

8th IASSC

**8th International Acid Sulfate Soils Conference
College Park, Maryland, USA**

July 17 – 23, 2016

*Acid Sulfate Soils:
Pathways to Exposure and Remediation*

Program



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Acid Sulfate Soil Working Group
International Union of Soil Sciences



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Acknowledgment

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8th International Acid Sulfate Soils Conference Organizing Committee

June 2016

8th International Acid Sulfate Soils Conference College Park, Maryland, USA

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8th International Acid Sulfate Soils Conference

Schedule Overview

SUNDAY		
Start	End	
8:30 AM	5:30 PM	Pre-Conference Tour: Hart-Miller Island
4:00 PM	6:00 PM	Conference Registration
5:30 PM	7:00 PM	Welcome Reception - Lower Level Concourse

MONDAY		
Start	End	
7:00 AM	8:00 AM	Breakfast (2nd floor foyer)
8:00 AM	8:30 AM	Welcome Session (Rm 2111)
8:30 AM	9:55 AM	Monday Morning Technical Session 1A (Rm 2111)
9:55 AM	10:25 AM	Coffee (2nd floor foyer)
10:25 AM	12:00 PM	Monday Morning Technical Session 1B (Rm 2111)
12:00 PM	1:00 PM	Lunch - Patuxent Dining Room
1:00 PM	2:25 PM	Monday Afternoon Technical Session 2A (Rm 2111)
2:25 PM	2:55 PM	Coffee (2nd floor foyer)
2:55 PM	5:15 PM	Monday Afternoon Technical Session 2B (Rm 2111)
6:00 PM	9:00 PM	Monday - Technical Reception - Posters Room 2100

TUESDAY		
Start	End	
7:00 AM	8:00 AM	Breakfast (2nd floor foyer)
8:00 AM	9:45 AM	Tuesday Morning Technical Session 3A (Rm 2111)
9:45 AM	10:15 AM	Coffee (2nd floor foyer)
10:15 AM	11:50 AM	Tuesday Morning Technical Session 3B (Rm 2111)
11:50 AM	1:00 PM	Lunch - Patuxent Dining Room
1:00 PM	2:25 PM	Tuesday Afternoon Technical Session 4A (Rm 2111)
2:25 PM	3:00 PM	Coffee (2nd floor foyer)
3:00 PM	4:50 PM	Tuesday Afternoon Technical Session 4B (Rm 2111)

WEDNESDAY		
Start	End	
8:00 AM	5:00 PM	Mid-Conference Field Tour
5:00 PM	9:00 PM	Cookout at Sandy Point State Park

THURSDAY		
Start	End	
7:00 AM	8:00 AM	Breakfast (2nd floor foyer)
8:00 AM	10:15 AM	Thursday Morning Technical Session 5 (Rm 2111)
10:15 AM	10:45 AM	Coffee (2nd floor foyer)
10:45 AM	12:15 PM	Thursday Morning Technical Session 2C (Rm 2111)
12:15 PM	12:30 PM	Pons Medal Award Presentation (Rm 2111)
12:30 PM	1:30 PM	Lunch - Patuxent Dining Room
1:30 PM	2:55 PM	Thursday Afternoon Technical Session 6A (Rm 2111)
2:55 PM	3:25 PM	Coffee (2nd floor foyer)
3:25 PM	5:00 PM	Thursday Afternoon Technical Session 6B (Rm 2111)
5:00 PM	6:00 PM	Business Meeting IUSS ASSWG, Closing Session/Ceremonies (Rm 2111)

FRIDAY-SATURDAY		
		Post Conference Tour: MD and VA
Friday	7:30 AM	Depart Marriott Hotel
Saturday	5:00 PM	Return to College Park

Acid Sulfate Soils: Pathways to Exposure and Remediation

MONDAY

Start		Speaker	Institutional Affiliation		Session/Title
		Moderator Marty Rabenhorst			Opening Session of the 8th International Acid Sulfate Soils Conference
8:00 AM		Dr. Martin Rabenhorst	8thIASSC Orgnizing Committee Chair, Environmental Science and Technology, Univ. of		Welcome and Orientation
8:10 AM		Dr. William Bowerman	Chair, Dept. of Environmental Science and Technology, Univ. of Maryland, College Park, MD		Welcome
8:15 AM		Dr. Craig Beyroudy	Dean, College of Agriculture and Natural Resources, Univ. of Maryland, College Park, MD		Welcome
8:20 AM		Dr. Leigh Sullivan	Acid Sulfate Soil Working Group of the International Union of Soil Sciences (ASS WG)		Welcome

		Moderator Rob Fitzpatrick -The University of Adelaide, AUSTRALIA			1A. Understanding Sulfidization - Environments for the formation of sulfide minerals and potential acid sulfate soils
8:30 AM	Keynote 1	Dr. David Rickard	Cardiff University	UK	Sedimentary iron sulfides revisited
9:15 AM		Dr. Jeffrey Cornwell	University of Maryland Center for Environmental Science	USA	Iron Sulfide Minerals in Chesapeake Bay Navigation Channels: Environmental Fate During Beneficial Utilization of Fine-Grained Sediment
9:35 AM	Discussion				

		Moderator Rob Fitzpatrick -The University of Adelaide, AUSTRALIA			1B. Understanding Sulfidization - Environments for the formation of sulfide minerals and potential acid sulfate soils
10:25 AM		Dr. Paul Shand	CSIRO	Australia	Regional controls on the formation of hypersulfidic soils and generation of extreme acidity in travertine mound spring discharge zones.
10:40 AM		Dr. Mark Stolt	University of Rhode Island	USA	Sulfide distribution in subaqueous soil systems
10:55 AM		Mr. Barret Wessel	Dept. of ENST, Univ. of Maryland	USA	An Inventory of Sulfidic Materials in the Subaqueous Soils of the Rhode River Estuary
11:10 AM		Mr. R. Kyle Derby	Dept. of ENST, Univ. of Maryland	USA	High Pore Water Hydrogen Sulfide in a Tidal Brackish Marsh with Substantial Methane Emissions
11:25 AM		Dr. Mark Stolt	University of Rhode Island	USA	Soil Description and Classification of Sulfidic Materials
11:40 AM	Discussion				

		Moderator Markku Yli-Halla - Univ. of Helsinki, Finland			2A. Understanding Sulfuricization - Natural and anthropogenic processes leading to acid sulfate soil problems
1:00 PM	Keynote 2	Dr. D. Kirk Nordstrom	U. S. Geological Survey	USA	Sulfide mineral oxidation, secondary minerals, and acid sulfate waters
1:45 PM		Dr. Seija Virtanen	Drainage Foundation	Finland	Oxidation of iron sulfides in subsoils of cultivated boreal acid sulfate fields – an examination based on soil redox potential and pH measurements
2:05 PM	Discussion				

Agenda - 8th International Acid Sulfate Soils Conference

MONDAY		Moderator Markku Yli-Halla - Univ. of Helsinki, Finland			2B. Understanding Sulfurization - Natural and anthropogenic processes leading to acid sulfate soil problems - Honoring the late Prof. Udo Schwertmann	
2:55 PM		Dr.	Darrell Schulze	Purdue University	USA	A Passion for Iron Oxides – Personal Reminiscences of Professor Udo Schwertmann
3:25 PM		Dr.	Robert Fitzpatrick	Acid Sulfate Soils Centre, The University of Adelaide	AUSTRALIA	Schwertmannite as an indicator of geochemical processes in acid sulfate soil environments: A tribute to legendary soil scientist Prof Udo Schwertmann
3:55 PM		Dr.	Vanessa Wong	Monash University	Australia	Coal seams, peat swamps and acid sulfate soils – where does the acidity come from? A case study from southern Australia
4:10 PM		Dr.	Angelika Kölbl	Technical University of Munich	Germany	Organic matter composition in acid sulfate soils
4:25 PM		Mr.	Thomas Job	The University of Sydney	Australia	A Geochemical Record of Acid Sulfate Soil Oxidation in the Lower Murray-Darling Basin
4:40 PM		Mr.	Stefan Mattbäck	Åbo Akademi University	Finland	The acidifying effects of oxidizing coarse-grained acid sulfate soil materials in western Finland
4:55 PM	Discussion					

6:00 PM	POSTERS	Lead Author				Presentation Title
		Mr.	Jaakko Auri	Geological Survey of Finland	Finland	Lithostratigraphy and mapping of acid sulfate soils in the coastal Bothnian Bay, Finland
		Dr.	Anton Boman	Geological Survey of Finland	Finland	Magnetic separation of greigite from sulfidic sediments for X-ray powder diffraction studies
		Prof.	Martin Rabenhorst	University of Maryland	United States	IRIS (Indicator of Reduction In Soils) Technology for Assessing Sulfidization in Subaqueous Soils
		Dr.	Wirastuti Widyatmanti	Universitas Gadjah Mada	Indonesia	Acid sulfate soil characteristics on the wave-dominated estuaries with pre-existing barriers in the south coast of Central Java
		Dr.	Walter E. Grube, Jr.	Soil Chemistry Consultant(retired)	USA	Acid Sulfate Soil Processes also Affect Other Soils
		Ms.	Jaclyn Fiola	University of Maryland	USA	Constructing and Evaluating a Monolith of an Active Acid Sulfate Soil with a Duripan
		Ms.	Elisa Azura Azman	The University of Tokyo	Japan	Chemical characteristics of acid sulfate soil as affected by addition of calcium silicate in-combination with and/or without ground magnesium limestone
		Dr.	Sten Engblom	Novia University of Applied Sciences	Finland	Precision chemical treatment of acid sulfate soils for the protection of waters in environmentally sustainable agriculture
		Ms.	Amarachi Nwokocha	Babcock University	Nigeria	Effect of soil amendments on growth and biomass yield of two varieties of maize at different cropping seasons on acid soil
		Ms.	Deborah Surabian	USDA Natural Resources Conservation Service	USA	Mesocosm Studies to Identify Potential Acid Sulfate Soils and Develop a National Cooperative Soil Survey Interpretation
		Dr.	Patrick Michael	Department of Agriculture, PNG University of Technology	Papua New Guinea	Effects of plants on the chemistry of acid sulfate soils
		Dr.	Anton Boman	Geological Survey of Finland	Finland	Mapping and characterization of acid sulfate soils in Finland
		Mr.	Krister Dalhem	Åbo Akademi University	Finland	A miniaturized distillation method for determining reduced sulfur species in sulfidic soil materials
		Ms.	Susan Demas	USDA Natural Resources Conservation Service	USA	A Coastal Zone Approach to Soil Surveys: Past, Present and Future
		Dr.	Bill Gardner	WestVic AgServicesP/L	AUSTRALIA	Remediation of "Red Barren" scalds comprising acid sulfate soils with iron clogged layers on the Dundas Tablelands, Victoria, Australia
		Dr.	Peter Österholm	Dept. of Geology and Mineralogy, Åbo Akademi University	Finland	Titrateable incubation acidity for acid sulfate soil materials
		Ms.	Debbie Surabian	USDA Natural Resources Conservation Service	USA	Use of National Soils Information System (NASIS) to Query Soils at Risk for Acid-Sulfate Formation in Dredged Materials
		Mr.	James Turenne	USDA Natural Resources Conservation Service	USA	The Rhode Island Mapping Partnership for Coastal Soils and Sediment - RI Coastal Zone Soil Survey.

Agenda - 8th International Acid Sulfate Soils Conference

TUESDAY

Start	Speaker			Title
	Moderator Brian Needelman - Univ. of Maryland			3A. Understanding issues and remediation strategies for inland acid sulfate soils and landscapes, AMD (acid mine drainage), ARD (acid rock drainage)
8:00 AM	Keynote 1	Dr. Jeff Skousen	West Virginia University	USA Geologic Testing for Land Disturbance: Acid-Base Accounting for Predicting Acid Mine Drainage on Surface Mines
8:45 AM		Dr. Jane Hammarstrom	USGS	USA Acid rock drainage – natural and human-induced
9:05 AM		Ms. Michele Coleman	NB Power	Canada Monitoring the Behaviour of Sludge in the Vadose Zone
9:25 AM	Discussion			
	Moderator Brian Needelman - Univ. of Maryland			3B. Understanding issues and remediation strategies for inland acid sulfate soils and landscapes, AMD (acid mine drainage), ARD (acid rock drainage)
10:15 AM		Dr. Zenah Orndorff	Virginia Tech University	USA Sulfidic Materials and Acid Sulfate Soils in Virginia, United States
10:30 AM		Dr. Luke Mosley	University of Adelaide	Australia Long timescales for recovery of acid sulfate sub-soils with sulfuric horizon following resubmergence: what we have learnt from the Millennium Drought
10:45 AM		Mr. David Palmer	Environment Protection Authority - South Australia	Australia Remediation and management options of salt drain and groundwater acidification in the Lower Murray Reclaimed Irrigation Area, South Australia.
11:00 AM		Dr. Zenah Orndorff	Virginia Tech	USA Reclamation of Disturbed Sulfidic Coastal Plain Sediments at Stafford Regional Airport, Virginia, USA
11:15 AM		Dr. Somchai Anusontpornperm	Department of Soil Science, Kasetsart University	Thailand Phosphorus sorption characteristics for determining rate and type of phosphorus fertilizer for paddy rice in residual liming acid sulfate soils
11:30 AM	Discussion			
	Moderator Paul Shand - CSIRO, Australia			4A. Understanding issues and remediation strategies for coastal and agricultural acid soils and landscapes
1:00 PM	Keynote 2	Dr. Peter Österholm	Geology and Mineralogy, Åbo Akademi University	Finland Management of Boreal agricultural acid sulfate soils
1:45 PM		Mr. Robert Quirk	Indep. researcher	Australia Discovery, Identification, Sustainable Remediation.
2:05 PM	Discussion			
	Moderator Paul Shand - CSIRO, Australia			4B. Understanding issues and remediation strategies for coastal and agricultural acid soils and landscapes
3:00 PM		Mr. Tanabhatsakorn Sukitprapanon	Department of Soil Science, Kasetsart University	Thailand Variations in Actual, Sulfidic and Retained Acidity in Thai Acid Sulfate Soils
3:15 PM		Dr. Del Fanning	University of Maryland	USA Phriends of Phragmites
3:30 PM		Ms. Debbie Surabian	USDA NRCS	USA Mesocosm Studies to Identify Potential Acid Sulfate Soils and Develop a National Cooperative Soil Survey Interpretation
3:45 PM		Mr. Gary Jellick	Acorn Environmental Inc.	USA Production of Salt Hay on Potential Acid-Sulfate Soils, Sulphuric Acid, and Associated Soils in Cumberland County, New Jersey
4:00 PM		Dr. Faustino Villamayor	Dept. of Soil Science, Visayas State University	Philippines A Review of Researches conducted on Aquaculture on Acid sulfate Soils in the Philippines.
4:15 PM		Dr. Udo Ufot	Akwa ibom State University	Nigeria CHARACTERIZATION AND CLASSIFICATION OF ACID SANDS OF EGBEADA SOUTHEASTERN NIGERIA
4:30 PM	Discussion			

WEDNESDAY

8:00AM - 5:00PM	Mid-Conference Tour	
5:00PM - 9:00PM	Cookout - Sandy Point State Park	

Agenda - 8th International Acid Sulfate Soils Conference

THURSDAY

Start	Speaker	Title			
	Moderator Maxine Levin, USDA-NRCS, USA	5. Policy, Regulation and Education - Best practices in avoidance and remediation			
8:00 AM	Keynote 1	Dr. Leigh Sullivan	Federation University Australia	Australia	Acid Sulfate Soil Regulation, Policy and Guidance in Australia: Status and Trajectory
8:45 AM		Dr. Lizeth Caballero	Facultad de Ciencias/Instituto de Geología UNAM	Mexico	River dynamics and soil properties to evaluate the impact of acid spills: The Sonora River example
9:05 AM		Dr. Stephanie Murphy	Rutgers Univ./NJAES Soil Testing Laboratory	USA	Regulations Relating to Acid-Producing Soils in New Jersey (USA)
9:25 AM		Ms. Amanda Peñafiel	Maryland Environmental Service	USA	Hart-Miller Island: Rebuilding, Restoring and Recreation
9:40 AM		Mr. David Smith	USDA-Natural Resources Conservation Service	USA	USDA Policy Concerns for Acid Sulfate Soils and Coastal Resources
9:55 AM	Discussion				

Start	Speaker	Title			
	Moderator Maxine Levin, USDA-NRCS, USA	2C. Understanding issues and remediation strategies for inland acid sulfate soils and landscapes, AMD (acid mine drainage), ARD (acid rock drainage)			
10:45 AM		Dr. Doug Ming	NASA Johnson Space Center	USA	Acid Sulfate Alteration on Mars
11:00 AM		Dr. Richard Morris	NASA Johnson Space Center	USA	Acid Sulfate Alteration in Gusev Crater, Mars
11:15 AM		Dr. Robert Fitzpatrick	Acid Sulfate Soils Centre, The University of Adelaide	AUSTRALIA	Schwertmannite formation and persistence in acid runoff from re-flooded Acid Sulfate Soil environments following river level decline during drought
11:30 AM		Dr. Darrell Schulze	Purdue University	USA	Bogus Soils! – Evidence for a Naturally Occurring Acid Sulfate Weathering Event in Northwest Indiana, USA
11:45 AM		Dr. Delvin Fanning	University of Maryland	USA	Modern ironstone formation by sulfurization phenomena
12:00 PM	Discussion				

Start	Speaker	Title			
	Moderator Peter Osterholm - Åbo Akademi Univ., Finland	6A. Monitoring and mitigating impacts of acid sulfate soil and water during reclamation and development (assessment techniques, laboratory analysis and soil classification and mapping issues)			
1:30 PM	Keynote 2	Dr. Markku Yli-Halla	University of Helsinki	Finland	Abundant stocks and mobilization of elements in boreal acid sulfate soils
2:15 PM		Mr. Robert Tunstead	USDA-Natural Resources Conservation Service	USA	The Coastal Zone Soil Mapping Initiative
2:35 PM	Discussion				

Start	Speaker	Title			
	Moderator Peter Osterholm - Åbo Akademi Univ., Finland	6B. Monitoring and mitigating impacts of acid sulfate soil and water during reclamation and development (assessment techniques, laboratory analysis and soil classification and mapping issues)			
3:25 PM		Dr. Amelie Beucher	Dept. of Agroecology, Aarhus University, Denmark	Denmark	Acid sulfate soil mapping in Denmark using legacy data and LiDAR-based derivatives
3:40 PM		Dr. W. Lee Daniels	Crop & Soil Env. Sci., Virginia Tech	USA	Characterization and Remediation of Acid Forming Dredge Materials
3:55 PM		Dr. Gustav Sohlenius	Geological Survey of Sweden	Sweden	Acid sulfate soils in northern Sweden
4:10 PM		Dr. Amelie Beucher	Dept. of Agroecology, Aarhus University, Denmark	Denmark	Spatial modelling techniques for acid sulfate soil mapping in northern Europe
4:25 PM		Dr. Wirastuti Widyatmanti	Faculty of Geography, Universitas Gadjah Mada	INDONESIA	IDENTIFYING ACID SULFATE SOIL UNIT BOUNDARIES USING BASIC IMAGE TRANSFORMATION ON MULTI-RESOLUTION SATELLITE IMAGERIES
4:40 PM	Discussion				
5:00 PM		Moderator Leigh Sullivan - Federation University Australia	ASSWG-IUSS Business Meeting, Closing Session/Ceremonies		

FRIDAY-SATURDAY

FRIDAY-SATURDAY		Post Conference Tour: MD and VA
Friday	7:30 AM	Depart Marriott Hotel
Saturday	5:00 PM	Return to College Park

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Abstracts

(Alphabetical by first author)

Phosphorus sorption characteristics for determining rate and type of phosphorus fertilizer for paddy rice in residual liming acid sulfate soils

Anusontpornperm, S.¹, Thanachit, S.¹, Wiriyaakitnateekul, W.², Ruksumruad, P.¹ and Choochat, J.¹

¹Dep. of Soil Sci., Fac. Of Agri., Kasetsart Univ., Bangkok, 10900, THAILAND

²Office of Sci. for Land Develop., Land Develop. Dept., Bangkok, 10900, THAILAND

A study on properties of residual liming paddy acid sulfate soils was conducted in 15 locations of Central Plain, Thailand, consisting of Ongkarak (Ok), Rangsit (Rs), Sena (Se), Bang Nam Prieo (Bp) and Thanyaburi (Tan) soil series. According to Soil Taxonomy, they were classified as Typic Sulfaquepts and Sulfic Endoaquepts. Their topsoil layers had pH of higher than 6.0 at the time of sampling compared to pH of less than 4.5 measured in the topsoil of virgin soils without liming. Most properties of residual liming acid sulfate soils were not different from virgin acid sulfate soils, especially in subsoil horizon. Most soils had clayey texture. Their pH values measured in 1:1 H₂O ranged between 3.4-5.1. Cation exchange capacity values of all soils varied between 18.0-24.5 cmol_c kg⁻¹. They had high level of extractable acidity (26-45 cmol_c kg⁻¹), and very low content of available phosphorus (3.0-10.2 mg kg⁻¹) except for Bang Nam Prieo soil (10.2-19.6 mg kg⁻¹). Residual liming acid sulfate soils were more suitable for paddy rice cultivation than that of virgin acid sulfate soils even though high level of acidity and low amount of available phosphorus were still the major limitation.

The response of rice, RD. 43 variety, grown on these acid sulfate soils with residual lime to rates of phosphate calculated from P adsorption characteristics such as P adsorption capacity (P_{max}), half of P_{max}, 0.2 mg P L⁻¹ (PBC) and the rate of 157 mg kg⁻¹ recommended by Department of Agriculture, Thailand, and to different types of phosphate, including triple superphosphate (TSP) and rock phosphate (RP) was also investigated. The experiments carried out in two soils were arranged in Completely Randomized design (CRD) with four replications. Rice seedling at 15 days old was planted in pot under greenhouse cover. Urea and KCl at the rates of 504 and 260 mg kg⁻¹ were used as top dressing for all treatments and the former at the rate of 98.5 mg kg⁻¹ was also additionally applied at flowering stage.

Two acid sulfate soils, Ongkaruk (Typic Sulfaquept, Ok) and Bang Nam Prieo (Sulfic Endoaquept, Bp) soil series, prior to conducting the experiment, had field pH of 5.0 and 8.5, respectively. The former soil had almost twice higher phosphate adsorption than did the latter soil with the value of 802 mg kg⁻¹ compared to 424 mg kg⁻¹ but the adsorption content at the concentration of 0.2 mg P L⁻¹ in soil solution was rather similar (398 and 327 mg kg⁻¹, respectively) (Fig. 1).

Rice grown on acid sulfate soils with residual lime clearly responded to P fertilizer applied with height, number of tillering and seed yield being higher than those without P fertilization. The rice grown on Ok soil series of which the soil remained very acidic responded well to TSP, giving a 192 g of seed per pot, rather than RP whereas the plant responded slightly lower to P fertilizer when grown in the other soil. P application at P_{max} induced the plant to reach flowering stage faster than did the other rates and gave the highest yield of 143 g per pot when grown on OK soil series while rice grown on Bp soil series only responded to P at the rate of PBC in the case of vegetative growth. P application at recommended rate gave the highest seed yield of 109 g per pot which was similar to

the yield of 102 g per pot when applied at PBC rate. The addition of P at high rate as well as the use of TSP resulted in the soils being more acidic and having greater available P but the application of P at $\frac{1}{2}$ Pmax rate gave the lowest P at PBC which was in contrast to no P addition that the highest amount of P was found at PBC.

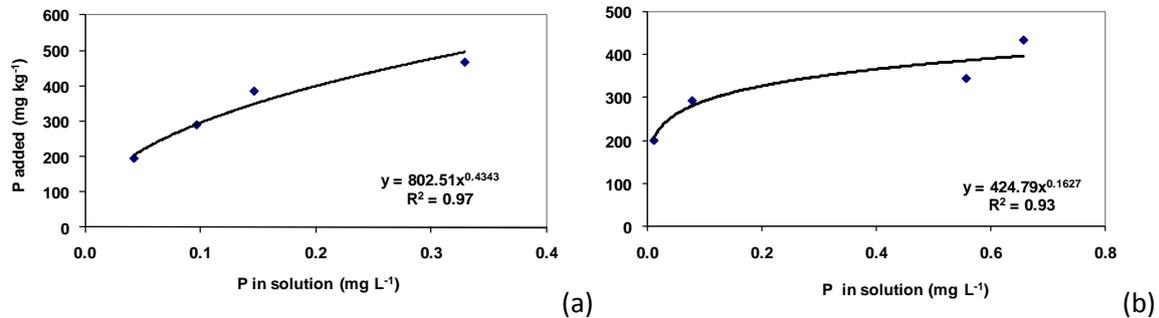


Fig. 1. P sorption characteristic curve of two acid sulfate soils with residual lime using Freundlich adsorption equation: Ongkaruk (Typic Sulfaquept, Ok) (a) and Bang Nam Prieu (Sulfic Endoaquept, Bp) (b) soil series.

References:

1. Attanandana, T. and S. Vacharotayan, 1986. Acid sulfate soils: their characteristics, genesis, amelioration and utilization. *Southeast Asian Studies* 24(2): 154-180.
2. Andriessse, W. and M.E.F. van Mensvoort. 2006. Acid sulfate soils: distribution and extent (Second edition). *Encyclopedia of Soil Science* 1: 14–19.
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Lithostratigraphy and mapping of acid sulfate soils in the coastal Bothnian Bay, Finland

Auri, J., Boman, A., Edén, P.

Geological Survey of Finland, P.O. Box 97, Vaasantie 6, 67101 Kokkola, Finland

The Geological Survey of Finland (GTK) started to map the properties and distribution of acid sulfate (AS) soils in the coastal areas of the Bothnian Bay in 2015 as part of a partly EU-funded project (INTERREG Nord). The field observation density is about 1 / 2 km² and so far around 1400 soil probings down to a depth of 2–3 m have been done. Besides assessing the acidifying potential (estimated using incubation-pH) and distribution of the soils we have also been making detailed notes on lithological properties and stratigraphic position of the sedimentary units.

In general, AS soils in Finland are found in the coastal area which has been subject to intense glacial isostatic rebound and marine regression since the last glaciation. The formation of sulfidic sediments in this setting has been mainly controlled by the varying salinity of the Baltic, iron influx from the continent and the organic productivity or the supply of organic matter (4).

During the mapping process, we have found that sulfidic sediments typically occur in different units with different lithological properties (Fig. 1). The lowermost unit in the strata is typically glacial till with a low acidifying potential unless it is contaminated by black-schist rock material which can be found sporadically in the study area. The till is often draped by a relatively thin layer of glaciolacustrine rhytmities (pale brown/reddish fine sand to clay) reflecting deposition from underflows and suspension during seasonal changes of glacial melt. The production of organic matter in the water during the late glaciation was low and the acidifying potential of this unit is usually very low (i.e. no significant drop in pH during incubation). The rhytmities are typically overlain by massive light-gray postglacial lacustrine clays. The unit has a relatively low organic content but it often contains some sulfur (generally $S_{(tot)} < 0.2\%$) which usually appears as black monosulfidic bands or mottles. This unit is interpreted to deposit in deep water during the Ancylus Lake phase (1, 2, 3). The organic-rich brackish-water sulfidic sediments (generally $S_{(tot)} > 0.2\%$) overlying the lacustrine clays is the most common AS soil-forming unit (5). This unit, representing the Littorina Sea or younger sediments, is typically massive or weakly stratified black gyttja-containing silt or clay deposited in relatively shallow water. It has typically an erosional lower bounding surface with a thin sandy horizon. Another unit comprising a significant amount of acidifying potential in the area is a typically upward coarsening unit of sand deposited during the littoral phase or in river mouths. This unit can be found overlying any of the preceding units.

The study on lithological properties and stratigraphic positions in the mapped area can be used to reconstruct depositional environments of sulfidic sediments and to predict their distribution based also on secondary data like Quaternary sediment maps and geotechnical surveys. Lithostratigraphic descriptions will also give more detailed 3D-information of AS soils, which can be readily used in sustainable land-use planning. Identification of different lithological properties is also important when identifying sulfidic sediments and AS soils in the field. The lithostratigraphic units in the area also have varying acidifying potentials which can be further used as a basis for risk classification.

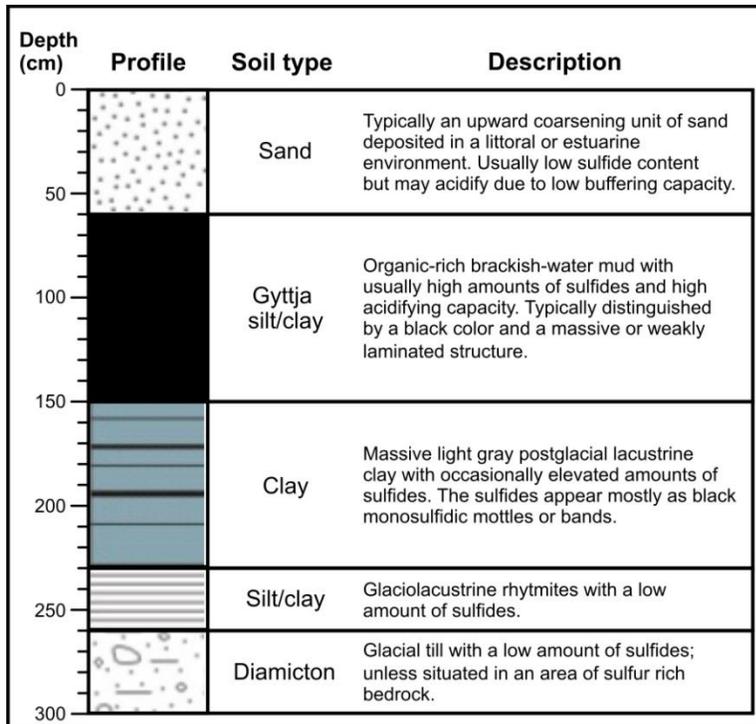


Fig. 1. A log profile showing the typical lithological units encountered in the corings during the acid sulfate soil mapping.

References:

1. Ignatius, H., Kukkonen, E. & Winterhalter, B. 1968. Notes on a pyritic zone in upper Ancyclus sediments from the Bothnian Sea. Bull. Geol. Soc. Finland vol. 40, p. 131-134.
2. Papunen, 1968. On the sulphides in the sediments of the Bothnian Sea, Bull. Geol. Soc. Finland vol. 40, p. 51-57.
3. Spiridonov, M., Ryabchuk, D., Kotilainen, A., Vallius, H., Nesterova, E. & Zhamoida, V. 2007. The Quaternary deposits of the Eastern Gulf of Finland. Geological Survey of Finland, Special Paper 45, p. 7-19.
4. Sternbeck, J. & Sohlenius, G. 1997. Authigenic sulphide and carbonate mineral formation in the Holocene sediments of the Baltic Sea. Chemical Geology, 135, p. 55-73.
5. Yli-Halla M., Puustinen, M., & Koskiahho, J. 1999. Area of cultivated acid sulphate soils in Finland. Soil Use and Management 15, p. 62-67.

**Chemical characteristics of acid sulfate soil as affected by addition of calcium silicate
incombination with and/or without ground magnesium limestone (GML) as soil
amendments in a closed incubation system**

Elisa A.A^a, Seishi Ninomiya^a, I. Roslan^b, J. Shamshuddin^b

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A study was conducted in a closed incubation system. The soil used for this experiment was acid sulfate soil obtained from Merbok, Kedah Malaysia. Most of the acid sulfate soils in this area are subjected to rice cultivation with average rice yield was below the national average of 3.8 t ha⁻¹ season⁻¹ due to the low soil pH accompany with presence of high amount of aluminum (Al). The objective of this study was to investigate the effect of calcium silicate incombination with ground magnesium limestone on an acid sulfate soil. The soil was incubated under submerged condition for 120 days and treated with ground magnesium limestone (0, 2, 4, 6 t ha⁻¹) incombination with calcium silicate (0, 1, 2, 3 t ha⁻¹). The soil was sampled and analysed every 30 days of incubation for soil pH, exchangeable Al, Ca, Mg and Si content.

The soil pH and exchangeable Al prior to incubation were 2.89 and 5.18 cmol_c kg⁻¹, respectively. Significant interaction between GML and calcium silicate were observed as their combination were able to, i) increase soil pH > 4, ii) reduce exchangeable Al below the critical level of < 2 cmol_c kg⁻¹ (Hiradate et al., 2007) as well as reduced Al saturation, iii) increase amount of exchangeable Ca and Mg above critical value of 2 cmol_c kg⁻¹ (Palhares de Melo et al., 2001) and 1 cmol_c kg⁻¹ (Dobermann and Fairhurst, 2001) for rice growth, respectively and iv) provide substantial amount of Si above the requirement level of 40 mg kg⁻¹ as suggested by Dobermann and Fairhurst (2001) (Figure 1). Therefore, addition of calcium silicate incombination with GML shows an ameliorative effect on acid sulfate soil.

Keywords

soil acidity, aluminum toxicity, silicon, submergence soil, soil amendments, calcium

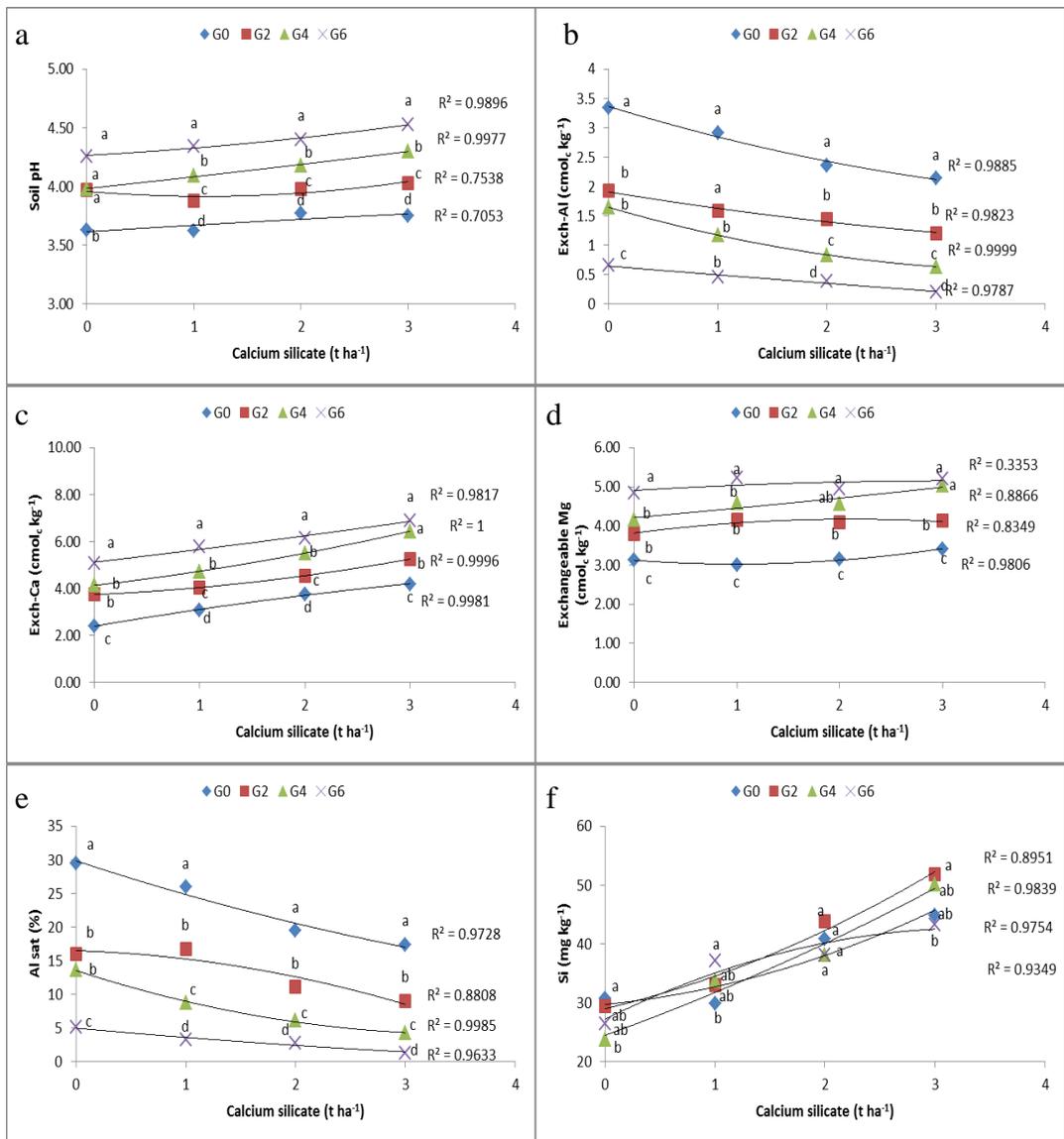


Figure 1: Selected chemical soil properties affected by calcium silicate in-combination with GML at 30D. Means marked with the same letter for each calcium silicate treatments are not significantly different at $p < 0.05$ (Tukey`s Test)

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Acid sulfate soil mapping in Denmark using legacy data and LiDAR-based derivatives

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Leaching large amounts of acidity and metals into the recipient watercourses and estuaries, acid sulfate soils constitute a substantial environmental issue worldwide. Mapping these soils enables measures to be taken to prevent pollution in high risk areas. In Denmark, legislation prohibits drainage of areas classified as potential acid sulfate soils without prior permission from authorities. The mapping of these soils was first conducted in Denmark about three decades ago [4]. Wetland areas, in which Danish acid sulfate soils mostly occur, were targeted and the soils were surveyed through conventional mapping (i.e. soil sampling and the subsequent determination of pH at the time of sampling and after incubation, as well as the calculation of pyrite content and acid-neutralizing capacity).

In this study, a probability map for potential acid sulfate soil occurrence was constructed for the wetland areas located in the Jutland peninsula (c. 6,000 km²), using the Digital Soil Mapping (DSM) approach introduced by McBratney et al. [3]. Among the variety of available digital soil mapping techniques, Artificial Neural Networks (ANN) were selected. ANN were previously utilized for the mapping of acid sulfate soils in Finland on a catchment extent [1, 2]. More than 8,000 existing soil observations and 16 different environmental variables, including geology, landscape type, land use, a digital elevation model created from laser scanning data (i.e. Light Detection and Ranging, LiDAR) and its derivatives, were utilized as input data within the modelling. Numerous prediction models based on different training algorithms and network topologies were assessed. Various combinations of environmental predictors and selections of soil observations were tested in order to estimate the best predictors, as well as the optimal amount of soil profiles required to yield satisfactory predictions. The overall prediction accuracy based on a 30% hold-back validation data reached 70% (Fig. 1). Furthermore, the conventional map indicated 35% of the study area (c. 2,100 km²) as potential acid sulfate soils while the digital map (Fig. 1) displayed about 50% (c. 3,000 km²) as the most probable areas for acid sulfate soil occurrence. Artificial neural networks, thus, demonstrated promising predictive classification abilities for the mapping of potential acid sulfate soils on a large extent.

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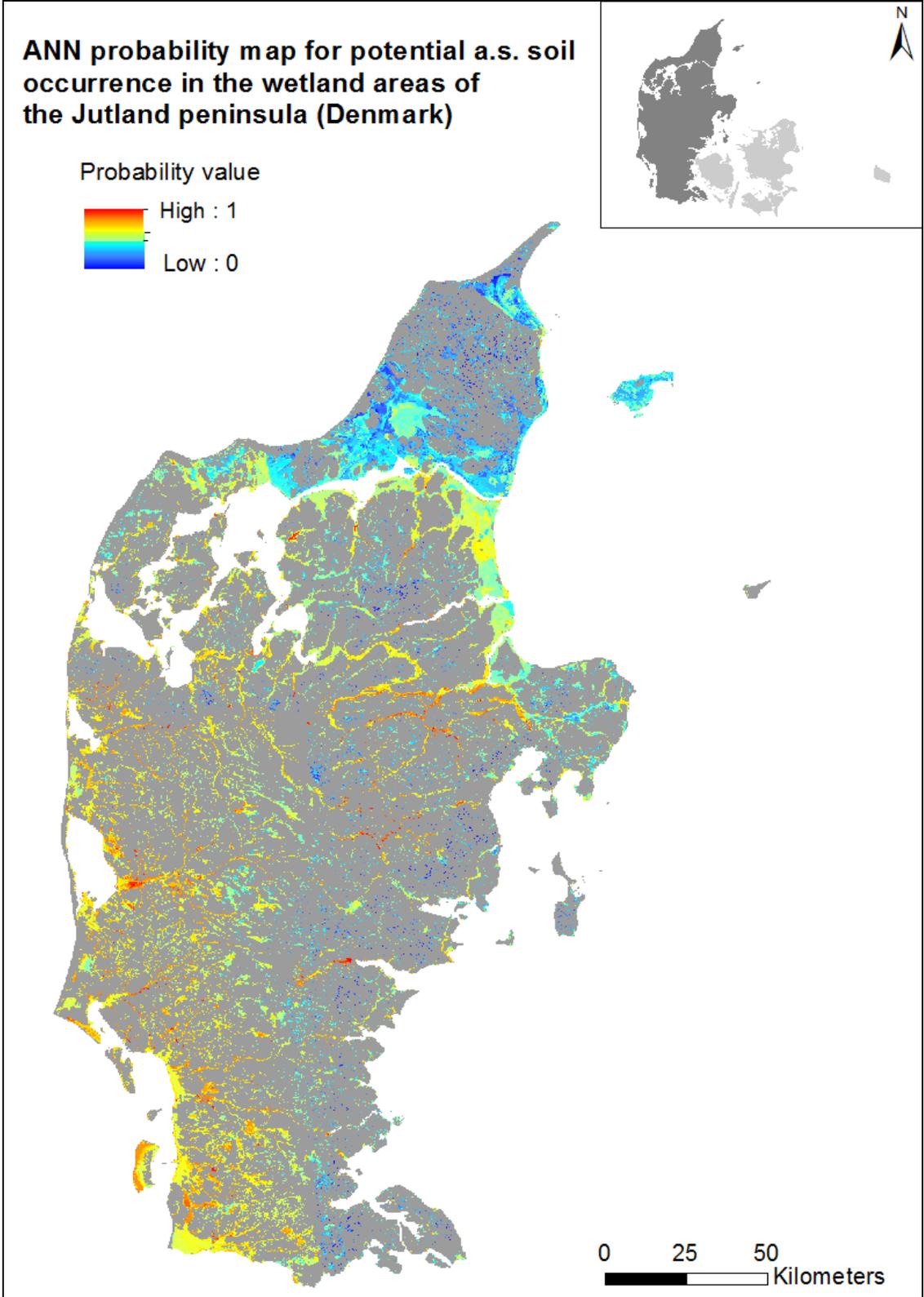


Figure 1. Probability map for potential acid sulfate (a.s.) soil occurrence created with Artificial Neural Networks (ANN) modelling

Spatial modelling techniques for acid sulfate soil mapping in northern Europe

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Acid sulfate (a.s.) soils presumably cover about 200,000 km² of coastal areas worldwide, major occurrences being located in Africa, Australia, southeastern Asia and Latin America [1]. As these soils can release a toxic combination of acidity and metals, causing severe ecological damage (e.g. killing fish and other aquatic organisms), they constitute a crucial environmental problem. Furthermore, a.s. soils can have considerable economic impacts through the resulting corrosion of concrete and steel infrastructures or their poor geotechnical qualities. Therefore, mapping these soils represents a key step in the management and mitigation of the related risks. In northern Europe, a.s. soils have been substantially studied in Finland, Denmark and Sweden, where they are mainly located on uplifted coastal areas related to Baltic Sea stages. These soils are also commonly found in Germany, England, the Netherlands, Poland and Russia, and they probably occur in Norway and the Baltic States. As suggested by Edén et al. [6], a multinational project could be carried out to produce an a.s. soil map of northern Europe and further define common guidelines for identifying and managing these soils.

Conventional mapping (i.e. soil sampling and subsequent pH measurements) has typically been used for a.s. soil mapping. Lately, spatial modelling techniques have also been assessed for mapping these soils in Finland and Denmark, appearing as effective tools for complementing conventional mapping at different levels (i.e. pre- or post-conventional mapping), extents (i.e. field, catchment or regional) and scales (i.e. resolution). The combined use of modelling techniques and conventional mapping might thus constitute an effective approach to build an a.s. soil map of northern Europe. Spatial modelling techniques have already been applied in different domains of geosciences (e.g. mineral prospectivity, groundwater and soil mapping) and can be implemented within various software environments (e.g. R, MatlabTM and Geographical Information systems, such as ArcGIS, SAGA GIS or QGIS). These techniques basically aim at gathering predictive knowledge from input data, learning relationships, recognizing patterns within it, then generalizing, classifying new data in order to generate a predictive map as an output. For a.s. soil mapping, soil observations (i.e. soil profiles or probing points) and environmental data (e.g. geology, landscape type, geophysics, digital elevation model and its derivatives) can be used as input data. The soil observations are collected in the field and classified as known a.s. soil occurrences or non-a.s. soil sites, based on pH (measured in the field and after several weeks of incubation). Additionally, sulfur, metal and organic matter contents are determined in the laboratory and can be used to map the risks due to a.s. soils. Environmental data (i.e. digital maps) also enables to target a.s. soil occurrences. Considering the geology predictor, these soils can occur in fine-grained sediments (i.e. clay, silt and gyttja), but also in sands, peat and till. In the landscape type map, a.s. soils can be found in various landforms, such as tidal flats and swamps, former marine environments (e.g. the bottom of saline and brackish seas, estuaries and lakes), as well as flood plains and inland valleys with influx of sulfate-rich water. In geophysical maps, fine-grained a.s. soils can be detected as high electromagnetic conductivity anomalies because of the salts contained in the ground, whereas coarse-grained a.s. soils are not detected as easily. Moreover, elevation and the derived slope gradient enable to target low-lying, low-relief areas where a.s. soils generally occur. Several spatial modelling techniques have already been tested for a.s. soil mapping. Conceptual, knowledge-driven techniques require the use of evidential data and enable the prediction of soil properties in areas with little or no available point data (i.e. soil observations). For example, fuzzy logic (FL) has been applied over large areas along the Finnish coast. FL has enabled the preliminary assessment of a.s. soil occurrence in scarcely sampled areas, point data being only used for model validation [3]. Empirical, data-driven techniques require the use of environmental data and soil observations, which are used for model training and validation. For example, Artificial Neural Networks (ANNs) constitute very good pattern recognition and classification tools. ANNs were assessed on a catchment in Finland (c. 400 km² [2, 4]) and also over a larger extent in Denmark (c. 6,000 km² covering the wetland areas in Jutland [5]). ANNs demonstrated promising predictive classification abilities for a.s. soil mapping at both catchment and regional extent. Furthermore, a fuzzy *k*-means algorithm for clustering analysis was applied to map a.s. soils in a field in Australia [7]. In particular, the use of proximal electromagnetic sensors measuring the apparent soil electrical conductivity (e.g. DUALEM device [8]) might enable to map a.s. soils in detail at field extent, possibly even distinguishing actual from potential a.s. soils in three dimensions.

Selecting the most appropriate spatial modelling technique is highly dependent on the input data, both its quantity and quality, and is also directly related to the study extent (i.e. field, catchment, regional or national extent) and the study scale (i.e. resolution). The input data plays a substantial role within the modelling; however, expert knowledge also represents a crucial factor to create robust and reliable models. Soil observations and updated knowledge originate from conventional mapping and enable the creation of robust and up-to-date empirical models. Nevertheless, conceptual models can deliver preliminary assessments particularly useful to plan conventional mapping. Therefore, modelling techniques and conventional mapping complement each other. Developing guidelines for a.s. soil mapping using both spatial modelling techniques and conventional mapping still constitutes a great challenge. These guidelines would be tested for mapping a.s. soils in northern Europe where the level of knowledge and amount of available data are varying from one country to the other.

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Mapping and characterization of acid sulfate soils in Finland

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In Finland, acid sulfate (AS) soils are disturbed in agriculture, forestry, peat production, dredging and infrastructure developments (roads etc.). The problems with leaching of acidity and metals into recipient waters related to AS soils have been known for centuries, but not until 2009 did systematic mapping and characterization commence on the responsibility of the Geological Survey of Finland (GTK). EU's Water Framework Directive, large fish kills in 2006–2007, national Water Management Plans and a National Strategy for reduction of harmful effects from AS soils led way for the mapping as an urgent part of the strategy.

The sulfidic sediments responsible for AS soil formation have been developing after the latest glaciation in parts of the Baltic Sea beginning during the Littorina Sea (c. 8000–3000 years ago) and today continuing in shallow coastal waters, such as estuaries and shallow bays. Post-glacial isostatic land uplift has brought these sediments above sea level and they are now consequently mostly found in coastal areas below the highest shore line of the former Littorina Sea. Until 2015, about 62% of the total potential 5 million hectares has been mapped (Fig. 1). To date, more than 15 000 observation points (observation density c. 1 / 2 km²) and an excess of 10 000 analyses have been made. At the observations points, soil probing and sampling down to 2–3 m is done and observations of soil type, texture and structure, pH, oxidation depth and ground water level are made. Samples are collected for further analyses of incubation-pH, trace- and major elements using aqua regia dissolution and ICP-OES, loss on ignition and grain size. Once the mapping is finished, the area of AS soils is very likely to exceed that of earlier estimations of 336 000 ha [3, 5].

The definitions and terminology for AS soils set by the International Acid Sulfate Soil Working Group in 2008, and published in Sullivan et al. [6] has with some minor modifications been adopted also for Finnish AS soils. AS soils are in Finland thus defined as soils, sediments, till, organic substrates or other materials containing sulfides in which sulfuric acid (H₂SO₄) is being produced, or may be produced from sulfide oxidation in such amounts that soil-pH is significantly lowered. *Sulfidic material* is defined as soil material containing $\geq 0.01\%$ S_{sulfide}. If the soil is severely acidified by sulfide oxidation, the sulfidic material is termed *hypersulfidic*, whereas it is termed *hyposulfidic* if the formed acidity is buffered and soil-pH remains elevated. These terms are used mainly in scientific communication. For communication with authorities, consultants, the public, etc. we use easier terminology.

AS soils are further divided into: **(1) potential AS soils**, which are waterlogged and often covered by a layer of peat and have not yet started to produce sulfuric acid and **(2) actual AS soils** where sulfuric acid is being produced. The actual AS soil materials are in most cases underlain by a layer of potential AS soil material (i.e. unoxidised hypersulfidic material) below the groundwater level. The diagnostic criteria for Finnish AS soils are: **(1)** a field-pH < 4.0 (< 3.0 for peat) in the oxidised soil and/or **(2)** a drop in soil-pH to < 4.0 (< 3.0 for peat) and more than 0.5 pH-units compared with field-pH when the sample has been incubated (oxidized) for 9–19 weeks following the procedures described in Creeper et al. [2].

The most common, and environmentally the most harmful, type of AS soils in Finland consist largely of fine-grained (clay and silt) and often gyttja-containing soil materials. In these soils, the reduced and unoxidised hypersulfidic material is often dark coloured (even black) indicating the presence of iron monosulfides. Fine-grained AS soils contain a relatively high concentration of S (median 0.5%) and a large pool of easily mobilised (heavy) metals [1]. During the mapping process it has become evident that in many places there are also coarse-grained soils (fine sand and sand) with low S-concentrations (~0.01–0.1%), which are strongly acidified to a pH well below 4 when oxidised in the laboratory, thus being classified as AS soils. The negative environmental impact of these coarse-grained AS soils is probably much less or more short-lived than that of fine-grained AS soils. For instance, the metal content is much lower and so is also the potential acidity that can be formed. However, because of the poor buffering capacity of these soils, even a low S-content can induce leaching of acidity strong enough to cause fish kills in recipient streams. Also sulfidic till and peat (with S-contents around 1–5%) have been encountered during the mapping and reportedly have had a negative impact on the environment (acidification of small streams and lakes). These AS soils occur also inland and seem to occur in association with black schists.

The fine-grained potential AS soil materials have commonly been deposited in (shallow) estuary systems where the input of organic matter is usually high and the conditions for sulfide formation are favourable. Coarse-grained AS soil materials, on the contrary, constitute of glaciogenic and/or re-deposited glaciogenic material, e.g. till derived from sulfide-bearing black schists or beach sand re-deposited from eskers by littoral forces [4]. The sulfide-bearing

beach sand deposits are typically low in organic matter, i.e. where initial conditions for sulfide formation (sulfidization) are less favourable. In-situ sulfidization in beach sand is still known to occur and have been observed during the national mapping of AS soils. This would explain the typical low S-concentrations (and thus also low iron sulfide concentrations) in coarse-grained AS soil materials.

The results from the mapping (incl. probability maps, site descriptions and analyses) are made public at <http://gtkdata.gtk.fi/Hasu/index.html>. The present AS soil maps produced by the Geological Survey of Finland are showing the probability (high, moderate, small, very small) of encountering AS soils and do not indicate the real environmental impact. There is therefore a need to develop maps or tools where the actual risk is taken into account. This work has been initiated in cooperation with Åbo Akademi University.

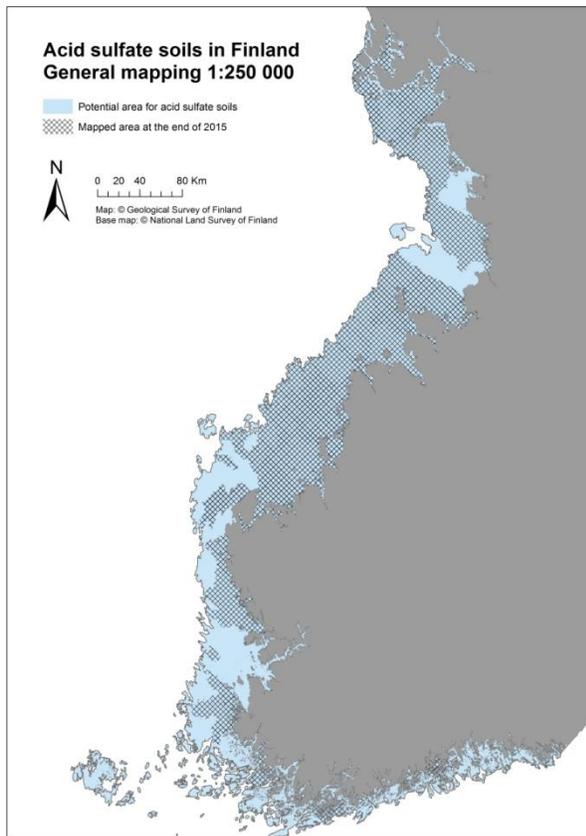


Fig. 1. Potential area for acid sulfate (AS) soils in Finland and the mapping situation at the end of 2015.

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Magnetic separation of greigite from sulfidic sediments for X-ray powder diffraction studies

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Iron monosulfide-rich sediments are common in the coastal areas of Finland. These sediments have a very black colour and usually high concentrations of acid volatile sulfide (AVS) and chromium reducible sulfur (CRS) [1, 2], thus indicating the presence of iron monosulfides and pyrite. Using SEM-EDS, Boman et al. [1] found three different iron sulfide minerals in sulfidic sediments, of which two had Fe:S ratios close to that of mackinawite and greigite and the third type had a ratio similar to pyrite.

In this study, the goal was to separate greigite from other iron sulfide minerals present in sulfidic sediments using strong neodymium magnets and in this way get an enriched magnetic fraction that could be analysed using X-ray powder diffraction (XRD; model Bruker D8 Discover A25). Similar procedures using strong magnets for enrichment of greigite have successfully been attempted elsewhere [3]. Epoxy mounts (4 pieces) of the magnetic fractions were also prepared for studies on FE-SEM (JEOL JSM 7100F Schottky).

Four sulfidic sediment samples were used in this study. During sampling, the samples were placed in plastic containers (15 mL) which were completely filled up to the lid and stored in a freezer. This keeps possible sulfide oxidation at a minimum. For the magnetic separation, both fresh sediment and freeze dried samples were used in order to determine which procedure was better. For comparison, original and magnetically untreated samples were also analysed with XRD and FE-SEM.

The equipment and reagents needed for the magnetic separations are **1**) a plastic container (15 mL), **2**) parafilm, **3**) deoxygenated ethanol, and **4**) a neodymium magnet (Fig. 1). The procedure for the magnetic separation was as follows: The sample (about ¼ of the container volume) was placed in a plastic container (15 mL) which was then filled with deoxygenated ethanol. A piece of parafilm was carefully placed on top on the container and held in place by attaching the lid to the container. A neodymium magnet was placed on top of the lid and held in place with excess parafilm sticking out underneath the lid. After this, the container was shaken for a while and all magnetic materials were transported towards the magnet and trapped on the parafilm. The container was left to stand for a while in order to let non-magnetic particles settle to the bottom. The lid was removed carefully (with the magnet still attached). The magnetic fraction on the parafilm was then washed with deoxygenated ethanol into a new plastic container. The whole separation process was repeated a few times and the fractions were washed into the same container as the initial fraction. This enriched magnetic fraction was subsequently washed and purified, using the same procedure as described above, in order to remove as much non-magnetic material as possible. The final enriched magnetic fraction was kept in deoxygenated ethanol prior to XRD analysis. Immediately before XRD analysis, the ethanol was removed from the container and the magnetic fraction was dried for a few minutes with Ar. The samples were analysed at an angle between 2θ 2-70° CuK α . The generator was set at 40kV/40 mA and the distance between measurements was 0.02° and the measurement time was 0.1 s.

FE-SEM analysis indicated that the majority of iron sulfides in the magnetic fractions were greigite but the results (both FE-SEM and XRD) showed that it was not possible to completely separate greigite from the other iron sulfides (mackinawite and pyrite) present in the samples. The reason why mackinawite and pyrite was present also in the magnetic fraction could be that **1**) the washing and purification of the magnetic fraction was incomplete, **2**) nanoparticulate mackinawite is intergrown with greigite, and **3**) sediment aggregates and root materials containing e.g. greigite and pyrite were present (this could be seen with FE-SEM). The positive part is, however, that it was actually possible to detect greigite, as well as mackinawite and pyrite with XRD in the magnetically enriched fraction. In comparison, iron sulfides could not be detected with XRD (pyrite was weakly detected in one sample) in any of the magnetically untreated (original) samples.

This study shows that although it is difficult to quantitatively separate greigite from other iron sulfides, it is possible to use this method for identification of iron sulfides with XRD. The method need, however, to be improved in order to break down sediment aggregates and to remove as much contaminants (other iron sulfides, plant material, silicates etc.) as possible before XRD analysis. For instance, other reagents than ethanol could be tested and ultrasonic could be used in order to break down any sediment aggregates present. It was also clear that the results were better when using fresh sediment instead of freeze dried sediment. This is most likely because fewer aggregates were present in the fresh sediment. Also, it is possible that some iron sulfides are oxidised during the freeze drying process. For these reasons, fresh samples should be instead of freeze dried samples.

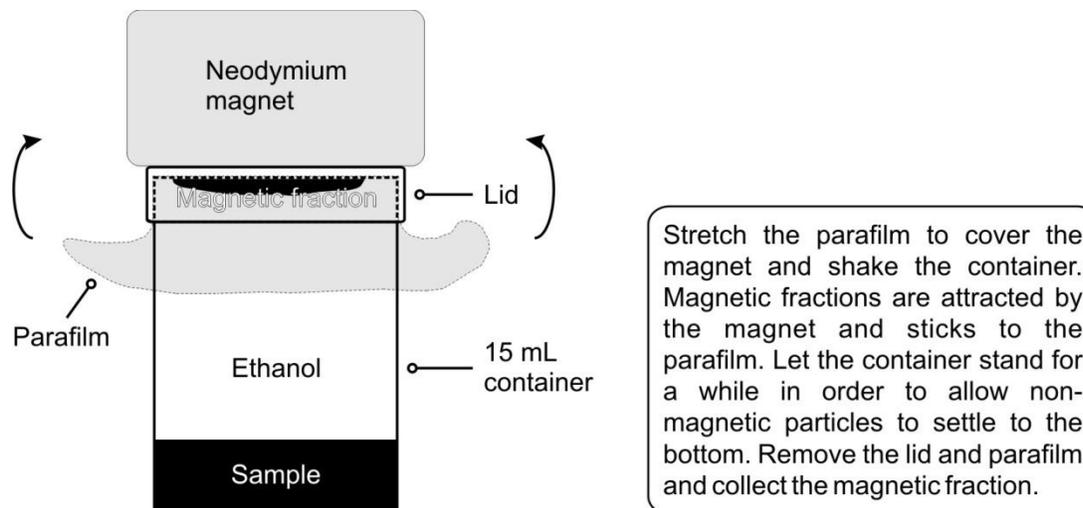


Fig. 1. Separation of magnetic fractions (greigite) from sulfidic sediments.

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River dynamics and soil properties to evaluate the impact of acid spills: The Sonora River example

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On August 6th, 2014, copper sulfate acid (40000m³) was spilled in the Tinajas River, a small tributary that belongs to Sonora River, one of the most important rivers in the Sonora State, Mexico. The impact of the copper sulfate acid spill was unknown since during the spill, there were several rains and data about river discharge was not available. Therefore a clear knowledge of fluvial conditions is necessary to estimate the initial distribution of the acid spill as well as the dilution process. Additionally, two hurricanes occurred briefly after the accident. Norbert and Odile, category 3 and 4 respectively. They caused heavy rains and favored transport and deposition of contaminated sediments along the Sonora River. In that context, the evaluation of the spill consequences must include the study of river dynamics, groundwater, soil properties and geochemical data.

Hydrologic conditions during and after the spill were modelled using hydrologically distributed models (tRibs and HEC-HMS) which predict spatial variability of runoff. Data from these models allowed us to know discharge rates for Tinajas river, before, during, and two months after the event. Simulation of sediment transport due to high discharge caused by hurricanes was also performed. Input data used for both type of simulations needs to be obtained from digital elevation models, channel characteristics, the analysis of rainfall, and the properties of soil, fluvial sediments and vegetation.

The soils of the region are originated from igneous and sedimentary materials; they are classified as Feozem, Regosol and Leptosol. Sediment characteristics along the fluvial channel show a bimodal distribution with modes in sediment fractions of 4-8 mm and 0.5 mm. Sand content diminishes downstream of Tinajas river, from 80% in the upper part, to 40% at the end. These changes in the sediment characteristics coupled with moisture content modified chemical properties such as pH and electric conductivity, and have a strong influence on the buffering capacity of spill residues. Batch equilibrium and transport experiments with samples taken from soils and fluvial sediments in the closer area to the Cananea mine (Tinakas creek) were performed in order to improve the current understanding of the sorption/retention behavior of metals contained in the mining waste.

Our results indicate that hydrologic conditions are very important to evaluate the impact of the copper acid sulfate spill since they determine its maximum distribution and the buffering capacity of soil and fluvial sediments. After the spill, due to the effect of extreme meteorological events, they will control the redistribution of contaminated sediments.

Keywords: Cananea spill, Sonora river, soil properties, fluvial dynamics

Monitoring the Behaviour of Sludge in the Vadose Zone

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Abstract

The approximately 120 ha backfilled Fire Road Mine strip coal mine in eastern Canada has been a source of acid mine drainage since the mid 1980's. Lime neutralization treatment of drainage has been continuously ongoing. Placement of the lime neutralization sludge back onto and into the backfilled mine site may be a factor in reducing the mine water acidity. Groundwater chemistry has been intensively monitored using a series of groundwater wells within and bordering the disturbed areas but the data is limited by the spacing of the wells.

Apparent conductivity and electrical resistivity surveys have been instrumental in identifying the locations of highly conductive mine water and what we are postulating is the treatment sludge, hopefully settled out in the vadose zone after lime neutralization sludge disposal. However, the conductivities of these zones vary across the site. And some areas thought to hold sludge have become less conductive over time. So does the sludge dry out and become less conductive? Does the sludge continue to migrate through the vadose zone? Excavations in the early 1990's indicated that the sludge only dried out near the surface but remained moist at depth.

To investigate these questions, apparent conductivity and electrical resistivity surveys will be re-acquired in areas that haven't been surveyed or received sludge deposition for more than a decade. Then, test pits will be used to allow in-situ measurements of electrical resistivity, and sampling for water content in areas where sludge is present and absent. These data will be compared to the results of conductivity/resistivity surveys acquired on surface.

This information would be beneficial to determining the behaviour of the sludge in the vadose zone and hopefully establish whether the benefits of sludge in this zone are temporary or long term. This would be useful information for determining sludge depositional locations in the future so as to possibly have a more targeted but larger impact on localized mine water characteristics. Improving the mine water chemistry to "zero lime demand" is the ultimate goal for mine water treatment at this location.

Iron Sulfide Minerals in Chesapeake Bay Navigation Channels: Environmental Fate During Beneficial Utilization of Fine-Grained Sediment

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In the upper Chesapeake Bay, dredging activities result in the average removal of $\sim 4 \times 10^6 \text{ m}^3$ of sediment removal on an annual basis. The salinity in oligohaline and mesohaline environments results in a ready supply of sulfate for anaerobic bacteria, which in combination with labile organic matter and iron oxides, results in the production of iron monosulfides and pyrite in these rapidly accumulating fine-grained deposits. In the Baltimore Harbor approach channels, AVS concentrations ranged from 0.01-0.41 % S and chromium reducible sulfur were 0.09-0.59 % S. Sediments from within Baltimore Harbor generally had similar values, but areas impacted by steel mill effluent had peak AVS and total sulfur concentrations of 3.1 and 4.5 % S. As in many coastal environments, the availability of labile Fe oxides limits the permanent burial of iron sulfide minerals.

In the state of Maryland, legislative limits on subaqueous disposal of dredged sediments has resulted in an emphasis on the beneficial use of dredged materials. Chesapeake Bay approach channel sediments are transported to facilities built on the footprint of islands that have eroded away in the last 100 years. Dredged sediments are used to construct both upland and wetland habitats on the constructed islands. Sediments are loaded into “cells” behind dikes and dewatered in a process termed “crust management”. The drying process can oxidize the iron sulfide minerals to depths of $> 0.5 \text{ m}$, yielding S oxidation of 76 mol S m^{-2} with an acid production of 152 mol m^{-2} of H^+ . Water and soil pH's during the drying process can be highly variable depending on the hydrological balance of the site, with pH varying from < 3.5 from pyrite oxidation to > 9 as a result of algal photosynthesis in pond water. A high degree of sulfate enrichment occurs in soils subjected to oxidation.

Two key management concerns in the use of dredged materials in beneficial use of dredged materials are 1) the water quality of water removed after placement and 2) the suitability of these soils for use as upland, wetland and pond restoration with appropriate plant communities. Three examples of successful utilization of use of these soils in restoration will be described. In all cases, early challenges by low pH were successfully overcome after the introduction of tidal flooding or in the case of upland habitat creation, a multi-year period of soil conditioning. The upland habitat in the southern part of Hart-Miller Island showed high plant diversity and coverage after ~ 1 decade of soil conditioning with mostly volunteer plants. A shallow pond in the same facility was pH challenged after its creation, but showed a strong ability to remediate pH through the net balance of sediment biogeochemical processes such as iron sulfide mineral formation. Similarly, wetland development after drying of sediments resulted in flooded soils with circumneutral pH, good growth of *Spartina spp.*, and over the course of several years, a conversion of abundant iron oxides to iron sulfide minerals.

Overall, upland soils without active neutralization with lime can become, with sufficient time, well suited for use in upland habitat creation. In both pond and wetland environments, iron sulfide minerals reformed because of high levels of pore water sulfate and iron as well as the production of reactive organic matter from photosynthesis of algae or macrophytes.

A miniaturized distillation method for determining reduced sulfur species in sulfidic soil materials

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Sulfur speciation methods are time consuming, expensive and labour intensive. With existing methods it is possible to separate and quantify reduced sulfur species, such as acid volatile sulfide (AVS), chromium reducible sulfur (CRS) and elemental sulfur (ES), from fine grained ($d_{50\%}$ grain size $< 63 \mu\text{m}$) hypersulfidic material (i.e. soil material with sulfidic S $\geq 100 \text{ mg/kg}$ and a pH < 4.0 upon oxidation [5]) with good precision and accuracy. Recent studies [3] have brought to attention coarse-grained ($d_{50\%}$ grain size $\geq 63 \mu\text{m}$) soil material with low sulfidic S that have an acidifying effect on the local environment due to their low buffering capacity. A distillation method for quantifying low amounts of sulfidic S with good precision and accuracy is therefore needed for risk analysis of low sulfidic soil materials. We present a miniaturized sulfur speciation distillation method for reduced sulfur species that is inexpensive to manufacture, easy to use, has a low detection limit and can be used to analyse several samples simultaneously.

The distillation apparatus presented in Fig. 1 is constructed from similar 50 ml conical polypropylene centrifuge tubes used in a diffusion-based sulfur speciation method [2]. The gas-tight centrifuge tube caps are fitted with acid resistive tubing plugged with ports and gas-tight luer-lock stopcocks which allow delivery of reagents to the reaction chamber and transport of the liberated H_2S gas using N_2 to the collection chamber. The centrifuge tubes are readily sterilized and can be discarded after use, thus reducing time spent cleaning expensive glassware, whilst the modified screw-caps can be rinsed and used numerous times before the tubing need replacing. The centrifuge tubes can also sustain over boiling-point temperatures thus enabling shorter reaction times [4] for CRS and ES distillations compared to cold purge-and-trap methods [1]. By using a miniaturized version of the distillation equipment we are able to perform sequential analysis with smaller sample sizes than with previous methods [1]. A modified analytical procedure for the sequential sulfur speciation enables AVS, ES, CRS, residual S (organic S), water leachable sulfate and acid leachable sulfate fractions to be extracted from a single 0.5 – 5 g sample. The water leachable sulfate is first extracted by centrifuging the sample with deionised and deoxygenated water and then analysing the leachate spectrophotometrically for sulfate. AVS, ES and CRS are sequentially liberated as H_2S with the distillation method and collected as ZnS in an alkaline medium. An iodometric titration procedure is then used to determine the quantities of the reduced sulfur species. Acid leachable sulfate can be separated after AVS distillation and analysed separately with a spectrophotometer and/or ICP-OES. After the extraction of all reduced sulfur species the sample residue can be mixed and fused with Eschka's reagent, thus oxidising all remaining sulfur to sulfate. After leaching the sample residue with deionised water the leachate can be analysed spectrophotometrically for sulfate which represents the residual S, or organic S, fraction. Preliminary results show good precision for reduced sulfur species and organic sulfur in fine-grained hypersulfidic material, detectable reduced sulfur species and organic sulfur in lake sediments with low sulfidic S, and good precision for reduced sulfur species in coarse-grained sulfidic material. The quantifiable detection limit for the iodometric titration method and spectrophotometric analysis has been determined to 0.01 % of sample dry weight, thus lowering the detection limit needed for low sulfidic soil material and enabling more precise risk assessments for hypersulfidic material.

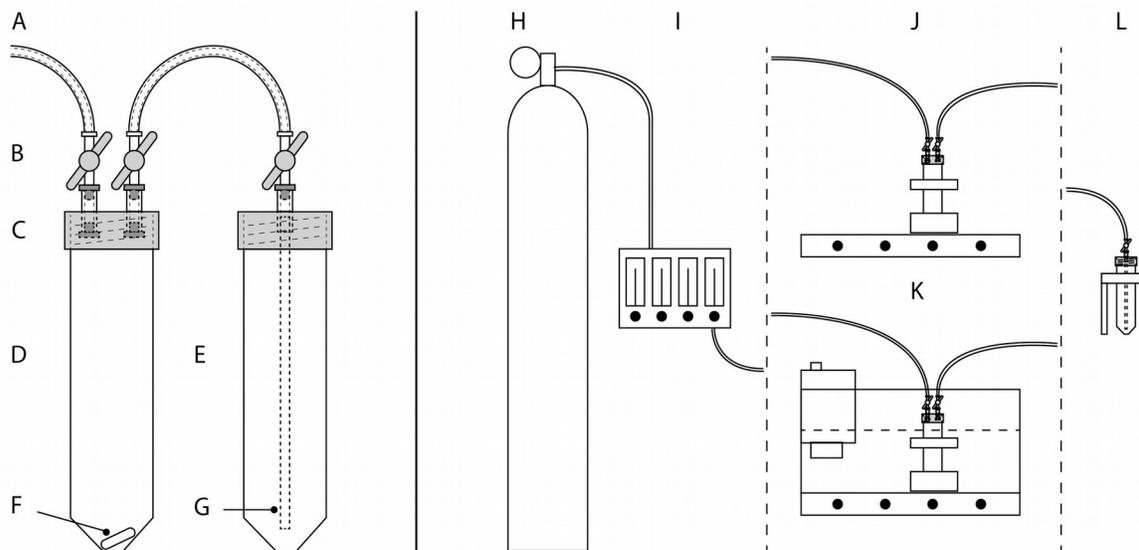


Fig. 1: Schematic figure of reaction and collection vessels (left) and distillation setup (right). A: Tubing for gas-flow, B: luer-lock stopcocks, C: polypropylene screw-caps, D: 50 ml polypropylene centrifuge tube as reaction vessel, E: 50 ml polypropylene centrifuge tube as collection vessel, F: stirring magnet, G: glass pipette, H: N₂-gas bottle, I: flow meter, J: distillation setup with reaction vessel on a stirring plate, K: distillation setup with reaction vessel in a water bath on a stirring plate, L: collection vessel.

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Characterization and Remediation of Acid Forming Dredge Materials

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Over 200 M m³ of dredge materials are removed for harbor and ship channel maintenance annually in the USA from a wide array of source environments. In the mid-Atlantic region, most of these materials are disposed of in large “spoil islands” although limited amounts are utilized for marsh reconstruction to offset sea level rise or for beach replenishment. A limited amount of dredge materials have been utilized in the upper Midwestern USA for soil reconstruction for parks and industrial site development as documented by Darmody et al. (1) and Darmody & Marlin (2). A similar effort has been monitored in Virginia by Koropchak et al. (3) since 2001 at an upland utilization facility (Weanack Land LLLP) in Charles City County where > 750,000 m³ of fresh- and salt-water source dredge materials have been placed to date and converted to agricultural use. All materials accepted for placement at Weanack must pass a rigorous screening protocol that includes an assessment of their acid forming potential via several acid-base accounting procedures. To date, we have screened approximately 20 different potential dredge materials and found that approximately 1/3 of the saline source materials contain significant amounts of potential acidity [e.g. > 5 Mg net calcium carbonate equivalent (CCE) lime demand per thousand Mg material]. Acid-formation from weathering saline dredge materials in the nearby Chesapeake Bay was also recently reported by Demas et al. (4). In our experience to date, fresh water source materials very rarely contain sufficient sulfides to warrant acid formation concerns.

One particular material proposed for dredging by the Maryland Port Administration (MPA) has historically presented a dredge disposal and utilization challenge due to metals and the potential acidity of their sediments. Post-placement low pH (<4.0) has been problematic for vegetation establishment and also reduces the pH of water moving through or over the sediment disposal or utilization facility. To determine best management practices for one material (Cox Creek; H₂O₂ potential acidity-PPA= -10 Mg CCE per 1000 Mg material; Total S = 1.31%; CCE = 7.13%) proposed for upland placement, we conducted lab and field experiments. In the lab, a series of liming rates (0.00, 0.50, 0.75, 1.00, and 1.25x of required lime additions as CCE) were evaluated through 32 wet-dry cycles. The pH of the 0.00 x liming rate treatment remained between 4.10 and 4.20 throughout the experiment, while the effects of the lime rates on bulk sediment pH were not evident until after four wet-dry cycles were completed. The lack of development of pH lower than 4.10 was unexpected. Based on the PPA results, we predicted the pH of the unlimed treatment to drop below 4.0 over more extended periods of time. By the end of the experiment, the 1.25 x liming rate sediment pH was 6.22 and the 0.50 x lime rate treatment pH was 5.11. Salinity of the material was clearly an additional issue. The EC of the 0.00x liming rate increased from 5.9 dS m⁻¹ at the start of the experiment to 7.9 dS m⁻¹, while the 1.25x rate EC increased from 7.0 to 8.9 dS m⁻¹, presumably due to sulfate release.

In the field, two lime application methods were tested (bulk-blending and layering) against an unlimed control treatment (see Fig. 1). Three zero-tension lysimeters were installed under each plot to monitor pH, EC and metal content of leachates. First-year results indicate that the pH of both the bulk-blended lime and layered treatments remained between 4.4 and 5.5 over the first four years, but the pH of the leachates under the non-limed control plots dropped to 3.7 after two year, before slowly rising again to approximately 4.2. The initial EC of the leachate samples (6 to 17 dS m⁻¹) again indicated an issue with soluble salts across all treatments, but all fell to < 4 dS m⁻¹ by the end of the 4.5 year monitoring period. The salts initially originated from entrained chlorides, but were enhanced by sulfates over time as sulfides reacted and were neutralized. High levels of Fe (> 10 mg L⁻¹) and Mn (> 100 mg L⁻¹) leached from the non-limed and layered lime treatments in the field, but were significantly lower in the bulk-blended lime treatment. The plots were seeded (Fall of 2010) to a diverse assemblage of acid-tolerant species utilized for direct seeding of acid-forming coal wastes at a combined seeding rate of 112 kg ha⁻¹. Species included *Eragrostis curvula* (weeping lovegrass), *Festuca arundinacea* “bronson” (tall fescue), *Festuca brevipila* “stonehenge” (hard fescue), *Lotus corniculatus* “norecen” with inoculant (birdsfoot trefoil), *Lespedeza cuneata* with inoculant (Korean lespedeza), and *Secale cereale* (cereal rye). This initial seeding attempt and a subsequent effort in the fall of 2011 both failed to produce > 20% cover on any of the plots. Another dose of lime (@ 10 Mg ha⁻¹) was added to the surface of the two lime treatments in the spring of 2012 and those plots finally supported ~70% mixed vegetative cover by the fall of 2013. The control plots remained barren through late 2014, but by the summer of 2015 had begun to support a limited cover (~15%) of plants like weeping lovegrass invading from adjacent plots. Net sulfurization processes were noted by the white sulfate salt crust on the soil surface and prominent jarosite mottles with depth in all plots in the first two seasons. More recent (2016) soil pit investigations confirmed that jarosite was

still present in subsoil horizons, but was no longer as prominent. The exact nature of the phytotoxicity was not directly determined, but we assume that it was due to a combination of (a) very high levels of soluble salts the first two seasons combined with (b) high soil heat levels due to the black color of the exposed surface materials.

Collectively, our experience with managing these materials for plant growth and water quality in an upland environment indicates they will be limited by low pH and the need to develop strategies for leaching soluble salts and predicting their local ground- and surface water impacts. Finally, for this material (MPA saline dredge) the PPA technique for estimating potential acidity was superior to a more conventional acid-base-accounting technique based on Total-S and CCE determinations.



Figure 1. The experimental cells containing saline and potentially acid-forming dredge materials from the MPA Cox Creek facility immediately after upland placement in the summer of 2010. The dredge material in the background is from another saline source, the Cheatham Naval Annex, Yorktown, Virginia. Lime at 12.5 Mg (CCE) per 1000 Mg of material was added to the first cell (on left) in layers on top of 15 cm lifts of dredge material while the lime for the center cell was uniformly bulk blended with the dredge materials before placement. The third cell on the far right was the unlimed control. Zero-tension lysimeters were placed at 75 cm under each cell to collect leachates which were analyzed for pH, EC and total Fe and Mn.

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A coastal zone approach to soil surveys: past, present and future

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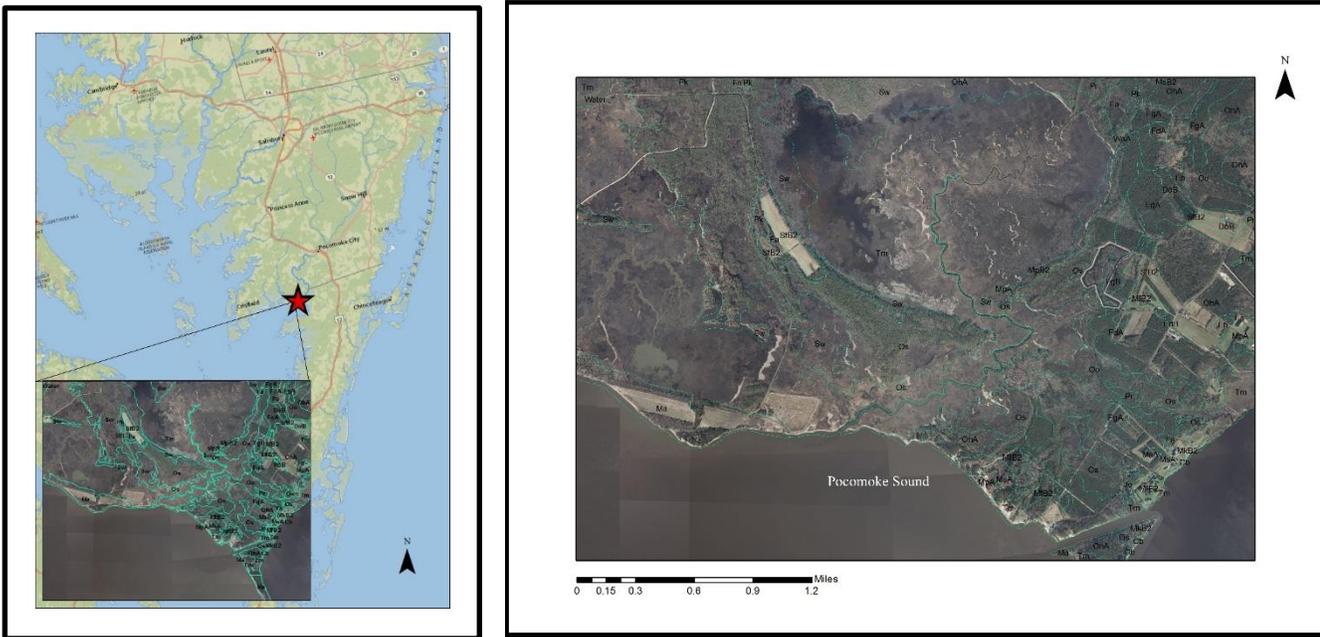
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The USDA Natural Resources Conservation Service (NRCS) is the lead federal Agency charged with the mapping and classification of soil resources on private lands. Soil surveys provide a field-based scientific inventory of soil resources. The first soil surveys were carried out just over a century ago and in addition to soil identification in uplands, earlier soil mapping included vast expanses of wetland areas such as marshes, mapped then as a “Tidal Marsh”, a Miscellaneous land type. Further, past published soil surveys like the 1966 Somerset County, MD soil survey report also recognized areas of disturbed land which may have included areas of dredge material placement as “Made Land”, another Miscellaneous land class. Unfortunately areas of Tidal Marsh or Made Land which were the result of dredging operations did not adequately address the hazards associated with acid sulfate soils and these older soil surveys failed to provide adequate information to the user concerning use and management of soil resources (Figures 1.and 2).¹



Figures 1 and 2. Location of Made Land (Ma) and Tidal Marsh (Tm) Miscellaneous Land Types, Pocomoke Sound Wild Life Management Area, 1966 Soil Survey of Somerset County, MD.

Technological advances in soil mapping methods and materials have occurred. Soil mapping of such areas today reflects better soil classification to the soil series level in *Soil Taxonomy*. Areas once mapped as Tidal Marsh such as in the 1966 Somerset County soil survey now include soils mapped to the series level such as Mispillion, (loamy, mixed, euc Terric Sulfihemist) and Transquaking (euc, mesic Typic Sulfihemists) soils. Today areas of former Made Land now includes areas of *Sulfic Endoaquepts* and *Typic Sulfaquepts*.



Figure 3. Sample soil mapping. Pocomoke Sound Wildlife Management Area, 2006 Somerset County Soil Survey Update. Soil mapping unit TP includes areas of Transquaking and Mispillion Soils.

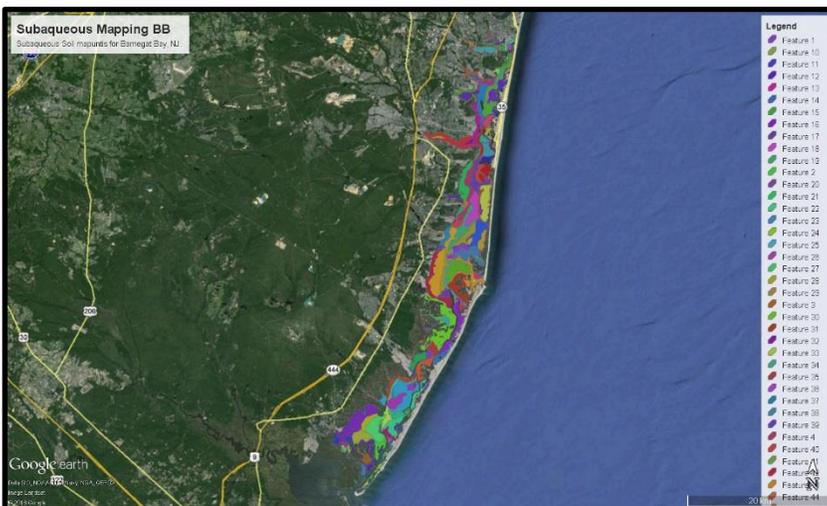


Figure 4. Barnegat Bay Subaqueous Soil Survey, Barnegat Bay, Ocean County, NJ.

islands, with subaqueous soils information. In light of climate change and near certain costly consequences, a comprehensive approach to inventorying coastal zones can only enhance our understanding of these rich and dynamic systems.

¹ Demas, S. Y., A. M. Hall, D. S. Fanning, M. C. Rabenhorst, and E. K. Dzantor. 2004. Acid sulfate soils in dredged materials from tidal Pocomoke Sound in Somerset, County, MD, USA. *Australian J. Soil Research* 42: 537-545.

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Since 1999 the definition of soil now includes subaqueous soils which are permanently submerged.^{2,3} Efforts now underway by NRCS include the subaqueous soil survey mapping of nearshore areas such as Barnegat Bay, New Jersey (Figure 4.) and the Coastal Bays of Maryland and Delaware.

The utility of a subaqueous and coastal zone soil survey is many fold and information gained may assist with the following: (1) the identification and protection of existing and potential submerged aquatic vegetation (SAV) habitats; (2) the identification of possible restocking sites for shellfish .i.e. clams and oyster and finfish; (3) the characterization of soil and dredge materials for their potential to develop acid sulfate conditions upon placement in a contained facility and atmospheric exposure and

(4) the development of a soil data baseline of chemical and physical properties which could assist in identifying sources of Bay eutrophication.

For example it is known that certain SAV species such as eel grass (*Zostera marina*) prefer sandier sediment types low in sulfides while certain aquatic organisms such as *Pfiesteria*, which is known in certain phases to be toxic to humans and fish, have a preference for siltier bottoms. A pedological approach to mapping of the coastal zone and subaqueous areas can lead to better allocation of resources and result in more science-based decisions for the management of shallow water habitats. In the near future, we propose to employ a “Coastal Zone approach”

to soil mapping to integrate soil data of previously mapped upland and near shore areas i.e. barrier

High Pore Water Hydrogen Sulfide in a Tidal Brackish Marsh with Substantial Methane Emissions

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Methane is a potent greenhouse gas and may offset a significant portion of the carbon sequestration benefit of many brackish marshes. Previous research indicates that sulfate availability can suppress methanogenesis in salt marsh soils but not in brackish marsh soils. In order to determine the impact of flooding and vegetation communities on methane emissions, we measured methane fluxes from two brackish marshes on the Deal Island Peninsula, located on the Eastern Shore of Maryland. Data were collected monthly from April 2015 until December 2015. Methane flux data was collected from 20 plots located in un-ditched (15 plots) and restored-ditched (5 plots) marshes. Four communities, three in the un-ditched site and one in the ditched site, were measured with five replicates per community. Porewater samples were taken concurrently at a 10-cm depth and analyzed for methane, pH, conductivity, ammonium, phosphate, ferrous iron, sulfate, and hydrogen sulfide. Preliminary results indicate the greatest methane emissions from the *Spartina alterniflora* community (2.72 times greater than the next highest community), which also consistently had the highest pore water hydrogen sulfide levels (mean = 2119 μM). Sulfate levels in the pore water varied significantly across both month and vegetative community. Our preliminary analyses indicate that some communities in our marsh are more prone to methane emissions than others; and suggest that methane emissions in these communities are not driven by the competition between sulfate-reducing bacteria and methanogens. This study will allow us to determine the controlling factors of methane generation in these important ecosystems.

Precision chemical treatment of acid sulfate soils for the protection of waters in environmentally sustainable agriculture

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Mitigating the acidic and metal-rich drainage from an acid sulfate soil in agricultural use is challenging. The approach we have chosen in the previous PRECIKEM project (2010-2014) and in the present PRECIKEM II project (2015-2018), is based on the fact that it is the soil layers below the plow layer, and especially at drainage depth, that contribute actively and predominantly to the accumulation of oxidation and leaching products in the drainage water. The oxidation process is most significant during dry periods with a groundwater table at or below drainage depth, while the oxidation products and leached metals are subsequently flushed out during wet periods with a high groundwater table. In the end of the summer when the groundwater is well below drainage depth (about 1.5 m) and the soil macropores (contributing to the high hydraulic conductivity in the drained soil layers) are empty, a solution/suspension of treatment chemicals is pumped into the soil layers via the control well and drainage pipes. This technique enables treatment of the most important hydrologically active soil layers.

Treatment chemicals

Our treatments so far have used ultrafine-grained suspensions of calcium carbonate or calcium hydroxide. The use of very fine particles (low μm dimensions) is essential in order to facilitate the transport through soil pores and to avoid sedimentation in the drainage system. It turns out that the calcite particles adhere to the exposed surfaces as the suspension flows through the cracks and macropores of the soil. As an example of the treatment result, in Fig. 1 it is shown that the surfaces of a newly formed crack in the sulfidic sediment underlying the acid sulfate soil in a treated field are covered with calcite. The oxidation front is clearly visible as the boundary between gray and black material only about 10 mm from the surface of the crack.

We hypothesize that this layer of calcite has several effects: the immediate increase in pH neutralizes recently formed sulfuric acid, it causes the precipitation of several metals, and it deactivates acidophilic microorganisms catalyzing reactions in the oxidation process. It may also form a physical barrier that slows down the passage of oxygen during times of a low groundwater table.

We are now following the long-term development of these treatments. There is a slow consumption of treatment chemical during the years following the treatment, and thus a progression towards an increase in acidity and metals content of the drainage water.

In the coming years complementary treatments with other substances will be conducted in order to prolong the effect of the treatment.



Figure 1. A newly formed crack just below drainage depth has been reached by the calcite suspension in a treated field.

Column and field experiments

Prior to field experiments, column leaching experiments are performed in the laboratory. Suspensions are passed through cylindrical soil samples from the soil horizon at 80-90 cm below the surface by applying a hydrostatic pressure. In the outflowing solution, pH, EC and ORP are measured continuously. Subsequently, selected parts of the treated soil are used for the microbiological assessment. Surfaces that have been in direct contact with the treatment suspension are compared with soil from the interior parts of aggregates.

In full scale field experiments, the test site at Risöfladan is utilized. Suspensions are created by mixing water from nearby Toby River with chemicals in a mixing vessel, before being pumped into the subsurface soil via the control well and subsurface drain pipes. Treatment effects are studied both chemically in the form of determinations of pH, EC, ORP, major anions and selected metals, and microbiologically in the form of the identification of microorganisms present by analyzing 16S rRNA gene sequences (Wu et al. (1)).

Future studies

The effect of the calcium carbonate and calcium hydroxide treatments on pH is evident. However, redox conditions are affected to a lesser degree and we will continue to work on developing new combinations that will allow us to adjust both pH and ORP in the soil layer that is treated.

The experimental field at Risöfladan is enlarged with new subfields. The subfields will have their own drainage system, and are hydrologically separated from each other by a plastic sheet enclosing each subfield and extending from about 40 cm below the surface down to about 140 cm. New drainage technology specifically designed for subsurface irrigation/chemigation will be developed.

We continue to follow the chemistry of the groundwater and the soil, as well as the microbiology of the soil. Clear chemical effects are evident in both laboratory and field, while no change in the populations of microorganisms are presently found (Wu et al. (2)). We recognize the importance of the microbiology, and more detailed studies are planned to elucidate the microbiological effects.

Acknowledgements

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Modern Ironstone Formation by Sulfuricization Phenomena

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This paper will report via pictures in a Power Point presentation where modern ironstone has formed as a result of sulfuricization phenomena. The ironstone looks like what in some soil science literature has been called laterite or hardened laterite or hardened plinthite, thought to have formed by laterization or lateritization in lateritic or Ground Water Laterite soils. We think that in cases like those shown in the pictures in this abstract, that the ironstone has formed by oxidation and hydrolysis of dissolved ferrous sulfate in waters that has emanated from active acid sulfate soil materials where the ferrous Fe has undergone oxidation and hydrolysis to form iron oxides or oxyhydroxides that precipitated to form the ironstone. Thus we prefer to think of this ironstone as a sulfuricization product, which, from the situations in which it occurs, has obviously formed in very recent times. These phenomena will also be referred to as examples of Big Bang Soil Genesis. Other examples will be presented in full paper.



A modern watch band cemented into recently deposited ironstone by iron likely released from oxidation of iron sulfides during sulfuricization. Slide from Darrin Lowery;

The picture above was taken on beach outside of dike containing sulfidic dredged materials beside tidal Pocomoke River (Handy property site) in Somerset Co., MD. Same is true for ironstone in other pictures.

Ironstone recently formed by the Handy DM deposition site deposited around stems of Phragmites reeds. This slide from Susan Demas



Ironstone formed in discharge pipe from Site B at Handy site, where sulfidic dredged materials were deposited behind dike in background in 1994.

The overall site where soils in sulfidic dredged materials from which the iron that formed the ironstone shown in pictures in this abstract was leached, presumably as dissolved ferrous sulfate, is described in Demas et al. (2004).

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Demas, S. Y., A. M. Hall, D. S. Fanning, M. C. Rabenhorst, and E. K. Dzantor. 2004. Acid sulfate soils in dredged materials from tidal Pocomoke Sound in Somerset, County, MD, USA. *Australian J. Soil Research* 42: 537-545.

Phriends of Phragmites

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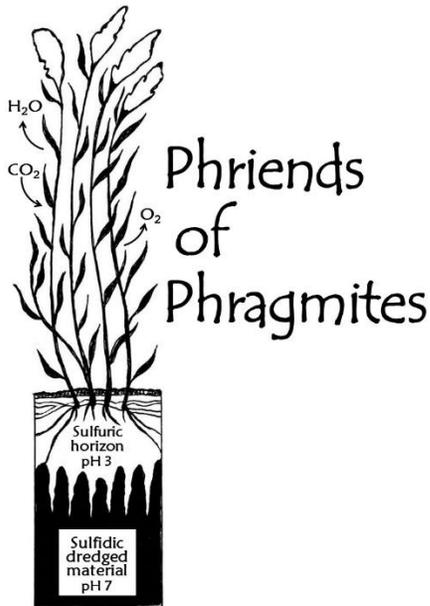
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In several publications (e.g. Fanning and Burch, 2000) the formation of a Phriends of Phragmites Society has been proposed to promote the use of the common reed, *Phragmites australis* in a reclamation strategy called “letting nature run it’s course” for acid sulfate soils on recently deposited sulfidic DM (dredged materials) in upland, usually diked in, deposition sites. In October 2015, upon visiting the HMI (Hart-Miller Island) deposition site for the first time in many years, to plan the 8th IASSC pre-conference tour there, the senior author was greatly disappointed to find that the opposite of the strategy of encouraging *Phragmites* has been practiced at that location for several years; instead, naturally invading *Phragmites* there have been driven back and reduced in their abundance by the use of herbicides and other practices, which has resulted in large parts of the land there presently lying barren or only covered with sparse, hardly noticeable, vegetation of little biomass. It was learned that those managing the HMI and other DM deposition site are required by state-mandated regulations to control *Phragmites* at their sites by the use of herbicides, apparently at HMI largely by aerially applied Rodeo. Learning these things stimulated us to renew our efforts to promote Phriends of Phragmites. Several attendees after a seminar about *Phragmites* by Baldwin in November, 2015 agreed to support our PofP efforts by signing to purchase tee shirts promoting P of P. Katie Haering, known for her drawing skills was recruited to do a drawing (shown below) for the tee shirt, representing

Phragmites growing on an active acid sulfate soil, ideally a *Hydraquentic Sulfaquept* by *Soil Taxonomy* developing in sulfidic dredged materials, for the tee shirt.



Phragmites are especially useful on these soils, which initially, following the deposition of the dredged materials are totally unvegetated. Thus on these soils *Phragmites* do not displace other plant species (a complaint of some Phoes of Phragmites) because other species are not present. Essentially no plants, including *Phragmites*, invade and grow upon these soils by seeds that fall upon the soils once they have acidified upon the oxidation of sulfides because of their ultra acidity, e.g. pH <3.5, of surficial *sulfuric horizons* that induce high levels of soluble aluminum in the soils. However, *Phragmites* do invade and colonize these soils by rhizomes running out upon them from the edges of the DM deposition areas where we think part of the root systems of the plants are in soil materials with less extreme chemical conditions, and once these plants do establish on the *sulfuric horizons*, healthy roots of *Phragmites* have been observed in *sulfuric horizons*, supporting above ground portions of the plants 2-3 meters tall. The picture shown on nest page (finger nail about 12 mm wide) shows a portion of a *sulfuric horizon* of an 8 year old soil in DM that had a pH, measured in water, of 2.8 with cross-section of a large hollow

Phragmites root, with smaller channels in its walls, close to the top of the photo, above and to the right of the finger.. A description of this soil that mentions the presence of common to many coarse and fine roots in this *sulfuric horizon* appears in Appendix A, pages 76-77 of Maura McMullen’s 1984 M.S. thesis (Mc Mullen 1984). The finger is pointing to the yellow mineral jarosite on a prism face of the soil, which also had concentrations of iron oxyhydroxides (possibly schwertmannite) on the walls of pores and channels and dark gray interiors of structure peds, shown where the ped faces were broken away, and also fine roots, some of which were observed to go into deeper black sulfidic materials where the pH was about 7, thus such a possibility is shown in the drawing.

We know that *Phragmites* grow on many other kinds of soils in addition to acid sulfate soils developing in dredged materials, including some where they are probably responsible for pushing out more desirable plants. We also know that there are native to North America, sub-species *americanus* as well as so-called foreign-invasive *Phragmites* that



apparently may grow larger than the native ones. Baldwin and others in the UM ENST Department have some research projects involving graduate students who are studying the various subspecies and conditions that may favor one vs. the other. However, for the promotion of the ripening of soils on soft newly deposited dredged materials, *Phragmites* are a special plants for utilization during the ripening and initial development of the soils, like they have been, used in the Netherlands, where they are sometime planted on newly exposed land, polders, where the sea has been pushed back to make new land for agriculture, to enhance the drying out and ripening of the soils..

At first only water, H₂O, was shown by chemical symbols leaving the plants in the drawing, as a main benefit of the *Phragmites*, by evapotranspiration, is the physical and chemical ripening of the soft soils at DM deposition sites, where they help get rid of the excess water, like at the Hart-Miller Island site, meaning that less water in liquid form has to be released to surrounding water ways Baldwin suggested that we also show CO₂, which is taken up by the *Phragmites* and O₂ which is released by photosynthesis, like it is with other kinds of plants. The large biomass produced by the *Phragmites*, is a major benefit to the soils in terms of additions of organic matter to the soils and in taking the heat-trapping CO₂ from the atmosphere etc. Andy suggested that we show O₂ coming out of the roots, where it hastens the oxidation processes in the soil. Katie could not find room in the diagram to show this. Perhaps that can be added in future updates/revisions. Also not shown, although implied, is that *Phragmites* take up P and N, which lowers that amount of these elements that enter waterways and contribute to eutrophication of waters of the Chesapeake Bay. All of these benefits and others (e.g. the beauty of *Phragmites* with benefits to many forms of wildlife – red-winged blackbirds and other birds and muskrats that build their houses using *Phragmites* -- are more reasons why we encourage people in all walks of life to be Phriends of *Phragmites*. Supporters will be offered an opportunity to purchase tee shirts at this 8th IASSC, perhaps at a poster version of this paper if it gets completed. PofP is not yet an official Society. Supporters are asked add their names to a list of those interested in becoming members and to contribute their ideas for goals of the organization, of which we hope to have a draft version ready to distribute at the conference.

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Constructing and Evaluating a Monolith of an Active Acid Sulfate Soil with a Duripan

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Soil monoliths are powerful tools for soil education and for representing soils as they are found in the field. They preserve and display major soil features and are relatively portable (Belohlavy 1994). The monolith described in this paper was collected from an active acid sulfate soil located along a road cut near the Smithsonian Environmental Research Center in Edgewater, Maryland (38°53'08.51"N, 76°34'08.06"W). The key features of this profile include a silica-cemented duripan, a sulfuric horizon, as well as prominent concentrations of jarosite and iron oxide, glauconite, and sulfidic materials. The scalped surface condition (down to the duripan) is thought to be an anthropogenic feature, resulting from the creation of a now-abandoned road, prior to the construction of Maryland Route 468 (Delvin Fanning, personal communication).

A morphological description of the soil was completed in the field before extracting the monolith and is summarized in Table 1. The surface includes a 1-2cm covering of decomposing pine needles (Oi horizon) underlain by the Ase horizon. The duripan begins at 6cm and extends to 47cm, but was split into two distinct horizons based on color differences caused by an increase in glauconite with depth. The duripan is composed of ~95% channers and flagstones that are interlocked but otherwise not bound to one another. These "plates" are coated with a thin layer of jarosite and consist of matrix-supported glauconitic wacke with ~50% subrounded glauconite fine sands.

Both the Bsej1 and Bsej2 horizons contain concentrations of jarosite occurring as intercalations which run roughly parallel to the soil surface (Fig. 2A). The Bsej2 horizon is distinguished by the presence of iron oxide intercalations (linear concentrations) in addition to the jarosite intercalations, as well as iron oxide coatings on peds. Interestingly, there were circular iron coatings which possibly suggest the past presence of roots (see Fig. 1B). The oxidized-unoxidized zone boundary occurs at 80cm, under which jarosite and iron concentrations are not found. The entire profile contains a pelletized form of the mineral glauconite as sand-sized grains that formed in a marine environment (Fanning et al., 2010). In the mid-Atlantic area, pyrite has been shown invariably to occur in the unoxidized zone of Tertiary and Cretaceous sediments containing glauconite (Rabenhorst and Valladares, 2005).

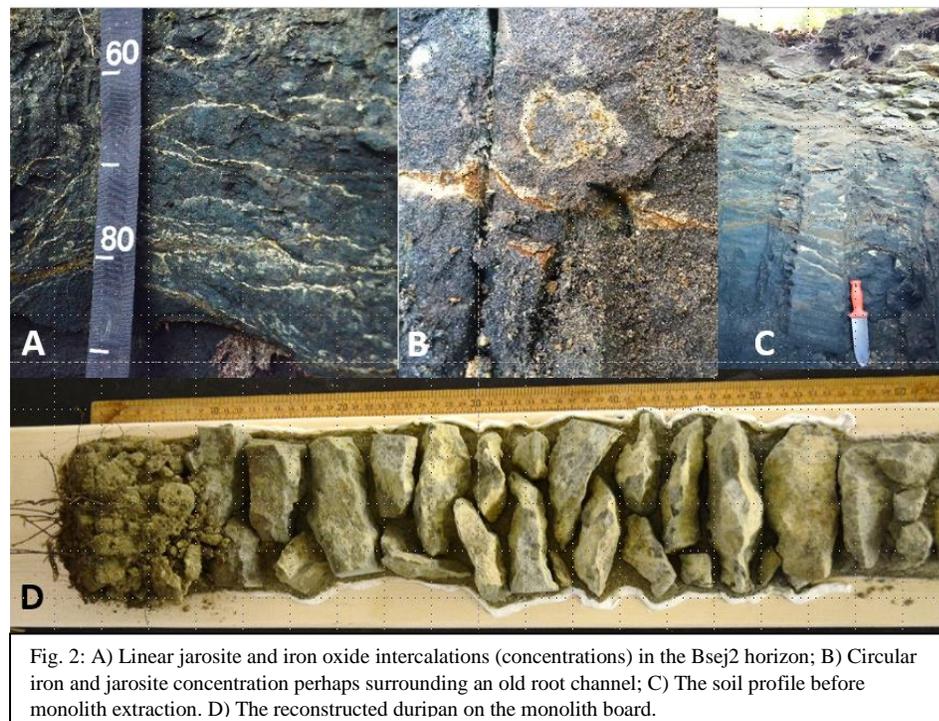
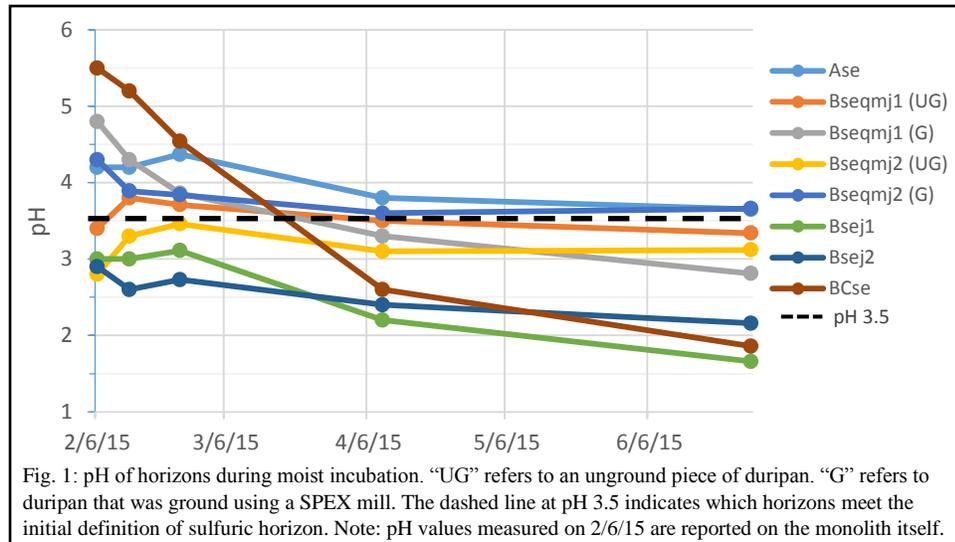
Table 1: Soil morphological description at field site where the soil monolith was collected.

Horizon	Depth (cm)	Description
Ase	1-6	5Y 4/2 loamy fine sand; moderate granular structure
Bseqmj1,2	6-47	Duripan with many prominent jarosite concentrations
Bsej1	47-65	2.5Y 4/1 sandy loam; weak subangular blocky structure; common prominent jarosite intercalations
Bsej2	65-80	2.5Y 3/1 sandy loam; weak subangular blocky structure; common prominent jarosite and iron oxide intercalations
BCse	80-108	2.5Y 2.5/1 sandy loam; massive structure

To create a monolith that best represented the soil, it was important to include the duripan as closely and accurately as it occurred *in situ*. During the extraction process, duripan fragments were collected using a spade and rock hammer. Soil from between the duripan rocks was collected, and the rest of the profile was removed using normal monolith extraction techniques. The duripan was later reassembled from fragments and fit into place by using a rock saw to cut flat surfaces. The pieces were then affixed to the monolith board with epoxy and the gaps between the rocks were filled with soil material (Fig. 3C).

According to *Soil Taxonomy*, a sulfuric horizon must be at least 15cm thick with a pH of 3.5 or less. Further, the pH can be 4.0 or less if sulfide or sulfur-bearing minerals are present and there is evidence that the low pH is caused by sulfuric acid. The presence of jarosite in the Bseqmj and Bsej horizons is enough evidence to call them sulfuric. Without jarosite, the layer directly underlying the horizon must contain sulfidic materials. Sulfidic materials are "mineral or organic soil materials that have a pH value of more than 3.5 and that become significantly more acid when oxidized." These materials usually accumulate under estuarine or marine conditions and persist even when the water recedes. Exposure to aerobic conditions, for instance by human activity, results in oxidation of the sulfides leading to the pH drop. To test for the presence of sulfides, a moist incubation was conducted on material from each horizon following guidance in *Soil Taxonomy*. The measured pH values are reported in Figure 1. According to the definition, the sulfuric horizon extends from the bottom of the Ase to the top of the BCse horizon.

Classifying this soil proved to be difficult since it does not fit any existing soil series and there are no other reported instances of duripans in the region. Due to the root-limiting layer (duripan) within 36cm, the family particle-size control section extends from the mineral surface to the root limiting layer which limits the control section to the 6cm of the Ase horizon. Additionally, the scalped surface and duripan are important features that should be included in the classification. Thus, the proposed classification is: Sandy mixed subactive mesic Scalpic (proposed, Fanning) Duric (proposed) Sulfudept.



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Schwertmannite as an indicator of geochemical processes in acid sulfate soil environments: *A tribute to legendary soil scientist Prof Udo Schwertmann*

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A giant in the field of iron oxides in soils, Professor Udo Schwertmann died on January 20th, 2016 at the age of 88. He led a group of international scientists who first described the formation, properties and structure, of the mineral “schwertmannite”, which is named after him by the International Mineralogical Association (Bigham *et al.* 1990, 1996, 2002).

This paper contains broad interpretations of the widespread occurrence and pedogenic significance of schwertmannite in acid sulfate soil and water environments by placing emphasis on relationships between field pedology, geochemistry and mineralogy. The paper will also cover the history of the important discovery of schwertmannite in acid sulfate soil and water environments mainly from an Australian landscape perspective (Fig. 1).

There is a unique and wide spectrum of occurrences and origins of schwertmannite in acid sulfate soils and water environments in both coastal and inland areas as well as in anthropogenic sites including mines, spoils and tailings. Schwertmannite may also be a component of sediments in equatorial regions of Mars where seepages of acidic, saline meltwaters are thought to have occurred as a result of permafrost melting (Bigham *et al.* 2000).

Schwertmannite is a metastable ferric oxyhydroxysulfate [$\text{Fe}_{16}\text{O}_{16}(\text{OH})_y(\text{SO}_4)_z \cdot n\text{H}_2\text{O}$ where $16-y = 2z$; $2.0 < z < 3.5$] that is often a ubiquitous mineral formed in oxidized acid sulfate soils with sulfuric horizons ($\text{pH} < 4$) and in acid drainage environments (Schwertmann *et al.* 1995, Bigham *et al.* 2002, Cornell and Schwertmann 2006, Mosley *et al.* 2014). Schwertmannite commonly forms in surface acid drainage waters with pH values between 3 and 4.5 and high dissolved iron and sulfate concentrations between 1000 and 3000 mg L. It plays an important role in controlling the chemistry of many acid sulfate soils and waters by buffering the pH and controlling the activity of metals and major ions. The presence and behaviour of schwertmannite is variable in terms of: (i) its specific occurrences, (ii) the environmental factors working during its formation, and (iii) post-formational alteration, for example:

- Schwertmannite is typically formed from oxidation and hydrolysis of dissolved Fe(II), which is accelerated in acid sulfate systems by acidophilic bacteria that have a metabolic requirement for sulfate, which is also a structural or stabilizing component of schwertmannite (Bigham *et al.* 1996; 2002). These reactions are favoured when Fe(II) and sulfate-rich groundwater discharging from acid sulfate soils enters more-oxygenated surface waters or drains (Schwertmann *et al.* 1995; Fitzpatrick *et al.* 2012; Mosley *et al.* 2014). These formation processes can cause less permeable Fe-rich layers to form in saline discharge areas and explains the mechanisms that lead to degraded soils, erosion and poor water quality (Fig. 1; Fitzpatrick *et al.* 1992, 1996).
- Schwertmannite has been found to form rapidly in acid sulfate soil environments in South Australia by the dissolution of metastable sideronatriite [$\text{Na}_2\text{Fe}(\text{SO}_4)_2 \cdot \text{OH} \cdot 3\text{H}_2\text{O}$] in rain water (i.e. after rain events) (Fitzpatrick *et al.* 2000; Fitzpatrick and Shand 2008). Sideronatriite formed via oxidation of pyrite (formed in subaqueous saline sandy soils), after being exposed to the air for the first time in more than 100 years during Australia's Millennium drought. This alternative pathway for the formation of schwertmannite was verified by dissolving synthetic high purity sideronatriite (made in the laboratory under similar conditions found in nature i.e. temperature, chemistry and pH) in distilled water.
- Schwertmannite is a metastable phase, and transforms to goethite (and or jarosite) over timescales of weeks to months, which was confirmed from laboratory incubation experiments using synthetic schwertmannite (Bigham *et al.* 1996). However, in coastal lowland acid sulfate soils schwertmannite can persist on a much longer time-scale than predicted by laboratory experiments, likely due to surface-site coverage by silicate, natural organic matter and phosphate (Collins *et al.* 2010). In anoxic acid-sulfate systems, the Fe(II)-catalyzed pathway has been found to exert a major influence on the transformation of schwertmannite to goethite and sulfide formation (Burton *et al.* 2008).

- Schwertmannite can be used: (i) to remove or scavenge arsenic from waters in acid streams and in mine tailings as it has a high sorption capacity for metal and anionic contaminants such as arsenic (Bigham *et al.* 2002), (ii) as a geochemical sampling medium for the detection of mineral deposits (Fitzpatrick and Shand 2008) and (iii) as an indicator of acid sulfate soil-water processes operating in landscapes (Fig. 1; Fitzpatrick *et al.* 1992; 1996).



Figure 1. Photograph of Professor Udo Schwertmann (right – after whom the mineral schwertmannite is named) and Dr Rob Fitzpatrick (left) both pointing in August 1993 to the reddish/orange-brown thin friable crust where schwertmannite was first identified in a natural acid sulfate soil (i.e. Alfic Sodic Sulfaquept) in the Mt. Lofty Ranges, South Australia. During wet winters, permanent saline seepages contain gelatinous precipitates of schwertmannite (below photograph), which forms from rising Fe^{2+} and SO_4^{2-} -containing ground waters that percolate through rocks containing pyrite and its oxidations products. In summer, the seasonal changes in soil redox conditions strongly modify the geochemistry of the soil solution causing both schwertmannite and goethite to form in the presence of excess sulfate and chloride, usually in the form of cemented crusts with high levels of scavenged cations such as As, Zn and Si (Fitzpatrick *et al.* 1992; 1996).

Finally, presence of schwertmannite has recently been included as an acceptable indicator of low acidity ($\text{pH} < 4$) for sulfuric material or horizon in several international (e.g. Soil Taxonomy and WRB) and national (e.g. Australian) soil classification systems.

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Schwertmannite formation and persistence in acid runoff from re-flooded Acid Sulfate Soil environments following river level decline during drought

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Introduction

Prior to Australia's Millennium drought, which commenced in 2007, the Lower Murray Reclaimed Irrigation Area (LMRIA) was actively farmed mainly as dairy enterprises (>80 years). During this extensive pre-drought period surface water tables were maintained from irrigation, river and groundwater flows, which kept the subsoils saturated (i.e. high water table level of 0-1m below ground level). At the end of the Millennium drought in 2010 a drop in the water table level of up to 3m from pre-drought levels led to the previously saturated soils being exposed to air for the first time causing severe soil cracking to depths of up to 3.5m and oxidation of pyrite in the subsoils, which contain high amounts of hypersulfidic material. This process enabled hypersulfidic material to transform to sulfuric material with the consequent formation of: (i) deep "Sulfuric clayey soils" and (ii) schwertmannite in bright reddish-yellow suspended/gelatinous precipitates in acidic drains (Fitzpatrick et al. 2012).

Methods and Results

The prime objective of this study was to examine in more detail the morphology [e.g. Soil Munsell colour and scanning electron microscopy (SEM)], mineralogy [X-ray diffraction (XRD)] and geochemistry (HCl dissolution) of iron-rich precipitates and salt efflorescences in a wider range of 5 acidic drains/retention ponds/sump areas near levee banks at Long Flat, Jervois, Toora, Pompoota and Burdett as shown in Fig. 1. A primary goal was to investigate whether relationships, exist between the following different sample types shown in Figures 2a and 3a: (i) reddish-yellow suspended/gelatinous precipitates in drains – as previously reported on by Fitzpatrick et al. (2012), (ii) reddish-yellow precipitates with white salt efflorescences on dead grasses, (iii) reddish-yellow precipitates coating wooden racks and dead vegetation, (iv) brownish-yellow hard cemented crusts and nodules on roots and/or stems of *Phragmites Australis* in salt drains, dead reeds and grasses.

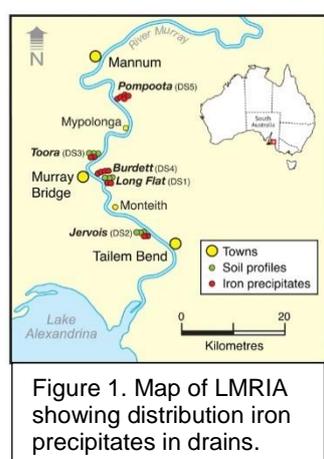


Figure 1. Map of LMRIA showing distribution iron precipitates in drains.

For all samples, XRD patterns displayed the eight broad peaks typical for schwertmannite [marked S in Figs. 2(a) and 3(a)] but with additional weak reflections indicating presence of small amounts of: (i) natrojarosite for Long Flat site, (ii) gypsum (G) and Hexahydrite (H) for Toora site, (iii) goethite (Goe) for Jervois evaporation pond, (iv) jarosite (J) for the side drain site at Pompoota. The different oxide assemblages of mainly schwertmannite with minor concentrations of natrojarosite, goethite and gypsum likely record deposition under variable pH conditions and sulfate concentrations resulting from different flow stages. Schwertmannite from the reed roots at Long Flat have radiating fibres (100nm) and globular (1-4µm) morphology [Fig. 2(b)] – likely due to periodic drying. In contrast, schwertmannite from Toora swamp has radiating fibres and balls 2µm [Fig. 2(c)], whereas coatings on grass and stems in the Pompoota drain shows "schwertmannite spheres" (0.3-1µm) [Fig. 3(b)]. Geochemical speciation calculations (PHREEQC) using the dissolved metal and major ion concentrations supported the

XRD and EDS results as the saturation index (SI) exceeded zero for schwertmannite in many drains. The schwertmannite-rich precipitates contain high concentrations of metals [Al (max: 81,900 mg/kg) > As (max: 116 mg/kg) > Zn (max: 164 mg/kg) > Cu (max: 89 mg/kg) > Pb (max: 20 mg/kg)] due to co-precipitation/scavenging of these elements during formation of schwertmannite. Precipitates also contained high concentrations of P (max: 5890 mg/kg), Ni (max: 131 mg/kg), Cr (max: 26 mg/kg), Co (max: 70 mg/kg), B (max: 56 mg/kg) and Mn (max: 271 mg/kg); where max = maximum concentrations after HCl dissolution. As was highest in the brownish-yellow hard cemented crusts and nodules on roots and/or stems of *Phragmites Australis* in salt drains at Long Flat. Zn, Ni and B concentration was highest in the reddish-yellow precipitates from the main drain at Toora. Cu was consistently higher in precipitates from the Burdett drain. Na was highest in the precipitates from the middle of the retention pond at Jervois.

The possible transformation of schwertmannite to goethite had only been observed in one sample (Jervois evaporation pond). The observation that schwertmannite precipitated and scavenged metals but has persisted for over 5 years in most of the LMRIA drains has significant implications for short-

term rehabilitation options. Schwertmannite is a “metastable phase” and has been shown that it will transform to goethite within weeks to months. Dilution and acid neutralisation, especially as the drain water is pumped back to the River Murray causing dilution of the acidic drain water, would likely promote dissolution of schwertmannite and release of associated trace elements. Gaps in understanding include whether incorporation of metals in the schwertmannite structure and Soil Organic Carbon (SOC) (strong SOC-mineral/metal associations) has increased tolerance for microbial degradation. Hence, preventing/reducing the transformation of schwertmannite to goethite.

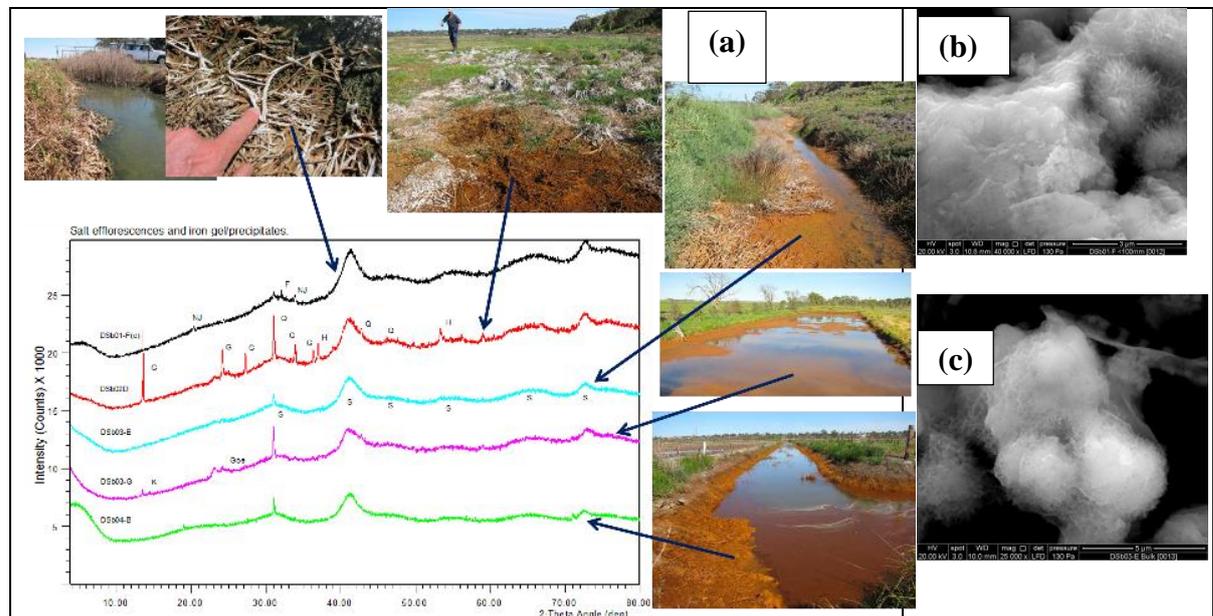


Figure 2. (a) Photographs and XRD patterns of schwertmannite-rich deposits from: (i) brownish-yellow hard cemented crusts and nodules on roots and/or stems of *Phragmites Australis* in shallow salt drains, dead reeds and grass in drain at Long Flat (Black), (ii) reddish-yellow precipitate and white salt efflorescences (Konyaite and Hexahydrate) on dead grass in field near Toora (Red) (iii) reddish-yellow gelatinous precipitates in drain near Toora (Blue), (iv) reddish-yellow gelatinous precipitate in the irrigation evaporation pond near Jervois (purple) and (v) reddish-yellow gelatinous precipitates in drain near Burdett drain (green). (b) SEM of crusts from Long Flat; (c) SEM of precipitates in drain from Toora. Where: S = Schwertmannite; G = Gypsum; H = Hexahydrate; J = Jarosite; Q = Quartz; NJ – Natrojarosite.

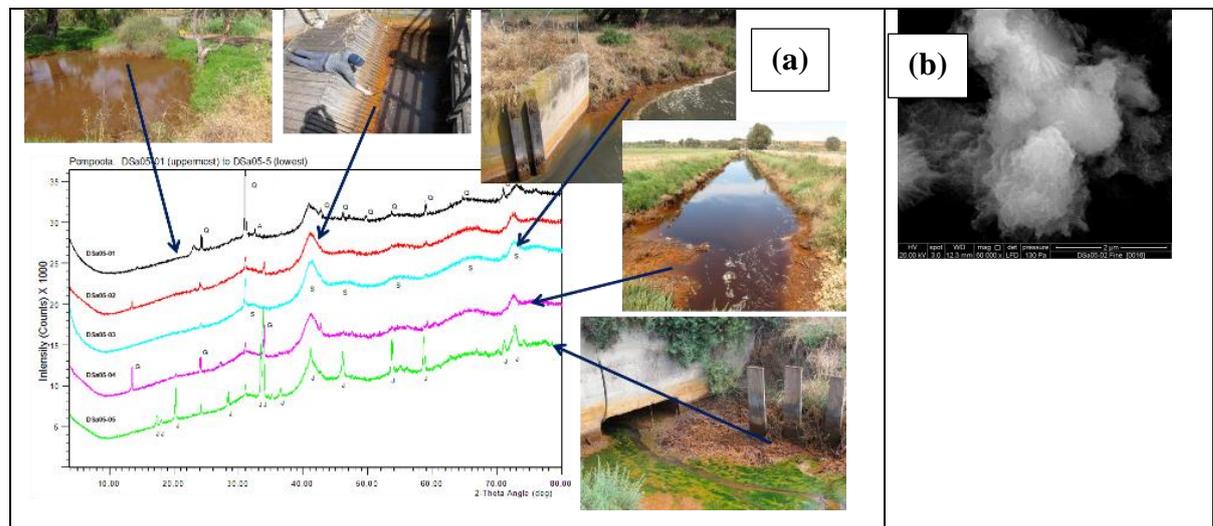


Figure 3. (a) Photographs and XRD patterns of schwertmannite-rich deposits near Pompoota comprising: (i) suspended/gelatinous precipitates in the wetland on the Murray River side of the Levee bank (black), (ii) precipitates coating wooden racks and dead vegetation in sump (red), (iii) precipitates coating dead reeds and concrete surfaces in main drain (blue), (iv) precipitates coating dead reeds in main drain (purple), (v) precipitates coating dead reeds on eastern side drain (green); (b) SEM of precipitate coatings in sump.

References

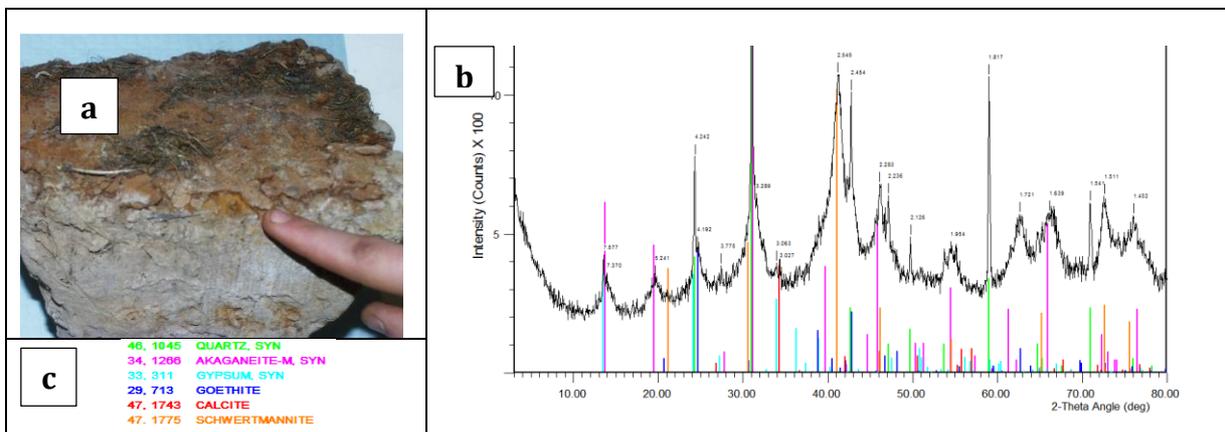
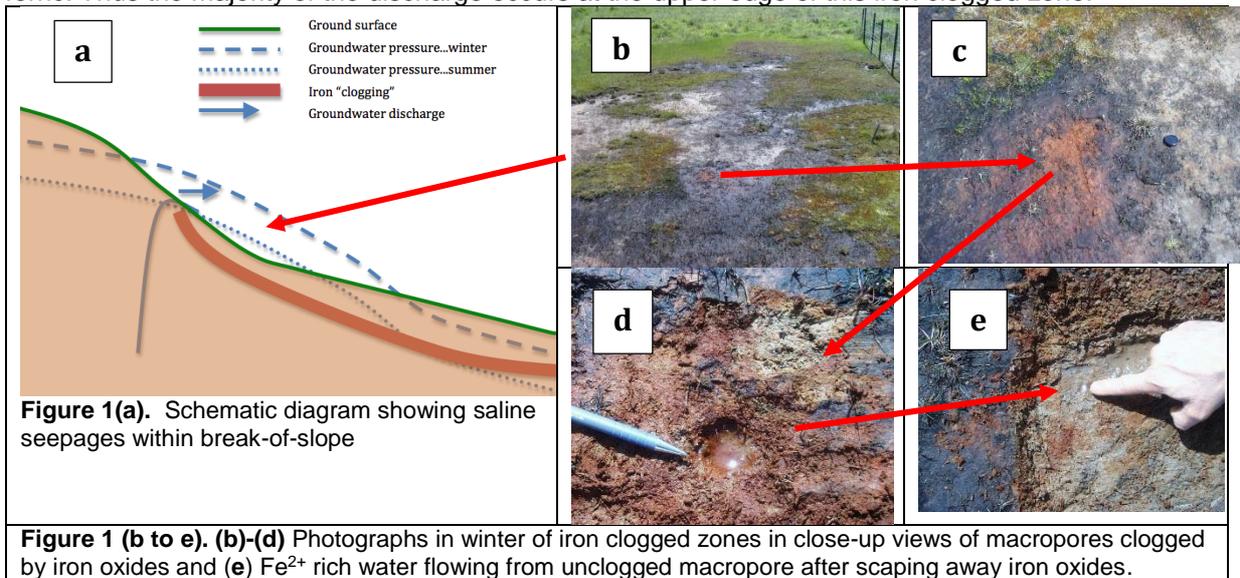
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Remediation of “Red Barren” scalds comprising acid sulfate soils with iron clogged layers on the Dundas Tablelands, Victoria, Australia

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Introduction

The schematic diagram (Figure 1a) and landscape photographs (Figure 1b-e) illustrates our concept of the processes occurring at the Red Barren scalds. The landscape is the result of pyroclastic eruptions, which have subsequently been uplifted and eroded. A regional groundwater exists with preferential areas of recharge and its pressure follows the topography with positive pressure (above ground level) occurring in various places, evident as land degradation. At these places, groundwater is prevented from discharging by a band of iron “clogged” soil, the result of ferrous ions being oxidised to ferric. Thus the majority of the discharge occurs at the upper edge of this iron clogged zone.



The deep groundwater is naturally electrically negative having passed through buried volcanic material. Reactive material has been stripped from flow pathways to the surface, as evidenced by the strong redox depletions (bleached matrix along flow pathways) surrounding redox concentrations (red mottles) in subsoil horizons. At the zone of discharge the reduced groundwater contacts reactive material, particularly iron, reducing it to ferrous (Figure 1). During wet winters, these areas of seepages contain acid sulfate soils with sulfidic material (“Alflic Sodic” Sulfaquents) and surface gelatinous precipitates of schwertmannite and some ferrihydrite, which forms from Fe²⁺ and SO₄²⁻ containing acidic (pH 2.8 to 4.5) ground water (Figure 1b-e). In summer, the seasonal changes in soil redox conditions strongly modify the geochemistry of the soil solution causing: (i) pyrite in the sulfidic material to oxidize and transform to sulfuric material (“Alflic Sodic” Sulfaquepts) and (ii) schwertmannite and

goethite to form (Figure 2b & c) in the presence of excess sulfate and chloride, usually in the form of cemented crusts (Figure 2a) with high levels of scavenged cations such as As, Zn and Si. A diurnal cycle in redox conditions has also been observed, with sharp decreases in pH, which causes salts to be released from the soil. These salts wash downslope and accumulate to toxic levels. The iron clogging forces the discharge further upslope where the process repeats itself.

This type of land degradation requires novel approaches to break the cycle of “sealing off” in discharge zones, and acidification and salt release from the gradually ascending edge of discharge. An essential component of remediation has to be the establishment of discharge points where the groundwater outflow can be kept in balance with the inflows across the landscape. It is a doubtful as to whether it would be feasible to alter the vegetation sufficiently across the land so that there is little or no nett inflow, particularly as this environment is prone to periods of excess winter rainfall, which would be very difficult to offset by increased plant water use. Given this, some 18 years ago, the following series of measures were begun to try and address this land degradation problem:

	Measures taken, Costs and/or Technical Issues	Hypothesis
1	Deep drains were excavated into the slope (to depths of 4-6 m), slotted pipe overlain with gravel placed in them and backfilled. Expensive and moderately demanding	Discharge flow created would reduce groundwater pressure in the general area and halt degradation
2	Explosives were placed 5-6 m deep with sufficient quantity to fracture soil without blowing out a crater. Less expensive but technically demanding.	Groundwater pressure would be reduced so halting the problem.
3	Trenches approximately 1 to 1.5 m deep were dug just below the advancing edge of the soil degradation. Discharge water was likely to be of poor quality.	Halt seepage at scald edge and processes driving the system upslope and/or divert toxic seepages away from revegetation
4	Six meter deep holes were drilled and pipes slotted at the base and backfilled with gravel for that portion, with bentonite above. These piezometers often developed a leak at the surface, either through a poor joint or a break.	To create a direct pathway for groundwater to reach the surface without contacting reactive material.

It is timely to now report on the following successes or failures that have occurred:

	Remediation results
1	Deep drains only had a very local effect (10-20m) on surrounding groundwater pressures due to the low permeability of the material and so had limited impact on the system given their cost.
2	Explosion points similarly had a limited effect, plus any discharge encountered reactive material at the surface and the discharge rates fell away quite quickly due to the iron clogging process
3	Trenches were successful in halting the advance of the scalds upslope, but the water discharging from the trench was of low quality indicating the groundwater was still contacting reactive material in the trench environment or that some upslope seepage was being captured.
4	Piped discharge points have shown a marked improvement with establishment of swamp plants typical of permanent springs, and there are indications that discharge rates are increasing and seepage areas are growing. One legume adapted to swampy conditions, <i>Viminaria juncea</i> , and rushes and sedges are of importance because they produce cluster roots. These root structures have been shown to mobilise iron in other species, so it is conceivable that such plants are breaking up the iron clogged layers.

Conclusions

The combination of shallow trenches at the upper edge of a scald (Figure 3: halting the advance upslope or diverting toxic seepage) and installation of pipes to allow reduced groundwater to reach the surface without contacting reactive material, coupled with plantings of swamp species shows promise as a long term solution to “Red Barren” scalds, as shown in Figure 4.



Figure 3: Shallow trench and piezometer in 2006

Figure 4: Expanding area of swamp vegetation in 2016

ACID Sulfate Soil Processes Also Affect Other Soils: Sulfuric acid weathering of parent materials prior to soil genesis

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Iron and other metal sulfide minerals are ubiquitous in many unweathered soil parent material rocks. Pyrite can be an accessory mineral in igneous rocks that form under reducing conditions and is occasionally found in metamorphic rocks. It is common in hydrothermal mineral deposits, and occurs in a wide range of sedimentary rocks and in widely varying amounts. The iron and sulfur oxidize when they are in aerated near-surface environments. Mineralized rock formations associated with ore bodies are readily recognized by bright reddish, yellow, and brown (Munsell) colors.

A general range of from 0.1 up to 10 weight percent of sulfur might be considered as common in a broad range of unweathered rocks which ultimately will be soil parent materials. Studies of sandstone, shale, and limestone sedimentary rocks, as well as igneous, suggest a model which describes sulfuric acid impacts on genesis of native soils as well as some minesoils. We clearly showed the difference in reduced sulfur concentrations between the weathered and unweathered parts of a sedimentary sandstone in a 1972 Nature publication. This distinction was also observed in other lithologies.

1. Soils developed within highly weathered surface rock parent material exhibit vivid high-chroma iron coloration, low cation exchange capacity, and a matrix relatively low in plant nutrient elements, as might be expected when strongly acidic (~0.1M sulfuric) leaching has been a part of their pedogenic history. Results are presented from research in mineral weathering, geochemistry, and soil development to show the importance of iron sulfide mineral alteration in many types of soils outside the traditional acid sulfate class emphasized in this Conference.

Mineral alterations resulting from strong acid reaction during soil parent material weathering may explain currently observable soil properties, including clay mineral degradation, soil color development, particle aggregation, saprolite formation, and others. The past 60 years' studies of oxidation of iron and sulfide minerals have revolutionized engineering approaches to mine drainage and wetland soil management. As the Critical Zone-- under several current Regional studies of the ecology of the earth's surface between the soil profile and underlying unweathered bedrock or groundwater-- descends into acid-altered underlying regolith, a better understanding of the quantities, rates, and products of mineral alterations will lead to improved resource management.

Understanding of the results of these geochemical processes will also provide a sound foundation upon which Moon or Mars soil development can be engineered to provide future subsistence

Acid Rock Drainage – Natural and Human-Induced

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Acid rock drainage occurs when rocks containing the most common iron sulfide minerals, pyrite (FeS_2) and pyrrhotite (Fe_{1-x}S), are exposed to air and water at the earth's surface by natural processes such as weathering of outcrops and landslides or by human construction activities through sulfide-bearing bedrock. The magnitude of remediation necessitated by inadvertent exposure of pyritic rock can approach that of dealing with acid mine drainage resulting from coal or metal mining. On the other hand, acid rock drainage associated with unmined sulfide-rich mineral deposits can be a tool for mineral exploration and a guide to premining baseline conditions. Three examples illustrate a range of acid rock drainage issues.

(1) Construction along Interstate 99 (I-99) during 2003 near State College, in Centre County, central Pennsylvania exposed sulfidic rock within a fresh roadcut on Bald Eagle Mountain at Skytop. The cut intersected pyrite veins associated with an unmined, sandstone-hosted, zinc-lead deposit. Excavated rock was crushed and used locally as road base and fill. Within months, acidic ($\text{pH} < 3$), metal-laden seeps and surface runoff from the crushed rock piles and roadcut raised concerns about surface water and groundwater contamination and prompted a halt in road construction and the beginning of costly remediation. A composite of < 2 mm material sampled from the cut face contained 8.1 wt. % total sulfide S, 0.6 wt. % sulfate S, and was net acidic based on acid-base accounting with a net neutralization potential of -234 kg CaCO_3/t . Primary sulfide minerals include pyrite, marcasite, sphalerite (2 to 12 wt. % Fe) and traces of chalcopyrite and galena. Inclusions (< 10 μm) of CdS and Ni-Co-As minerals in pyrite and minor amounts of Cd in sphalerite (0.1 wt. % or less) also provide sources of trace metals. Wet/dry cycles associated with intermittent rainfall promoted oxidative weathering and dissolution of primary sulfides and their oxidation products. Resulting sulfate solutions evaporated during dry periods to form intermittent "blooms" of soluble efflorescent sulfate salts (copiapite, melanterite, and halotrichite) on exposed rock and other surfaces. Salts coating the cut face incorporated Fe, Al, S, and minor Zn. They readily dissolved in deionized water in the laboratory to form solutions with $\text{pH} < 2.5$, consistent with field observations. In addition to elevated dissolved Fe and sulfate concentrations ($> 1,000$ mg/L), seep waters at the base of the cut contain > 100 mg/L dissolved Zn and > 1 mg/L As, Co, Cu, and Ni. Lead is relatively immobile (< 10 $\mu\text{g}/\text{L}$ in seep waters). The salts sequester metals and acidity between rainfall events. Episodic salt dissolution then contributes pulses of contamination including acid to surface runoff and groundwater. The Skytop experience highlights the need to understand dynamic interactions of both primary and secondary mineralogy with hydrology in order to avoid potentially negative environmental impacts associated with excavation in sulfidic rocks.

(2) Weathering of sulfidic (primarily pyritic) schist, slate, and phyllite of the Anakeesta Formation in the Great Smoky Mountains in North Carolina and Tennessee produced acid rock drainage severe enough to affect aquatic life. Landslides create temporary, but catastrophic, physical and chemical impacts on aquatic ecosystems. The lithology also poses engineering problems for construction projects because of the high potential for acid generation associated with exposing fresh pyrite-bearing rock surfaces. Efflorescent sulfate salts coat freshly exposed outcrops in landslide breakaway zones, and Fe- and Al-hydroxysulfate minerals precipitate downstream of landslide debris flows. Streams that drain the Anakeesta Formation are highly variable in pH, ranging from 4.0 to about 7.0. Drip waters and streams

immediately below landslides typically have low pH values (~4) and elevated concentrations of dissolved metals relative to other surface waters.

(3) The unmined Red Mountain volcanogenic massive sulfide deposit in the Alaska Range near Fairbanks, Alaska displays a remarkable environmental footprint of natural acid generation and high metal concentrations in surface waters. The name of the deposit derives from an extensive alteration zone characterized by red, orange, and yellow colors due to ferric iron alteration of pyrite, as confirmed by surface sampling and alteration mapping by remote sensing methods. Dissolution of pyrite and associated secondary reactions under near-surface, oxidizing conditions are the primary causes for the acid generation and metal leaching in the undisturbed natural setting at Red Mountain. Alteration zone waters (pH generally < 3.5) contain elevated concentrations of Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, Y, and particularly Zn and the REEs. Surface waters collected upstream from the alteration zone have near-neutral pH values, lower specific conductances, lower metal concentrations, and measurable alkalinities. Water samples collected downstream of the alteration zone have pH values and metal concentrations intermediate between the extremes (pH = 2.4 to 7.8). Red Mountain Creek and its tributaries do not support significant megascopic aquatic fauna. Therefore, any plans for future proposed mining in the area should consider the premining condition of the undisturbed setting in establishing goals for mine closure.

Geologic maps showing regional distribution of sulfidic lithologies, databases of sulfide mineral occurrences, and the use of remote sensing methods to determine areas of hydrothermal alteration are all tools that can be used to screen areas likely to produce acid-rock drainage in land-use planning and development.

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**Production of Salt Hay on Potential Acid Sulfate Soils,
Sulfihemists and Associated Soils in Cumberland County, New Jersey**

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Saltmeadow cordgrass (*Spartina patens*), locally known as salt hay, is a native species along the eastern coast of North America that grows in the upper areas of the intertidal zone, predominantly above mean high water. Salt hay grows to a height of 0.3 to 1.2 m (1 to 4 ft.) and spreads extensively by long rhizomes to form dense communities of wiry grass. This grass is adapted to a wide range of mineral and organic soils with a pH between 4.5 and 7.1, and will tolerate irregular inundations with 0 to 53 mS/cm conductivity (35 parts per thousand salinity). In Cumberland County, New Jersey, soils that support the growth of salt hay are included in the Appoquinimink-Transquaking-Misphillion complex mapping unit (Thapto-Histic Sulfaquents-Typic Sulfihemists-Terric Sulfihemists). These soils are expected to generate, upon exposure to oxidizing conditions, sufficient sulfuric acid to drive the pH of near-surface horizons to ultralow levels (potential acid sulfate soils).

In the 17th and 18th centuries, settlers from Holland and England recognized that salt hay was a valuable crop that could be used for many purposes and installed systems of dikes and ditches, similar to the widespread practice used in the Netherlands to increase land area for farming and for flood protection. Early uses of salt hay included bedding and feed for livestock, thatch for barn roofs, packing for glassware and pottery, insulation for icehouses and fiber for making rope. Later uses included protecting freshly poured concrete in winter. During World War II the U.S. government purchased large quantities of salt hay for construction of airport runways and concrete roads. Today, salt hay is in high demand for use as landscaping mulch and is shipped to nurseries in New England, Pennsylvania, and northern New Jersey. Nurseries and home gardeners favor salt hay because it is slow to decompose and the seeds cannot grow in dry conditions, essentially making salt hay a weed-less mulch.

Most of the marshes on the New Jersey side of the Delaware Bay were diked for farming at one time. Many of these dikes were later abandoned as dike maintenance became too costly. However, dikes on several thousand hectares were maintained to facilitate harvesting of salt hay through the formation of meadow companies, a collective of farmers that were responsible for maintenance and repair of the dikes, and the salt hay industry continued to thrive through the late 20th century. With the implementation of wetland protection regulations in the 1970's, construction of new dikes is no longer permitted in New Jersey. In fact, many dikes were removed in the 1990's to restore approximately 1,789 hectares (4,420 acres) of salt marsh as mitigation for activities at the Salem Generating Station located on the Delaware Bay.

The Durham farm on Abbot Creek is one of the last farms in Cumberland County to harvest salt hay. The Durham family has cut salt hay since the late 1700's, but dikes and water control structures are not used to control tidal flow in the marsh. Instead, they selectively cut salt hay in free-flowing portions of the salt marsh where a tractor equipped with high flotation tires can operate. Harvesting salt hay is done in the summer after several days of below normal tides, and in the winter when the marsh is frozen. The soil profile below was described with a McCauley auger in an area where salt hay is routinely cut on the Durham farm (Fig. 1). This profile represents an unnamed soil in Cumberland County (Terric Sulfisapristis), with colors of organic horizons based upon rubbed color.

- Oe – 0-20 cm (0-8 inches) mucky peat
- Oa – 20-46 cm (8-18 inches), 5YR 2.5/1, muck; 16% rubbed fibers
- 2Btgb1 – 46-102 cm (18-40 inches), 5Y 5/2, clay loam, few distinct faint Fe (III) masses, organic coats, depletions (N 2.5/-)
- 3Btgb2 – 102- 127 cm (40-50 inches), 5Y 4/2, sandy loam (18% clay), common prominent Fe (III) masses (10YR 4/6)
- 3Cg1 – 127- 145 cm (50-57 inches), 2.5Y 4/2, gravelly coarse sandy loam (15% 12-mm gravels, 8% clay), many distinct Fe (III) masses (2.5Y 4/4)



Figure 1 **A.** Location of Durham Salt Hay Farm on Abbot Creek in Cumberland County, New Jersey (USGS Dover Quadrangle, 1982). **B.** *Spartina patens* meadow. **C.** Portion of Durham salt hay farm showing selective harvest areas and location of soil profile description.

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A Geochemical Record of Acid Sulfate Soil Oxidation in the Lower Murray-Darling Basin

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Metals released into the environment as pollutants following oxidization of acid sulfate (AS) soils are sequestered to the sediment of proximal basins (Nordmyr et al., 2008). Enrichment of pre-industrial metal concentrations in the sediment archive of these basins can therefore be used as a proxy for AS soil oxidation in the past. With an established link between AS soil oxidation and climatic drought (Simpson et al., 2010), the record produced brings insight into the frequency and magnitude of acidification events through comparison to established climate history of Southeastern Australia, providing an empirical basis for assessing the articulation between climate variability and AS soil mobilisation of trace metals. In addition, the impact of land use change and river regulation since European settlement on the frequency and/or magnitude of acid mobilisation events is assessed.

A Holocene-aged record of sedimentary trace metal concentrations is presented from Lake Albert - part of the terminal Lower Lakes system of the Murray-Darling Basin, Australia - a known 'hotspot' for AS soils during the Millennium Drought (Fitzpatrick, 2008; Mosley et al., 2014).

A sediment core (code LA1) was collected from near the centre of Lake Albert (coordinates: 35°38.473'S, 139°18.257'E; Murdoch, 2009), a location identified as proximal to oxidised AS soils during the Millennium Drought (Fitzpatrick, 2008). Water depth at the time of sampling was 40cm below the lake surface (water levels at a lake minimum in 2009, ~-0.5m mAHD), with the site remaining inundated throughout the Millennium Drought period due to levels (~- 0.5 mAHD) being maintained via pumping (EPHC, 2011).

Targeted metals (Cr, Co, Ni, Cu, Zn, Cd and Pb) were sequentially extracted from sediment using the modified BCR Sequential Extraction Procedure (Rauret et al., 1999) and analysed using inductively-coupled plasma mass spectrometry.

Combined element concentration records were constructed highlighting collective increase in concentrations of AS soil acidification mobilised elements. Stochastic variation in individual elements was reduced by applying composite indices decomposed from the raw data using Principal Component Analysis (PCA). This emphasises response across the range of target metals while reducing the impact of single metal variation in the data set. Prior to analysis all data were normalised to the long-term mean (ie: whole data set) for that element. Synchronous increase in a range of target metals weighted by their consistency in overall variability can be identified using PCA by determination of the principal component values and combining these based on their eigenvalues, which are indicative of how well the component represents the total data (Zhiyuan et al., 2011). The resulting combined value is a function of the concentration of the element and how consistent it is in overall variation in the dataset; i.e. high values are given to elements of high concentration that are in high relative consistency in the primary variability.

It is identified that AS Soil mobilised metals may act as a marker for the occurrence of past acidification events. The magnitude of the chemical signal identified in these records is indicative of the intensity of the acidification event. As an acidification event signifies a system tipping point being exceeded, the established geochemical record only provides direct inference on the magnitude or precedence of an individual climatic event if system conditions were constant, as climate forcing alone does not determine the intensity of acidification.

The observed correlation between geochemical variability and known periods of climate variability during the late Holocene suggests that climate forcing is playing a significant role in AS soil activation in the Lower Lakes of the Murray-Darling Basin. As the intensity of a drought is not the only variable responsible for acidification intensity, and the geochemical data did not respond to all instances of known past droughts, these records cannot form the basis on which historical climate is inferred. However they can contribute to the understanding of how historic climate has interacted with AS Soils in the region.

Sediment deposited during the Millennium Drought exhibited concentrations of Ni and Pb unprecedented since ~2.2ka. Cd reached levels that had not been seen since ~3.2ka, whilst Cr exhibited the highest concentration on record. Indices that reflect an acidification response across the suite of elements reach their highest levels in more than two millennia during the Millennium Drought.

As continued water management of the MDB remains the current political response to environmental and economic contention, an understanding of the impact current practices are imposing on the system is critical. In comparing the geochemical responses for the Millennium Drought, and the Federation and World War II Droughts,

it is concluded that anthropogenic water management - principally the construction of the Goolwa Barrages – has dramatically reduced the resilience of the Lower Lakes to AS soil activation.

As the Murray-Darling Basin Plan implements policy based on projected sustainable water use levels (MDBA, 2012), environmental allocations require critical foresight into potential future requirements. With historic water management decisions having likely contributed to the intense nature of the Millennium Drought acidification, future allocations needs to consider its role in minimising initial system vulnerability, and allocating sufficient resources for potential remediation. This need is amplified when taking into consideration the increasing probability of lower winter/spring rainfall and more frequent climatic extremes projected for Southeastern Australia.

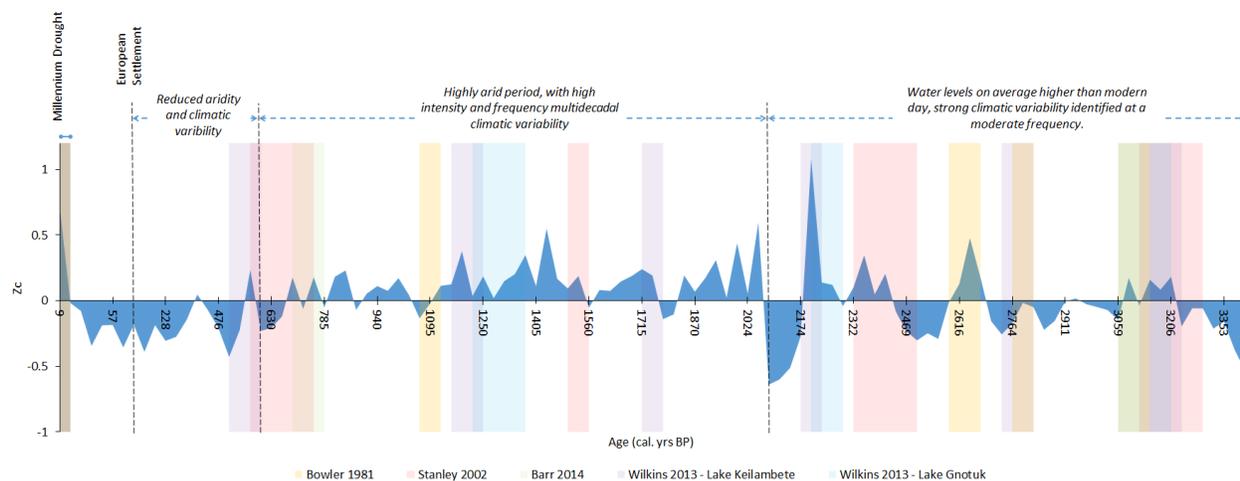


Figure 1: Combined Principal Component Value (Z_c) plotted against age of sediment. Coloured regions overlaying data identify prolonged dry periods highlighted in published regional palaeoclimate data (Barr et al., 2014; Bowler, 1981; Stanley and De Deckker, 2002; Wilkins et al., 2013).

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Organic matter composition in acid sulfate soils

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Acid sulfate soils (ASS) are productive wetland soils, but pose a major threat to the environment when they fall dry, as for example after drainage for agricultural use, or during drought periods. When they dry, ASS generate large amounts of acidity and toxic concentrations of metals that can enter ground and surface water. After re-saturation of ASS and thus re-establishment of reduced conditions activity of sulfate reducing bacteria can lead to formation of pyrite and pH increase. However, re-saturation of dry ASS, and even increasing the soil pH by lime application to pH levels optimal for microbial sulfate reducers may not result in sulfate reduction in the field. Sulfate-reducing bacteria are heterotrophic, requiring organic carbon (OC) for growth and metabolism (Plugge et al., 2011). Therefore we hypothesize that quality and availability of OC can limit activity of sulfate reducers in re-saturated ASS. This is supported by studies showing that organic matter addition can result in an increase in pH during wet periods and lead to a higher pH in oxic periods (e.g. Jayalath et al., 2016). However, besides the general recognition of the importance of OC for sulfate reduction, little is known about the nature of OC in ASS and the availability of OC to microbes.

The present study aims at determining OC composition and its availability for microbial processes in ASS. Our approach consists of the assessment of OC in ASS of Southern Australia collected in November 2015 from areas that are permanently saturated or flooded but experienced previous drying and rewetting cycles. First results were obtained from two different sites: (1) "Long Flat" in the Lower Murray Reclaimed Irrigation Area is a regularly flooded pasture with high groundwater level, resulting in permanently water saturated subsoils and topsoils with periodic dry-wet-cycles, which classified as a Typic Sulfaquert (Soil Survey Staff 2014). (2) "Wallys Landing" (Finniss River) in the Lower Lakes area is a permanently flooded wetland zone located in the Finniss River, which classified as a Typic Sulfiwassent. Both sites experienced deep drying and severe subsoil acidification during extreme drought conditions between 2007 and early 2010 (Mosley et al., 2014; Leyden et al., 2016). After water levels returned to normal in 2011, both sites slowly recovered and have now pH values >5.5. However, their acidification potential is still classified as high because of the presence of hypersulfidic materials (Baker et al., 2012; Fitzpatrick et al., 2013). After sampling in November 2015, topsoils and subsoils were analysed for total OC and N. Total OC composition was characterized by solid-state ¹³C NMR spectroscopy. All ¹³C NMR spectra were integrated to obtain signal intensities of four major OC groups: alkyl-C (terminal -CH₂ and -CH₃ groups; non-specific lipids and hemicelluloses), O/N-alkyl-C (carbohydrates, polysaccharides), aryl-C (condensed aromatic structures, phenolic carbon), and carboxyl-/carbonyl-C.

Topsoils have OC concentrations between 6 and 10%, and even subsoils show high concentrations between 1.6 and 5%. C/N ratios are narrow between 10 and 12; however, OM composition is considerably different between sub- and topsoils and also differs between sites (Fig.1). Topsoil ¹³C NMR spectrum of organic matter at "Long Flat" is characterised by high proportions of O/N-alkyl-C (50%), indicating high inputs of fresh plant material rich in polysaccharides, which is typical for grasslands. Thus, in this regularly oxic topsoil sufficient easily decomposable OC is available. In contrast, subsoil organic matter at "Long Flat", but also top- and subsoil material at "Wallys Landing" reveal significantly lower proportions of O/N-alkyl-C (down to 24%), but high proportions of Alkyl C (up to 35%). This leads to the assumption that these permanently flooded soil materials, which experienced one severe drought and acidification event are characterised by highly degraded OC and receive only small amounts of fresh, readily biodegradable organic matter. The present organic material is poorly decomposable and may hamper regeneration of soil pH after severe acidification during drought periods. Further investigations will focus on the proportion of free vs. mineral-bound OC to obtain more detailed information on the availability of organic matter.

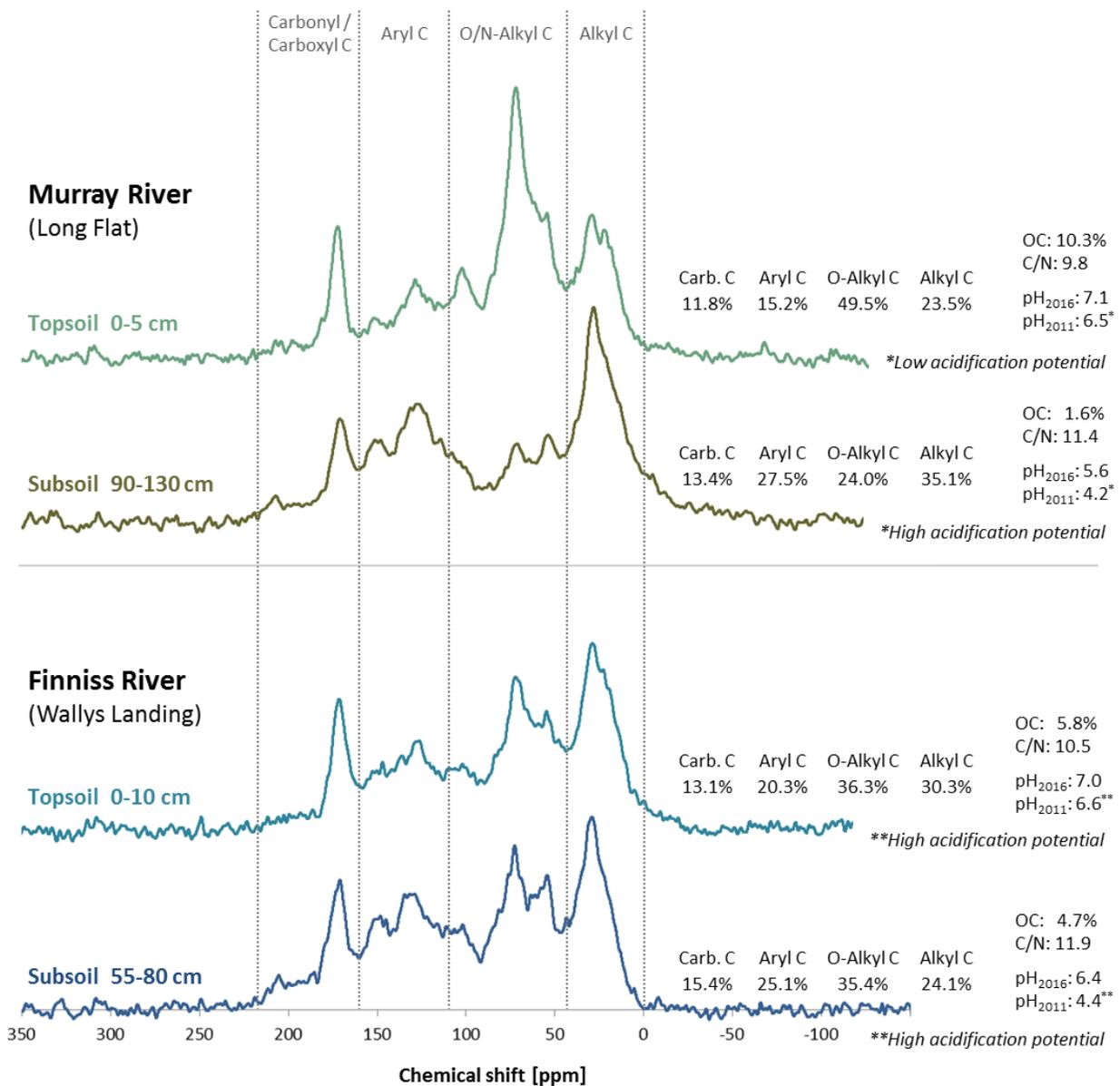


Fig. 1: Composition of topsoil and subsoil (sulfuric horizon) organic matter at Long Flat and topsoil and subsoil (sulfidic / hypersulfidic material) at Wallys Landing from analysis by solid-state ^{13}C NMR spectroscopy (pH₂₀₁₁ and acidification potential according to *Fitzpatrick et al., 2013, and **Baker et al., 2012).

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The acidifying effects of oxidizing coarse-grained acid sulfate soil materials in western Finland

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Previous research on acid sulfate (a.s.) soils in Finland have mainly focused on fine-grained a.s. soils. While it is true that these soils pose as one of the largest threats to coastal waterbodies in Finland, local negative effects caused by the oxidation of coarse-grained ($d_{50\%}$ grain size $\geq 63\mu\text{m}$) a.s. soil materials have recently come to the attention as acidification and elevated metal concentrations of groundwater and pit lakes (formed by sand mining) have been observed.

Sampling was carried out in an area with known acidic sand pit lakes, where the main cause for acidification is believed to be the oxidation of hypersulfidic parent material. In order to investigate the acidity and metals released during oxidation of any occurring coarse-grained a.s. soil materials, six soil profiles were sampled down to a maximum depth of 10m. The pH was measured in the field during sampling and grain sizes were estimated by the feel test for all samples and by sieving for selected samples. Samples ($n=74$) were allowed to oxidize according to the incubation procedure described by Creeper et al., 2012 [1]. In order to determine the rate of oxidation as indicated by the decrease in pH, pH measurements were carried out in the field and after 3 days and 2, 4, 6, 8, 12 and 16 weeks of incubation. Duplicate samples were also analyzed for the aqua regia leachable fraction of 31 elements with ICP-OES. Acidity was determined, by the titratable incubation acidity [2] after 4, 8 and 16 weeks of incubation. Total reduced sulfur (TRS) was also analyzed in selected samples. Water samples ($n=12$) were collected from the sand pit lakes and the pH and EC was measured in the field. In addition, groundwater samples ($n=7$) were collected from groundwater monitoring wells on two occasions, in 2013 and 2014, in order to investigate the impact of oxidizing coarse-grained soil materials on the groundwater. All sand pit lake and groundwater samples were analyzed with ICP-OES and ICP-MS.

Table 1 Median values for several grain sizes of hypersulfidic reduced parent materials within the investigated soil profiles

Grain size	Number of samples	Sulfur (mg/kg)	Incubation pH at t=16 weeks	pH 5.5 incubation acidity at t=16 weeks (mol[H ⁺]/ton)	pH 6.5 incubation acidity at t=16 weeks (mol[H ⁺]/ton)
Medium sand	23	224	3.6	5.1	7.5
Fine sand	15	473	3.4	9.6	12.6
Silt	5	535	3.7	8.5	12.8

None of the sampled soil profiles displayed a field pH below 4.0, which is the pH limit for sulfuric materials (actual a.s. soil materials or thionic horizon [3, 4]). However, all but one of the profiles contained hypersulfidic soil materials (i.e. potential a.s. soil materials with sulfidic S $\geq 100\text{mg/kg}$ and pH < 4.0 upon oxidation). The lack of sulfuric soil materials is most likely explained by a poor buffering capacity, due to the quartzofeldspathic mineralogy and the lack of carbonates [5, 6]. Median acidities and sulfur concentrations in the hypersulfidic coarse-grained a.s. soil materials presented in Table 1 are also considerably lower than in typical Finnish fine-grained a.s. soil materials, where acidities may be several hundred mol[H⁺]/ton and where previous studies show sulfur concentrations between 1,300–18,000mg/kg [7, 8].

High metal concentrations in both sand pit lake waters and the groundwater suggest the presence of an easily leachable fraction of several metals, released due to the acidification formed by sulfide oxidation. Metals such as Al, As, Cd, Cu, Mg, Ni, Pb and Zn correlated significantly with sulfate concentrations in the pit lakes and As, Fe, Mn and Ni were strongly elevated in several groundwater monitoring wells. This shows that even though the acidities

and sulfur concentrations in the investigated coarse-grained hypersulfidic soil materials were low, these soil materials still had a substantial negative effect on the local environment.



Fig. 1 One of the sampled acid sand pit lakes with a pH 3.8 and an iron concentration of 2 mg/l. Iron precipitates can clearly be seen on the pit lake rim.

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Effects of Plants on the Chemistry of Acid sulfate Soils

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Unless properly managed, acid sulfate soils can exert a range of negative environmental impacts, including soil acidification and mobilisation of metals and metalloids. Incorporation of organic matter in the form of plant mulches can substantially neutralise sulfuric soils and prevent the oxidation of sulfidic soils. These positive effects of dead plant materials are largely mediated by bacterial reduction of sulfates to sulfides, using the organic matter as a microbial nutrient source. However, very little is known about the effects of live plants on acid sulfate soils. In this study we compared pH, Eh and sulfate content of sulfidic and sulfuric soils that were not planted (i.e. unplanted) with those soils planted with the following three common wetland plants: Phragmites, Melaleuca and Typha. Each of these plants are capable of growth in aerobic and flooded soils. In all our experiments plants caused an increase in soil acidification rather than neutralizing soil acidity. Changes in soil chemistry were positively correlated with root distribution. The mechanism for this appears to be transport of oxygen down the soil profile by aerenchymatous tissue formed in these species, and the release of oxygen into the rhizosphere.

Acid Sulfate Alteration on Mars

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A variety of mineralogical and geochemical indicators for aqueous alteration on Mars have been identified by a combination of surface and orbital robotic missions, telescopic observations, characterization of Martian meteorites, and laboratory and terrestrial analog studies. Acid sulfate alteration has been identified at all three landing sites visited by NASA rover missions (*Spirit*, *Opportunity*, and *Curiosity*). *Spirit* landed in Gusev crater in 2004 and discovered Fe-sulfates and materials that have been extensively leached by acid sulfate solutions [1]. *Opportunity* landing on the plains of Meridiani Planum also in 2004 where the rover encountered large abundances of jarosite and hematite in sedimentary rocks [2]. *Curiosity* landed in Gale crater in 2012 and has characterized fluvial, deltaic, and lacustrine sediments. Jarosite and hematite were discovered in some of the lacustrine sediments [3].

The high elemental abundance of sulfur in surface materials is obvious evidence that sulfate has played a major role in aqueous processes at all landing sites on Mars. The sulfate-rich outcrop at Meridiani Planum has an SO₃ content of up to 25 wt.% [4]. The interiors of rocks and outcrops on the Columbia Hills within Gusev crater have up to 8 wt.% SO₃ [5]. Soils at both sites generally have between 5 to 14 wt.% SO₃ [6], and several soils in Gusev crater contain around 30 wt.% SO₃ [7]. After normalization of major element compositions to a SO₃-free basis, the bulk compositions of these materials are basaltic, with a few exceptions in Gusev crater and in lacustrine mudstones in Gale crater. These observations suggest that materials encountered by the rovers were derived from basaltic precursors by acid sulfate alteration under nearly isochemical conditions (i.e., minimal leaching). There are several cases, however, where acid sulfate alteration minerals (jarosite and hematite) formed in open hydrologic systems, e.g., in Gale crater lacustrine mudstones [8]. Several hypotheses have been suggested for the aqueous formation of sulfate-bearing phases under acidic conditions on the surface of Mars including (1) sulfuric acid weathering of basaltic materials; (2) oxidative weathering of ultramafic igneous rocks containing sulfides; (3) acid fog weathering of basaltic materials, and (4) near-neutral pH subsurface solutions rich in Fe²⁺ that were rapidly oxidized to Fe³⁺, which produced excess acidity as iron was oxidized on exposure to O₂ or photo-oxidized by ultraviolet radiation at the martian surface [9,10]. Next, we briefly describe evidence for these hypothesis.

Sulfuric Acid Solutions from Volcanic Processes: The formation of jarosite in Meridiani Planum outcrops is strong evidence for the aqueous alteration of basaltic materials under acid sulfate conditions and may be analogous to the formation of jarosite in basaltic materials on Mauna Kea volcano in Hawaii under oxidizing, hydrothermal conditions [11]. The Mauna Kea sulfuric acid solutions are the result of interactions of SO₂-rich volcanic gases with water. Acid sulfate solutions percolated up through the basaltic tephra, dissolved Fe and other cations, and precipitated jarosite when environmental conditions permitted its formation. The pH of the system plays a major role in defining the stability field between jarosite and hematite (or goethite) formation. The composition of Meridiani sediments was basaltic on a SO₃- and Cl-free basis, suggesting that sulfuric (and possibly hydrochloric) solutions permeated the sediments with minimal leaching (i.e., closed hydrologic system). The sulfuric acid solutions in Meridiani were apparently not sufficiently “neutralized” by the basaltic sediments, and thus the pH was low enough to favor precipitation of jarosite. Similar trends were observed in Gusev crater and described in detail elsewhere [11].

Sulfuric Acid Solutions from Sulfides: Acid-sulfate weathering on Earth, in general, results from processes that release sulfuric acid into a soil or sediment. Nearly all of the occurrences of acid sulfate soils and sediments on Earth have resulted from the oxidative weathering of sulphidic materials and are often the culmination of complex biogeochemical processes. Burns [12] suggested that oxidative weathering of sulfides might be a significant process on the surface of Mars. In his model, iron-rich ultramafic igneous rocks containing pyrrhotite-pentlandite contacted aerated groundwater, generating strongly acidic, sulfate-rich solutions. In the oxidized section above the groundwater table, sulfates (e.g., jarosite) and hydrated ferric oxides are precipitated from solution by the oxidation of the sulfide and dissolution of Fe. The recent discovery of jarosite and hematite in a lacustrine mudstone in Gale crater suggests authigenic or diagenetic acid sulfate alteration; however, it is not clear if the acid sulfate environment resulted from oxidative, aqueous alteration of Fe-sulfides or via sulfuric acid fluids migrating through the sediments [3].

Acid fog on Rock/Soil Surfaces: Acid fog alteration on rock and soil surfaces has been suggested as an acid sulfate weathering process for surface materials [13,14,15,16]. The acid sulfate reactions are driven by acidic volatiles (e.g., SO₂, HCl) deposited from the atmosphere and then reacted with the mineral surfaces in the dry Mars environment. Laboratory simulated acid weathering of palagonitic tephra by Banin *et al.* [14] resulted in the formation of gypsum and alunogen; those authors hypothesized that the top layer of Mars “soil” may have formed by extremely slow ongoing weathering interactions at the atmosphere-rock interfaces. Golden *et al.* [15] subjected basaltic tephra materials to acid fog conditions in the laboratory and found that Al, Fe, and Ca sulfates and amorphous silica formed

from plagioclase-rich tephra, and Mg and Ca sulfates and amorphous silica formed from the olivine-rich sand. Hurowitz *et al.* [16] have presented evidence for very low pH (pH = 0 to 1) alteration at rock and outcrop surfaces in Gusev crater based upon laboratory experiments. They suggest that there is a leached layer where outcrops and rocks are depleted in Mg and Fe at their surfaces compared to their interiors, probably as a result of pyroxene and/or basaltic glass dissolution by acidic fluids (*e.g.*, sulfuric acid fog). Under this process, acidic vapors reacted only at the surfaces of rocks and outcrops, leaching some elements (*i.e.*, Fe and Mg) and resulting in the observed depletion trends of Mg and Fe from the rock's interior.

Rapid oxidization of Fe²⁺ to Fe³⁺: Hurowitz *et al.* [10] have hypothesized that jarosite and hematite in Meridiani Planum sedimentary rocks formed via a two stage process. First, water was brought to the surface by groundwater upwelling and may represent the last vestiges of the widespread occurrence of liquid water on Mars. The groundwater transported Fe²⁺ from basaltic dissolution to the surface where the Fe was rapidly acidified during oxidized on exposure to O₂ or photo-oxidized by ultraviolet radiation at the martian surface. Oxidized Fe under acidic conditions then reacted with SO₄²⁻ also brought to the surface by groundwater upwelling to produce jarosite and hematite in the Meridiani sediments.

Summary: Acid sulfate weathering was an important aqueous alteration environment on ancient Mars. Key indicator minerals such as jarosite and other Fe-sulfates provide evidence for these environments. The type of acid sulfate environment, *i.e.*, "sulfidization" vs. sulfuricization, is more problematic to identify because the mineralogical/geochemical properties of the "host" materials may be unknown (*e.g.*, presence of Fe-sulfides). However, Mars had extensive volcanism early in its history and almost certainly sulfuric acid fluids have interacted with basaltic materials.

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Acid Sulfate Alteration in Gusev Crater, Mars

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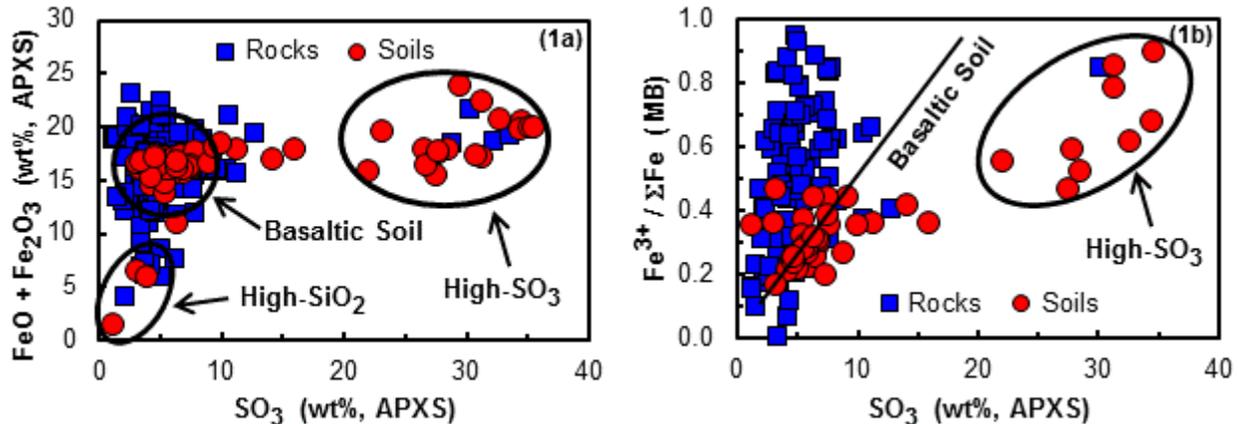
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The Mars Exploration Rover (MER) *Spirit* landed on the Gusev Crater plains west of the Columbia Hills in January, 2004, during the martian summer (sol 0; sol = 1 martian day = 24 hr 40 min). *Spirit* explored the Columbia Hills of Gusev Crater in the vicinity of Home Plate at the onset on its second winter (sol ~900) until the onset of its fourth winter (sol ~2170). At that time, *Spirit* became mired in a deposit of fined-grained and sulfate-rich soil with dust-covered solar panels and unfavorable pointing of the solar arrays toward the sun. *Spirit* has not communicated with the Earth since sol 2210 (January, 2011) [1]. Like its twin rover *Opportunity*, which landed on the opposite side of Mars at Meridiani Planum, *Spirit* has an Alpha Particle X-Ray Spectrometer (APXS) instrument for chemical analyses and a Mössbauer spectrometer (MB) for measurement of iron redox state, mineralogical speciation, and quantitative distribution among oxidation ($\text{Fe}^{3+}/\Sigma\text{Fe}$) and coordination (octahedral versus tetrahedral) states and mineralogical speciation (e.g., olivine, pyroxene, ilmenite, carbonate, and sulfate) [2].

The concentration of SO_3 in Gusev rocks and soils varies from ~1 to ~34 wt% (Fig. 1a) [3,4,5]. Because the APXS instrument does not detect low atomic number elements (e.g., H and C), major-element oxide concentrations are normalized to sum to 100 wt%, i.e., contributions of H_2O , CO_2 , NO_2 , etc. to the bulk composition are not considered. The majority of Gusev samples have $\sim 6 \pm 5$ wt% SO_3 , but there is a group with high SO_3 concentrations (~30 wt%) and high total iron concentrations (~20 wt%). There is also a group with low total Fe and SO_3 concentrations that is also characterized by high SiO_2 concentrations (>70 wt%) (Fig. 1a). The trend labeled “Basaltic Soil” is interpreted as mixtures in variable proportions between unaltered igneous material and oxidized and SO_3 -rich basaltic dust. The Mössbauer parameters are not definitive for mineralogical speciation (other than octahedrally-coordinated Fe^{3+} but are consistent with a schwertmannite-like phase (i.e., a nanophase ferric oxide).

The high oxidation state (Fig. 1b) and values of Mössbauer parameters (center shift and quadrupole splitting) for the high- SO_3 samples imply ferric sulfate (i.e., oxidized sulfur), although the hydration state cannot be constrained. In no case is there an excess of SO_3 over available cations (i.e., no evidence for elemental sulfur), and Fe sulfide (pyrite) has been detected in only one Gusev sample. The presence of both high- SiO_2 (and low total iron and SO_3) and high SO_3 (and high total iron as ferric sulfate) can be accommodated by a two-step geochemical model developed with the Geochemist’s Workbench. (1) Step 1 is anoxic acid sulfate leaching of martian basalt at high water-to-rock ratios (>70). The result is a high- SiO_2 residue (Fig 1a), and anoxic conditions are required to solubilize Fe as Fe^{2+} . (2) Step 2 is the oxic precipitation of sulfate salts from the leachate. Oxic conditions are required to produce the high concentrations of ferric sulfate with minor Mg-sulfates and no detectable Fe^{2+} -sulfates.



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Long timescales for recovery of acid sulfate sub-soils with sulfuric horizon following resubmergence: what we have learnt from the Millennium Drought

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An extreme “Millennium” Drought” occurred from 2001 to 2010 in the Lower Murray region of South Australia and falling surface and groundwater levels exposed acid sulfate soils (ASS) with saturated sulfidic material to air for the first time in more than 100 years (Mosley et al. 2014). This formed acid sulfate soils with dry and cracked sulfuric horizon resulting in landscapes with severe water quality, infrastructure, ecological, and socio-economic effects. Droughts are likely to occur more often and be longer in the future in many regions of the world due to climate change but there has been limited research on the ability of acid sulfate soils to recover from drought. We collected field data, and conducted controlled laboratory experiments, to assess recovery timescales and processes of acid sulfate soils impacted by the Millennium Drought.

Acid sulfate soils with sulfuric horizon in the Lower Murray agricultural floodplains have still not recovered since the drought ended in 2010 (i.e. classified as a Sulfic Sulfaquert in 2011 and Typic Sulfaquert in 2015/16). This is illustrated in Figure 1 where pH has showed little change over the 5 year post-drought period (2011–2015). Strongly acidic sulfuric horizon (pH 3.5–4.0) is still present between approximately 1–2.5 m below ground level (Figure 1) with highly acidic drainage water returned to the River Murray. The acid drainage from these soils results in environmental and infrastructure damage (Figure 1), including risks to major drinking water supplies for over 1 million people (Frizenschaf et al. 2015).

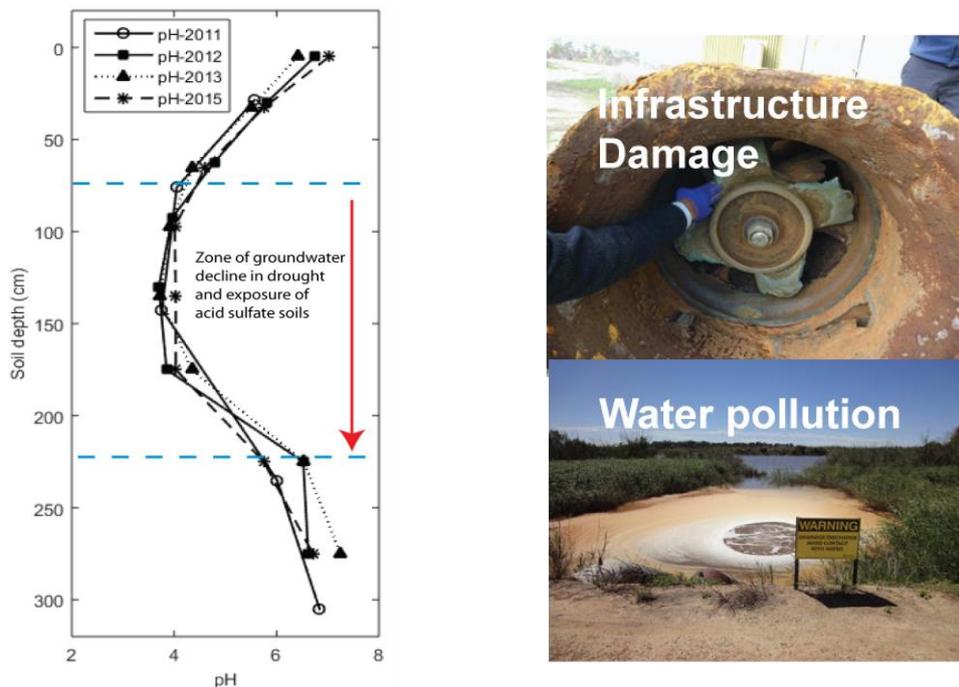
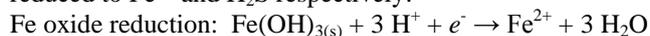


Figure 1: (left) pH in a soil profile at Long Flat sampled repeatedly between 2011 and 2015 after the Millennium drought ended and groundwater levels returned to pre-drought conditions (approx. 70 cm soil depth), and (right) ongoing environmental impacts arising from the acid drainage.

Following resubmergence of sub-soils, oxygen is rapidly consumed and not replenished from the atmosphere. The soils are converted through microbial respiration to a biogeochemically reduced state. The source of electrons for microbially-mediated reduction is organic matter, and these electrons are “accepted” by oxidised (redox-active) species, which are reduced. For example in the following reactions Fe oxides and sulfate are reduced to Fe^{2+} and H_2S respectively:



Sulfate reduction: $1/8 \text{SO}_4^{2-} + 5/4 \text{H}^+ + e^- \rightarrow 1/8 \text{H}_2\text{S} + 1/2 \text{H}_2\text{O}$

Protons are consumed during these reduction reactions. Hence they are potentially important reactions for recovery of acidic soils. However, we have shown that the low availability of organic carbon and low pH (<5) can prevent these reduction reactions progressing in the acidic subsoils with a sulfuric horizon of the Lower Murray (Yuan et al. 2015a,b). Although total organic carbon contents in the sulfuric horizon is approximately 1%, it appears to be stabilised by interaction with mineral surfaces and unavailable to microbes. When fresh/available organic matter is added in the laboratory and pH is >5 (enabling sulfate reducing bacteria activity), rapid increases in pH and decreases in redox potential occurred (Figure 2 and see Yuan et al. 2015a,b).

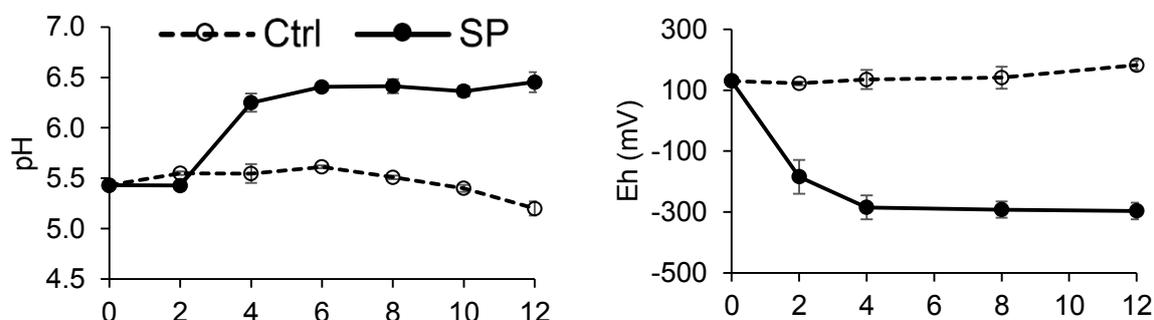


Figure 2: pH and Eh of soil pore water in soil over 12 weeks incubated submerged in the control (Ctrl) or with 3% straw/fibre pellet (SP) added. The soil pH was initially raised to 5.5 with NaOH.

Apart from the lack of available organic carbon and low pH, other causes of slow recovery of acidic soils in the Lower Murray may be due to the persistent presence of relatively insoluble forms of acidity in the minerals jarosite, natrojarosite and schwertmannite, which buffers the pH in the acidic range. Limited diffusion and advection may also limit jarosite, natrojarosite and schwertmannite dissolution. The following acid sulfate soil environments in the Lower Murray River Basin have also shown similar prolonged recovery from the Millennium drought: (i) Lower Lakes groundwater acidification (Leyden et al. 2016;), (ii) Lower Lakes acid sulfate soils with sulfuric horizon (Baker et al. 2013) and (ii) Banrock Station wetlands sulfate soils with sulfuric horizon (Fitzpatrick et al. 2015). The broader implications of the results are that acid sulfate soils (and their water quality, ecological and infrastructure impacts) may not recover in inter-drought periods. This is very concerning given climate change is predicted to increase drought frequency and severity. Effects of recurrent drought in soils, which have not recovered are uncertain at present and requires further investigation.

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Regulations to Avoid and Mitigate Hazards of Acid-producing Soils in New Jersey

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New Jersey is located on the east coast of the United States (USA) with its western border defined by the Delaware River. Lying in a northeast to southwest pattern across New Jersey in the transition zone between piedmont and coastal plain (Figure 1), certain geologic formations of strata which were deposited in estuarine and marine environments during Cretaceous and Paleogene periods have sulfidic minerals with potential to form acid-sulfate soil if exposed during excavation, grading, or other disturbance. New Jersey regulates acid-producing soils by way of its Soil Erosion and Sedimentation Control (SESC) Act (1975) and until recently by the Flood Hazard Area Control (FHAC) Act rules (2007). The Soil Erosion and Sediment Control Standards¹ are the rules promulgated by the SESC law and are enforced by local Soil Conservation Districts under authority of the New Jersey Department of Agriculture. The first Standard addresses Acid-producing Soils, providing guidance to site workers on identifying acid-producing material and directing developers to minimize exposure, to isolate, and to re-bury any acid-producing soils which are exposed during development or other disturbance. Other regulatory attention to acid-producing soil has been in the “Draft Technical Manual, Flood Hazard Area Control Act Rules”² proposed and enforced by New Jersey’s Department of Environmental Protection (NJDEP-Division of Land Use Regulation, 2008) due to the potential environmental dangers associated with acid runoff and erosion into water bodies. When development or other land disturbance was proposed near rivers and streams within mapped areas of acid-producing geologic formations, Section 7 of the FHAC Technical Manual not only provided guidance on site management to minimize exposure and/or hazards of acid-producing deposits but also either 1) imposed a 150-foot (45.72 meter) riparian buffer zone or 2) required testing to ascertain whether and where (across the landscape and depth) acid-producing materials exist prior to disturbance. Detailed instructions on sampling and analysis were included. In 2015, New Jersey’s administration proposed revisions³ to the FHAC regulations to eliminate Section 7 and transfer all authority relating to acid-producing soils to Soil Conservation Districts. The proposed amendments were recently adopted (2016). While it may be “common sense” to consolidate authority for enforcement of regulations, there was valuable guidance in the FHAC (2008 draft) rules that would be useful to include in future revisions of SESC Standards to continue protection from hazards of acid-sulfate soils.

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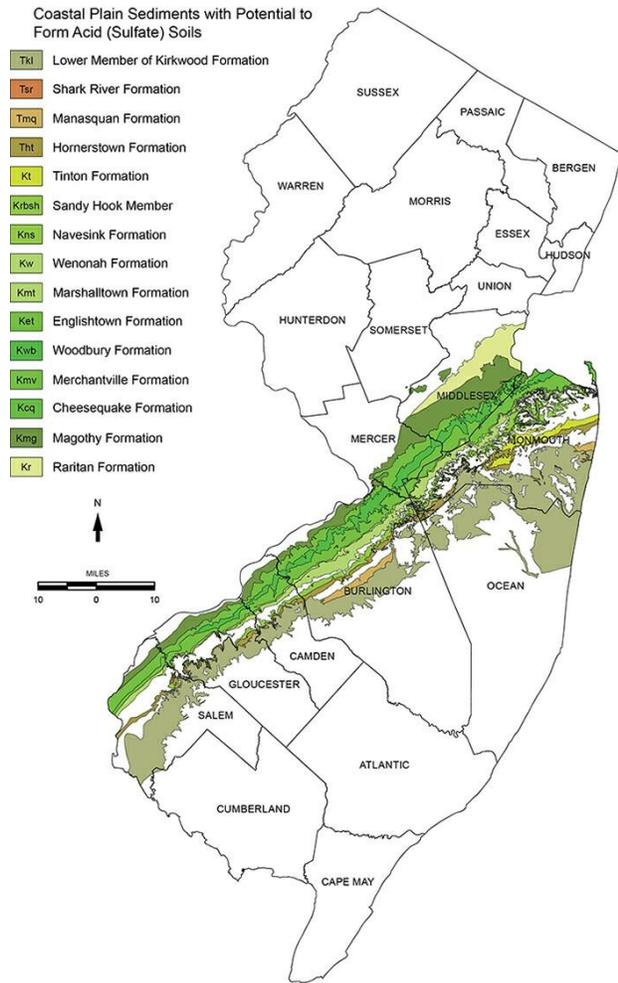


Figure 1. Geologic formations in New Jersey with potential to form acid sulfate soil.

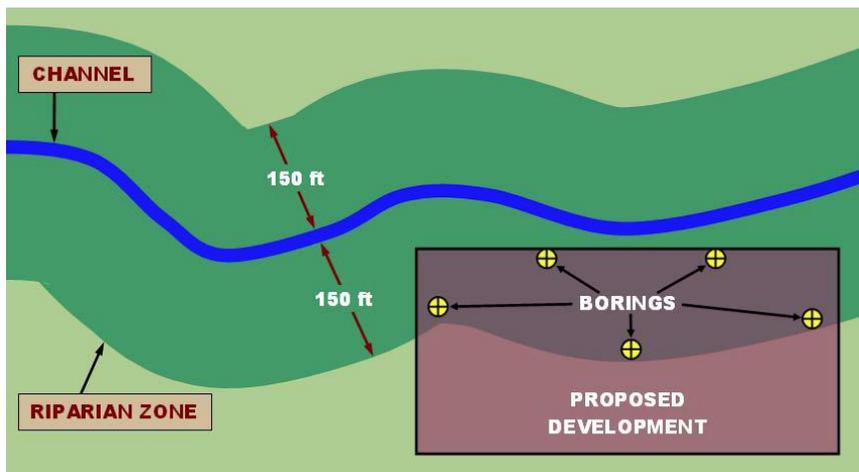


Figure 2. Sampling guidance to assess sites along regulated waterways for acid-producing strata were provided in the Draft Technical Manual for Flood Hazard Area Control Act Rules (2008).

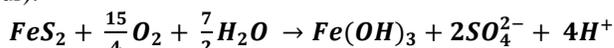
Sulfide Mineral Oxidation, Secondary Minerals, and Acid Sulfate Waters

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Natural acid sulfate waters develop from the oxidation of sulfide minerals, hydrogen sulfide, and elemental sulfur in the presence of air and water. There are only 3 sulfides and one sulfide group that are responsible for acid sulfate waters: pyrite, pyrrhotite, marcasite, and low-temperature iron monosulfides such as greigite and mackinawite. Among these, pyrite is the most nearly ubiquitous in rocks, soils, and sediments. Other sulfides such as chalcopyrite, arsenopyrite, and sphalerite tend to contribute much less to the formation of sulfuric acid. Oxidation is a complex hydrobiogeochemical process that degrades the chemistry and productivity of soils, gives rise to acid mine drainage and acid rock drainage, corrodes highways and building foundations, and solubilizes and mobilizes elements harmful to aquatic biota and human health. The process involves a series of chemical reactions aided by microbiological catalysis. Acid sulfate waters have pH values of -3.6 to 4.5, may contain toxic concentrations of dissolved metals including Fe, Cu, Zn, Cd, Pb, Cr, and As, and will rapidly dissolve soluble elements from the host rocks and sediments, especially Al and SiO₂.

The oxidation of pyrite involves the transfer of 15 electrons per mole of pyrite (one from iron and 14 from sulfur):



These electrons cannot be transferred simultaneously but must proceed stepwise with one or two electrons at a time. Hence, intermediate species must form and for sulfur these have been identified as sulfite, thiosulfate, and polythionates. These intermediates are rapidly destroyed by sulfur-oxidizing bacteria, by dissolved ferric iron, and by low pH. Electrons leaving sulfur atoms reduce molecular oxygen to water through hydrogen peroxide as an intermediate. Another set of reactions proceed with iron oxidation. As long as pyrite maintains contact with an aqueous solution, the iron that dissolves from pyrite will stay reduced as Fe²⁺ because of the reducing power of pyrite. When no longer in contact, Fe²⁺ oxidizes at low pH by iron-oxidizing microbes and at circumneutral pH abiotically. The oxidation of Fe²⁺ to Fe³⁺ consumes protons and raises the pH. Consequent hydrolysis, polymerization, and precipitation (abiotic reactions) lower the pH. These four reactions can be distinguished because of the difference in their rates.

Sulfide minerals can also be oxidized by dissolved ferric iron at low pH and by nitrate in anoxic systems over a range of pH. Indeed, the primary mechanism for pyrite oxidation under acidic conditions is abiotic attack by dissolved Fe(III) [1-4]. Nitrate pollution of groundwaters has often caused pyrite oxidation in sediments [5] either with or without oxygen.

The complex rates of dissolved ferrous iron oxidation has been simulated and compared to lab experiments with good results. The next step of applying this kinetic model to an actual pipeline carrying acid mine drainage has been accomplished [6]. The results make it possible to show how mixing proportions of effluents can be modified to minimize the precipitation of iron minerals that form scale and clog the pipe.

Two groups of secondary minerals form from iron sulfide oxidation, soluble efflorescent sulfate salts and insoluble oxyhydroxides and hydroxysulfates. Soluble salts form from the evaporation of acid sulfate waters and temporarily store acidity until precipitation dissolves them or submergence from rivers, lakes, or seawater ingresses and dissolves them. There are a large suite of soluble sulfate minerals that form in acid sulfate environments but those most directly related to pyrite oxidation include melanterite, rozenite, copiapite, coquimbite, voltaite, and rhomboclase. The compositions of the solutions from which these minerals form have been analyzed [7-9] and their pH is near 0.0 or less (down to -3.6).

Insoluble secondary minerals include ferrihydrite, schwertmannite, microcrystalline goethite, jarosite, magnetite, and hematite. Akaganéite, maghemite, and lepidocrocite can also form but they are minor or negligible in most environments, especially in the presence of acid sulfate solutions. These minerals precipitate relatively quickly from solution but which ones occur depends on pH, temperature, and solution composition. In metamorphic rocks that have relatively large crystals of pyrite, the oxidation rate is very slow, governed by solid-state diffusion, and exact goethite pseudomorphs of pyrite can form. These pseudomorphs still contain the same surface striations from the original pyrite and often have unoxidized pyrite in their core even though they must have weather for many thousands of years. From the work of Bigham, Schwertmann, and others and our own experience with acid mine

drainage, jarosite typically forms at pH values of 1-2, schwertmannite (often mixed with microcrystalline goethite) at pH values of 2-4, and ferrihydrite, goethite, and other hydrated ferric oxides at higher pH values [10-11].

The mass balance approach to acid mine drainage or rock drainage demonstrates that although several minerals dissolve, oxidized iron minerals and silica must precipitate [12]. Numerous iron minerals can form as previously mentioned but the silica is often ignored. Silica precipitation has been documented and can occur as microcrystalline silica or aluminosilicate phases.

Microbiology is an integral aspect of sulfide oxidation and mineral precipitation. Through the work of Banfield and her colleagues, iron-oxidizing archaea and leptospirilli bacteria have been shown to be more important than acidithiobacilli near or at the source of pyrite oxidation [13-14]. Downstream from the sites of pyrite oxidation, acidithiobacilli and leptospirilli are more prevalent. Iron-oxidizing bacteria and archaea have the ability to oxidize dissolved Fe(II) rapidly at rates that are close to that of pyrite oxidation by dissolved Fe(III) [3]. This indirect mechanism is the important role that microbes play in the overall process of acid sulfate water formation.

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Effect of soil amendments on growth and biomass yield of two varieties of maize at different cropping intervals on acid soil

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Abstract

Soil acidity has wide spread limitation on optimum plant production particularly in the tropics and this causes limitation and/or phosphorus deficiencies. This work was carried out with acidic soil of south western Nigeria to evaluate the effects of sole and combined applications of lime and p fertilizer sources as soil amendments on the growth and biomass yield of maize (*Zea mays* L) on an acidic soil. Eight treatment combinations: control, Lime (L), Rock phosphate (RP), Organo mineral fertilizer (OMF), L+ RP, L+OMF, RP+OMF and L+RP+OMF, each supplying 200kg P/ha and/or 1.0t/ha of Lime were applied in three replicates using a completely randomized Design. Data were collected on plant height, stem girth, leaf area at 4 weeks after sowing while fresh root and shoot and dry biomass yield data were collected at 5 weeks after sowing (WAS) for first and second cropping intervals of the two maize varieties. Data collected were subjected to analysis of variance. Means were separated using Duncan Multiple Range Test (DMRT) at 5 % probability level. Treatments that involve rock phosphate (RP), organomineral fertilizer (OMF) and control, positively influenced soil pH to 6.2, 6.5 and 5.9, respectively. These pH values fall within the pH range of 5.5-6.5 required for optimum maize production. Results obtained for the growth of the two maize varieties (95TZEE-WI and ACR97TZE Comp 3x4) in first cropping was in this order L+OMF > OMF > RP+OMF > L+RP+OMF > control with respect to growth, fresh and dry biomass yield while in second cropping result obtained was in the order OMF > L+OMF > L+RP+OMF > control. Generally, organomineral fertilizer (OMF) applied either solely or in combination with lime and RP substantially improved the growth and biomass yield of maize crop compared to control. Farmers may not need to apply the nutrient element in two or three successive seasons. The superior performance of the organo-mineral fertilizer and its combination with L and RP relative to control is suggestive of the enormous benefit that could accrue from their direct use to low input farmers.

Keywords: Acidic soil, soil amendment, maize growth, biomass yield, cropping interval.

Sulfidic Materials and Acid Sulfate Soils in Virginia, United States

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Sulfidic materials are found in various geologic and geomorphic settings across the state of Virginia (USA). These settings include unconsolidated sediment formations in the Coastal Plain, certain slate and phyllite bearing formations in the Piedmont and Blue Ridge, some of the black shales in the Valley and Ridge, and coal seams in the coalfields of southwest Virginia. Historically, problems associated with sulfide oxidation following disturbance and the exposure of *sulfidic materials* were primarily associated with coal and metal mining. In the 1990's attention was called to sulfide related problems from other forms of land disturbance as exposure of *sulfidic materials* from highway, commercial, and residential construction resulted in localized but significant acid rock drainage (ARD) that adversely affected water quality, sedimentation, integrity of building materials, and vegetation management throughout Virginia. In 1997, the Virginia Department of Transportation funded a comprehensive study to map and characterize sulfide-bearing materials in Virginia. Geologic formations associated with acid roadcuts were correlated to the state geologic map and characterized by peroxide potential acidity (PPA), expressed as calcium carbonate equivalence (CCE), and total Sulfur (S) to develop a statewide sulfide hazard rating map (Fig. 1). A limited amount of water sampling was completed at several sites to document the high acidity and metal concentrations associated with drainage from these roadcuts.

Problematic geologic formations were grouped into four categories based on potential acid-producing severity: i) PPA < 10 Mg CCE 1000 Mg⁻¹; S < 0.5% (Tabb Formation), ii) PPA < 10 Mg CCE 1000 Mg⁻¹; S > 0.5% (Ashe Formation), iii) PPA 10 – 60 Mg CCE 1000 Mg⁻¹ (Chesapeake Group, Lower Tertiary deposits, Millboro shale, Marcellus shale, and Needmore Formation) and iv) over 10% of samples with PPA > 60 Mg CCE 1000 Mg⁻¹ (Chattanooga shale and Quantico slate). In most cases, except for the Tertiary marine deposits, sulfide distribution was not uniform over the extent of the studied roadcuts. Consequently, proper spatial sampling is critical to adequately characterize the range of S and PPA values that may occur. In addition to acid-producing potential of the geologic material, the actual impact of ARD at a given location depends on site-specific conditions such as drainage design, proximity and volume of surface water, and the presence of neutralizing materials. While this map provides guidance for potentially problematic locations, it is not intended for site-specific planning. Since the state map is based solely on surficial geology it does not address issues such as depth of weathering within a formation (i.e. natural oxidation of a “high-risk” unit) or geologic changes with depth (i.e. a “low-risk” area may be underlain by “high-risk” materials). Where sulfidic materials are likely to occur as indicated by the statewide sulfide hazard rating map, detailed sampling and characterization of materials can minimize ARD-related problems. Guidance for identification and management is provided at http://landrehab.org/acid_sulfate_soils.

Over the course of the initial study it became increasingly evident that while sulfide-bearing materials are found in a variety of geologic settings across Virginia, the majority of current problems were occurring in the Coastal Plain due to increased demand for commercial and residential development, the ever-deepening nature of road cuts, and the common presence of *sulfidic materials* (with depth) throughout most of the province. In 2001 our focus shifted to remediation and revegetation of acid sulfate soils in the Coastal Plain as developers increasingly excavated into *sulfidic materials* with little or no understanding of how to identify or properly handle these materials. The most significant exposure was at Stafford Regional Airport, with over 150 ha of disturbance in sulfide-bearing Tertiary marine sediments generating large expanses of pH < 3.5 soils. This site was successfully reclaimed with the incorporation of lime-stabilized biosolids. Smaller sites identified in several housing developments have been remediated in a similar manner with the use of lime, fertilizers and organic amendments (compost).

Over the past 15 years significant efforts have been made to educate engineers, developers, and public officials about the major problems associated with the exposure of *sulfidic materials*. The development of active acid sulfate soils in several housing developments, and subsequent public outcry, resulted in the establishment of regulations and/or policies to test for potential acid sulfate soil materials for new construction in Stafford County (2006), the City of Fredericksburg (2007) and Spotsylvania County (~2010). To date these are the only regulations concerning *sulfidic materials* and acid sulfate soils within the state of Virginia.

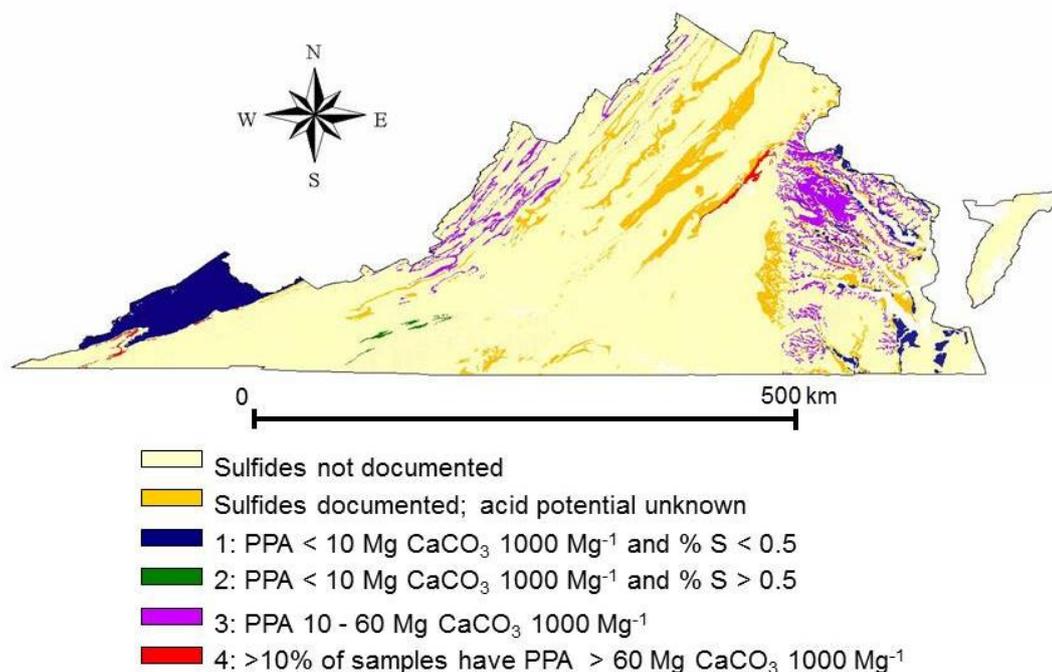


Fig. 1. Sulfide hazard risk map for the state of Virginia, United States

Table 1. Summary of Potential Peroxide Acidity (PPA) and %S for sulfidic geologic formations, and pH and metal concentrations of representative road drainage samples.

Geologic Formation	Geologic Samples			Road Drainage Samples						
	# of samples	PPA ¹ (avg)	%S (avg)	pH	Fe	Al	Mn	Cu	Zn	S
					----- mg/L -----					
Tabb	10	3.2	0.10	3.09	12.4	15.2	2.4	<0.1	0.6	136
Tertiary Marine Sediments(1) ²	27	13.3	0.52							
Tertiary Marine Sediments(2) ²	18	35.7	1.22	3.05	13.9	49.5	2.1	<0.1	<0.025	298
Quantico Slate	13	32.7	1.09	2.61	114.2	66.9	17.4	0.4	3.5	639
Ashe (phyllite)	21	4.8	0.30	3.22	39.7	20.1	1.4	<0.1	0.6	182
Devonian Black Shales(1) ³	21	4.4	0.80							
Devonian Black Shales(2) ³	22	11.5	0.47	2.67	59	162.5	38.5	<0.1	8.3	1011
Chattanooga Shale	6	42.4	1.60	NA	NA	NA	NA	NA	NA	NA

¹ Mg CaCO₃ 1000 Mg⁻¹ material

² Tertiary Marine Sediments(1) are surface sediments, typically to a depth of 20 – 30cm, that show indications of partial oxidation. Tertiary Marine Sediments(2) are underlying sediments that retain darker color and show less indication of oxidation.

³ Devonian Black Shales(1) have a positive fizz test. Devonian Black Shales(2) do not have a positive fizz test.

Reclamation of Disturbed Sulfidic Coastal Plain Sediments at Stafford Regional Airport, Virginia, USA

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Excavation of *sulfidic materials* during construction has resulted in acid rock drainage (ARD) problems throughout Virginia. The most extensive known example not associated with mining impacts is in the Coastal Plain at the Stafford Regional Airport (SRAP). Between 1998 and 2001, construction activities at SRAP disturbed over 150 ha of sulfide-bearing Tertiary marine sediments. Long spur ridges were excavated to depths ≥ 25 m, exposing gray *sulfidic materials* which were placed into intervening valley fills to support the runway. Excess *sulfidic materials* were placed into steeply sloping above grade spoil fills along a first-order stream draining the southeastern section of the site. Since the sulfidic nature of these materials was not recognized during construction, the acid-forming materials were not isolated from drainage or surface exposure and were scattered randomly throughout the site. After multiple revegetation efforts failed, the authors were contacted for assistance and first visited the site in November 2001. Acid sulfate related problems were readily apparent including barren cut and fill slopes, red iron oxy-hydroxide precipitates on concrete drains and culverts, and significant etching and degradation of cement components. Galvanized steel standpipes in stormwater basins below the site were degraded by the acid drainage in < 1 year, releasing *sulfidic materials* into the receiving streams and local floodplains (Fig. 1).

In February 2002, surface soils (0–15 cm) were sampled from 42 map units (based on spoil composition and slope class) across the site and analyzed for pH, total-S, and peroxide potential acidity (PPA). We recommended variably liming each sampling cell to meet predicted requirements, applying fertilizer and organic amendments, and seeding to acid- and salt-tolerant grasses and legumes. The airport authority opted to use lime-stabilized biosolids (LSB) as a cost-effective alternative treatment to conventional topsoiling or purchase of commercial lime + compost. Application of LSB at higher than agronomic rates was necessary, creating concern about the impact of potential N and P losses to surface and ground water. Two objectives of this study were: (i) evaluation of LSB to stabilize and revegetate active acid sulfate soils; and (ii) determination of associated impacts on local surface water quality.

In April and May 2002, Class B LSB were applied and incorporated to a depth of 10 – 25 cm across the site at rates of 35 – 270 dry Mg ha⁻¹ to supply 1.25X the lime required for neutralization of the soil surface. The soil was straw-mulched and hydro-seeded with acid- and salt-tolerant grasses (primarily *Festuca arundinacea* Schreb. and *Festuca ovina*). Late planting (past mid-May) and severe drought conditions minimized establishment of vegetative cover during the spring/summer so the site was overseeded in September 2002. Visual and photographic observations were made over the course of the following year to evaluate revegetation. In September 2003, surface (0–15 cm) and subsoil (40–50 cm) samples were collected from the original sampling locations. In September 2004 and March 2006, surface and subsoil samples were collected again from subsets of the original sampling locations. All samples were analyzed for pH and EC, and subsoil samples were analyzed for PPA.

Soil pH, EC, and PPA results are presented in Table 1. Surface soils initially were highly acidic (avg pH = 3.10). After 1.5 yr, remediated soil pH had increased notably (avg pH = 7.26). Although EC values > 2.0 dS m⁻¹ may somewhat inhibit plant growth, overall the values fell well within an acceptable range (< 4.0 dS m⁻¹). A salt-tolerant grass species mix was specified since high EC values were anticipated. Soil sampling 2.5 yr after remediation (August 2004) yielded similar pH and EC values; sampling 4 yr after remediation (March 2006) yielded similar EC values, but slightly lower pH values. The drop in pH is at least partially accounted for by the sampling method which involved fewer samples that targeted poorly vegetated areas. Based on visual observations, the remediated zone typically ranged to depths of 15 – 30 cm.

In many areas, partially oxidized *sulfidic materials* directly underlie the reclaimed zone. Subsoil sampling (40 to 50 cm) from the three post-reclamation sampling dates indicated that subsoil pH typically was still less than 4.5 with an average pH around 3.5. Electrical conductivity values from the three dates ranged as high as 11.8 dS m⁻¹ with an average of ~ 3.0 dS m⁻¹. Peroxide potential acidity values from the subsoil, determined only for the 2004 and 2006 samples, ranged as high as 60 Mg CaCO₃ equivalent (CCE) 1000 Mg⁻¹ material, but averaged 10 Mg CCE 1000 Mg⁻¹. With few exceptions, the shallow depth of these problematic materials did not appear to negatively impact the vegetative cover on the overlying reclaimed surface.

Initial revegetation efforts were largely unsuccessful for two reasons. First, the reclamation prescription specified that all planting must be completed by mid-April; however, most seeding was not completed until late May and early June. Areas seeded by mid-April established a vegetative cover by early June, while areas seeded later remained barren. Second, the summer of 2002 was one of the hottest and driest on record for Virginia. Soil samples collected in early July indicate that pH (Table 1) was conducive for establishing vegetation; therefore,

we believe the combination of late seeding and harsh hot/dry weather conditions prevented germination over most of the site. After overseeding in September 2002 the site was fully revegetated (>90% living cover) by late October 2002. Since October 2002, the site has remained fully vegetated, although a few highly acidic outcrop and seep areas on steep cut and fill slopes remained barren (<5% of the total disturbed area; Fig. 1). These sites will demand intensive spot-liming and other remedial treatments over time.

A water quality program was established in 2002 to monitor baseline pH, EC, NO₃-N, NH₄-N, PO₄-P, Fe, Al, Mn, and SO₄-S. Initial pH values as low as 2.9 were noted in receiving streams. Water quality responded quickly to treatment; runoff waters were buffered into an acceptable pH range and dissolved metal loadings were drastically reduced. Despite heavy total P loadings, no effect of the land application was seen on runoff water P. Although N losses to surface water were a secondary effect of the use of heavy loading rates coupled with very poor first season plant establishment, these losses declined rapidly within 9 months following application. Furthermore, the net long-term water quality effects of N losses must be weighed against the environmental cost of taking no action.



Figure 1. Degraded steel standpipes in stormwater basin in 2001 (upper left), barren acidic soils surrounding a remnant beaver pond within SRAP in 2001 (upper right), aerial photo of SRAP two years after remediation shows successful revegetation over most of the site, but discrete problematic areas remain barren (lower left), isolated acid seeps persist > 10 years after remediation (lower right).

Table 1. Summary of soil characterization data.

	<i>n</i>	pH	EC dS m ⁻¹	PPA Mg CaCO ₃ 1000 Mg ⁻¹
Surface soils (0–15 cm)				
Feb. 2002 (before reclamation)	42	3.10 ± 0.86 ^a	nd ^b	9.5 ± 10.3
July 2002 (<3 mo after remediation)	12	8.04 ± 0.13	3.5 ± 1.7	nd
Aug. 2003 (1–1.5 yr after remediation)	32	7.26 ± 0.43	1.7 ± 0.8	nd
Aug. 2004 (2–2.5 yr after remediation)	18	7.30 ± 0.73	1.6 ± 0.8	nd
Mar. 2006 (3.5–4 yr after remediation)	11	6.65 ± 0.84	1.6 ± 0.7	nd
Subsoils (40–50 cm)				
Feb. 2002 (before reclamation)	42	nd	nd	nd
Aug. 2003 (1–1.5 yr after remediation)	32	3.49 ± 0.50	3.0 ± 2.3	nd
Aug. 2004 (2–2.5 yr after remediation)	18	3.56 ± 1.11	3.5 ± 3.4	11.4 ± 14.2
Mar. 2006 (3.5–4 yr after remediation)	11	3.62 ± 0.42	2.7 ± 2.1	10.2 ± 8.0

^a Mean ± SD.

^b nd = not determined.

Management of Boreal agricultural acid sulfate soils

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Sulfidic sediments that may form acid sulfate (AS) soils ($\text{pH} < 4$) upon oxidation cover over 17 million ha worldwide [1]. They are typically sediments of marine origin, thus occurring in coastal environments where they have emerged from the sea due to post glacial sea level change and/or due to postglacial land uplift and subsequently been covered by peat and vegetation. Under natural conditions, these sediments can be prevailed under harmless anoxic conditions for thousands of years. But upon reclamation that lowers the groundwater they will very rapidly oxidize and unless there is natural buffering capacity, they will become very acidic within a few months and mobilize very large quantities of soluble toxic metals such as Al, Cd and Ni to water courses with serious consequences on water ecology. The drainage systems enable oxidation as well as a rapid transport of acidity and metals from the soil to water courses. For centuries there has been an incentive to reclaim such areas in order to create fertile agricultural land but without proper management preventing the acidity and soluble metals from affecting crops, results have been poor. Nevertheless, in countries such as Australia and Finland, they are among the most valuable farmlands due to their fertility. Management of agricultural acid sulfate soils has traditionally been concerned with issues related to crop productivity but in recent decades when such problems have largely been overcome, the question has shifted to how to maintain a high crop productivity without harming the environment, in particular the recipient water courses. In this paper the latter question is in focus, with special regards to Boreal agricultural acid sulfate soils in Finland but the general principles may be largely adaptable for other regions

In the 50's when large areas of sulfidic sediments were reclaimed for fertile agricultural land and environmental concerns were not considered, one conscious agricultural management strategy in Finland was to drain away the acidity and soluble toxic aluminium from surface soil layers for several years before applying heavy doses of neutralizing agents and using the land for crop production. Installation of deep efficient subsurface drainpipes, instead of open drains, reduced the need for liming as more acidity was exported from the soil rather than being raised to the surface by capillary forces. Long term water monitoring data shows that the installation of subsurface pipes that became popular in the late 60's and early 70's coincides with an increased acidity and large scale fish kills in recipient rivers and estuaries [2, 3].

Being difficult to mitigate once the soil material has been oxidized, from an environmental perspective the main aim of management should be preventive actions to minimize the oxidation and subsequent leaching of acidity and metals. On agricultural land, this means that the groundwater level should be kept as high as possible without endangering plant growth. Moreover, flow peaks should be avoided. Thus, water management is the key to environmentally sustainable management of agricultural AS soils [4]. However, while the aims are clear, best management practices need to be adapted to the regional climate, hydrology, plants, availability of irrigation/tidal water, finance and availability of technology. In Scandinavia, there is a large excess of water in spring after snow smelt but with efficient drainage systems including subsurface drain pipes, the groundwater is rapidly lowered below 0.6 meter or more that is needed for tractor bearing and sowing. Rainfall deficit is typical in the warm summer months and as a combined effect of drainage and evapotranspiration, the groundwater may drop to two meters in the end of summers, corresponding with the depth of oxidation [5]. In order to minimize oxidation, controlled subsurface drainage (CD) and subsurface irrigation (CDI) have been trialled on soils that have previously been oxidized. If properly managed CD has the potential to delay the groundwater drop, shortening the time of oxidation [5, 6]. In CDI-system the groundwater could be kept at c. 1 m or shallower throughout the summers, thereby preventing oxidation of critical sulfide horizons in the lower subsoil [5]. It is notable that especially with CDI, it is necessary to prevent by-pass flow into the main drain. This can be done with a vertical plastic sheet inserted in to the soil to a depth of c. 1.8 m along main drains [5, 7]. CD and CDI may also be useful if more extreme weather conditions due to potential climate change that otherwise would cause even deeper oxidation. It is expected that CD and CDI in particular would reduce the oxidation and ideally reverse the process into acid consuming sulfate reduction as has been shown in soil columns in lab experiments [8]. However, from field tests lasting for less than five years, there are not yet any clear evidence that CD or CDI would have significant positive effects on the soil or drainage water chemistry.

Trials to neutralize the soil with applying lime or other neutralizing agents on the soil surface have shown that even with extremely high doses, the acidic oxidized subsoils, where most of the acidity occurs and that can reach down to two meters or more, are not affected. Neither are there any measurable effects on the water quality [6]. In a project called PRECIKEM (precision chemical treatment of AS soils 2011-2014), an attempt to overcome this problem has been made by injecting suspensions of ultrafine grained calcium carbonate ($D_{50} = 2.5 \mu\text{m}$) and $\text{Ca}(\text{OH})_2$ in to the soil with CDI via subsurface drain pipes. It is expected that the treated irrigation water will reach the same hydrologically active soil pores that are responsible for most of the acidity export during high flow conditions [9]. With this method it is possible to reduce the acidity and acid soluble metals significantly for a couple of years. Ideally, the chemicals would hamper the microbiologically mediated oxidation process and thereby reducing the need for further treatment with neutralizing agents. In a follow up project, PRECIKEM2, additional chemicals, including reductants, will be trialled with the aim to have stronger and more long lasting impacts on the soil geochemistry [9].

Ideally, economic and environmental interests should go hand in hand, otherwise implementation of environment friendly management techniques will require policies that offer rewards and/or sanctions. CD systems are expected to provide a better water balance during dry summers and therefore it has been widely adapted for both economic and environmental reasons. Given a sufficient supply of irrigation water, existing CD systems can relatively easily be used for CDI. While CDI with treated irrigation water may prove to become an efficient treatment method, it additionally requires a mixing vessel and more labor and competence to add the treatment chemicals. The method may also pose a risk for clogging the drainage system and, therefore some additional modifications of the drainage system may be needed. Consequently, it would require subsidies to be implemented on a large scale. To be widely accepted and adaptable, involvement of farmers and other stake holders is crucial in the development of new management techniques.

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Titrateable incubation acidity for acid sulfate soil materials

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Metal sulfide, such as pyrite (FeS₂), containing anoxic sediments are found in several regions around the world. When the metal sulfides are exposed to atmospheric oxygen, microbiologically mediated oxidation of sulfides [1] takes place and acid sulfate (AS) soils (pH < 4) are formed if the amount of acidity exceeds the natural buffering capacity. Utilization of these soils for different purposes such as agriculture or building of infrastructure, the soil acidity and metals needs to be considered because they discharge very large quantities of sulfuric acid and soluble metals such as Al, Cd and Ni in to water courses with detrimental environmental consequences on water ecology. They may also affect plant growth and may cause serious corrosion on concrete and metal constructions.

Identifying AS soils typically involves pH measurements under field conditions and subsequent pH measurements after incubation where a 2 – 10 mm thick soil-slab of moist soil material is in contact with air in room temperature for up to 19 weeks [2]. If the field pH is above 4 but incubated soil pH ≤ 4 and the pH drop due to incubation ≥ 0.5 pH units, the soil material can be considered as a potential acid sulfate soil, also termed hypersulfidic material [3] (Sullivan et. al. 2010). Incubation is a reliable, cost efficient and widely used method to identify hypersulfidic soil materials as it lets the soil “speak for itself” [4] (Dent 1986).

Further, the acidity hazard of AS soils can be estimated by acid base accounting where the net acidity is obtained from the sum of potential, actual and retained acidity minus acid neutralization capacity. Two main approaches are the “Acidity Trail” which is a direct approach of determining acidity by titration and the “Sulfur Trail” which is an indirect approach combination of the sulfur content and the stoichiometry is used to predict the acidity risk. Potential Acidity is commonly determined through titration of acidity after oxidation with peroxide, which is termed titrateable peroxide acidity (TPA) [5]. The aim of this study is to demonstrate a more simple method for assessing soil acidity hazard in sulfide-bearing soil materials by the measurement of the “actual acidity” after incubation in accordance with the “let the soil speak for itself” approach. The combination of these two widely adapted methods are here termed Titrateable Incubation Acidity (TIA).

Within a project assessing environmental risks related to peat harvesting on peatlands with sulfides in the harvested peat and/or in the underlying mineral soil, a large number sediment samples with low contents of carbonate buffering capacity were analyzed for TIA in order to assess their environmental risks [6]. Of these samples, eleven reduced clayey-silty samples with no actual acidity under field conditions were analyzed for pH and TIA after 4, 8 and 16 weeks of incubation with c. 10 mm soil-slabs as well as for TPA, total sulfur after aqua regia leaching (S_{tot}) total reducible sulfur (TRS = acid volatile sulfur + chromium reducible sulfur). Samples were incubated and analyzed in duplicate for TIA and TPA.

Medians/min-max values were: TRS (0.78/0.0 – 3.49, mainly as chromium reducible sulfur), S_{tot} (0.99/0.03 – 4.58), LOI (4.8/0.5 – 65), TPA (606/34 – 2620 mmol H⁻¹) and TIA at 16 weeks (339/28 – 962 mmol H⁻¹). pH decreased rapidly upon incubation; with one exception pH was ≤ 3.5 (median 3.1) after four weeks and < 3 (median 2.3) after 8 weeks with no significant difference between 8 and 16 weeks. In contrast, TIA generally increased continuously during the 16 week period, as compared to TIA after 4 weeks; it was about two times higher after 8 weeks and three times higher after 16 weeks. There was no correlation between incubation pH with TIA or TPA. Thus, incubation pH cannot be used to assess the severity of AS soil materials in this environment.

The correlation for TRS and S_{tot} to TIA and TPA was good (R²: 0.8 – 0.9), indicating that TIA is comparable to the other variables for assessing/classifying the severity of the soil materials. TIA generally gave lower acidity values than TPA and the differences between the two methods varied greatly; there was 13 – 64 % less acidity for 9 out of eleven samples, equal acidity for one sample and twice as much acidity for one sample. The precision with TPA was very good, the deviation between standard and duplicate samples was < 6%. The precision with TIA was less good, the deviation between original and duplicate samples (subsamples incubated in separate vessels) was up to 38 % and 19 % on average. Since the titration procedure is similar to that of TPA, that had a high precision, the reason for the deviation was likely to be caused by the incubation procedure, e.g. different soil moisture conditions, heterogeneities in the soil material in the c. 10 mm thick soil-slabs and/or incomplete/uneven oxidization/buffering during the 16 week incubation time. The use of thinner soil-slabs for incubation would, in accordance with recommendations by [7] Sullivan et al (2009), probably lead to a more even/complete oxidation of the soil material. Although, the incubation procedure may inevitably lead to a lower

precision, it can be argued that since TIA mimic natural oxidation conditions, enabling microbiologically mediated oxidation and time for natural buffering reactions to occur, it gives a more realistic estimate of the acidity that actually will be produced if oxidized in nature than methods involving peroxide oxidation and theoretical stoichiometric calculations. It is, however, notable that as compared to natural conditions where leaching continuous leaching typically will occur, there will be a buildup of more acidity and oxidation products with incubation that may affect the oxidation process. It is also notable that the conditions for microbes will differ from that in nature as because during the incubation, samples will be exposed to some light and for Boreal soils used here the temperature will be significantly higher if incubated in room temperature. From a practical point of view, a disadvantage with TIA is that it requires a long incubation time. On the other hand, having used TIA on hundreds of samples during the last five years, we can conclude that a great advantage with TIA is that it is very simple and cost efficient as compared to other methods that estimate the acidity hazard of acid sulfate soil materials.

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Remediation and management options of salt drain and groundwater acidification in the Lower Murray Reclaimed Irrigation Area, South Australia.

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Abstract

Due to very low inflows throughout the Murray–Darling Basin from 2007–2010, water levels in the Lower Murray River (below Lock 1) fell from a normal pool level of 0.75 m AHD in 2007 to a low of –1.2 m AHD by April 2009. The low water levels and restricted irrigation water allocations during this hydrological drought period meant that most of the Lower Murray Reclaimed Irrigation Area (LMRIA) was not irrigated. The low river levels and lack of irrigation led to a drop in the shallow water table of 1.5–3 m from pre-drought levels. The heavy clay soils subsequently salinised, dried and cracked causing major damage to the rehabilitated irrigation bays and associated infrastructure.

Screening by the South Australian Environment Protection Authority in late February 2011 highlighted the presence of acid water in 14 salt drains across 13 of the 27 LMRIA irrigation areas. Investigations determined that the falling groundwater levels led to the exposure and oxidation of reduced inorganic sulfur minerals, commonly termed acid sulfate soils, at a depth 1–3 m below ground level. The acid and metals which were produced in the soil profile were then mixed with the shallow groundwater as water levels recovered in late 2010. This resulted in acidic drainage water entering the LMRIA salt drains. The acidic drainage water is pumped back into the River Murray, a practice which is necessary to keep the saline water tables low enough to maintain agricultural practices in this region.

A remediation project was developed to assess potential mitigation strategies and trial options to reduce the potential risks that acidic drainage water poses to the water quality and environmental values of the Lower River Murray in South Australia.

Following scoping of a range of potential options, five remediation strategies were trialled:

- 1) Controlled flood irrigation to flush acidity from the soil profile
- 2) Surface limestone application followed by irrigation
- 3) Lime dosing of drain water prior to discharge to the river
- 4) Sub-surface injection of a hydrated lime and limestone slurry
- 5) Sub-surface injection of fresh organic material (OM)

To investigate remediation strategies 1 and 2, a trial site to examine whether flood irrigation and lime spreading could combat acidic groundwater conditions was established at one of the acidic areas. A series of piezometers at depths ranging from 0.3 to 3 m below ground level were installed to assess and monitor the groundwater during the trial.

To investigate remediation strategy 3, a trial aimed at treating the water in the salt drains (in situ) was initiated to alleviate any immediate impacts from drainage water to the River Murray and potential risks to drinking water supply off-takes and ecosystem health.

To investigate remediation strategy 4, a trial of sub-surface injection of a neutralising agent was undertaken. A total of 7000 kg of lime was injected into a trial paddock using an adaption of a LMRIA practice called “mole ploughing”. This method of lime injection deep into the soil profile was a “world’s first practice”. The aim was to stimulate the sulfate reducing bacteria by raising the pH (the activity of these bacteria is known to be limited below pH 5) in localised areas

An adaption of the method used for the lime injection trial to inject fresh OM (pelletised wheat straw) into the subsoil to stimulate sulfate reduction was used in remediation strategy 5. A total of 4000kg of fresh organic material was injected into two trial site paddocks.

The results from these trials will be discussed, along with their advantages and disadvantages.

Figure 1: Images of the River Murray discharge point at a LMRIA irrigation area while discharging



treated water with a lime slurry (left) and untreated water three days after the treatment trial ceased (right), highlighting the temporary effects and disadvantages of ‘remediation strategy 3’.

Hart-Miller Island: Rebuilding, Restoring and Recreation

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Located approximately 14 miles east of Baltimore's Inner Harbor, Hart-Miller Island Dredge Material Containment Facility (HMI-DMCF) lies at the mouth of Back River. Once two separate islands, Hart Island and Miller Island, were purchased by Maryland Port Administration (MPA) in the late 1970's. In 1981, construction began on a perimeter dike connecting Hart and Miller Island, creating an island of 1,040 acres. HMI-DMCF received dredge material from shipping channels to the Port of Baltimore from 1984-2009. Currently restoration efforts are underway to create wildlife habitat and eventually turn HMI into a State Park. This presentation will review HMI's history, background, and future plans.

Discovery, Identification, Sustainable Remediation

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Keywords: Fish Kill, Low pH, Drainage Management,

Abstract

When the first European explorers discovered the Tweed in 1843, little did they know, that behind the lush river bank vegetation, there were very toxic soils. These very low pH soils were classified by Dutch scientist Lennaeus in 1737 as the soils from hell (Quirk et al. 2004). The Tweed Valley was in-filled with high sulphur ocean sediments during the last interglacial period and when drained and exposed to oxygen, these sediments can produce large amounts of sulphuric acid. The subject site was one of the last areas in the valley to be in-filled as the ocean receded and has a current height of 0.5 of a metre Australian Height Datum (AHD).

For the first 120 years of European settlement, agriculture and the local sugar mill were seen as the cause of fish and benthic mortalities. One study of rainfall records showed that the major fish kills occurred following a long dry period which ended with a heavy rain event, in particular, an event that was associated with intense low pressure systems and two successive flood peaks (Heath L. ~2006)

Following a major fish kill in 1987, Clive Easton, an entomologist at the Tweed Shire Council correctly identified the cause of the fish kill in an article he wrote (Easton 1989) as being runoff from the acid sulphate soils in the area. The local Government authority moved quickly and in a "global first" in 1992, introduced the first guidelines for work in acid sulphate soils.

Results came quickly with scientist, agriculturists and governments at all levels providing funding to address a problem that had by this time been identified as aluminium and iron rich water being mobilized by the acidity in the landscape. By 2005 the NSW sugar cane industry had put in place a management plan that, under self-regulation, was granted an exemption from protective legislation relating to work in ASS (Beattie et al 2005)

Discovery

The indigenous occupants told European settlers during the 1860's that "fish die every now and then but are edible if recovered while they are still moving". There were also stories of farmers shovelling fish off the river banks and taking them to use as fertilizer on their fruit trees following a major flood in 1893. This flood had been preceded by a 3 year "dry". At this time, there were no drainage channels constructed on the flood plain.

The first documented report of a fish kill event in the Tweed River was in December 1901 (Walsh, 2011). Similar events occurred at regular intervals over the next 20 years as the flood plain was gradually drained. These events were blamed on discharges of chemicals from the local sugar mill as the causal factor.

Identification

In 1924 a fisheries inspector took water samples which identified the likely cause as high levels of "Alum" and sulphuric acid coming from McLeod's Creek and Ledday's Creek. Interestingly the recorded samples were sourced from McLeod's Creek where the study site was established by Dr's White and Melville 60 years later. Following the 1987 fish kill when the Tweed River was acidified and all aquatic life was killed for 30 km of its length, a public meeting was held attended by 500 concerned stakeholders. The meeting broke up after 2 hours of accusations and threats and it was decided to reconvene the following week. A committee was formed including representatives from agriculture, fishermen, environmentalists, local government and local drainage boards). This model of engagement has since been recognized globally as a model for conflict resolution (White et. al Journal of cleaner production). The committee that was formed and it initiated a process based on scientific research.

- The initial research monitoring indicated regular pH readings in McLeod's Creek as low as 2 (Willet et al 1993)
- Over the next ten years the McLeod's Creek research site became one of the most studied ASS sites in the world with 10 PHD studies and numerous masters and honours studies all being undertaken at the site.
- The studies identified many of the active processes (Wilson 1993) and assisted quantification of acid loads, discharge mechanisms, and drainage system contributions to acid in the water column. Remedial liming rates and impact mitigation activities were also identified.

Sustainable Remediation

The 25 years post the 1987 fish kill saw many developments:

- Changes in attitude of the land managers along with Local, State and Federal Governments. As an example a quote from Dr Mike Melville in a conversation to Robert Hawken and Robert Quirk "yes we know it is a natural phenomenon, the sulphur came from the ocean and it is on its way back so we must find a way to reduce both the discharges and the mortality to the aquatic life as it does so ".From that instance, land managers took control of the problem. It was their acid soil and discharges killing their fish.

- With the help of the scientists and their students, land management techniques were developed to reduce acid discharges.
- These techniques have turned McLeod's creek from one of the most toxic streams (devoid of any marine life including benthic organisms) on the east coast of Australia to a juvenile fish breeding habitat with 7 species of ocean fish growing in these creeks (Kroon report to ASSMAC).
- The landscape had 50 tons of oxidized sulphuric acid for every hectare with the potential to produce a magnitude much greater (Macdonald et al 2002)
- The amount of existing, oxidized, acidity with the potential of finding its way into Tweed River would require approximately 500,000 tons of lime to neutralize. It has been calculated that the major 1987 fish kill event was due to a discharge of approximately a half a ton of acid per hectare (Quirk et al 2005).
- At the time of the initial research, sufficient oxidation had already produced enough acid to cause fish kill events for the next 100 years, even if oxidation could be arrested.
- Reverting the farmland to wetlands was not contemplated as it would not reverse the oxidation.
- Doing nothing was also not an option.

The solutions evolved slowly as studies progressed.

- It was found that there was negligible lateral water movement through these soils, the predominant movement being vertical (Cook et al 1999) the movement being approximately 0.30 cm per day about the same speed as through concrete.
- It was also found that the oxidation front was well below the bottom of the drainage ditches, and that the drainage ditches were the conduit for the acid's releases but not the cause of the oxidation (Keene et al. 2003)
- It was found that the discharge of acid came from a wedge shaped section of the soil profile 60 cm deep and 5 m from the drain bank. The filling of 50% of the drains reduced the problem by half.
- The drain banks of the remaining drainage ditches were heavily limed at the rate of 10 tons/ha. This raised the drainage pH from 3.5 to 5.5 and is now accepted best practice on the flood plain (Melville et al 1996).
- An automated dewatering system was designed and installed at the study site. This was set to start pumping when the water in the drains reached minus 0.50cm AHD and shut down when the water level reached minus 60cm AHD.
- The cane was planted on natural ground level and the soil mounded over the cane. This gave about 20 cm more drainage head than using the conventional system of planting below the ground. This system gives a much larger storage for the flood water. It gives the site storage for a 50 mm rain event before any damage occurs to the crop.
- All fields have been laser levelled to drain towards the pumps at a grade of 0.05%. The lower ends of the fields are used as storage for the run off water.

Organic Matter

While the benefits of organic matter are not fully understood in reducing acid discharges some observations are:

- During high rainfall events the discharges are slowed as the water moves through the residue in the inter row spaces of the sugar cane and any iron and aluminium tend to adhere to the residue in many cases forming iron mono sulphides under the residue. Mono sulphides are quite dangerous to marine life when mobilized, trapped in the field, they are an excellent source of potassium for sugar cane .
- The residue from a crop of sugar cane yielding approximately 80-90 Tonnes per Hectare (tph) is around 15 tph per year. The study site was tested recently (80 carbon tests cores) and found to be very close to carbon saturated.
- The tests showed an additional 1.5 tons of carbon capacity remained over the 100 ha site (Mulvey P.).

Further Observations

- A PHD study in progress (Jackie Webb SCU) is indicating that over a 12 month period the sugar cane is absorbing up to 75% of all the ambient CO₂ and 54% of all the ambient methane.
- Harvesting records show that production on the 100 ha study site has increased from 50 tph to over 80 tph along with very productive legume crops of soy beans and lupins.
- The study site has gone from very poor dairying country in the early 1960's into some of the most productive rain fed sugar cane growing land in the country. The global standard for growing rain fed sugar cane is 38 tph the site is achieving double that.
- The model developed at the study site has had around 2,000 visitors; these have included scientists, government officials, the community and local students, during the study period. The practices developed at the site have been adopted globally as best practice for growing sugar cane in AS soil landscapes.

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IRIS (Indicator of Reduction In Soils) Technology for Assessing Sulfidization in Subaqueous Soils

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Processes related to sulfidization, including dissimilatory sulfate reduction and the reaction of soluble sulfide with ferric and ferrous Fe to form Fe sulfide minerals, are common in estuarine subaqueous soils. The formation of Fe sulfide minerals often results in the presence of potential acid sulfate soil materials. Sulfide in the soil porewater can be toxic to various types of submersed aquatic vegetation (SAV) and also to many benthic organisms. IRIS technology, where PVC devices are coated with Fe oxides, have been used mostly in the recognition of reducing conditions in non-tidal freshwater wetlands (Castenson and Rabenhorst, 2006, Jenkinson, 2002, Rabenhorst, 2008, Rabenhorst and Burch, 2006). More recently, these devices have been shown to be useful in measuring the sulfide concentration in soil porewater, mostly in coastal marshes (Rabenhorst, Magonigal, et al., 2010). This paper demonstrates how this *in situ* technology can be adapted to rapidly quantify levels of porewater sulfide in subaqueous soil profiles.

Four study sites were selected in Chincoteague Bay, MD within four different soil map units (Fig. 1), and also to be near locations where soils were previously characterized (Balduff, 2007). In June, three sets of five replicate IRIS tubes, specially adapted for use in subaqueous environments, were installed at each site. One set of 5 replicate tubes was removed after 1 hr, 6 hrs, and 24 hrs. Tubes were then removed from the water, gently blotted dry and photographed as a group, rotated 180 degrees and photographed a second time (to obtain images of both front and back of the tubes). Photographs were completed within approximately 2 minutes. Expeditious photography is important because the black Fe monosulfide that forms on the tubes begins to fade upon exposure to oxygen and may disappear altogether within a couple of hours.

The images of the tubes were digitally cut into 10 cm increments from 0 to 50 cm, and were analyzed following the protocol described in Rabenhorst et al. (2010) in order to estimate the sulfide content. The images from the tubes extracted after 1 hr and 6 hr were used to calculate sulfide concentration, because the

Fe sulfide on those tubes was sufficiently present and exhibited an adequate range for analysis. This procedure was repeated in September and November.

Photographic images of the tubes from the June sampling are shown in Fig. 2. Darker colors of the precipitated FeS reflect higher concentrations of porewater sulfide. Longer exposure (i.e. 6 hrs) are darker than shorter exposures (i.e. 1 hr). Sulfide concentrations with depth are shown in Fig. 3, as well as sulfide concentrations averaged for the 0-50 cm depth.

Site	Pedon	Landform	Soil Map Unit	Soil Classification of Pedon	Series
A	CB21	Submerged wave cut headland	SpB	Fine-loamy, Thapto-Histic Sulfiwassents	Southpoint Taxajunct
D	CB52	Barrier cove	MmB	Fine-silty, Fluvic Sulfiwassents	Tingles
C	CB58	Lagoon bottom (barrier side)	Ct?	Coarse-loamy, Fluvic Sulfiwassents	Sinepuxent
B	CB100	Lagoon bottom (central)	TgD	Fine-silty, Fluvic Sulfiwassents	Coards

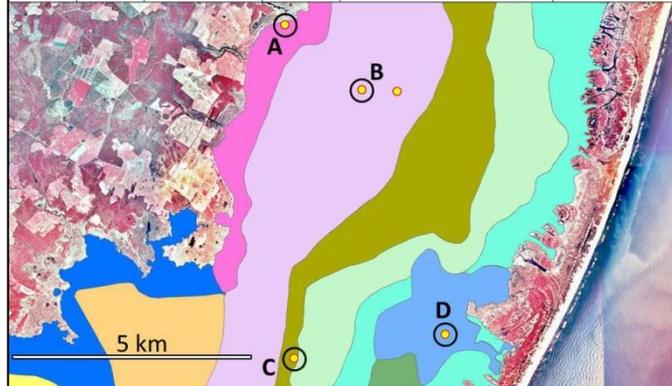


Figure 1. Subaqueous soils map of Chincoteague Bay, MD showing the four study sites associated with different soil map units (map modified from Balduff, 2007).

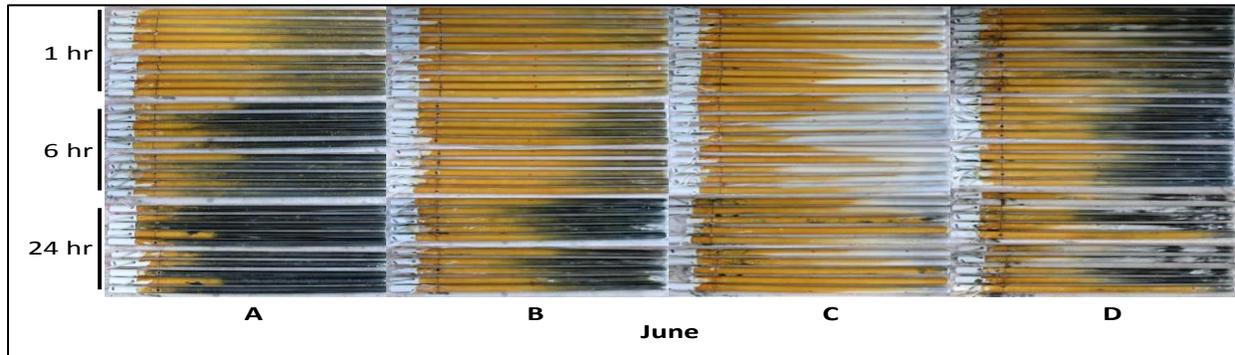


Figure 2. Photographs of IRIS tubes extracted from the four sites (A, B, C, D) in June. FeS forming on the tubes became darker with longer exposure. The bottom of the tubes from site B are white due to abrasion of the Fe oxide coating by the sandier soil.

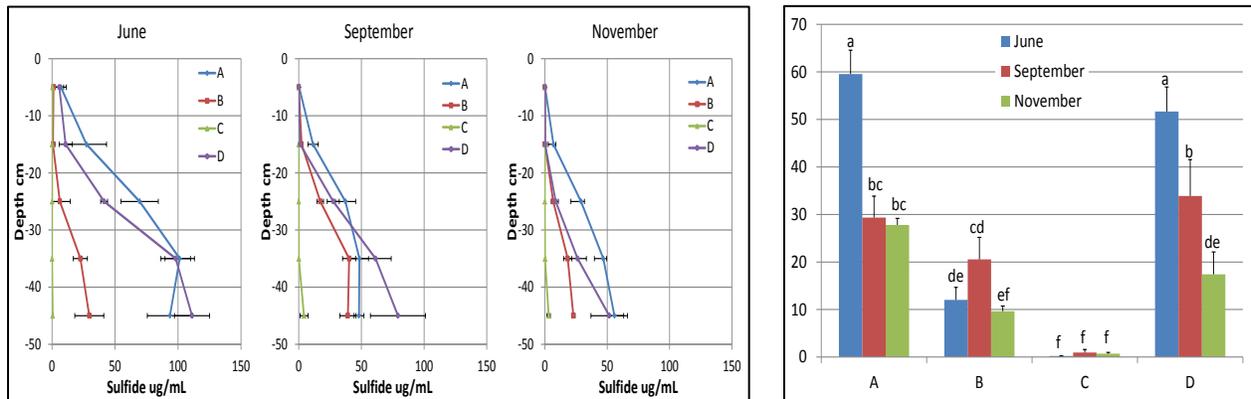


Figure 3. Porewater sulfide concentration with depth (left) at the four study sites during 3 periods and average sulfide concentrations over the 0-50 cm depth (right). Error bars represent the SEM. Bars with the same letter are not significantly different at the 0.05 level.

Porewater sulfide generally increased with depth, and significant differences were observed between different soils. Highest porewater sulfide was observed in the Southpoint soil at site A (Fine-silty, Thapto-Histic Sulfiwassents) and in the Tingles soil at site D (Fine-silty, Fluvic Sulfiwassents). Minimal porewater sulfide was observed in the Sinepuxent soil at site C (Coarse-loamy, Fluvic Sulfiwassents). Porewater sulfide levels are function of both sulfide generation via microbial sulfate reduction and also the quantity of free Fe present in the soil to form Fe sulfide minerals. Some seasonal differences were observed. In both sites A and D, June levels of porewater sulfide were significantly greater than during September and November. These differences may be related to subaqueous soil temperatures.

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Sedimentary sulfide formation revisited

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From the viewpoint of acid sulfate soils (ASS), sedimentary iron sulfides can be conveniently divided into iron sulfides in sedimentary rocks and iron sulfides in sediments. In both cases by far the most abundant iron sulfide is pyrite and the assumption that it is all pyrite is, surprisingly, usually accurate within normal analytical error.

The masses of reduced sulfur in various reservoirs of the Earth's crust are listed in Table 1. Sedimentary rocks make up just 0.7 wt % of the continental crust but contain almost half the reduced sulfur, S(-II). Of these sedimentary rocks, shales contain over one third of the S(-II) in the continental crust. From the point of view of ASS source rocks, shales are by far the most important with 10x as high S(-II) concentrations as the average continental crust. Sedimentary pyrite formation, defined as pyrite where the sulfide moiety has been produced microbiologically, is at least 3.5 Ga old.

The most immediate sulfide source for many ASS is modern sediments. These have a mass of S(-II) equivalent to almost half that contained in sedimentary rocks. This S(-II) is derived from the activities of sulfate-reducing prokaryotes, mainly bacteria, which use sulfate to oxidize organic matter. Their abundance on the modern Earth is extraordinary and they oxidize half the organic matter reaching sediments (Jørgensen, 1982). They can be divided into two broad groups, the complete oxidizers that oxidize organic C to all the way to CO₂ and the incomplete oxidizers that typically produce acetate.

Table 1. Mass of reduced sulfur (S(-II) in Earth's crust, sedimentary rocks and sediments (Rickard, 2012).

	Mass x 10 ²² g	Conc S(-II) wt %	Mass S(-II) x 10 ²⁰ g
Continental crust	2090	0.04	84
Oceanic crust	553	0.096	53
Sedimentary rocks	144	0.3	40
Sandstone	36	0.2	7
Shale	72	0.4	29
Carbonate	35	0.1	4
Evaporite	1	0	0
Sediments	110	0.2	18

At the bottom of the thermodynamic food chain sit the methanogens, archaeans that are organisms more nearly related to us than to bacteria. These methanogens produce methane from the CO₂ and CH₃COOH left over by the sulfate-reducers. This is an important process because it partly explains why sulfide depth profiles in sediments are highly variable. The methane is oxidized anaerobically at depth by a synergistic consortium of sulfate-reducing bacteria and methanotrophic archaeans.

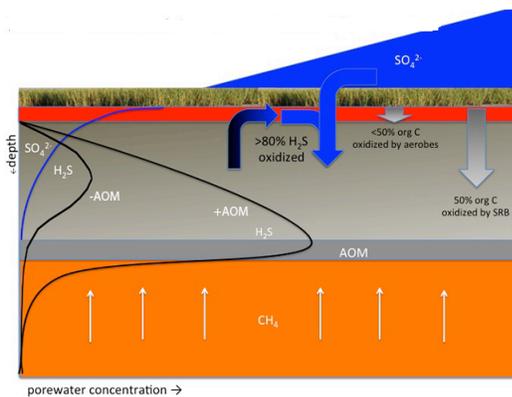


Figure 1. Elements of sulfide production in sediments with (+AOM) and without (-AOM) anaerobic oxidation of methane (AOM).

Egger et al. (2016) estimated that this process of anaerobic oxidation of methane (AOM) results in a fivefold increase in the amount of sulfide produced in the sediment. From the point of view of ASS, sulfide production in wetlands is of particular interest. Wetlands are the largest source of atmospheric methane and Segarra et al. (2015) showed that AOM results in a reduction in atmospheric CH₄ emissions of 50%. If we assume an average sulfate-reduction rate of 1-10 mmol S m⁻² d⁻¹ for a global wetland area of 5.9 x 10¹² m², this would suggest a global wetland sulfide production rate of 5 x 10¹² - 10¹³ g S a⁻¹. Most of this sulfide is immediately re-oxidized (Jørgensen, 1982) with less than 20% being fixed in the sediment as pyrite. Even so this results in the global burial of between 10¹²-10¹³ g S a⁻¹ equivalent to 1 - 15% of the total sulfide buried in marine sediments.

The major elements of pyrite formation in sediments are summarized in Fig. 2. Sedimented Fe oxyhydroxides have to penetrate a zone populated by Fe-reducing bacteria before reaching the sulfide zone. In the cases where mackinawite, metastable FeS_m , is precipitated, it dissolves rapidly where $\{\text{Fe(II)}\}\{\text{S(-II)}\} < 10^{-5.7}$ and Fe(II) is available for reaction to form pyrite. The sulfur reactant is $\text{S}_2(-\text{II})$, the most abundant polysulfide species, which has a significant equilibrium concentration in sulfide solutions. The re-oxidation of $> 80\%$ of the S(-II) produced by sulfur-oxidizing bacteria produces a cocktail of sulfur species with various oxidation states which are subsequently reduced again. Most of the pyrite formed is also re-oxidized and adds to the sulfur and iron cycle within the sediment.

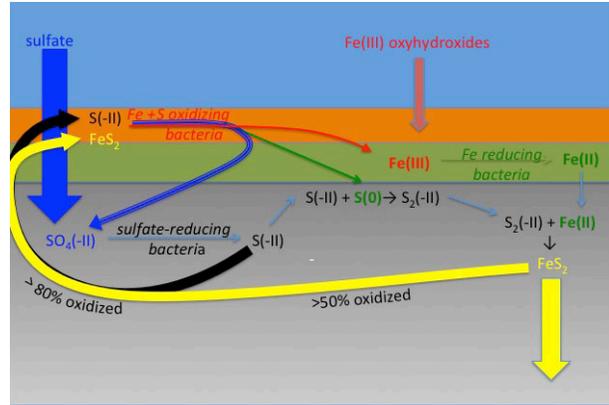
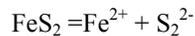
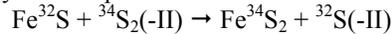


Figure 2. Elements of pyrite formation in sediments.

The key to pyrite formation is the extraordinary stability of the mineral with $K_{sp} = 10^{-24}$ at STP for the congruent dissolution reaction



The pyrite-forming reaction itself is a simple substitution reaction, as finally demonstrated by Butler et al. (2004) by isotopic tagging of S(-II) and $\text{S}_n(-\text{II})$ polysulfide species



The older idea of pyrite being produced by some magical transformation of metastable iron sulfides such as mackinawite, FeS_m , and greigite, Fe_3S_4 , to pyrite has been disproven theoretically, experimentally and in observations of natural systems where there is usually a distinct disconnect between rare metastable iron sulfide formation and abundant pyrite.

Pyrite oxidation provides a key element of the global biogeochemical sulfur cycle (Fig. 3) and is consequently a basic factor in the global carbon and oxygen cycles as well as the cycles of many nutrient elements and trace metals. The measurement of the concentrations of pyrite in ancient rocks, together with its variable isotopic and trace element compositions, is the fundamental variable on which much of our current knowledge about the geochemical and biological evolution of the Earth is based. And running these great biogeochemical algorithms forwards in time enables us to predict what the future holds for our successors.

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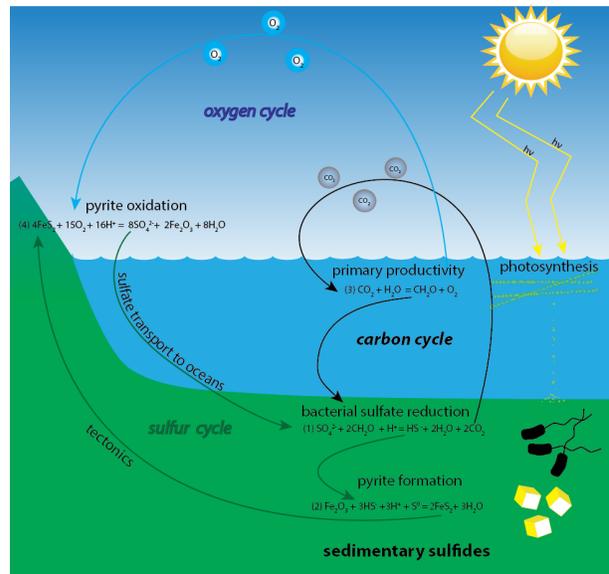


Figure 3. The sulfur biogeochemical and its relationship to the C and O cycles, with the relevant balanced chemical equations that are used in constructing quantitative secular algorithms for determining ancient and future Earth surface conditions (Rickard et al. in press).

A Passion for Iron Oxides – Personal Reminiscences of Professor Udo Schwertmann

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Prof. Udo Schwertmann was one of those few individuals who have the curiosity, vision, drive, and perseverance to substantially move a field of science forward. I had the good fortune of being a student with him from September 1977 through June 1982. This was an extremely productive time in his career and the Institut für Bodenkunde was an exciting place to be. Enver Murad, Walter Fisher, David Lewis, Reg Taylor, Nestor Kämpf, and Shelly Cornell were all in the lab at that time either as permanent scientific staff, visiting scientists, post docs, or Ph.D. students working on various aspects of iron oxide minerals. Other faculty, visiting scientists, graduate students, and under graduates worked on other aspects of soil and clay science, while several laboratory and field technicians kept the various projects on track. Prof. Schwertmann had the unique ability to inspire and motive all of us, and to make us feel that we were doing the most important work in the world. I will share some of my personal experiences from my time in Freising and of my interactions with Prof. Schwertmann over the succeeding years.

Bogus Soils! – Evidence for a Naturally Occurring Acid Sulfate Weathering Event in Northwest Indiana, USA

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At the end of the Wisconsin Glaciation about 15,000 years b.p. the Lake Michigan Lobe of the Laurentide Ice Sheet built a large, prominent end moraine in northwestern Indiana. Multiple lines of evidence indicate that this resulted in a post-glacial acid sulfate weathering event that still impacts the area today. The evidence includes: (1) soils in wetlands that became “unproductive black soils” when settlers drained them for agriculture, (2) soils with anomalously low base saturation that are classified into ultic subgroups in a region where typic subgroups are extensive, (3) arsenic concentrations in streambed sediments of the Kankakee River that are higher than other streams in the region, (4) a modern day “unproductive black soil” with a surface soil pH of 2.1, and (5) the presence of pyrite and acid sulfate weathering products (jarosite, and/or gypsum) in 8 of 18 specimens of shale pebbles and cobbles collected from 2 gravel pits in the area.

We propose that the acid sulfate weathering event was initiated when the Wisconsin Glacier eroded pyrite-rich sedimentary rocks and deposited the derbies in a large outwash fan south of the Valparaiso Moraine. Sorting by water depleted calcium carbonate-rich fine material relative to pyrite-rich coarse material. On the higher lying landscape positions, weathering of pyrite led to well drained soils depleted of Ca and Mg, and resulted in anomalously low base saturation. Calcium, iron and sulfate moved to lower lying landscape positions where reduction of iron and sulfate in wetlands resulted in the precipitation of secondary pyrite in the accumulating organic material. Extensive drainage of these wetlands in the late 1800s exposed the secondary pyrite to oxygen and initiated a second cycle of acid sulfate weathering that led to the unproductive black soils. In addition to low native K contents, these unproductive black soils also developed extremely low pH when drained, and some of these active acid sulfate soils exist today. Arsenic released from the original pyrite is still moving through the landscape, resulting in the higher than expected arsenic contents in the sediments in the streambed of the Kankakee River that drains the area. Thus, seemingly unrelated observations are all manifestations of a single natural phenomenon.

Regional controls on the formation of hypersulfidic soils and generation of extreme acidity in travertine mound spring discharge zones

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The iconic groundwater-dependent mound springs of Lake Eyre in the central arid zone Australia are host to unique ecosystems displaying a high degree of endemism. The springs are fed by deep groundwater from the Great Artesian Basin and many form travertine mounds as high pCO₂ waters degas at the surface. Spring flows have been decreasing over millennia as the interior has dried due to natural climate change. Superimposed on this slow decrease is a more recent rapid response to groundwater abstraction. The recent discovery of extreme acidification around some spring systems highlights a serious risk to the flora and fauna at these sites.

Abundant thick crusts of rare Fe- and Al-oxyhydroxysulfate minerals have formed under extremely low pH (pH < 0.5) conditions as sulfide present in discharge zones, built up over millennia, is now oxidising under lower flow and highly evaporative conditions. Minerals such as metavoltine, sideronatrite and ferrinatrite form in the most acidic upper soil layers, changing to natrojarosite and jarosite deeper in the profile. Very high Cr-reducing sulfur concentrations (> 40 wt. %) are present at depth along with very high net acidities (>25,000 mol/tonne H⁺). The presence of large travertine mounds and calcareous soils limit the spatial extent of acidification, but the unique ecological assets within discharge zones and spring tails are at a high risk of environmental degradation. In some regions, travertine mounds are not present in discharge zones, and salt efflorescences include Na carbonate and bicarbonate minerals such as trona and thermonatrite.

The key to acid sulfate soil hazard lies in regional variations of groundwater chemistry. The spring zone represents a complex discharge area above a major crustal fracture, the Torrens Hinge line, where groundwater from different parts of the basin converge. Water chemistry evolves along different flow paths controlled by water-rock interaction, strongly influenced by the degassing of CO₂-rich fluids from deep crustal fractures. Helium isotope evidence shows that at least some of the fluids are mantle-derived. Depending on depth of circulation, influence of deep fluid inputs, aquifer mineralogy and sources and sinks of S (mineral dissolution/sulfate reduction), the waters are of contrasting composition. Spring discharges and bore water in the east have very high alkalinities and are of Na-HCO₃ type with very low SO₄, and pose little risk of acidification. Those in the west contain moderate sulfate and alkalinity. The western groundwaters emerge through organic-rich soils, and over millennia this have caused a build-up of sulfide in the soils. The alkalinity is transported to the surface where it forms travertine, hence acidity and alkalinity are effectively fractionated at a local scale, and the stored acidity forms a locally high risk of soil and water acidification. There is thus an association between travertine mounds and hypersulfidic soils in the west, and very high alkalinity with no travertine formation in the east of the spring zone.

This study highlights a deep connectivity between the shallow critical zone and deep geochemical processes within the crust and upper mantle. This coupling of deep groundwater flow systems and mantle processes to surface ecosystems shows that biogeochemical cycles should be viewed in a much broader context to understand the dominant controls on Earth's chemical fluxes and geochemical hazards.

Geologic Testing for Land Disturbance: Acid-Base Accounting for Predicting Acid Mine Drainage on Surface Mines

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Acid mine drainage and acid sulfate soils are common consequences of disturbing geologic materials containing pyrite and other sulfide-bearing minerals. In order to predict the acid-producing potential of geologic layers, Acid-Base Accounting (ABA) was developed by researchers at West Virginia University. ABA is an analytical procedure that provides an assessment of the acid-producing and acid-neutralizing potential of overburden rocks prior to coal mining, highway construction, and other large-scale excavations. ABA provides techniques to measure the reactive sulfur content (which is converted to the acid-producing potential, Maximum Potential Acidity or MPA) and the reactive carbonate content (which is converted to acid-neutralizing potential, Neutralization Potential or NP). These two primary factors of ABA are used to predict the quality of drainage and soil quality by subtracting MPA from NP. If the MPA value is higher for the sample, the rock sample is predicted to produce acidic drainage upon weathering and leaching. If the number for NP is higher, the rock is predicted to produce alkaline drainage. Other parameters such as paste pH, electrical conductivity (EC), rock type and color help to refine the prediction and interpretation. Other techniques to predict drainage and soil quality involve simulated weathering or leaching tests, but these procedures are generally more time-consuming and costly. After the passage of laws requiring an assessment of surface mining on water quality, ABA became the preferred method to predict post-mining water quality, and permitting decisions for surface mines are largely based on the values determined by ABA. With this information, mining plans are developed which may include removal of acid-producing materials from the site, selective handling of these materials and placement in specific areas within the backfill, and amending these acid materials with limestone or other alkaline material. ABA has proven to be a good tool to evaluate overburden quality before disturbance and to provide values that can be used to mix or blend overburden materials during the mining and reclamation process. In one study, prediction of water quality from ABA was correct in 96% of the cases where pre-mining ABA data from actual surface mines were compared to the drainage quality from the site.

USDA Policy Concerns for Acid Sulfate Soils and Coastal Resources

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Legacy USDA policies for soil erosion, soil health, wetlands, agricultural reclamation, soil mapping and farmland protection have some potential for application to coastal protection and the recognized hazards of acid sulfate materials and dredging. However there are no specific or direct references for use, identification or reclamation of acidified soil material. Most of the interest in Acid sulfate soils is associated with dredged materials and the making and reclamation of “made land” from these materials. There is also some interest in urban development in the Coastal regions where deep landscape leveling has uncovered these materials in Coastal Plain cretaceous layers. Soil Surveys in USDA provide background information of land classification, combined soil properties (both estimated and measured), and land management classification that could be applied to these materials. Using soil security as a framework (capability, condition, capital, connectivity, codification), there is potential in a number of policy avenues with the US National Cooperative Soil Survey database and identification of acid sulfate materials and processes to address sustainability or climate change at local, regional, or global scale. The Soil Conservation districts in the US coastal regions have been exploring reclamation strategies with high pH/base amendments and encouraging the policy to keep it covered, saturated or buried as an alternative to high maintenance cost of amendments. Locally-led, incentive-based conservation program work strategies have been used by the Natural Resources Conservation Service in the U.S. as a successful model for getting things done. In addition, the USDA Farmland Protection Policy Act (FPPA) provides a model strategy to assure that federal programs are administered to be compatible with state, local units of government, and private programs and policies, and the Important Farmlands Mapping will work as well as a “programmatic” strategy to help identify and address resource concerns.

Keywords: acid sulfate soils; coastal systems; dredging; farmland protection

Acid Sulfate Soils in Northern Sweden

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Background

Many small streams along the coast of northern Sweden are periodically affected by low pH and high metal concentrations due to the occurrence of acid sulfate soils (AS-soils) in the drainage area. During Holocene sulfidic silt and clay was deposited at the floor of the Baltic Sea. These fine-grained sediments have in many areas been uplifted due to ongoing isostatic land uplift. AS-soils form when sulfidic reduced sediments (potential AS-soils) are exposed to oxygen, which primarily occur due to artificial lowering of the groundwater table.

The sediments were originally deposited at large water depths but also at more shallow bottoms situated in sheltered bays. In northern Sweden the magnitude of the isostatic uplift has been large (more than 200 m) since the disappearance of the last ice sheet. Vast areas with sulfidic sediments have consequently been uplifted above the present sea level. These areas are now situated in the lowest topographical parts of the landscape and are characterized by a groundwater table close to the surface. To obtain land favorable for cultivation and forestry the groundwater table has often been artificially lowered by ditches, which has prompted the development of AS-soils.

Methodology, fieldwork and analysis

During 2012 and 2013 the Geological Survey of Sweden (SGU) conducted fieldwork along the Baltic Sea coast in the counties of Västerbotten and Norrbotten in northern Sweden, during which AS-soils were documented by low resolution mapping. One aim of the documentation was to determine where AS-soils are distributed in the landscape in regards to land use, altitude and type of deposits. Another aim was to identify streams that may be, or have already been, negatively affected by AS-soils.

Land used for agriculture or forestry (commonly drained by ditches) were studied alongside unaffected wetlands to determine if AS-soils develop as a consequence of land use. Sites in transects from the coast to successively higher altitudes were studied to further understand the geographical distribution of AS-soils. Data that was used to identify areas where AS-soils and sulfidic sediments may occur are stated below:

1) Maps of Quaternary deposits were used to delineate areas with deposits associated with sulfidic sediments and AS-soils.

2) Chemical composition of plants from streams was used to indicate areas with high metal content due to leaching from AS-soils.

3) Shoreline displacement data was used to identify recently uplifted areas.

In situ measurements of pH were conducted to identify AS-soils in the field. Complementary laboratory pH measurements on field samples were done in order to examine whether some of the reduced sediments exhibited potentially acid characteristics when oxidized over a long period of time (several weeks).

Selected samples were analyzed for sulfur (S), carbon (C), metals and other elements by IPC-OES and ICP-MS.

Data from this study has been used together with other geographical information for modeling the distribution of AS-soils (Nguyen 2015).

Results

The results show that AS-soils and potential AS-soils can generally be recognized in the field. Most of the studied AS-soils were characterized by pH levels <4.0 and vertical soil fissures covered by rust, which sometimes are associated with the yellow mineral jarosite. The potential AS-soils are often characterized by a distinct black or dark grey color and a neutral pH which after incubation in the laboratory drops to values below pH 4.

The AS-soils occur in areas which according to SGUs maps of Quaternary deposits constitute clay and silt. Potential AS-soils also occur in areas where these sediments are covered by younger deposits, such as fluvial deposits or peat, which can prevent the formation of AS-soils. The results show that AS-soils mainly occur at sites situated in areas that have been uplifted during the past 5 000 years, as a

consequence of the land upheaval. The total area in which AS-soils in Norrbotten and Västerbotten, is assumed to be at least 600 km². This estimate does not take into consideration areas where potential AS-sediments are covered with younger deposits such as peat or fluvial sediments.

The low soil pH conditions have caused leaching of certain elements, e.g. nickel (Ni), cobalt (Co) and cadmium (Cd), from the studied AS-soils that may have reached surrounding waters. There is a correlation between drainage areas with a high proportion of AS-soils and negatively affected streams which is further reflected in the chemical composition of plants growing in the streams. This correlation has been investigated within earlier studies (Lax 2005).

The study by Nguyen (2014) shows that in areas with fine-grained sediments slope and ditches are the most important factors influencing the outcome of the AS vulnerability maps, i. e. AS-soils are commonly occurring in flat areas with ditches.

Discussion

The AS-soils are often underlain by potential AS-soils, which will oxidize if the groundwater level is lowered. Today the establishment of arable land is uncommon in Sweden and numerous farm lands have long since been abandoned. However, in many areas currently used for agriculture the groundwater table is lowered due to compaction of the AS-soils and oxidation of overlying peat. This causes exposure of sulfidic sediments to oxygen. Peat excavations and infrastructure projects may also expose potential AS-soils to oxygen.

The results of this study can be used as an aid to identify streams that are negatively affected by AS-soils, and will hopefully contribute to the identification of AS-soil hot spots, where measures can be taken to decrease the negative environmental impacts from these acid soils.

Further studies

Within two projects, partly financed by the European Union, SGU is currently documenting the occurrence and properties of AS-soils in selected drainage areas along the coast of northern Sweden. The projects are carried out in cooperation with the Geological Survey of Finland (GTK) to secure that AS-soils around the Baltic Sea are classified and investigated with the same methodology. An overview map showing the distribution of AS-soils around the Bothnian Bay will be produced, as well as more detailed probability maps for AS-soils in the selected drainage areas.

The two projects aim to reduce the negative impacts on water quality from AS-soils. Methods to decrease oxidation of sulfide minerals will be tested at sites where the groundwater table has been artificially lowered. By keeping the groundwater level as high as possible during dry periods the negative impact from the AS-soils will hopefully be mitigated. This method will be tested in selected agricultural lands and at a few sites restoration of wetlands will be implemented.

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Sulfide Distribution in Subaqueous Soil Systems

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Sulfidization, or the accumulation of sulfides, is an important soil forming process in estuarine subaqueous soils. Sulfide content is important in many ecological, use, and management aspects of these soils. For example, sulfides precipitate with a number of toxic metals, limiting the bioavailability of these metals. Sulfide contents in subaqueous soils $> 400 \mu\text{M}$ has been shown to have significant decreases in eelgrass productivity. If sulfide bearing subaqueous soils are dredged and placed in a subaerial environment, sulfides will oxidize, creating sulfuric acid, drastically lowering soil pH, and resulting in acid sulfate soils. Prior to 1992, Soil Taxonomy defined sulfidic materials based on sulfide and CaCO_3 levels. The definition has since changed to allow for the use of incubation pH as an alternative method for identifying sulfidic materials. The objectives of this research were to determine the distribution of sulfides in subaqueous landscapes and to evaluate sulfide levels in relation to other soil properties including carbon content, calcium carbonate content, soil texture, soil salinity, incubation pH, and soil salinity after oxidation with peroxide. Seventeen pedons were sampled from Cove, Drowned Channel, Fluvio-marine Bottom, Bayfloor, Mainland Shoreface, Spit, and Shoal soil-landscape units from three shallow estuaries in Rhode Island. Fifty-two soil samples were analyzed for acid volatile sulfides (AVS), chromium reducible sulfur (CRS), incubation pH, and salinity after oxidation with peroxide. Total sulfide measurements (CRS+AVS) ranged from $20 - 11592 \mu\text{g g}^{-1}$ with an average of $2965 \mu\text{g g}^{-1}$. In most cases, CRS represented nearly 100% of the total sulfides measured. Nearly half of all samples measured (47%) had incubation pH readings ≤ 4.0 , meeting the Soil Taxonomy requirement as sulfidic materials. Only two out of 17 pedons (7 of 52 soil samples) contained sulfidic materials as defined by sulfide content, while incubation pH measurements showed 11 of 17 pedons (27 of 52 soil samples) to meet criteria for sulfidic materials. Soils that reached an incubation pH ≤ 4 showed no significant difference in carbon content from those that had an incubation pH > 4 , and samples with higher incubation pH values had significantly higher levels of calcium carbonate than those with low incubation pH. Carbon content and particle size appear to be the two factors that were the most strongly related to the distribution of sulfides. Total dry weight of salts after oxidation with hydrogen peroxide showed a stronger relationship with total sulfides ($R^2=0.70$) than incubation pH ($R^2=0.19$). Sulfide content and incubation pH showed similar trends among landscape units with high sulfide levels, low incubation pH, and high carbon and calcium carbonate contents on low energy, silty landscape units.

Soil Description and Classification of Sulfidic Materials

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Since the advent of subaqueous soils a range of new descriptors and taxa have been added to standard methods for describing and classifying soils with sulfidic materials. In the 11th edition of Keys to Soil Taxonomy taxa were added to accommodate both mineral and organic subaqueous soils in the Entisol (Wassents) and Histosol (Wassists) orders. For subaqueous soils containing sulfides taxa were included at the great group level as Sulfiwassents and Sulfiwassists as well as Sulfic subgroups of Fluviwassents, Haplowassents, Psammowassents, Hydrowassents, and Haplowassists. The period of incubation pH for defining sulfidic materials was changed from 8 to 16 or more weeks. A subordinate distinction (se) was added to our horizon designation standards to identify mineral and organic soil horizons containing sulfides. The most recent USDA-NRCS Field Book for Describing and Sampling Soils (2012) now contains a section just on subaqueous soils with numerous references for describing soils with sulfidic materials. With the recent formation of a task force within the Soil Science Society of America to develop Fundamental Changes to Soil Taxonomy <http://casoilresource.lawr.ucdavis.edu/wiki/SoilTaxonomyTaskForce> now is the time to consider changes in the way soils with sulfides are classified. In this paper we will discuss and illustrate these additions to our standards and provide a forum to consider changes in classification relative to soils with sulfidic materials.

Variations in Actual, Sulfidic and Retained Acidity in Thai Acid Sulfate Soils

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Acid sulfate soils (ASS) in Thailand have been utilized over 140 years with agricultural management including drainage, liming and irrigated agriculture, particularly paddy rice cultivation and recently oil palm (Fig. 1). This management has resulted in the transformation of potential acid sulfate soils (PASS) to active acid sulfate soils (AASS) and eventually to post-active acid sulfate soils (PAASS) which are considered to be the mature stage of ASS. The classification of these three types of soils in this research is based on the definition by Fanning (2012). All three stages of ASS exhibit soil acidity. Worldwide acid sulfate soils (ASS) have been extensively drained and utilized for agriculture purposes (Auxtero and Shamshuddin, 1991; Yvanes-Giuliani et al., 2014), consequently PAASS will become the dominant form of ASS in many regions. Therefore, to facilitate management, it is necessary to better understand the nature of acidity of PAASS and their ASS precursors.

Eighteen sites representing PASS, AASS and PAASS in the Lower Central Plain and the Southeast Coast of Thailand, were investigated (Fig. 2). The complete suspension peroxide oxidation combined acidity and sulfur method (SPOCAS) was used to analyze acidity fractions including actual, sulfidic and retained acidity. Acid neutralizing capacity (ANC) was also measured (Ahern et al., 2004).

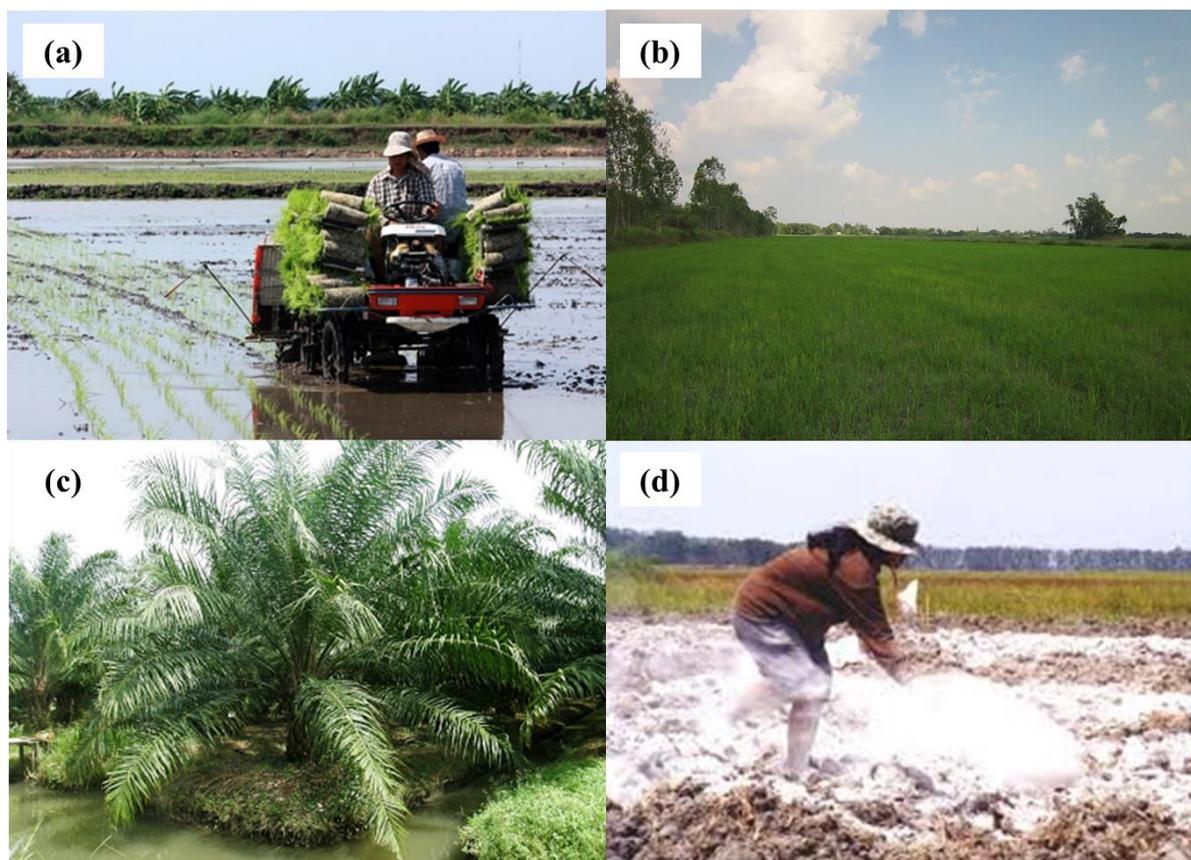


Fig. 1 Land use on Thai acid sulfate soils (a) (b) paddy rice cultivation, (c) oil palm and (d) liming before growing rice.

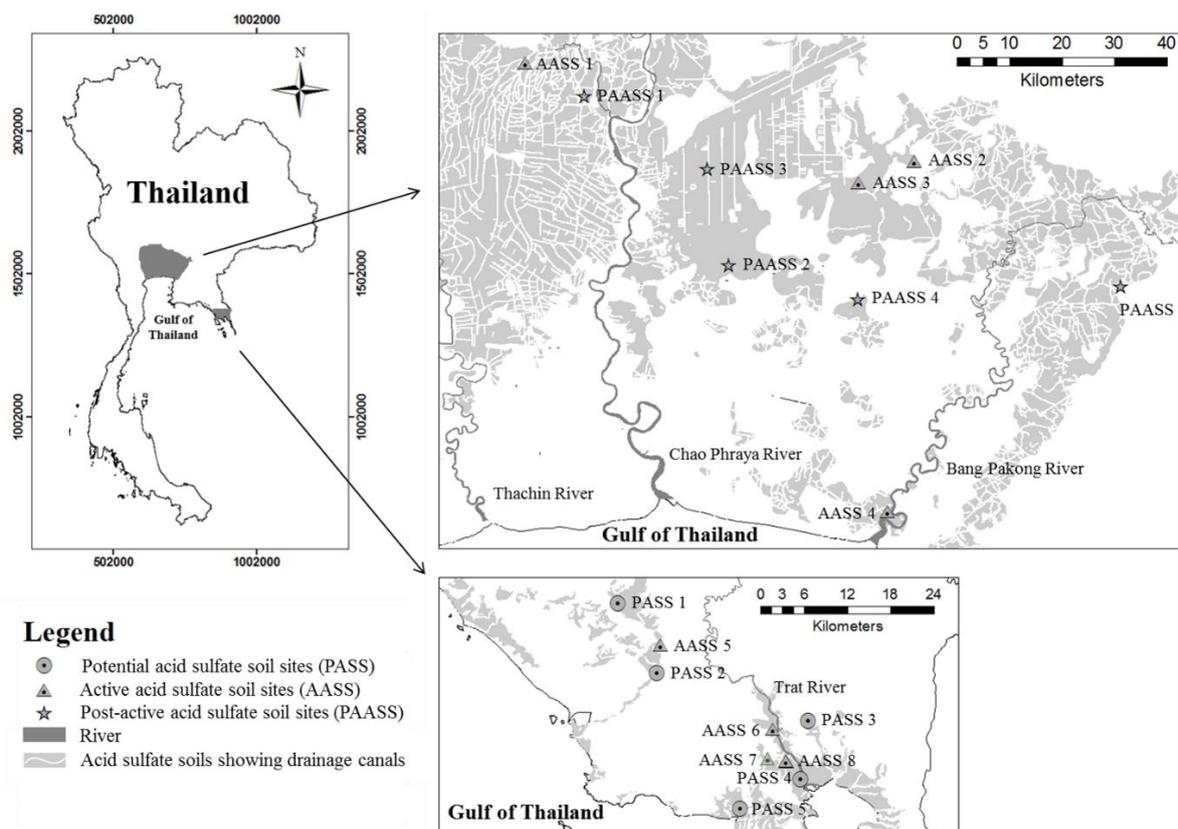


Fig. 2 Sampling locations for potential, active and post-active acid sulfate soils in the Lower Central Plain and the Southeast Coast regions of Thailand.

The result shows that most Thai ASS do not contain ANC due to the lack of carbonate minerals. The PASS and AASS contain higher amounts of sulfidic acidity than the critical level for management planning (300 mg kg^{-1}) (Stone et al., 1998). The PAASS contain smaller amount of this acidity because the soils have a longer history of management involving drainage and liming. The AASS contain higher amounts of actual acidity comparing to the PASS and PAASS. Jarosite is the major form of retained acidity being produced by the oxidation of sulfidic materials, especially in the partly oxidized layer of AASS. This indicates that the present management practices, involving drainage, liming and irrigated agriculture (e.g. periodic flooding for rice growing) on ASS can ameliorate their acidity.

Acknowledgement:

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Acid Sulfate Soil Regulation, Policy and Guidance in Australia: Status and Trajectory

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Introduction

Acid sulfate soil materials (ASSMs) are a subset of soil materials that have been widely recognized to present unique properties and associated hazards especially if mismanaged. A wide range of environmental hazards are posed by ASSMs including: severe acidification of soil and drainage waters; mobilization of metals; deoxygenation of water bodies, and; production of noxious gases, and; scalding (Sullivan et al. 2012).

Australia is comprised of a federation of states with environmental policy and regulation largely the responsibility of these provincial governments. Here I examine some of the different approaches being pursued by provincial governments in Australia to minimize the impacts of disturbing ASSMs during development e.g. major projects such as canal estates through to the installation of underground infrastructure. I then examine the directions in which I believe ASSM management regulation and guidance are moving in Australia including the development of comprehensive national guidance literature for ASSM management.

Planning instruments for ASSMs

The management of ASSM disturbance is commonly regulated through state-based planning instruments. This captures contemporary disturbance of ASSMs during developmental activity. ASSMs are specifically mentioned within some jurisdictional instruments such as in Western Australia in the Acid Sulfate Soil Planning Bulletin 64/2009 under the *WA Planning and Development Act 2005*. In other jurisdictions ASSMs are generally considered under either general environmental protection acts, or planning and approval acts.

At this time, Western Australia of all the states in Australia has, I believe, adopted and developed most of the best management approaches for ASSMs. In Western Australia, a whole-of-government approach to ASSM management has been adopted that utilises planning, environmental protection and groundwater licensing regulatory tools to control soil disturbance and groundwater dewatering in high risk ASSM areas. Indeed ASSM management issues were directly incorporated into the State planning process requiring developers in high risk ASSM areas to undertake soil and groundwater investigations in accordance with the state's best management guidelines to the satisfaction of the state regulator, before clearance for new developments will be provided.

Significantly, in Western Australia, sites inadequately managed for ASSM risks such that groundwater quality has deteriorated, need to have their groundwater quality disclosed to potential purchasers. Furthermore, such sites may be classified as 'contaminated sites' under the provisions of their state *Contaminated Sites Act, 2003*.

Scope of the regulations

In most jurisdictions regulations only apply to new developments. Only in Western Australia, under the Contaminated Sites Act, *in situ* ASSMs that have been previously disturbed and have elevated arsenic, aluminium and acidity in groundwater or soil above background concentrations, are considered contaminated land and must be managed as part of any future development.

Recommended laboratory analysis for assessment and management purposes

In Australia, the assessment and management of the acidification risk should ASSMs be disturbed is the main aim for management by regulators. The critical Net Acidity (Ahern et al. 2004) levels that initiate the development of detailed management plans, should acid sulfate soil materials be disturbed, vary according slightly between jurisdictions and are based on soil texture and the amount of soil disturbed. For sandy soil materials, and where large amounts of soil are to be disturbed, the critical Net Acidity level is $> 18 \text{ mol H}^+/\text{t}$ (Ahern et al. 2004). However current recommendations on the analytical methodology to be used vary between jurisdictions in Australia. Whereas most guidelines recommend the approaches detailed in the 2004 guidelines of Ahern, McElnea and Sullivan (2004) and use the Acid Base approach, the current guidelines of two states still refer to out-dated methods despite these methods having been 1) shown to be not fit for purpose, and/or 2) superseded by the 2004 Queensland guidelines. The 2004 guidelines represent best management practice and have been endorsed by the National Council for Acid Sulfate Soil (NatCASS), the peak national advisory group on ASSM issues.

Who approves or declines ASSM Assessment and Management Plans?

As ASSMs are most commonly regulated through the planning process, in many states the responsibility for assessing ASSM Assessment and Management Plans (ASSAMPs) falls to the local government sector (a level beneath that of the state governments). Only in 3 of the 8 Australian jurisdictions - Western Australia, South Australia and Northern Territory - are the majority of plans assessed by state and territory regulators. In some states the clear delineation of roles in this task is still under development. In Queensland the state government devolved in 2012 its responsibility for assessing ASSAMPs to the local governments.

Level of detail required in ASSAMPs in different jurisdictions

For developments of comparable nature, the level of detail required in ASSAMPs to gain consent varies markedly between jurisdictions. Whereas the management aspects within ASSAMPs in some jurisdictions requires comprehensive detailing of e.g. strategies selected and their rationale, performance criteria, monitoring and reporting procedures, contingency procedures, coverage of dewatering practices verification testing procedures, etc., such a level of information is not required to be provided in ASSAMPs in other jurisdictions in order to gain development consent. Such wide variation in the level of effort required to gain development consent for ASSM-containing sites has raised widespread concern as to whether the level of protection afforded by planning instruments against deleterious ASSM-related impacts, is uniformly adequate across jurisdictions.

Trajectory

As shown, there are considerable differences in how ASSAMPs are assessed, managed and regulated across jurisdictions, especially with regard to the level of effort required to gain development consent. The national government with the full co-operation of the state jurisdictions is currently developing a national approach for technical guidance across a range of ASSM assessment and management issues, partly to ensure that an adequate level of effort is required before gaining development consent. The national guidelines being developed currently include: Sampling of ASSMs; ASSM Laboratory Analysis; Monosulfidic Black Oozes, and; Dredging of ASSMs. It is recognised that these national guidance documents will be necessarily broad as jurisdictional differences in geographical, legislative, and regulatory landscapes will continue to require jurisdiction-specific guidance approaches at a more detailed level. Despite these differences the appropriate assessment and management of ASSMs needs to be ensured, and in this regard, the developing national guidance documentation will undoubtedly assist in setting national best practices for the management of ASSMs within all of the Australian jurisdictions.

Assessment for environmental risks associated with ASSM disturbance other than acidification are increasingly being included in ASSAMPs, even though the methodology for assessing the likely risks of deoxygenation and metal mobilisation arising from future ASSM disturbance still require development and/or adoption. One recently developed is Claff et al.'s (2010) sequential extraction procedure that has been shown to provide valuable information on the potential for mobilisation of metals under differing management scenarios (Claff et al. 2011).

Should severely affected ASSMs be considered “contaminated soil”?

Accepted national regulatory definitions of contamination include – *“the condition of land or water where any chemical substance or waste has been added as a direct or indirect result of human activity at above background level and represents, or potentially represents, an adverse health or environmental impact”* (NEPM 1999). The term ‘added’ in the definitions refers to “increase in size, number or quantity”. I believe it can be successfully argued that, at the geochemical species level (i.e. the level appropriate for assessment of contamination), in e.g. severely acidified ASSMs, the *increase in the quantity* of many toxic chemical species (e.g. Al³⁺ or As(III)) by e.g. acidity-driven dissolution of clay particles, fits squarely within the definitions of ‘contamination’.

As in many countries in Australia the management of contaminated land or soil is more strictly regulated than the management of ASSMs. For example in Australia, contamination laws are closely observed and enforced by the threat of severe fines and imprisonment. As mentioned previously, only in Western Australia are ASSMs considered (when severely degraded) to be contaminated soil materials. To me this poses a fundamental question as to whether the evident successful management of ASSMs in Western Australia using contaminated land regulatory instruments could be used as a guiding precedent to govern the management of severely degraded ASSMs in other locations, both within and outside of Australia? And if so, then under what conditions?

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Mesocosm Studies to Identify Potential Acid Sulfate Soils and Develop a National Cooperative Soil Survey Interpretation

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The National Cooperative Soil Survey is currently developing a soil interpretation for land utilization of dredge materials. The intent of the interpretation is to provide resources such as maps and tables to assist in achieving best environmental practices to support management decisions regarding coastal resources. This interpretation is being based on our Coastal Zone Soil Survey investigations. One objective of these investigations is to identify sulfide bearing subaqueous soils and those with the potential to create acid sulfate soils if dredged and placed on the land surface. Before now, little soil survey attention was placed on identifying soils with the potential for oxidation of sulfide-rich materials and the subsequent implications related to extremely low pH values (< 4.0), metal toxicity, and creation of salts of dredged material. In this study, we simulated the dredging and upland placement of subaqueous soils to determine if subaqueous soil type controlled their impact when placed in the subaerial environment. A mesocosm experiment was used to simulate upland placement of marine dredged material. Dredged materials were sampled to 25 cm from a range of subaqueous soil-landscape units of two embayments and two coastal lagoons in New England. Higher energy soil-landscape units included Mainland Shoreface, Spit, Washover Fan, and Flood Tidal Delta. Lower energy environments included Lagoon Bottom and Cove soil-landscape units. Simulated dredged materials were placed outside into mesocosms to allow them to be exposed to natural climatic conditions and precipitation. Mesocosm leachate was analyzed for pH, conductivity and sulfate content over a two year period. Dredged materials ranged from sand to silt loam textures with increasing percent carbon and calcium carbonates with increasing fineness of the material. Inorganic sulfide concentrations ranged from 6 – 3411 µg/g, with an average of 1303 µg/g. Embayments had higher concentrations of inorganic sulfides than coastal lagoons. Lower energy environments (Bottom and Cove landscape units) dredged materials classified as sulfidic materials. The four most common heavy metals observed in the dredged materials were lead, copper, chromium, and zinc. Mesocosm leachate showed two trends. Leachate from finer textured dredged materials from low energy landscape units showed a large drop in pH (pH ≤ 4.0) associated with sulfide oxidation and creation of acid sulfate conditions. These conditions persisted for the duration of the experiment, while leachate from coarser textured materials of high energy landscape units increased in pH to > 8.0. Salts washed out of the dredged material fairly quickly such that leachate reached conductivities of <5 dS/m in 10 months. Leachate sulfate content was initially high following dewatering of the mesocosms but decreased afterwards. Leachate sulfate content from finer textured materials was higher due to high levels of sulfides found in these soils. Sulfate content also spiked during summer months, due to increased temperatures, oxidation, and microbial activity. In the second year of the study, selected materials from the higher energy landscape units were mixed with those that contained sulfidic materials. Results from the mixed mesocosm experiment suggest that as little as 5% of fine textured material (Sulfiwassents) may influence the extent and duration of the development of acidic conditions. To help better manage coastal areas, accurate subaqueous soil surveys and a specialized soil interpretation for land utilization of dredge materials would allow managers to dredge certain areas accordingly. These tools would provide coastal resource managers with a means to assess the beneficial uses of the dredged spoil. While dredge materials may provide a resource that is varying in texture and chemical properties (such as carbon), caution must be taken to manage them accordingly and separately from one another due to the development of acid sulfate conditions, potential to leach heavy metals, and high salt content.

Use of National Soils Information System (NASIS) to Query Soils at Risk for Acid-Sulfate Formation in Dredged Materials

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Use of dredged materials from shallow marine and estuarine waters can result in failed or compromised infrastructure, limited plant growth and detrimental soil and water quality issues. By identifying soils with reduced monosulfides and low oxidized pH in a corporate database, interpretations can be developed that successfully identify dredged materials at risk for acid sulfate formation. Iron monosulfides (FeS) are often associated with organic-rich estuarine sediments that oxidize rapidly when exposed to oxygen. Oxidation pH is used to test for the presence of sulfidic material in these sediments and to predict the occurrence of sulfuric horizons. It is an indicator for potential acid sulfate soil formation. The addition of a reduced monosulfide indicator in the NASIS database has allowed soil scientists to identify spatially which subaqueous soils are at risk for acid-sulfate formation if dredged and exposed to air. Presently, a draft NASIS interpretation has been developed that queries the occurrence of the reduced monosulfide indicator in a horizon or layer within 2 meters soil depth. A discussion on criteria refinement will be presented.

The Coastal Zone Soil Mapping Initiative

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USDA, Natural Resources Conservation Service

The U.S. Department of Agriculture's Natural Resources Conservation Service (NRCS) is in the initial planning phase of conducting an inventory of soil resources and ecological sites along our nation's coastal zone. The work will be conducted under the umbrella of the National Cooperative Soil Survey (NCSS) partnership.

The concept of gathering resources inventory in the coastal zone is not revolutionary but rather evolutionary. NCSS soil survey work and ongoing research by universities since the 1990s have developed considerable advanced mapping and classification protocols in coastal zone areas. They have even provided some new official update soil survey information along the coast, but not nearly the extent or volume of information that is truly needed.

The Coastal Zone Soil Mapping Initiative will include nearshore or subaqueous soils along with adjacent terrestrial soils including upland tidal marshes or barrier beaches. Like terrestrial soil surveys, these areas are best inventoried using procedures and protocols established by the NCSS. This soils resource inventory will provide valuable information for a better understanding of the distribution, occurrence and behavior of acid sulfate soils in the coastal zone. State-of-the-art soil interpretations and ecological site information will be developed to accompany the coastal zone soil survey, providing important information for NRCS programs, partners, and the public.

The Rhode Island Mapping Partnership for Coastal Soils and Sediment - RI Coastal Zone Soil Survey

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The MapCoast Partnership began in 2004 when the Natural Resource Conservation Service (NRCS) approached the University of Rhode Island about establishing the institutional framework needed to begin to map, inventory, describe, and classify coastal soils and sediment in Rhode Island and New England. The MapCoast partnership brings together groups and individuals who recognize the importance and need to collect more detailed soil and sediment data for coastal marshes, dunes, inter-tidal flats, and shallow water habitats (to approximately 5 m of water). MapCoast partners recognize that map data and attributes for coastal and shallow water soils (subaqueous soils) and sediment are essential for management and protection of these vital coastal ecosystems.

CHARACTERIZATION AND CLASSIFICATION OF ACID SANDS OF EGBEADA SOUTHEASTERN NIGERIA, WEST AFRICA

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ABSTRACT

A soil survey covering Egbeada in Mbaitoli Local Government of Imo State was conducted. The prime objective of the soil survey was to determine the soil characteristics for the purpose of classifying the soils. Free survey technique was used aided by topographic map of the area. Three profile pits were excavated on different topographic positions (Upper slope, Middle slope and Lower slope) represented as pedons 1, 2 and 3 respectively. Soil samples were collected and subjected to routine and standard laboratory analysis. The results of the finding revealed that sand particles dominated other particles. The surface soils have sand fraction of 83%, 84% and 81% for pedons 1, 2 and 3 respectively. The texture of the top soil varies from loamy sand to sandy loam while the subsoil is predominantly sandy clay loam. Bulk density was slightly higher in soils of pedon 2 (1.70g/cm^3) and pedon 3 (1.71g/cm^3). All the pedons are acidic and highly leached due to high rainfall. The soils were generally low in chemical properties particularly TN, available P, exchangeable bases and organic matter. The soils of pedon 1 and pedon 2 were classified as Typic Paleudults according to USDA soil taxonomy system and correspond to Dystric Nitisols in the WRB system while soils of pedon 3 were classified as Aquic Udipsamments (USDA) and correlated with the World Reference Base for soil resources (WRB) as Gleyic Fluvisols. Based on the study, the soil of these pedons can be used for sustainable agricultural production, if proper land use management and crop options are adopted. Keywords: Characterization, Classification, Topography, Egbeada, Imo State.

A Review of Research Conducted on Aquaculture on Acid sulfate Soils in the Philippines

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A review of researches on aquaculture of acid sulfate soils conducted in the Philippines was made. These researches started from the occurrence of fish kill on the newly opened brackish water fish ponds of the University of the Philippines at Visayas in Leganes, Iloilo. The fish kill was attributed to the fishpond being on acid sulfate soils. Brackish water fishponds occupy about 15,000 – 18000 hectares in Panay Island, Philippines alone whereas the total extent of acid sulfate soils in the Philippines is about 500,000 hectares. Even as early as 1977, a test for acid sulfate soils had been developed. The test consists of determining the pH of a soil that had been incubated for 30 days. If the pH dropped to 4, then the soil has large reserve of acidity or is an acid sulfate soils. Fishponds on acid sulfate soils were found to have poor response to P fertilizer application. This is due to high P fixing capacity of the soil. It was found that on acid sulfate soils, the most common form of fixed P are Al- phosphate, Ca-phosphate and Fe-phosphate. P use efficiency is also low on fishponds on acid sulfate soil. The high P fixing capacity can be remedied by applying P in small quantity per application and in preventing P fertilizer contact with the soil using platforms where fertilizer in bags were placed in platforms and dissolved in water by wind and current effects. Lime levels determined using lime requirement determination for agriculture overestimate the amount of lime needed for fishponds. It was found the for soils with high acidity, the lime level resulting from lime requirement determination for agriculture can be increased, whereas for those with less acidity the lime level can be lower than the requirement. Leaching studies showed that the acidification on pyritic soils is due to pyrite oxidation and production of sulfuric acid. Increasing oxidation or number of leachings decreased the pH and increased the solubility of Al and Fe, decreased the availability of Fe and causing the loss of Ca, Mg, Zinc and Cu. A method for preparing acid sulfate soils for aquaculture or for remedying acid sulfate soils will be thoroughly discussed in the paper.

Oxidation of iron sulfides in subsoils of cultivated boreal acid sulfate fields – an examination based on soil redox potential and pH measurements

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Acid sulfate (AS) soils in Finland are mainly formed on the bottom of the ancient Litorina Sea. Since then isostatic land uplift has resulted in the expansion of land area on the coast of the Baltic Sea by 50100 km² in Finland. Depending on the criteria, at least 600 to 1300 up to 3300 km² of that are cultivated AS soils (1, 2). These soils have gone through several anthropogenic processes such as reclamation of AS soil marshes into arable land by burn clearing, draining and poldering. These measures have initiated the sulfuricization of soils. In addition, natural processes such as evapotranspiration particularly in exceptionally dry summers lower the groundwater table of the fields deeper than drainage alone and also cause sulfuricization, acid discharge pulses and hazards to the aquatic ecosystems of the recipient waters. Major fish kills have been reported as early as in 1834 and most recently in 2006.

Sulfuricization is initiated by the oxidation of sulfidic materials by oxygen. This process is accelerated when microbially catalysed oxidation by ferric iron begins in acidic conditions. Such conditions are not prevailing in the neutral or nearly neutral subsoils which commonly contain the largest pool of sulfides. However, nitrate reduction to N₂ (g) or NH₄⁺ coupled with the oxidation of sulfidic materials has been reported in circumneutral aquifers (3), wetlands and brackish sediments (4). Sulfide-induced nitrate reduction was suggested to occur also in subsoils of boreal AS fields based on redox equivalent calculations (5). In this study reactions that might cause sulfuricization were explored by using theoretical redox ranges and a large data set of soil pH and redox potential at different soil profile depths on cultivated Finnish AS fields.

The data of this study originates from a profound field drainage survey (2), from which the fields meeting the criteria of *Typic Sulfaquepts* or *Sulfic Cryaquepts* (1) of Soil Taxonomy were selected. Nearly all fields had been cultivated more than 30 years. If subsurface drained, preceding drainage had been open ditch drainage. Some fields were subsurface drained already before the 1940's. The clayey AS fields (n=9, clay 30-65%) were subsurface drained whereas among the silty AS fields (n=48) part of them was drained by open ditches or some had a sufficient natural drainage to allow cultivation.

During the survey, soil pH and redox potential (E_h) had been measured *in situ* on each field from two soil profiles every 10 centimetres down to the depth of two meters. The measurements were depicted in E_h-pH diagrams with the lines for dissociation of water to H₂ (g) or O₂ (g), a stability line for nitrate reduction to ammonium, as well as lines for reduction of iron and sulfate (6, 7).

In clayey AS fields, reducing conditions were found closer to the soil surface than in silty AS soils. In clayey AS soils at the depth of 100 cm the soil redox status of most profiles was in the range of iron reduction, while it was in the nitrate reduction range in four profiles, in sulfate reduction range in two profiles and in only one profile Fe³⁺ was dominant dissolved iron species (Fig. 1a). In all clay fields at the depth of 200 cm the soil redox status was in the iron or sulfate reduction range (Fig. 1 b). Quite differently, in silty AS fields the redox status at 100 cm was mostly in the nitrate reduction range (Fig. 1c) and at 200 cm the redox status was still in the nitrate reduction range in five profiles and redox status was favouring iron reduction in the majority of the profiles (Fig. 1d).

According to our findings the redox status in subsoils of AS fields is related to soil texture. This is in agreement with findings that clay soils have more redox capacity than coarser soils (8) and therefore also higher poise. In addition, the structure of clayey subsoils is commonly massive and therefore the air entry value is higher than that of coarser silty soils (9). Consequently, oxygen is able to penetrate into silty soils more easily than into clay soils when groundwater table drops. Furthermore, the saturated hydraulic conductivity of clay soils is much lower than that of silty soils, thus the transport of oxidizing solutes, such as nitrate, is faster in silty than clay soils. These physical features may cause the difference in the depth of reducing layer between AS soils with different textures.

These findings suggest that nitrate might assist the oxidation of sulfides and contribute to sulfuricization. On the other hand, the high nitrate concentration of the discharge waters from AS soils (10) does not support the idea of abundant consumption of nitrate by reduction coupled with the oxidation of sulfides in subsoils above the drain pipes. However, in the study referred above shows that there is nitrate available for the oxidation of sulfides below the drainage depths, and that the reduction of nitrate coupled with the oxidation of sulfides can occur even deeper. That would be in accordance with the findings that sulfides oxidation coupled with reduction of nitrate occurs below redox interface (8) and the findings that the subsoils of Finnish AS fields contain high NH₄⁺ pools (11).

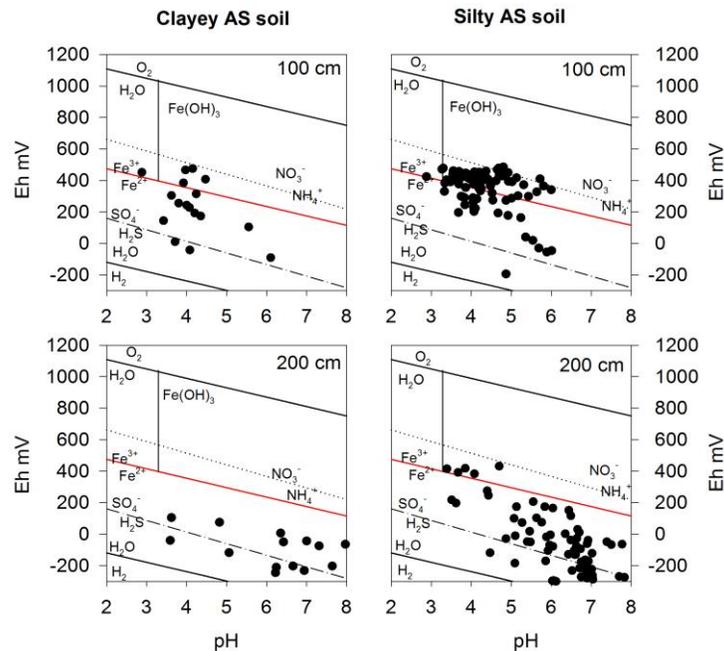


Figure 1. E_h and pH in clayey and silty AS fields at 100 and 200 cm below soil surface. Dissociation of water to H_2 (g) or O_2 (g), theoretical lines for NO_3^- reduction to NH_4^+ and SO_4^{2-} reduction to H_2S/HS^- , line for Fe^{2+}/Fe^{3+} as well as empirical line for Hydric Soils (red line). In the diagram the lines indicate equal activities of dissolved species.

It is commonly known that redox potential of soils is spatially and temporally highly variable, and the empirically measured values may be influenced by multiple oxidizing and reducing agents. Therefore, the theoretical values may differ from those in the fields. However, this examination, which is based on large data of AS soils, shows that sulfurization coupled with reduction of nitrate might exist particularly in silty AS soils. Our findings highlight the need of further studies on this issue also with other methods.

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An Inventory of Sulfidic Materials in the Subaqueous Soils of the Rhode River Estuary

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Sulfidic materials, while common in the subaqueous soils of mesohaline aquatic environments, are not ubiquitous. It is important to understand their distribution and the magnitude of potential sulfurification that they can undergo for a variety of management interpretations including dredging, and construction of shorelines and nearshore structures. These activities can disturb sulfidic materials and result in their deposition in areas where they may undergo sulfurification (Rabenhorst and Stolt, 2012). Fisheries and aquaculture activities such as tonging or dredging for bivalves may also disturb sulfidic materials, allowing them to oxidize in a process that can reduce the level of dissolved O_2 in the water column, with negative effects on the aerobic organisms that live there (Holmer et al., 2003).

The Rhode River estuary is a subestuary of the Chesapeake Bay located along its western shore near Edgewater, MD. Several submerged land leases have already been approved by the U.S. Army Corps of Engineers Baltimore District and the Maryland Department of Natural Resources Aquaculture Division for private aquaculture operations within the estuary. The estuary is also home to several marinas and many waterfront homes, and the extensive shoreline and marine construction associated with them. Consequently, an understanding of the distribution and types of sulfidic materials in the Rhode River estuary is of great interest to local scientists and policy makers.

The bottom of the Rhode River estuary was once described in a National Ocean Service hydrographic survey report as “soft silt...such that a man will sink 1’ or 2’ while walking in it” (Austin, 1972). While certainly true for large areas of the estuary, this is an oversimplification that overlooks the great diversity of landforms and subaqueous soils within this landscape (Figure 1). While the presence of monosulfides was confirmed by color change with 3% H_2O_2 in nearly all of the 71 pedons collected and described, the recognition of sulfidic materials was more complex. Moist aerobic incubations were completed on every horizon of 25 pedons representing the range of soil properties observed in the estuary.

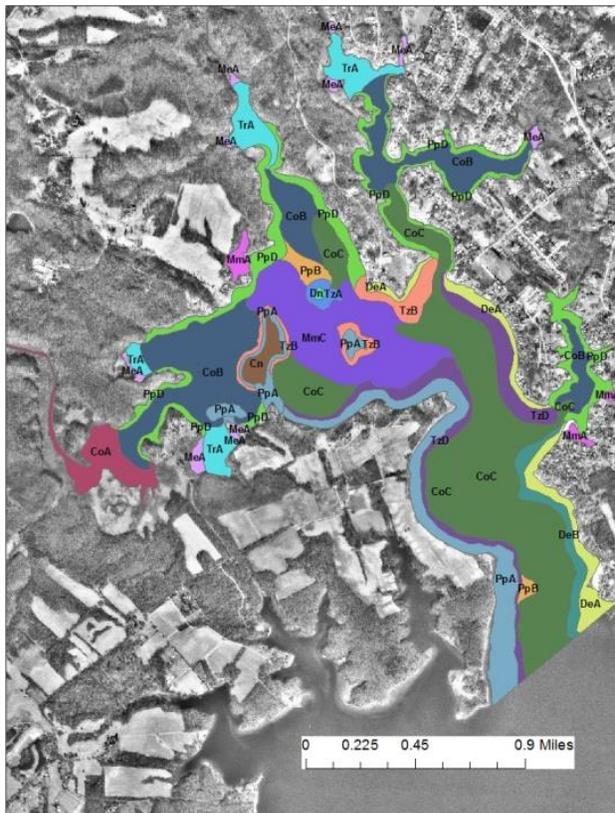


Figure 1. A subaqueous soil map of the Rhode River estuary. Soils in these map units differ in their propensity to become acidic under oxidizing conditions.

Psammowassents, even those without visible shell fragments, tended not to qualify as sulfidic materials according to the definition used in *Soil Taxonomy* (United States NRCS, 2014). Some of these materials maintained a pH above 7 throughout the incubation (Figure 2), and therefore do not qualify as sulfidic materials of any sort; however, some of these did exhibit a color change upon the addition of 3% H₂O₂ and received the “se” suffix symbol. Many of the soil materials, with textures ranging from coarse sand to silty clay loam, exhibited drops in pH from above 8 to 4-7 (Figure 2). Some of these samples contained visible shell fragments, but many did not. These materials all underwent some degree of sulfurization but were either well buffered or had a lower concentration of oxidizable sulfides. Samples with visible shell fragments were buffered at least in part by that reserve of CaCO₃, but other buffering agents may have included clay minerals, organic matter, or shell fragments too small to see. These buffered soil materials therefore were considered to be hyposulfidic materials (United Nations FAO, 2015) which are not explicitly identified in *Soil Taxonomy*.

Most of the soil materials in this survey that met the definition of sulfidic materials used in *Soil Taxonomy*, and that would be identified in other taxonomic systems as hypersulfidic materials, consisted of buried marsh surfaces and underlying submerged upland soils that developed in glauconitic pre-Holocene sediments, including the Eocene aged Nanjemoy Formation. Evidence for the presence of submerged upland materials includes easily observable root fragments and distinct or prominent iron concentrations in the subsoil. One sample from a paleosol with a bright matrix color of 7.5 YR 4/3 was violently effervescent when treated with 30% H₂O₂. Upon moist aerobic incubation, some of these materials dropped to a pH below 4 and some of the buried A and O horizons dropped to a pH between 2-3 (Figure 2). Sulfidization in the A and O horizons is likely occurring in the present environment, but the origin of the sulfides in the submerged upland subsoil horizons is less certain. It is unknown whether these sulfides formed recently following submergence of these soils, or whether these soils contained relict sulfides accumulated at the time of their deposition as Eocene or Paleocene marine sediments.

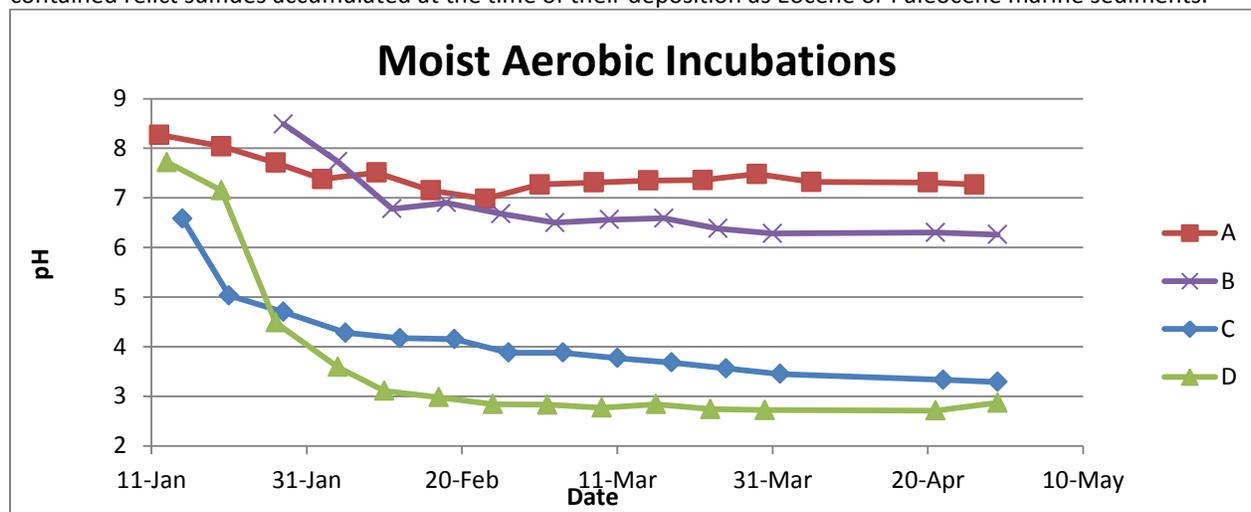


Figure 2. Soil pH over time during moist aerobic incubation of four subaqueous soil materials. A) Psammowassent sand, B) channel deposit silty clay loam, C) submerged upland subsoil sandy clay loam, D) buried A horizon loamy sand.

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IDENTIFYING ACID SULFATE SOIL UNIT BOUNDARIES USING BASIC IMAGE TRANSFORMATION ON MULTI-RESOLUTION SATELLITE IMAGERIES

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The development of Acid Sulfate Soil (ASS) mapping has been involving remote sensing imageries to identify landscape units that represent the sites of ASS occurrences. However, there have not been many studies which examined the relationship between their spectral characteristics and the ASS properties on multi-spatial resolution satellite data in relation to ASS unit boundaries determination. This study examines the function of basic image transformation using spectral rationing to identify the ASS unit boundaries on Landsat ETM+, ALOS AVNIR-2 and QuickBird® imageries. Landform unit boundaries identification using visual interpretation on those satellite imageries was conducted to provide a landform unit reference which was compared to the one from spectral rationing. Field and laboratory soil analysis are undertaken to identify the soil physical properties in each landform units.

The result shows that after conducted several spectral rationing trial, the band ratio of b3/b4 presents the most similar boundaries to the one from visual interpretation. Using this boundaries, soil sample were taken using stratified random sampling method. The statistical analysis shows that there are significant correlations between the soil properties and the spectral information from rationing process (r value more than 0.79). The brightness levels shown on the spectral rationing values present negative relationship to the presence and absence of ASS (-0.68). This study also reveal the prerequisite needed in choosing the imagery for ASS mapping purpose, such as: time of acquisition (seasons), imagery correction, and scale and resolution knowledge. All the information delivered in this study provide significant contribution on the rapid assessment of ASS mapping for sustainable coastal resources management.

Acid sulfate soil characteristics on the wave-dominated estuaries with pre-existing barriers in the south coast of Central Java

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The development of an estuary classification scheme for Central Java is an important component of a broader study on mapping the distribution of acid sulfate soil (ASS). Preliminary result shows in the wave-dominated estuary class, some of the rivers are blocked by hilly landforms just before they discharge into the sea. This uncommon estuary type is described as a wave-dominated estuary with pre-existing barrier, which has not been identified in previous Indonesian estuary classification schemes. This geomorphic condition creates some low energy environments that sufficient for pyrite to develop. The aim of this study is to identify the presence characteristics of ASS in this scarce estuary type. This research method uses multi-level remotely sensed imagery to identify the low environment areas in conjunction with field surveys. Field and laboratory soil analysis are undertaken to identify the soil physical properties in each hydro-geomorphological units and to understand the soil forming processes.

The result show that the pre-existing barrier is actually a complex hilly landform that predominantly comprise of calcareous materials. Howeverm this carbonate content material didnt influence the presence of the ASS. The material accumulated surround this hill is characterized by low, moderate and high energy environments thus forming different soil environments upper catchment. The field and laboratory analysis present that the the compex energies controlled by dry and rainy seasons that form the estuary influence the formation of the pyrite shown by different content of pyrite in different layers of horisons but in a certain pattern, ranges from 0-2%, 2-4% and above 4%. This study conclude that ASS characteristics can be predicted from understanding the energy responses to various barrier conditions in wave-dominated estuaries. This study is also adding to the understanding of coastal evolutionary processes in Central Java.

Keywords: acid sulfate soil, estuary classification, geomorphology unit, wave-dominated estuary with pre-existing barrier

Coal seams, peat swamps and acid sulfate soils – where does the acidity come from? A case study from southern Australia

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Introduction

Globally, coastal and estuarine floodplains are frequently underlain by sulfidic material. Similarly, sulfidic material can also be found in inland wetland and swamp environments, and in conjunction with coal and metalliferous deposits. When these materials are exposed to oxygen, such as a result of changes in water levels from drainage or drought or stockpiling of spoil, sulfidic material oxidises to form acid sulfate soils, adversely impacting on floodplain health and adjacent aquatic ecosystems. In eastern Australia, our understanding of the formation of coastal and estuarine floodplains, and hence, acidification potential of acid sulfate soils, is relatively well established. However, our understanding of the evolution of estuarine systems and acid sulfate soil formation in southern Australia and hence, sources of acidity, remains limited.

Case Study

The Anglesea River, located approximately 115 km SW of Melbourne in southern Australia, is subjected to frequent episodes of poor water quality and low pH resulting in closure of the river and, in extreme cases, fish kill events. The Anglesea River catchment contains sulfidic coal seams, coastal acid sulfate soils (CASS), inland acid sulfate soils (IASS) and sulfidic peat swamps. An open cut brown coal mine, which was recently closed in August 2015, dominates the catchment. Poor water quality has been linked to acid leakage from mining activities and Tertiary-aged coal seams in the upper catchment, and peat swamps and acid sulfate soils in the region.

The Anglesea River estuary, and other estuaries in this region, crosses the iconic Great Ocean Road, and therefore, closure of the estuary to fishing and other recreational activities directly impacts on the local economies. While some preliminary studies have been undertaken in the past (Fitzpatrick *et al.* 2007), our understanding of the sources of acidity and distribution of acid sulfate soils in this region remains poor.

Four sites on the estuarine floodplain, representative of the main vegetation communities in the lower catchment, were sampled. An additional seven sites located in the tributaries (Salt Creek and Marshy Creek) in the upper catchment of the Anglesea River were also sampled.

We found that the potential for acidification on the estuarine floodplain varied. Sites located on the lower estuarine floodplain had a higher acid neutralising capacity due to the presence of seawater and shell materials, which provided up to 10.65 % CaCO₃-e, resulting in negative acid generation potential. Sites located further upstream on the estuarine floodplain had a higher net acidity (> 200 mol H⁺/t) with limited neutralising capacity due to the decreasing effects of seawater and absence of shell materials. High concentrations of organic matter in peat-like layers also potentially contributed to higher net acidities at these locations (Yau *et al.* in press).

The two tributaries in the upper catchment, Salt Creek and Marshy Creek, flow ephemerally following periods of high rainfall. The sites sampled were generally characterised by dense vegetation dominated by tea trees (*Leptospermum spp.* and *Melaleuca spp.*) and reeds (*Phragmites spp.*). We found that the acidification potential was very high in the sites sampled in the upper catchment. This was largely attributed to the high net acidity as a result of high concentrations of organic matter which produce organic acids, presence of reduced inorganic S (RIS) species and negligible acid neutralising capacity of the sediments.

The direct contribution of the coal mine in terms of acidification potential in the upper catchment and downstream effects requires further investigation. Coal seams, which are common throughout the area, are often associated with metals which can be leached and either concentrated or mobilised by groundwater. High concentrations of soluble metals were found near the surface and at depth at both the Salt Creek and Marshy Creek sites, such as Al (> 1400 mg/kg), Cr (> 0.3 mg/kg), Cu (> 0.6 mg/kg), Ni (>200 mg/kg) and Zn (>150 mg/kg).

The results from this study suggest that the upper catchment is a substantial source of acidity to the lower catchment and estuary. The direct contribution of the coal seams throughout the region are yet to be quantified and are likely to be a substantial source of acidity, RIS and trace metals. The effect of the closure of the coal mine on the lower catchment is unknown and requires further research.

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Abundant stocks and mobilization of elements in boreal acid sulfate soils

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Substantial changes in soil chemistry take place upon drainage and subsequent oxidation of sulfidic materials producing plenty of sulfate and divalent iron. The pH is lowered from neutrality to values below 3.5, conducive to dissolution of metals from the solid matrix. Elevated concentrations of elements in pore water result in increased leaching of substances. The oxidizing horizons also gradually become saturated with exchangeable Al. Upon oxidation of Fe²⁺ to Fe³⁺ new solid phases are precipitated as coatings or as pipestems around former root channels. Moreover, abundant reserves of NH₄⁺-N have been measured in the reduced subsoil, creating potential for N leaching or gaseous N losses. In this paper, these processes are reviewed on the basis of results from cultivated boreal acid sulfate (AS) soils in Finland.

The results come from three sites, Ylistaro, Helsinki and Joensuu in W, S and E Finland, respectively. Sulfic Cryaquepts of Ylistaro and Helsinki are coastal AS soils sedimented less than 5000 yrs ago while the Typic Sulfaquept at Joensuu is a former peat mining area where the mineral subsoil originating from black schists has been exposed to rapid oxidation. In Helsinki, the response of pore water composition to the gradual oxidation of sulfidic material was monitored over 28 months in a lysimeter study (1, 2). In Ylistaro, pipestems were collected from the depth of 50 – 190 cm and investigated with a scanning electron microscope (SEM). The elemental composition was determined using an ISIS energy dispersive X-ray EDX microanalysis system. The mineralogy of the pipestems was investigated by powder X-ray diffraction (XRD). In Joensuu, the soil samples were collected from the oxidized horizons and from the reduced subsoil and analysed for Cu, Zn and Ni bound to 1) easily soluble forms (acetic acid extraction), 2) sesquioxides (hydroxyl ammonium chloride), 3) organic matter (H₂O₂ followed by ammonium acetate) and 4) primary minerals (aqua regia) (3). Timothy vegetation growing in the area was analysed for the same metals. N₂O emissions were also monitored and mineral N in soil was determined.

In one treatment of our lysimeter study, high groundwater (HGW) level was maintained to inundate the sulfidic materials and horizons that had been oxidized in the field while in the other one, low groundwater (LGW) allowed oxidation. In the HGW, iron was mobilized and dominated the pore water composition in the horizons that had been oxidized in the field. In the LGW, no dissolved iron was measured but aluminium dominated in these horizons. In the LGW subsoil with sulfidic materials, calcium and magnesium concentrations increased substantially over time suggesting leaching from cation exchange sites and dissolution of primary minerals upon oxidation and acidification.

Pipestems (Fig. 1a) represent the precipitation of a new solid phase, partly consisting of iron mobilized earlier from sulfidic materials. The bulk of the pipestem consisted of silicate particles cemented together. XRD analysis confirmed by EDX analysis showed that the cortex cell walls remaining in the interior of the pipestem (Fig. 1b) were filled with schwertmannite, Fe₈O₈(OH)₆(SO₄) nH₂O (Fig 1c). The excess of iron and sulfate may be conducive to the formation of schwertmannite in our fine silt soil of low potassium supply. Jarosite, KFe₃(OH)₆(SO₄)₂ (Fig 1d), was much less abundant in SEM images, even though it was clearly detected by XRD.

It is most commonly stated in text books of soil chemistry that acidity promotes the solubility of heavy metals in soil. Therefore it may be expected that plants growing in AS soils would be rich in heavy metals. However, plant analysis revealed that Cu and Zn concentrations were the same (Cu) or much lower (Zn) than commonly found in Finnish timothy, while Ni concentration was somewhat higher but not excessive. The fractionation of the Joensuu soil revealed that the combination of acidity and the boreal humid climate prevailing in Finland had resulted in mobilization of metals from the topsoil and subsequent leaching to subsoil or to watercourses. Much higher concentrations of the labile metal fractions were indeed found in the deepest horizon sampled (70-85 cm) (Fig 2). The soil had been limed and the topsoil pH was 4.6, while at unlimed sites the pH was as low as 2.7-3.0, certainly conducive of metal dissolution. It has indeed been observed in other studies that substantial amounts of heavy metals are leaching out of AS soils of Finland. The mobility of heavy metals seems thus to be rather an environmental than an agricultural problem.

Like in all Finnish AS soils investigated thus far, the Joensuu soil contained plenty of mineral N, up to 200 kg/ha in the uppermost 100 cm. Most of the stock occurred in the reduced subsoil and consisted predominantly of ammonium. The emissions of N₂O during snow-free periods corresponded to only 2.6-3.8 kg N ha⁻¹a⁻¹. This is only 1/10 of what has been measured in a coastal AS soil in W Finland (4). The reasons behind the diverse N₂O emissions remain still to be disclosed.

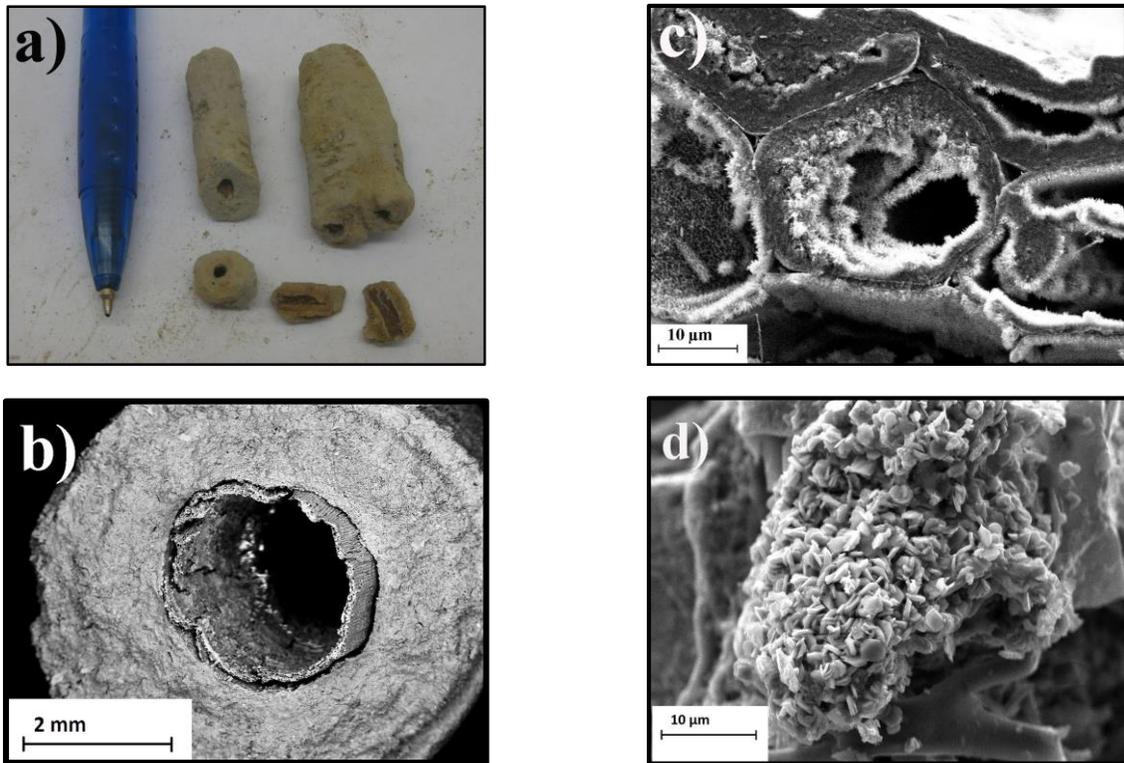


Fig.1. Pipestems of the Ylistaro fine silt soil: a) pipestems by the naked eye, b) a pipestem with the remaining cortex cell walls, c) cortex cells half-filled with schwertmannite, d) jarosite in the pipestem matrix.

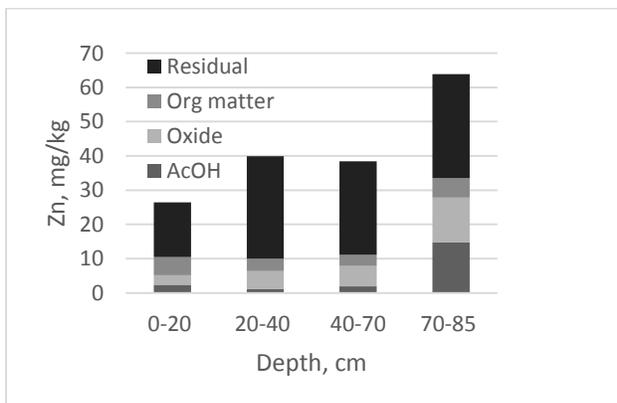


Fig. 2. Concentration of Zn in different fractions in the Joensuu coarse silt soil. AcOH stands for acetic acid dissolving the most labile fraction.

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