Acid Sulfate Soils in the Coastal Zone 2018 Coastal Zone Soil Survey (CZSS) Work Planning Conference Savannah, GA – January 8th – 12th, 2018

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Outline

- Introduction to Acid Sulfate Soils
- Formation and accumulation of sulfides (sulfidization)
 - Biogeochemical processes
 - Locations
- Exposure and development of AS Soil conditions
 - (sulfuricization)
 - Dredging
 - Draining
 - Upland AS soils



Background

- Recognized as early as the 1700s
- Acid sulfate soils Those in which sulfuric acid
 - <u>may be produced</u>,
 - <u>is being produced</u>, or
 - <u>has been produced</u>,
 - in amounts that have a lasting effect on soil characteristics.
 - Three broad genetic kinds of acid sulfate soils
 - Potential
 - Active
 - Post-active

- Potential Acid Sulfate Soils
 - Non-oxidized (anerobic) soils, currently or previously coastal (tidal) sedimentary environments affected by sulfidization.
 - Contain sulfide minerals in near surface horizons/layers that generate sulfuric acid upon exposure to oxidizing conditions
 - Hypersulfidic Materials (insufficient neutralization; become extremely acid, pH < 4)
 - Hyposulfidic Materials (buffering or neutralization potential; don't become extremely acid)



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- Active Acid Sulfate Soils
 - Form where sulfide minerals (mostly pyrite) have oxidized in near surface horizons and formed enough sulfuric acid (insufficiently neutralized or buffered), to cause pH drop to ultra low levels
 - A sulfuric horizon is recognized



- Potential Acid Suli
 - Non-oxidized (an (tidal) sedimenta
 - Contain sulfide n generate sulfuric
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 - Form where sulfinear surface horion
 (insufficiently neultra low levels)
 - A sulfuric horizor
- Marlton Collington/Annapolis
- Post-Active Acid Sulfate Soils
 - Where weathering and pedogenesis have moved beyond the active stage
 - Sulfide minerals are no longer present in surface soil horizons
 - Sulfuric horizons no longer present
 - pH of these horizons has risen above 3.5

Formation of Sulfides

Microbial Decomposition of Organic Matter $O_{CH_2O + O_2}^{4} ----> CO_2 + H_2O$

- When the C is oxidized, something must be reduced (Reduction of an electron acceptor)
- In aerobic settings O₂ is the "electron acceptor"
- When soils or sediments are saturated
 Diffusion of O₂ into the soil is retarded
- Microbial activity begins to deplete dissolved O₂
- Eventually becomes anaerobic

Alternate e⁻ acceptors progressively more reducing (facilitated by various microbes) $NO_{3}^{-} + 2H^{+} + 2e^{-} ---> NO_{2}^{-} + H_{2}$ Nitrate $MnO_{2} + 4H^{+} + 2e^{-} ---> Mn^{2+} + 2H_{2}O$ Mn Oxides $Fe(OH)_3 + 3H^+ + e^- ---> Fe^{2+} + 3H_2O$ Ferric Iron +6 $SO_4^{2-} + 10H^+ + 8e^- --> H_2^{-2} + 4H_2^{-2}$ Sulfate What you smell!

Eh-pH stability phase diagrams of redox-affected minerals



Summary

Factors Necessary for Sulfate Reduction

- C Source (oxidizable organic matter)
 - Plant roots in soils
 - Plankton in sediments
- Reducing conditions
 - Exclusion of oxygen
 - Usually from saturation or ponding
- Sulfate-Reducing microorganisms (ubiquitous)
- SO₄⁻² Source
 - estuarine waters (coastal settings most common)
 - atmospheric deposition
 - weathering of S bearing rocks (ASW)
 Upland settings, less common

Requirements for Sulfate Reduction C Source (oxidizable organic matter) Reducing conditions Sulfate-Reducing microorganisms (ubiquitous) SO⁻² Source

You smell the H₂S! Will Fe sulfide minerals form? (these don't smell) Is there Fe available? (main source is sediment)

Formation of Fe Sulfide Minerals

Reaction of Ferrous Iron (II) with Sulfide

$Fe(OH)_2 + H_2S ---> FeS + 2H_2O$

(no electron transfer)



Partial oxidation of the sulfide (S^{-2} to S^{-1}) is tied to the reduction of iron from Fe⁺³ to Fe⁺². Also other mechanisms.

Due to greater stability of pyrite, FeS is transformed to FeS₂ over time (weeks, months, years).

Common Fe-sulfide minerals



Pyrite framboid

0020 20KV X3,500 10Pm WD16

Euhedral Pyrite Crystals

0006 15KV X1,200 10Pm WD15

Pyrite

e

g

(Richard T. Bush-UNSW-2000)

h

10 v



5 um



a



1 um



FeS (Richard T. Bush-UNSW-2000)

2 um

Where Sulfide Minerals Form

Coastal Marshes



IRIS Tubes Installed

Ĩ.



Subaqueous Soil Environments









1hr

6hrs

Site A

24hrs



Site B 24 hrs 30 --5 H Site C 24 hrs 14 14 1 T 14 0 Product in 0 Site D 24 hrs

Sale

War and a fair for

Special problems of MBO's

- Mono-sulfidic black oozes (MBO) contain iron monosulfides, FeS
 - (making them jet black in color)
 - They are AVS (acid volatile sulfides) evolve H_2S when exposed to 10% HCL.
 - Extremely labile
- When MBO's are stirred into water
 - the sulfide oxidizes very rapidly and consumes the dissolved oxygen in the water (rapid hypoxia/anoxia)
 - Turbulence in natural water bodies can result in fish kills
 - Well documented in Australia



Sulfides form mainly in coastal environments – Marshes and Subaqueous Settings

Sulfuricization (Acid Sulfate Weathering)

- Sulfide-bearing materials are oxidized,
- Minerals are weathered by the sulfuric acid produced, and
- New mineral phases are formed from the dissolution products.

(Fanning and Fanning, 1989)

1st Step – Oxidation of the Sulfur in Pyrite

- $FeS_2 + 3\frac{1}{2}O_2 + H_2O \rightarrow Fe(II)SO_4 + H_2SO_4$
- Generates 1 mol of sulfuric acid
- Generates 1 mol of ferrous sulfate (highly soluble)

2nd Step

Oxidation and Hydrolysis of Ferrous Sulfate

- Fe(II)SO₄ + $\frac{1}{4}$ O₂ + 1 $\frac{1}{2}$ H₂O \rightarrow FeOOH + H₂SO₄
- Generates a second mol of sulfuric acid
- Generates a mol of Fe oxihydroxide (e.g. goethite)

Overall Combined Reactions Oxidation and Hydrolysis of Pyrite

- $FeS_2 + 3 \frac{3}{4}O_2 + 2 \frac{1}{2}H_2O \rightarrow FeOOH + 2H_2SO_4$
- Generates 2 moles of sulfuric acid
- Generates oxidized iron phases
 - Schwertmanite
 - Jarosite
 - Ferrihydrite
 - Goethite

Sulfuric acid neutralized with calcium carbonate

- $H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2$
- This forms the mineral gypsum.
- Releases CO₂
- From this reaction and knowing
 - the AW of Sulfur is 32
 - The molecular weight of CaCO₃ is 100
- 3X the weight of CaCO₃ is needed to neutralize the acidity of a given weight of S as sulfuric acid.
- 1% pyrite S in a 6" layer of soil, would require 30 tons/acre of CaCO₃ to neutralize it.

Acid Sulfate Weathering Produces Sulfate Salts

- Ferrous and ferric sulfates
 - are water soluble
 - rozenite, Fe(SO₄)x4 H₂O
 - melanterite, $Fe(SO_4)x7 H_2O$
 - Reaction with silicates can release Al to form Al sulfates or mixed Fe Al sulfates or hydroxysulfates etc.





Salts Accumulate at the Soil Surface During Dry Periods

- The flushing of sulfate salts into waterways followed by the oxidation and hydrolysis
- Essentially is like AMD
- acid waters in streams coated with iron (hydr)oxide precipitates – very poor for fish and other aquatic organisms.













* Age ranges from Kulp, J. L., 1961, Geologic time scale: Science, v. 133, no. 3459, p. 1105-1114.

† Radiometric dates made on Maryland rocks.

1 inch equals 25 miles

‡ A detailed Geologic Map of Maryland, 1968 at a scale of 1 inch equals 4 miles, is also available.



Representative Cross-Section through a Landscape Overlying the Mattawan/Monmouth (upper Cretaceous) Formations



(T.M. Valladares)



Representative Cross-Section through a Landscape Overlying the Aquia/Nanjmoy (Eocene) Formations



(T.M. Valladares)

Jarosite and Fe oxides

2.8 m

Sulfidic

Sulfide-bearing sediments exposed in excavation/grading of housing development in Crofton, MD east of Washington, DC

Great Oaks Development, Stafford VA

HICKORY

Corrosion of concrete structure by acid drainage in an area where sulfide-bearing sediments were exposed

The Problem

Acid drainage along road cut in Anne Arundel Co. MD



Also found in the Outer Coastal Plain





Data LDEO-Columbia, NSF, NOAA Image NOAA Data SIO, NOAA, U.S. Navy, NGA, GEBCO Image Landsat / Copernicus

35.0"W



Conclusions

- Sulfides form most commonly in the coastal zone (marshes and subaqueous soils)
- Significant potential for serious environmental impacts
- Extent
 - Known to some degree
 - May be more extensive than thought
- Needs to be a consideration in the CZSS effort