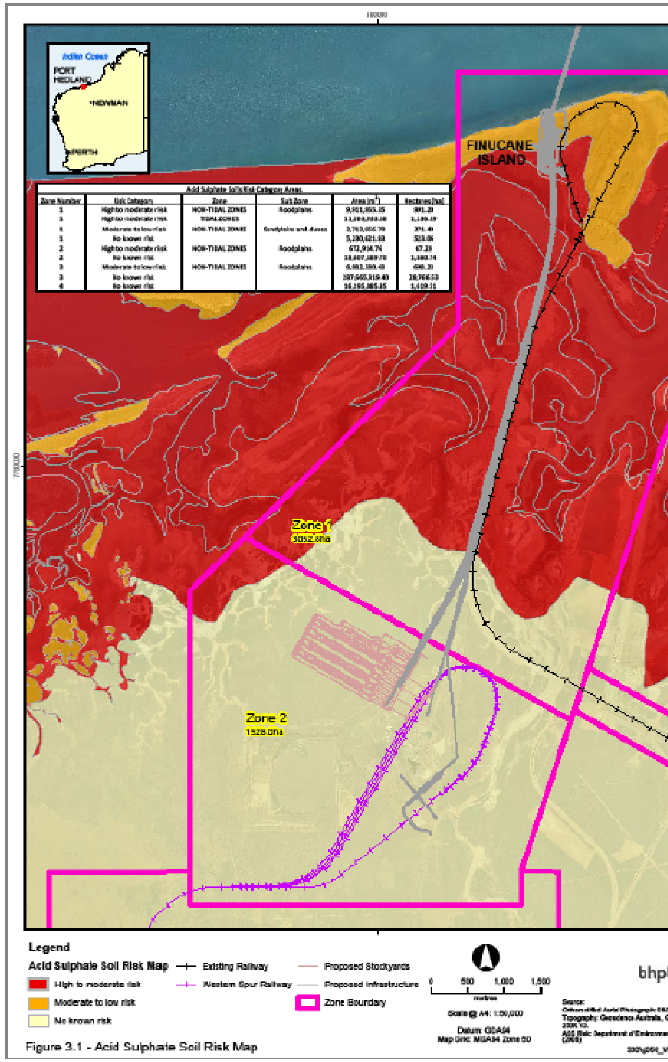


Figure 3.1 - Acid Sulphate Soil Risk Map

TEXAS HIGHWAY CONSTRUCTION GUIDELINES

Table 1. Level of risk associated with lime stabilization in sulfate-bearing clays.

Risk Involved	**Soluble Sulfate Concentrations**	
	Parts Per Million	**Percent dry weight**
Low Risk	Below 3,000 ppm.	Below 0.3%
Moderate Risk	Between 3,000 and 5,000 ppm	Between 0.3% and 0.5%
Moderate to High Risk	Between 5,000 and 8,000 ppm	Between 0.5% and 0.8%
High to Unacceptable Risk	Greater than 8,000 ppm	Greater than 0.8%
Unacceptable Risk	Greater than 10,000 ppm	Greater than 1.0%

SO_4-S = 35.5 %S   Multiply x 0.355 = % S

Recommended Practice for Stabilization of Sulfate-Rich Subgrade Soils Texas _ National Cooperative Highway Research Program (NCHRP) National Academy Press http://nap.edu/22997 DOI 10.17226/22997

METHODS FOR SULFATE QUANTIFICATION IN SOILS

- These methodologies use different sulfate measurement techniques
  - Chromatography,
  - Gravimetric (Turbidity)
  - Colorimetry
  - ICP
- Most of the test methods are based on determining water soluble sulfates in the soil.
- Commonly Used Soil Test Extractants

Soil Test Extraction Reagents

- Reagents containing Sulfates cannot be utilized
    - *Mehlich-1 extracting solution*: 0.0125 *M* H_2SO_4.
- Newer Mehlich's (2 and 3) are OK
- In the Northeast USA:
    - Extraction for Sulfate-S (Morgan's / Modified Morgan's) OK
- North Central USA Soil Extractants: Bray, Olsen, Mehlich OK
- South and Southeast
    - Mehlich developed in North Carolina
    - Lancaster Method Developed in Mississippi
    - Lancaster Reagents OK

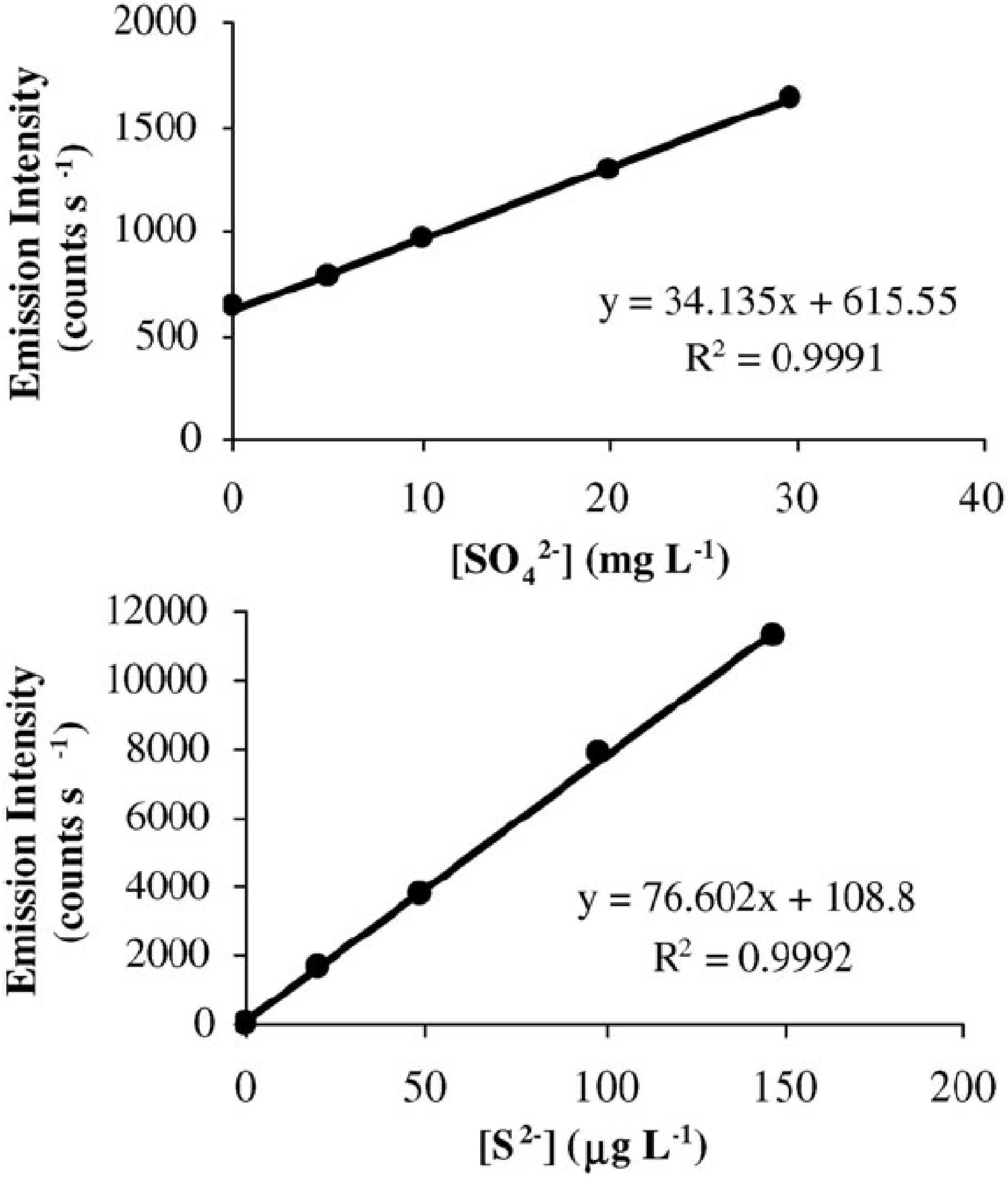


Fig. 2 Calibration curves for sulfate and sulfide.

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

Sulfur is determined by the Intensity of the Sulfate and Sulfide Emission at 180.7 nm

Colon at al, 2008. Sulfide and Sulfate Determination.. by ICP.. J. Anal. Atomic Spec 23:416-418

Lignite Coal Mine, Choctaw County, MS

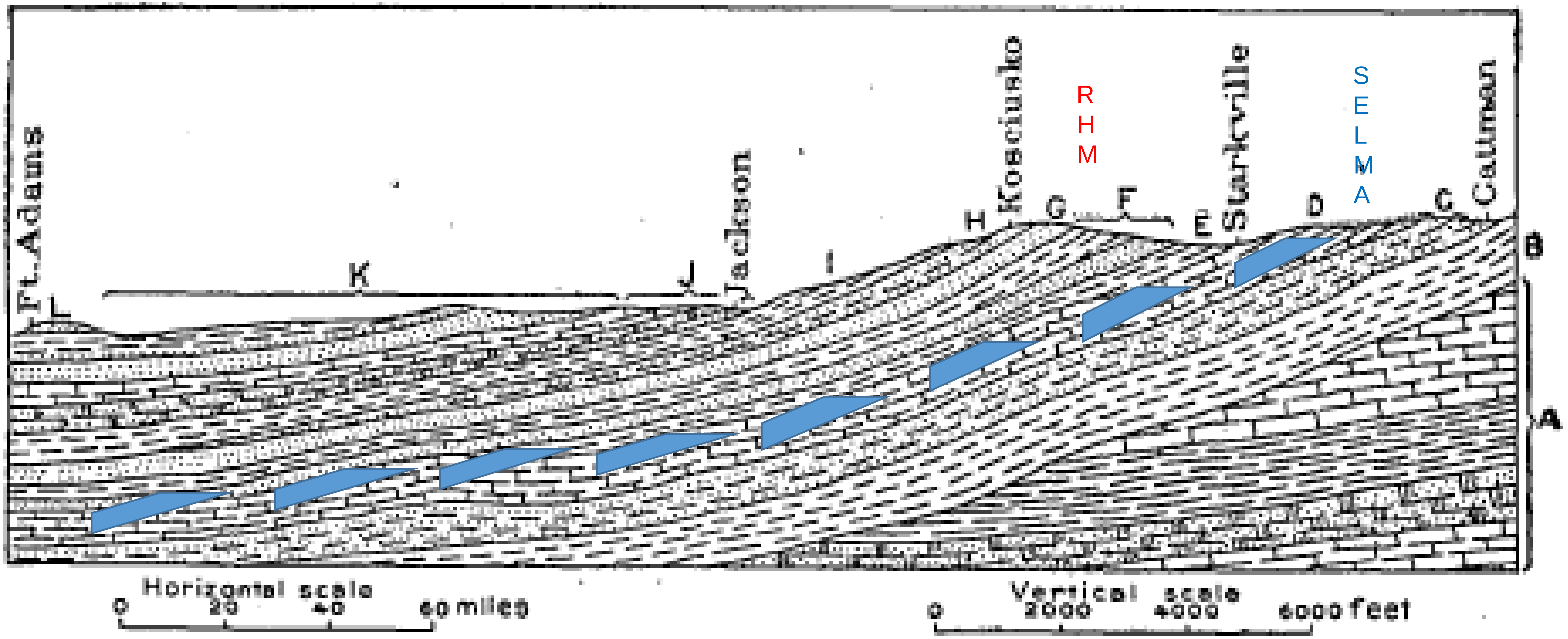
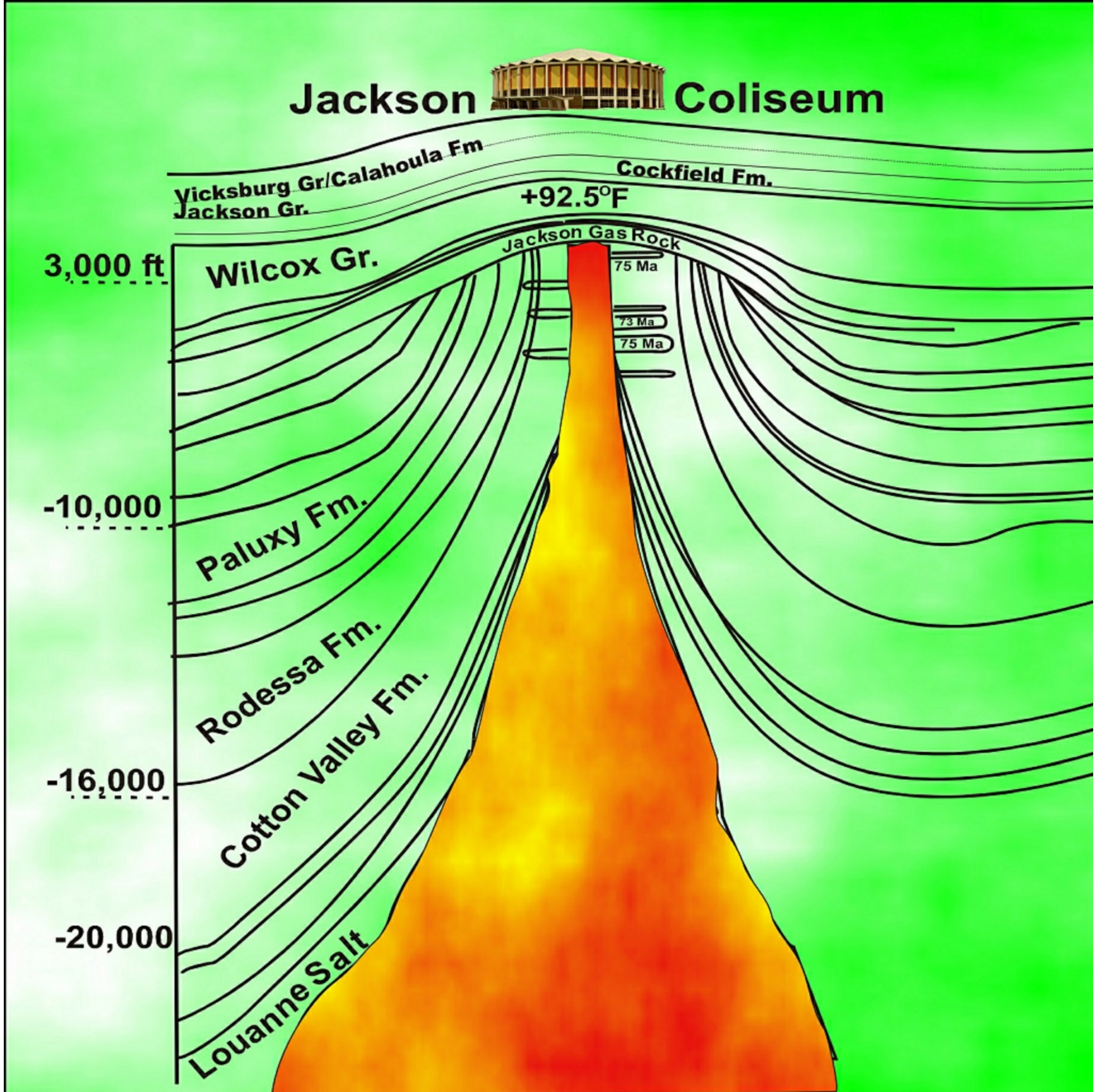


FIG. 4.—Section from Gattman to Fort Adams. L, loess; K, Grand Gulf (sandstone and clay); J, Vicksburg (limestone); I, Jackson (clays and marls); H, Claiborne; G, Tallahatta (sandstone); F, Wilcox (sands and clays); E, Midway (limestone and clays); D, Selma (limestone); C, Eutaw (sands and clays); B, Tuscaloosa (sands and clays); A, Paleozoic (limestone, etc.).

https://pubs.usgs.gov/bul/0283/report.pdf Crider 1906 Geology of Mississippi



Jackson
Coliseum
Vicksburg Gr/Calahoula Fm
Cockfield Fm.
Jackson Gr.
+92.5°F
Jackson Gas Rock
3,000 ft
Wilcox Gr.
75 Ma
73 Ma
75 Ma
-10,000
Paluxy Fm.
Rodessa Fm.
Cotton Valley Fm.
-16,000
-20,000
Louanne Salt

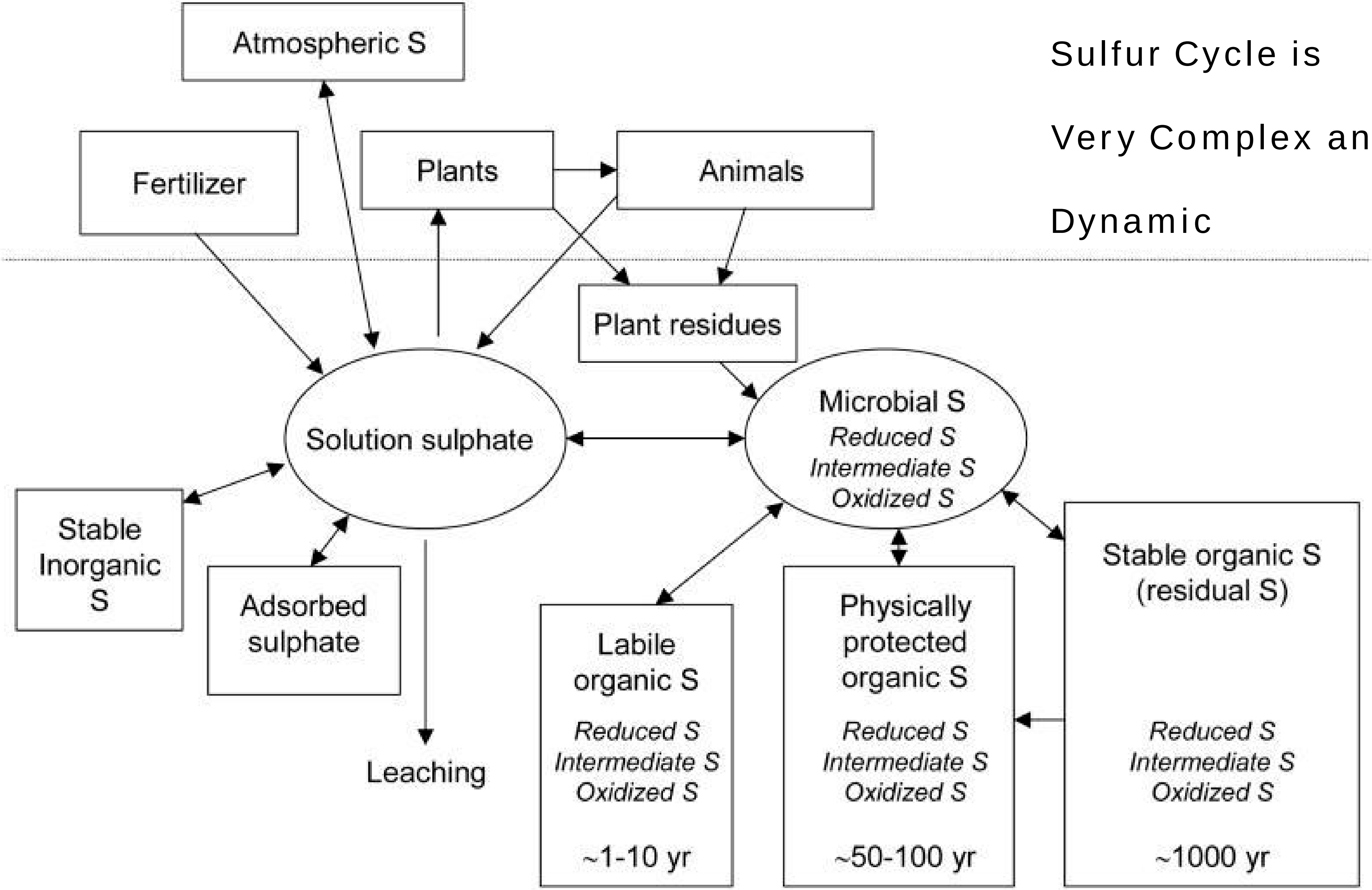
Introduction

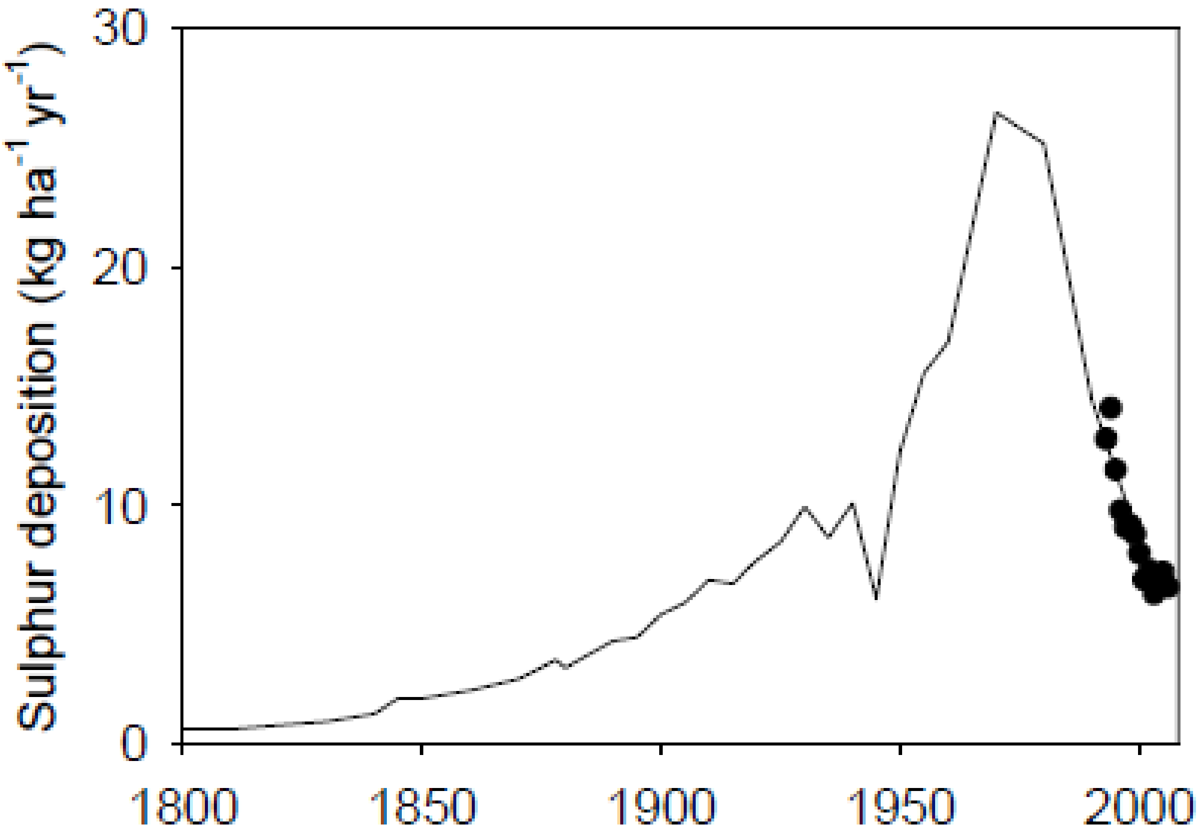
- Overburdens in the Mississippi Embayment are mined for lignite in Mississippi, Louisiana and Texas. Similar Eocene deposits are mined for lignite in Wyoming, Montana and North Dakota.
- There are unconsolidated sediment layers that are unoxidized gray materials and may be suitable inclusion as final respreads (NOT APPROVED!).
- Variable amounts of pyritic sulfur may be present in these overburdens selected for reclamation that can be difficult to predict from visual characterizations.
- Generally, red oxidized materials contain little pyritic S, so these are favored as suitable topsoil substitutes (RedOX Approved as Respread)

Introduction

- Standard agricultural soil testing determines exchangeable potassium (K) and phosphorus and extractable potassium (K), but neither pH nor the predicted lime requirement provides an indication of potentially oxidizable sulfur.
- Normal agricultural soils contain 50 to 200 mg kg^{-1} extractable sulfate depending upon seasonal sulfur mineralization stages and it can vary by extraction method utilized (Bray, Mehlich, Lancaster, etc).

Sulfur Cycle is Very Complex and Dynamic





Sulfur ↓

Emissions

Success !

Fig. 1. Historic atmospheric sulphur deposition in Denmark. Based on actual values (symbols, Ellermann et al., 2006) and scaling of the relative time series developed by Alveteg et al. (1998).

https://dl.sciencesocieties.org/publications/books/abstracts/agronomymonogra/sulfuramissingl/25

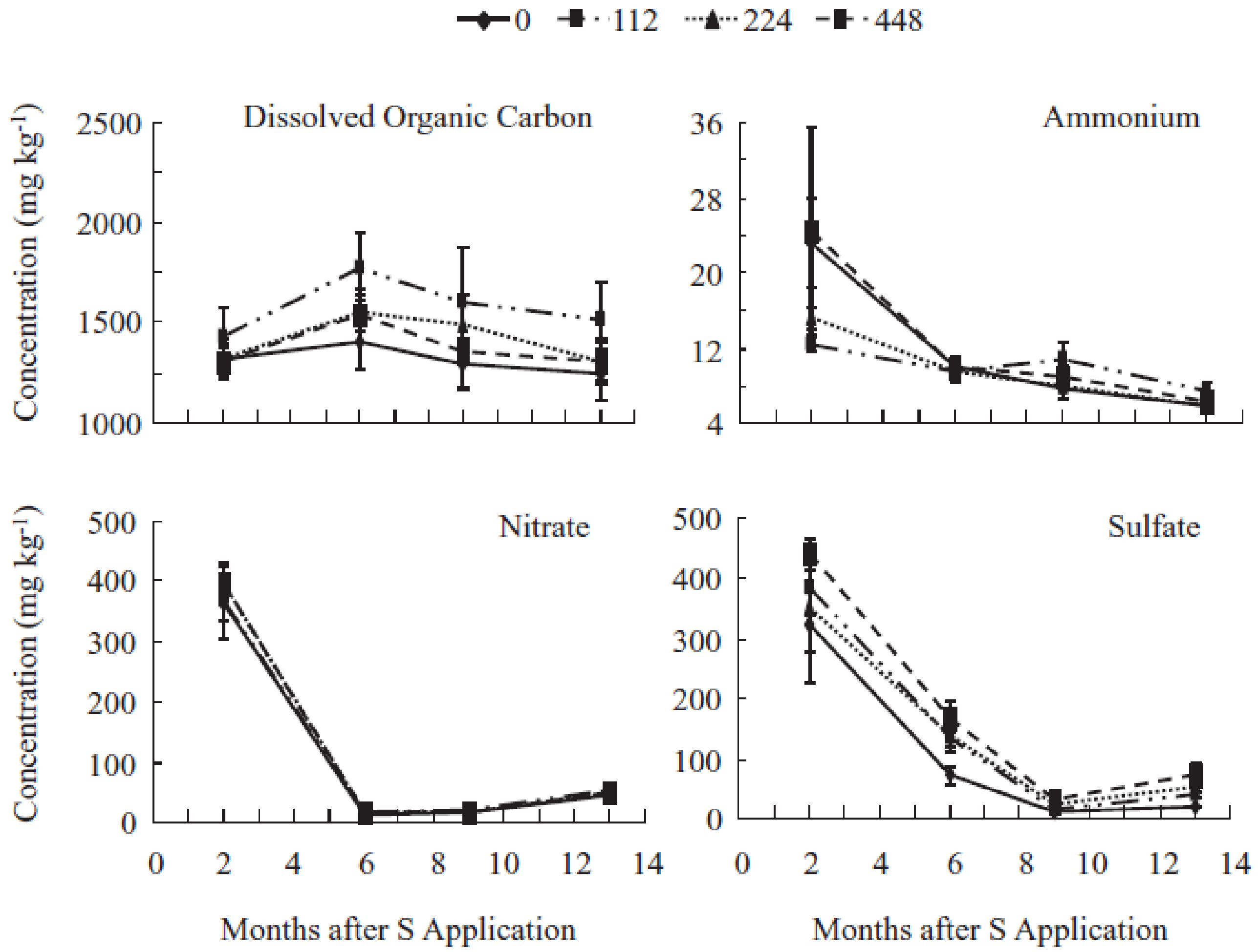


FIGURE 2 Seasonal dynamics of dissolved organic C, extractable NH_4—N, NO_3—N, and SO_4—S after S application at 0, 112, 224, and 448 kg S ha^{-1}. Error bars represent the standard error of the mean.

Muck Soil (Histosol) in Florida Releases

NO_3^-, NH_4^+ and SO_4^-

even without Sulfur or N Added

SO_4^- and NO_3^-
at 200 to 400+ mg kg^{-1}

Seasonal Mineralization Changes

SEASONAL CHANGES IN NUTRIENT AVAILABILITY FOR SULFUR-AMENDED EVERGLADES SOILS UNDER SUGARCANE
Ye, Wright,and McCray. 2011 *Journal of Plant Nutrition*, 34:2095–2113. DOI: 10.1080/01904167.2011.618571

Lime Requirement of Agricultural Soils

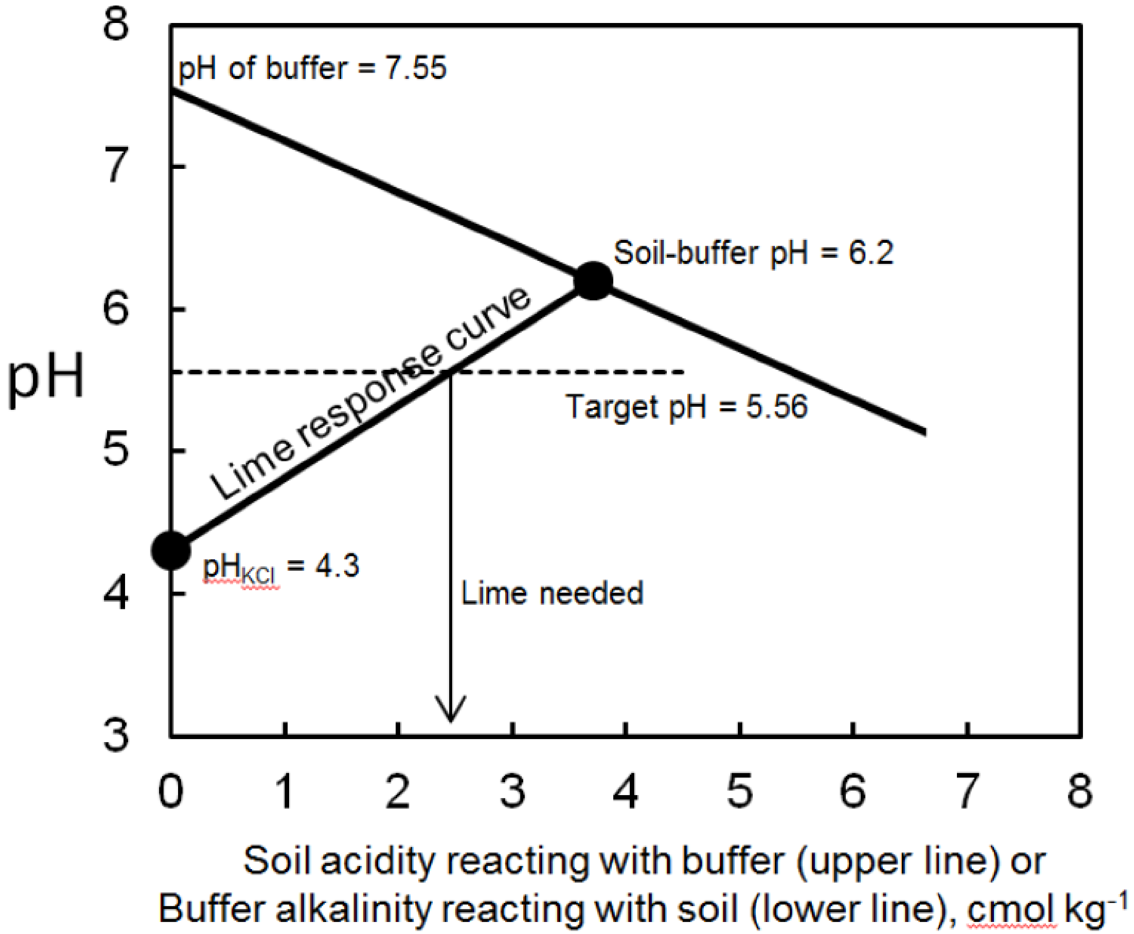


Fig. 1. An example lime-response curve with pH_{KCl} of 4.3 and Sikora-2 soil-buffer pH of 6.2. 2.46 cmol kg^{-1} alkalinity (equivalent to 1.23 tons $acre^{-1}$ $CaCO_3$) is required to increase pH to a target pH_{KCl} of 5.56 which is equivalent to pH_w of 6.4.

Not Applicable for

Reclaimed Mine

Land with some

Pyritic Sulfur

Experiments in Mississippi with Reclaimed Lignite Lands

- Early work with Red Gray Mixtures
- Greenhouse Incubation
- USDA Manure and Gypsum

Objectives

- Determine Potential Adverse Effects of Utilizing Gray Unoxidized Deep Subsoil as a Plant Growth Medium
- Determine the Optimum Ratio of Gray to Red Soil as Suitable Plant Growth Substitute Material
- Utilize Common Soil Test Extractable Sulfate as an Early Indication of Pyritic Sulfur FeS_2

Site “B” was a Sweatman Silt Loam Soil
Low Pyritic Sulfur 0.05%
Light colored gray


Site “A”
Site “A” was from a
Smithdale Sandy Loam Area
There was a small band of
lignite “I or H” Seam
Gray Material with
0.16% Pyritic Sulfur


Site “A” was from a
Smithdale Sandy Loam Area
with Medium to High Pyritic
Sulfur 0.16%
Gray unoxidized was very dark
gray, almost black
345B
CAT

Methods and Materials

- Red and Gray Overburden Mixtures (w/w)
- Gray Portion: 0, 25, 50, 75 and 100 %
- 10 kg per pot
- Overburdens were Analyzed for Pyritic S, Acid Base Accounting (ABA) and Texture by Energy Labs, College Station, TX
- Soil Fertility was Analyzed by the Mississippi Extension Soil Fertility Lab (Lancaster Extractant)
- Included extractable Sulfate-S and Mn

Sulfur Levels in Gray Unoxidized Soil

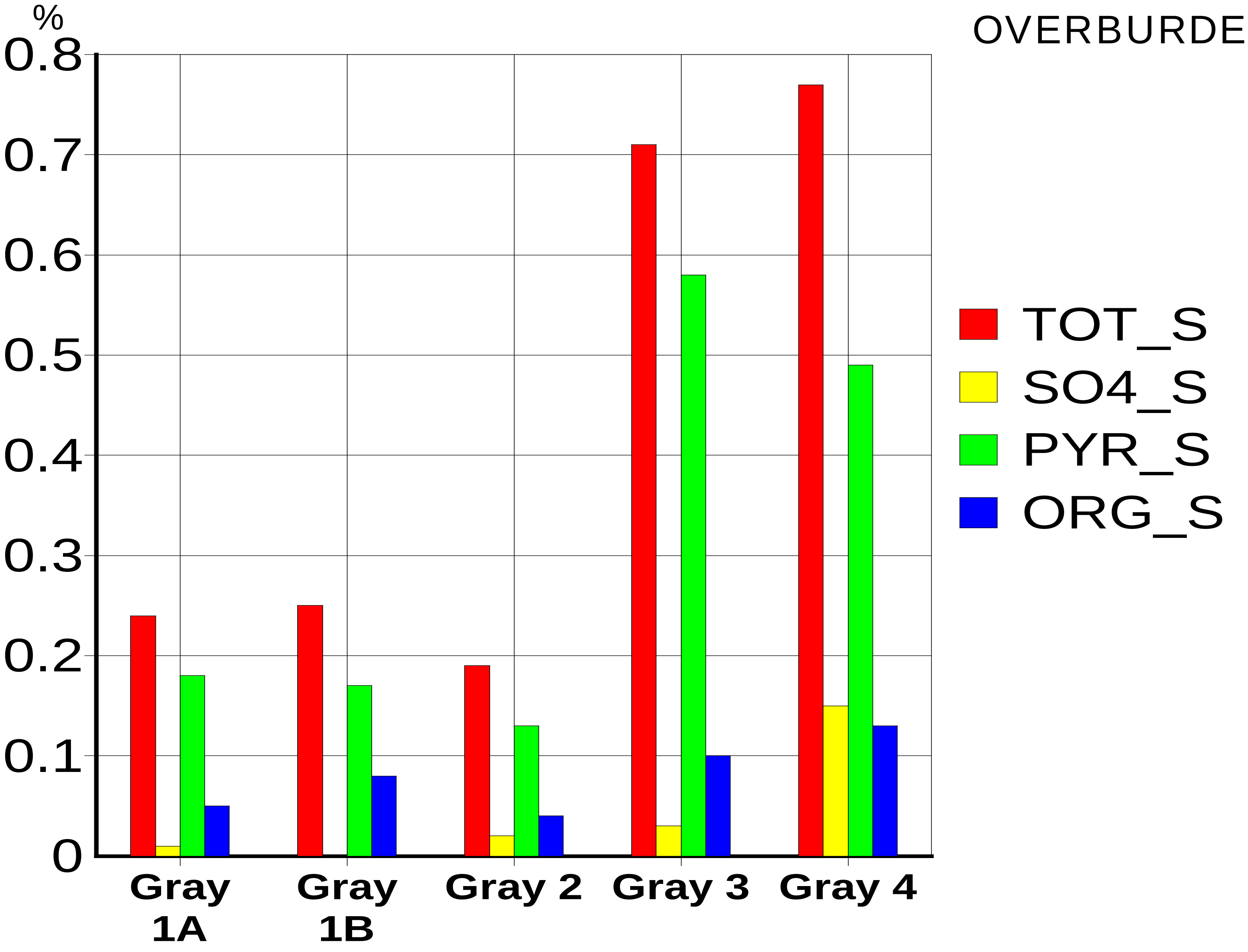
XXIX

OVERBURDEN

All samples exceed the current 0.10% Pyritic S level

Samples 2, 3 and 4 had a “benign” light gray color

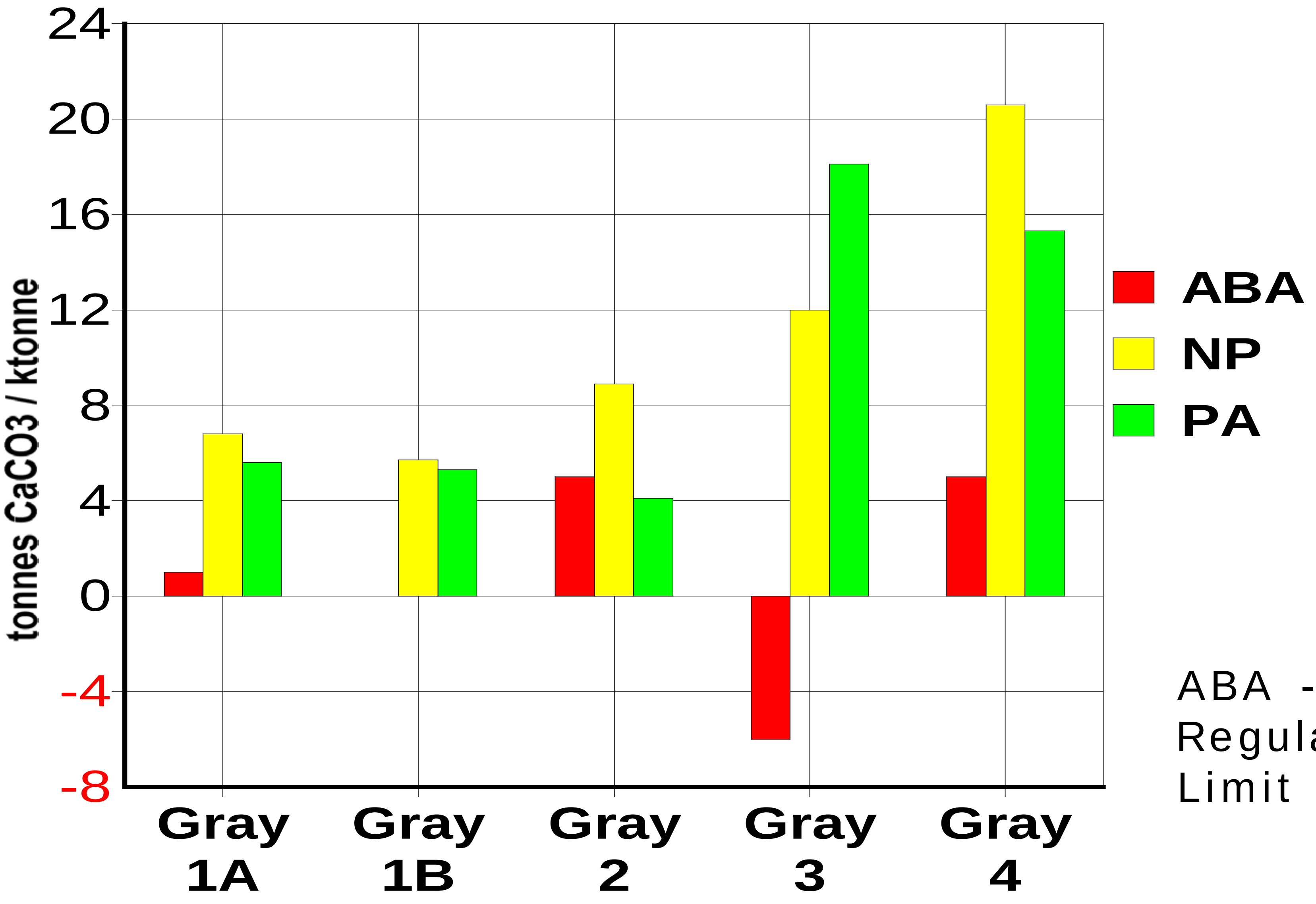
There was no relationship between Total S levels and Organic matter



Acid Base Accounting

Four of the five samples have acceptable ABA levels

Balanced by High $CaCO_3$ Levels from Selma Chalk



ABA - 5 is the Regulatory Limit

Methods

- The Mississippi Soil Testing laboratory routinely utilizes the Lancaster solution to determine agricultural fertilizer and lime recommendations.

- It determines most of its parameters with an Optima 4300 DV ICP Spectrophometer including Ca, Mg, P, K, Na, Zn, Mn and SO_4-S, though Mn and SO_4-S are not routinely reported.

    - Since 2005, all samples from reclamation research in Mississippi have had SO_4-S and Mn reported.

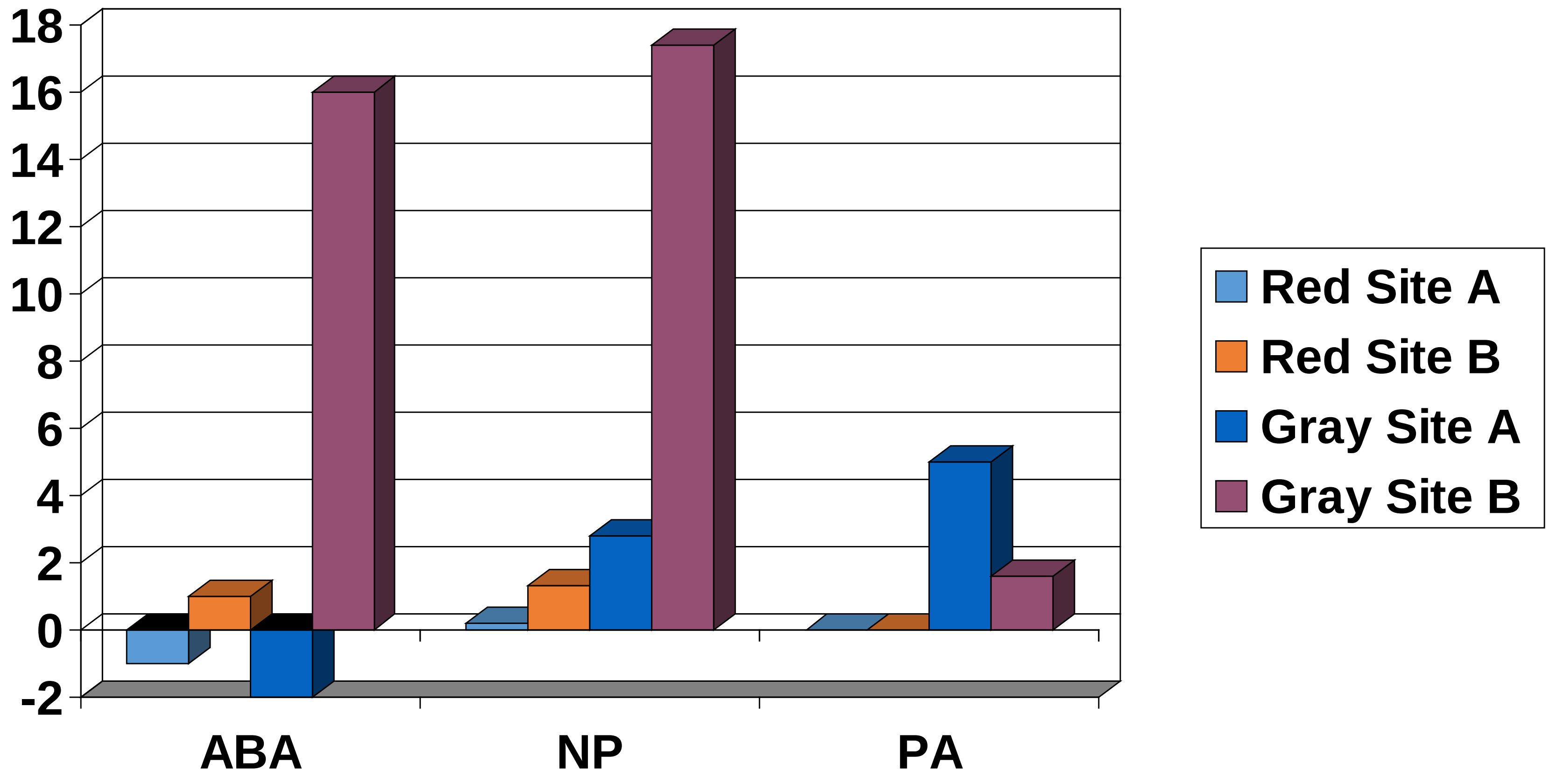
- Samples with known pyritic-S levels of 0.05 (B) to 0.16% (A) were found in some gray unoxidized materials not suitable for topsoil replacement utilization.

- These were mixed with various portions of suitable red oxidized materials with 0.00 % pyritic-S and tested for extractable sulfate and incubated in the greenhouse for 12 months.

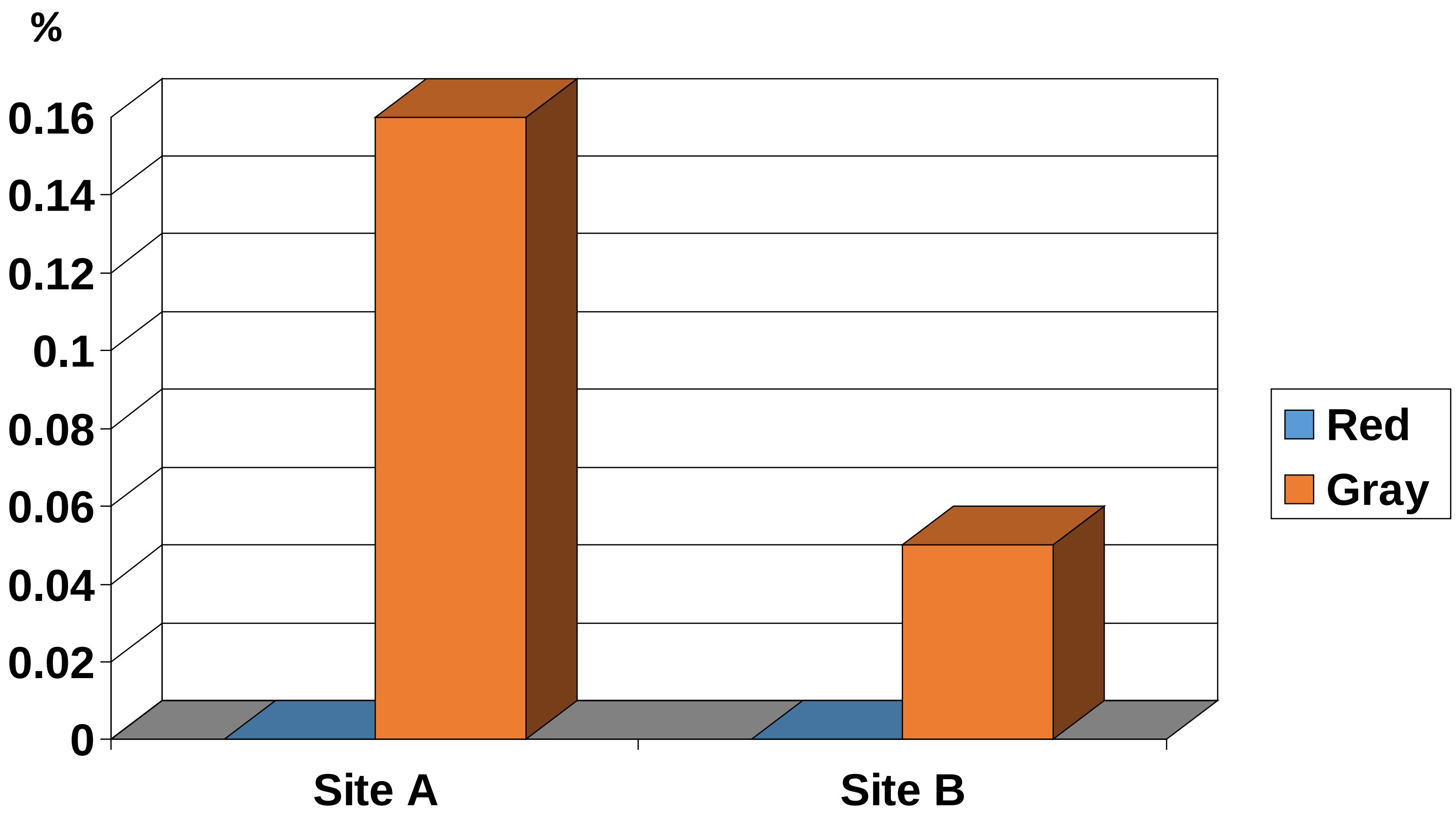

Pearl Millet is
Tolerant of Low
pH and is a good
indicator plant
for Loblolly Pines

Acid Base Accounting of Red and Gray Overburden

ktonnes $CaCO_3$ ktonne^{-1} soil



Pyritic S Levels FeS_2

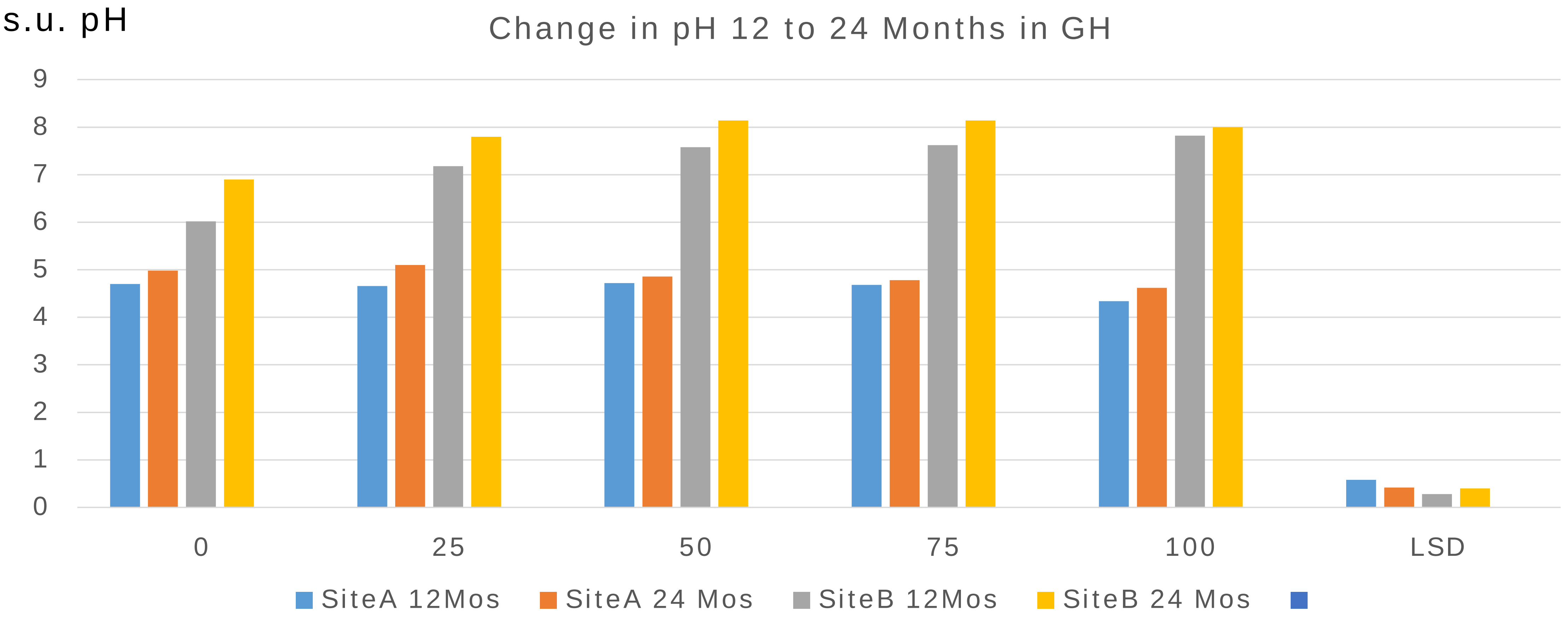


Soil Fertility Analysis

- All Major Nutrients (P, K, Ca, and Mg) Increase with Increasing Levels of Gray Overburden
- Pyrite Levels at Site A Exceed Acceptable (Desirable?) Levels – Increased Potential Acidity
- pH and Neutralization Potential at Site B Indicates that this Overburden would be Suitable for only high pH Loving Plants

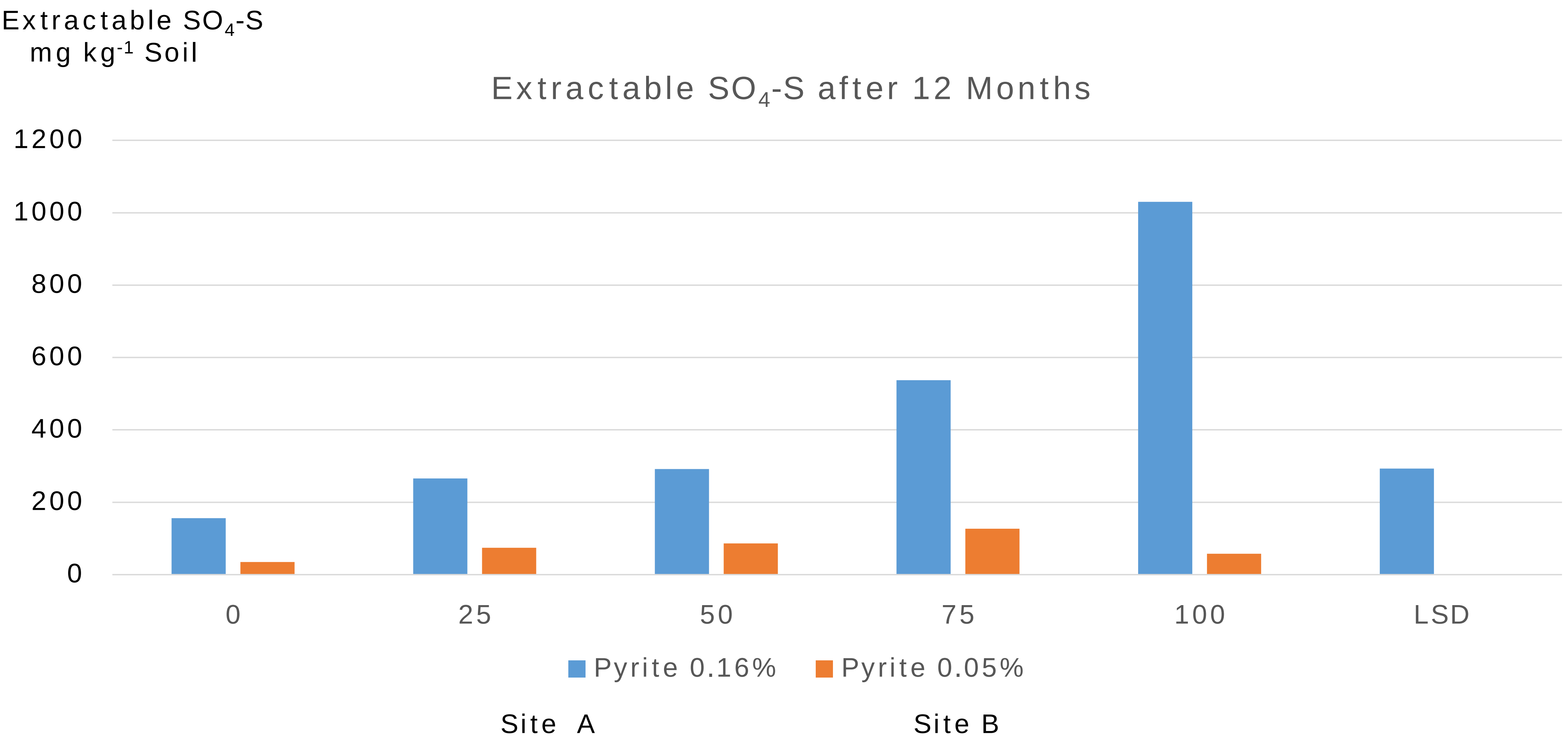
Red Gray Mixtures with Pyrite in Gray at 0.05 and 0.16%

Red → → → → Gray

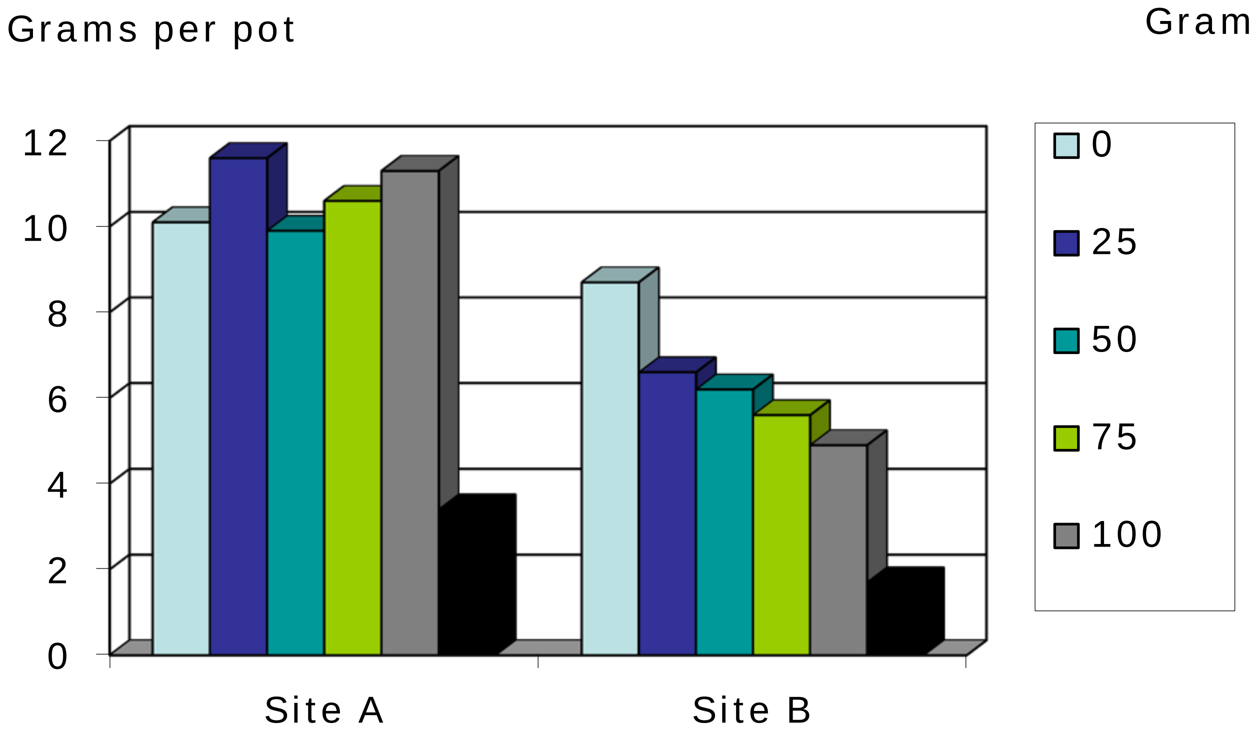


Site A = 0.16% Pyrite Site B = 0.05% Pyrite
In only the Gray Material ; Red = 0.0% Pyrite

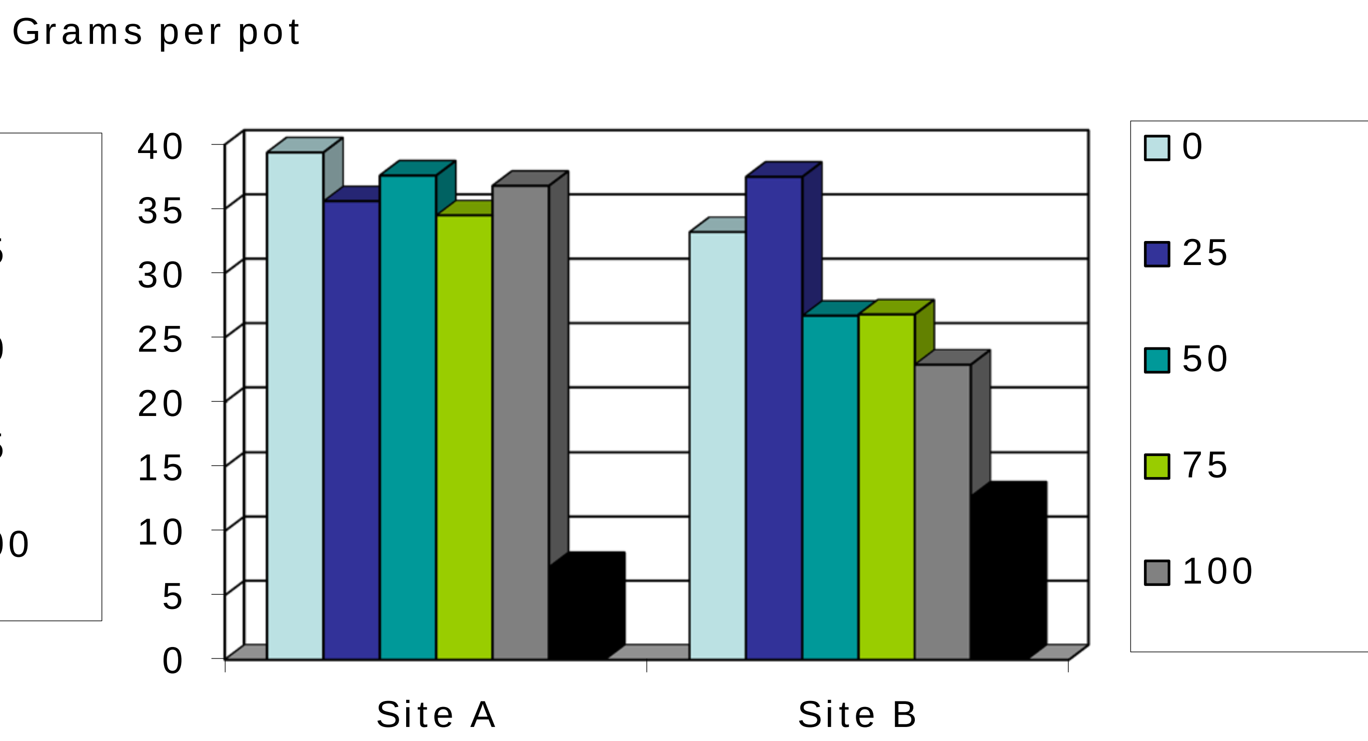
Red Gray Mixtures with Pyrite (FeS_2) at 0.05 and 0.16%



Greenhouse Growth Response of Pearl Millet to Red Oxidized / Gray Unoxidized Mixtures



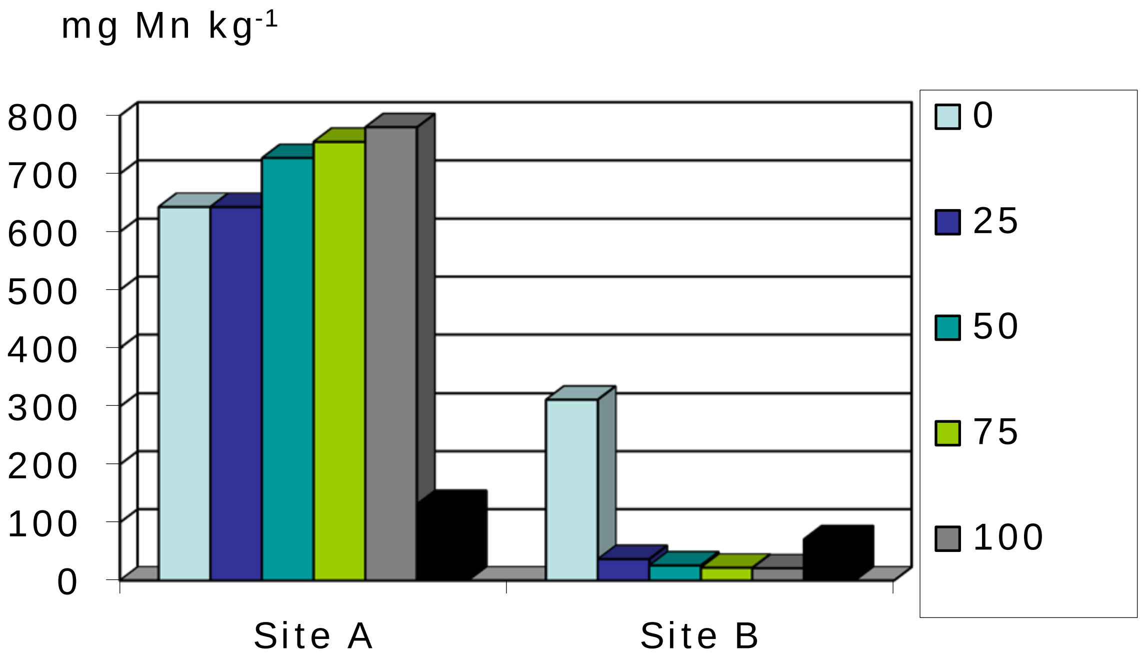
August

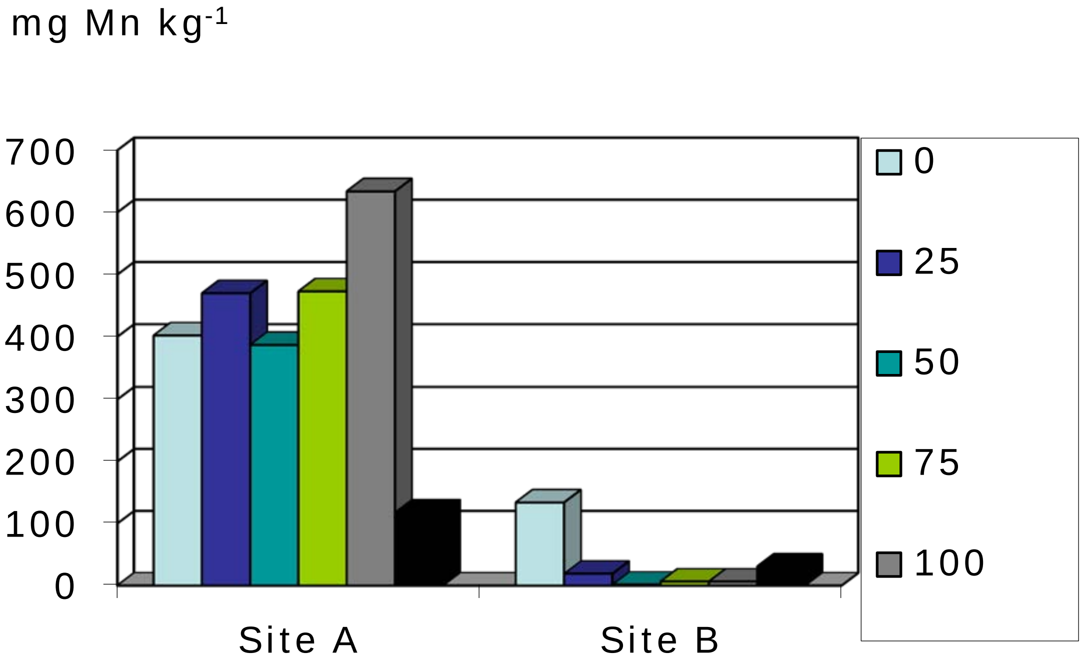


October

Site A = 0.16% Pyrite Site B = 0.05% Pyrite
In only the Gray Material ; Red = 0.0% Pyrite

Manganese (Mn) Levels in Pearl Millet Growing in Red and Gray Mixtures with Low (Site B) and Moderate (Site A) Pyritic Sulfur





Site A 0.16% Pyrite
1600 ppm

Site B 0.05% Pyrite
500 ppm

August

October

Sufficient at 100 mg Mn kg^{-1}; Toxic to pearl millet at > 500-1000 mg Mn kg^{-1}.
Toxic to wildlife and Livestock at 2000 ppm (2000 mg kg^{-1})

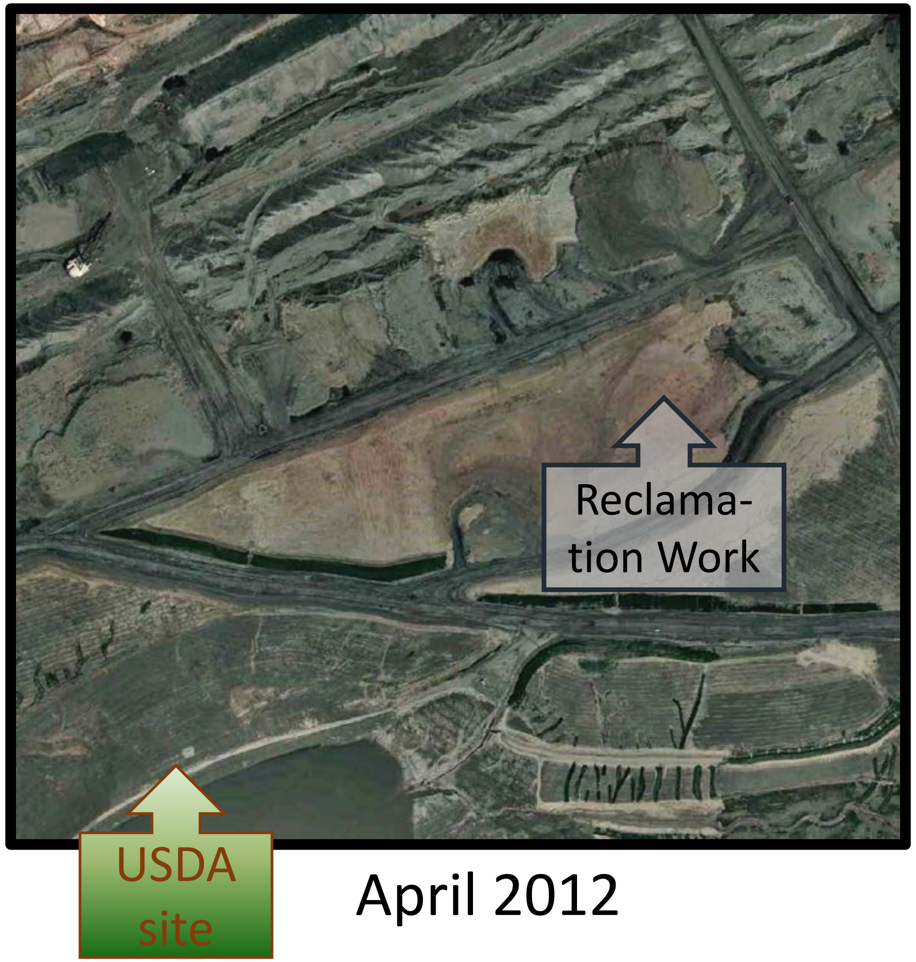
Results and Discussion

- Extractactable SO^4- from site B (Moderate pyritic S) was 500 to 1000 mg kg^{-1} initially and 150 to 180 mg kg^{-1} SO_4-S from the low pyritic-S site (A).
- Apparent pH remained high (7.2 to 7.8) at site A, but it declined to 4.6 to 5.1 in the higher pyritic-S materials.
- Economical utilization of routine agricultural soil testing provides a viable initial screening tool prior to expenditure of scare resources for expensive overburden testing procedures.

Restoration of soils after strip mining of coal

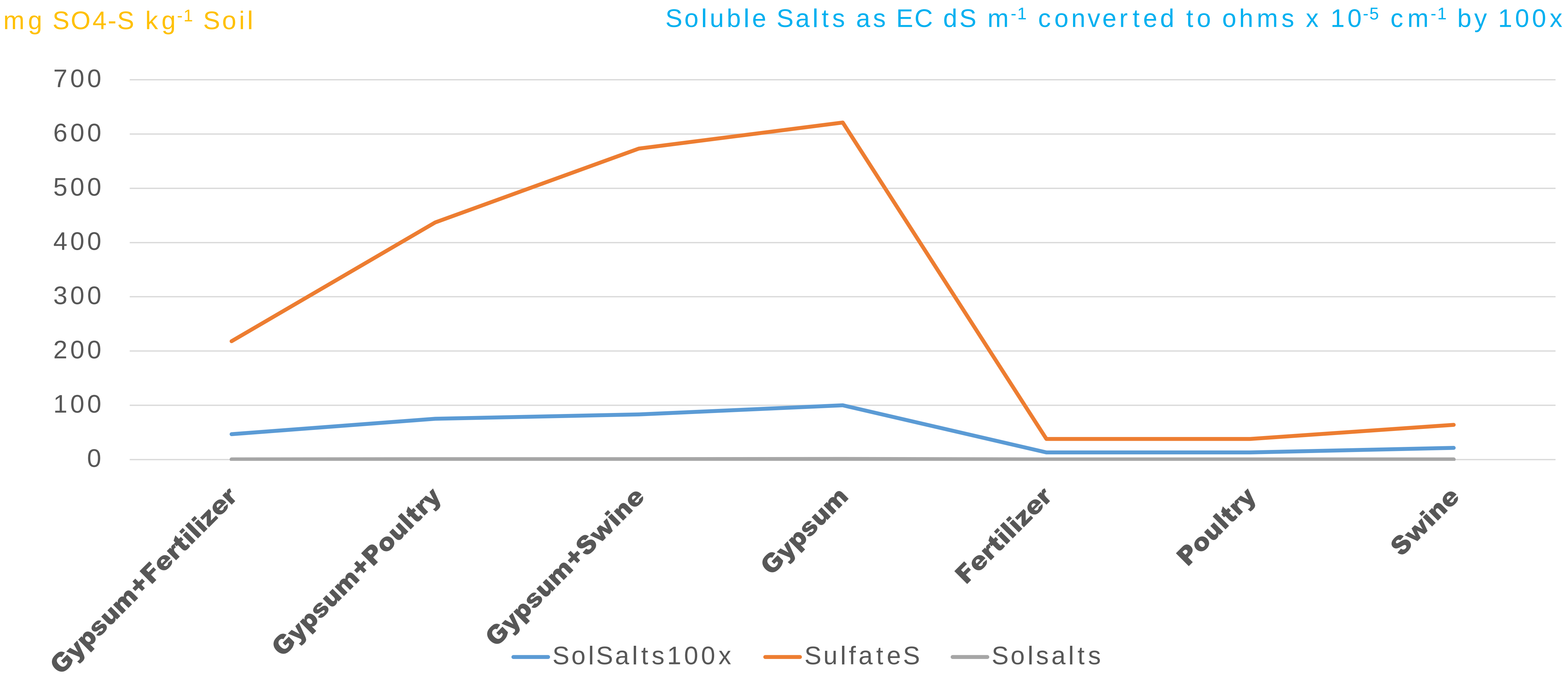
- USDA is cooperating to find potential uses for animal and industrial by-products.

January 2012



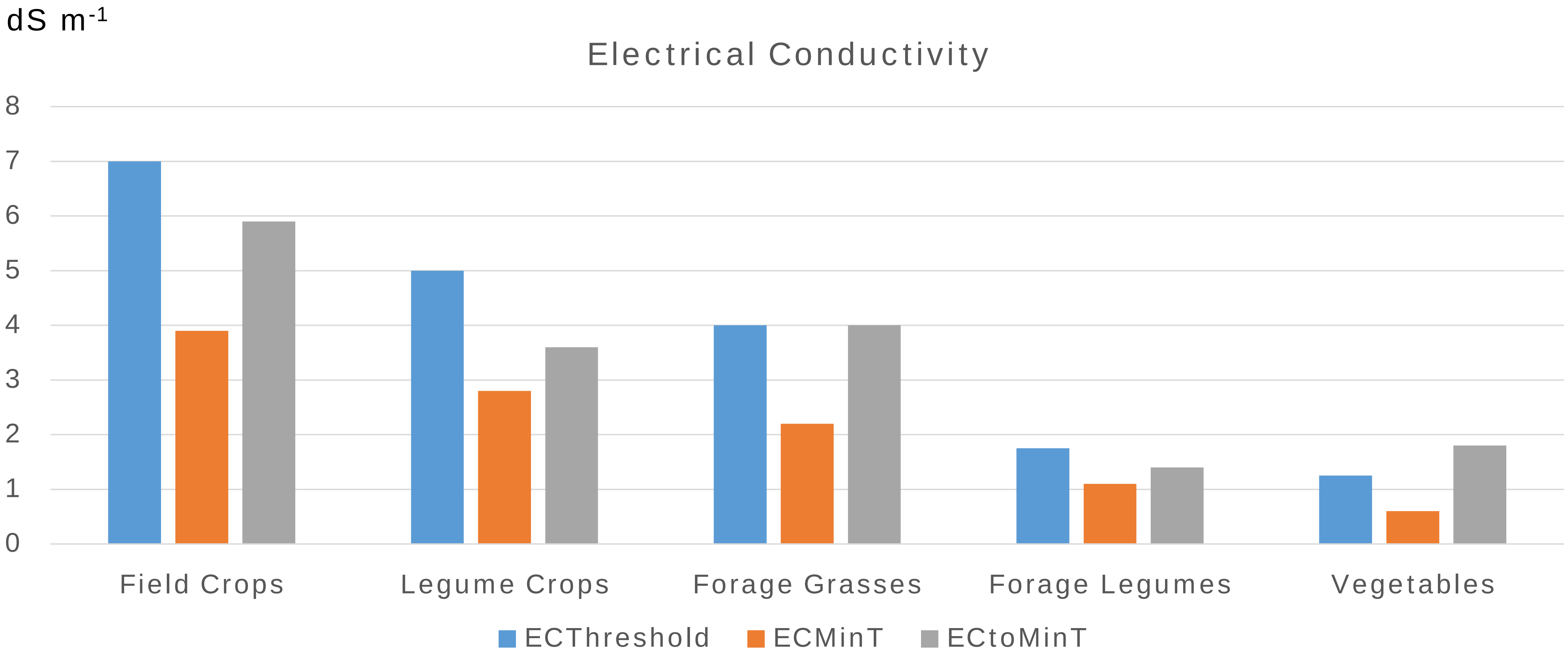
April 2012

Sulfate Sulfur and Soluble Salts



Duncan Sulfate-S: 344 Soluble Salts: 36

Threshold Sensitivity of Various Crops



NRCS Soil Electrical Guidelines

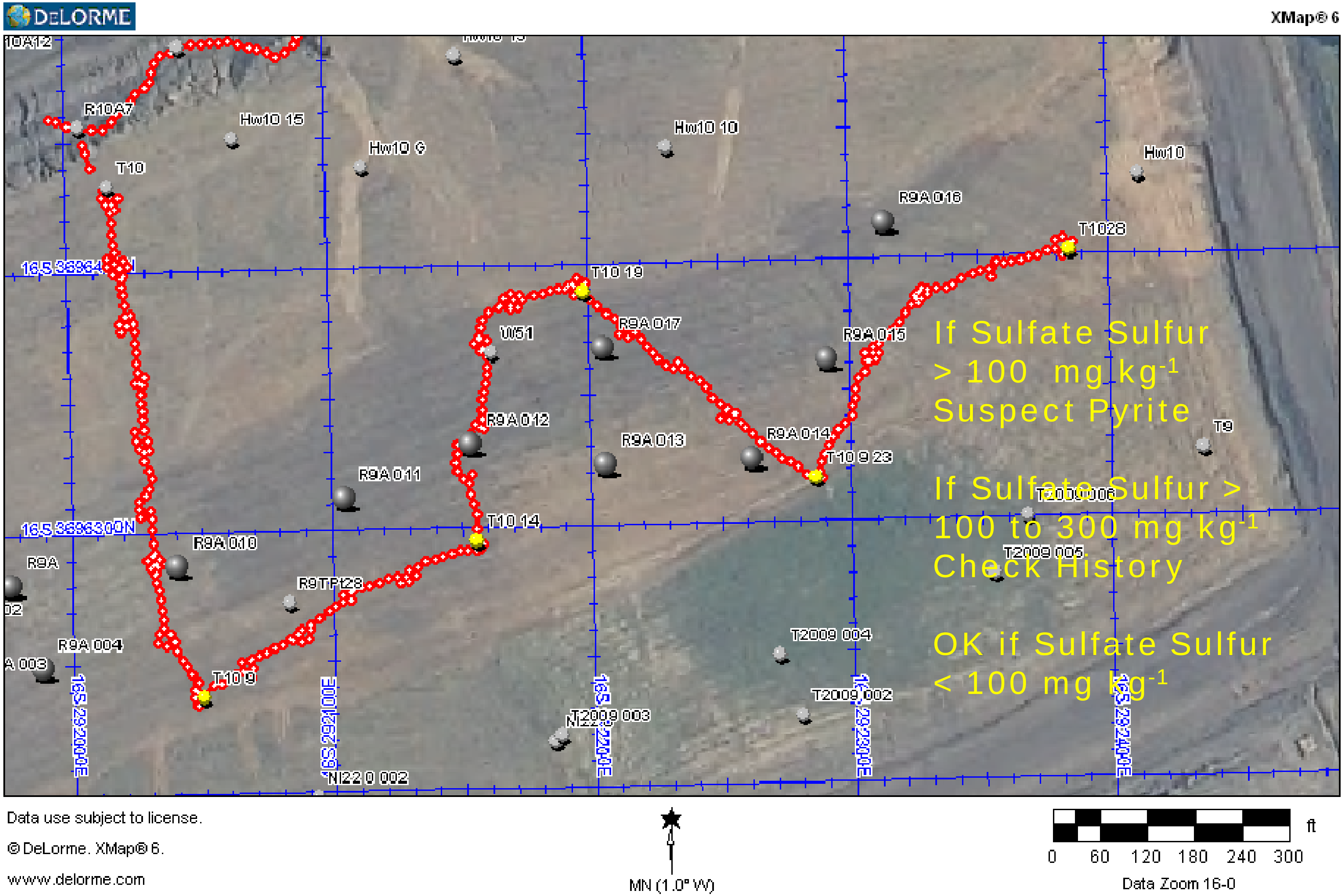
Conclusions

- **Site A with a Pyrite Level of 0.16% dropped in pH and Pearl Millet had Increased Levels of Mn as Gray Portion Increased**

- **Inclusion of Gray Unoxidized Overburden is Not Desirable for Suitable Plant Growth, particularly loblolly pines**

- **Utilization of Routine Soil Tests Provides the Mining Company and Landowners Assurance of Good Reclamation**

- **Soluble Salts and Extractable Test SO_4-S can be Used as Initial Indicators**


DeLORME
XMap® 6
If Sulfate Sulfur > 100 mg kg-1 Suspect Pyrite
If Sulfate Sulfur > 100 to 300 mg kg-1 Check History
OK if Sulfate Sulfur < 100 mg kg-1
R10A7
Hw10 15
Hw10 6
Hw10 10
Hw10
T10
R9A 016
T1028
T10 19
R9A 017
W51
R9A 015
R9A 012
R9A 013
R9A 014
T10 9 23
T9
R9A 011
T10 14
R9A 010
R9A
R9TPt28
R9A 004
T10 9
T2009 004
T2009 002
T2009 003
T2009 006
T2009 005
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Data Zoom 16-0

THANK YOU!

Questions ??

NORTH AMERICAN COAL CORPORATION

RED HILLS MINE