9th International Acid Sulfate Soils Conference Abstract Book

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Geochemical and mineralogical composition of acid sulfate soils in Luleå, northern Sweden.

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Biography:

I was born in Buenos Aires and I have lived in Patagonia for many years. I am a Geologist, with a bachelor's degree from the National University of Patagonia San Juan Bosco, Argentina, and a master's degree in geology applied to energy resources from the University of Granada, Spain.

I am focusing on the mineralogy and geochemistry of acid sulfate soils present in the coastal areas of northern Sweden. I analyze the seasonal development of groundwater chemistry and isotopic composition (Fe and S) in soils. The main aim of my study is to have a better understanding of the processes and kinetics involved in the oxidation of sulfide-bearing soils.

Geochemical and mineralogical composition of acid sulfate soils in Luleå, northern Sweden.

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Acid sulfate soils (AS-Soils) are a common feature along Swedish and Finnish coastlines that can potentially cause significant negative environmental and economic impacts. When sulfide-rich sediments get exposed to oxygen, their pH value drops below 4, and sulfuric acid is generated, causing element leaching and precipitation of secondary minerals (Cook et al.,2000). Anthropogenic activities that lower the groundwater level and expose the soils to atmospheric oxygen contribute to soil oxidation (e.g., deforestation, drying of wetlands, excavation during construction) (D.L. Dent, L.J. Pons, 1995).

In northern Sweden, parts of the sulfide-rich sediments have already been oxidized, leading to element mobilization and chemical composition changes both in soils and adjacent water bodies. Therefore, this study aims to analyze AS-Soils from a geochemical and mineralogical perspective.

We present the chemical elements distribution and the mineralogy (SEM-EDS, ICP-SFMS) of one oxidized and one waterlogged soil profile separated at a distance of 100 meters, close to the Lule river (Södra Sunderbyn). Three different zones with varying pH are found in the soil profiles; oxidation (OZ), transition (TZ), and reduction zone (RZ). Further, the materials were classified according to the classification of Finnish and Swedish AS-Soil materials (GTK and SGU), where field pH (pH_f) is compared to an incubation pH (pH_i) for at least 10 weeks. According to the measurements between pH_f and pH_i it was possible to determine that both sites present sulfuric materials in their surface horizons and underlying unoxidized materials that have the potential to become Active AS-Soils.

In both profiles, chemical element concentrations (e.g., S, Mn, Fe, Co, Ni, Zn) tend to decrease in the OZ (e.g., Fe: 2.45%), increase and accumulate in the TZ (e.g., Fe: 5.00%) and reach their maximum values in the RZ (e.g., Fe: 5.47%). These trends are comparable to what has been shown in previous research both in Finland and Sweden (Åström 1998; Österholm and Åström 2002; Sohlenius and Öborn 2004). The chemical distribution of Fe, S, and Mn along the oxidized profile is consistent with the SEM images, which show framboidal pyrite enriched with an Mn zoning belonging to the RZ (Figure 1).

SEM images show that the OZ contains possible sulfate minerals (e.g., jarosite) resulting from sulfide oxidation. In the TZ and RZ, iron sulfides (e.g., pyrite) dominate, although sulfates and iron oxides were also recognized. Barite appears as a frequent mineral in the OZ and TZ of both sites. Its precipitation could be due to a Ba source from silicates and variations in redox conditions combined with the introduction of saline groundwater resulting from fluctuating groundwater levels (Stoops and Zavaleta, 1978; Carson et al. 1982). The identified silicates (mainly quartz and albite) reflect a parent material composition associated with the granitic bedrock.

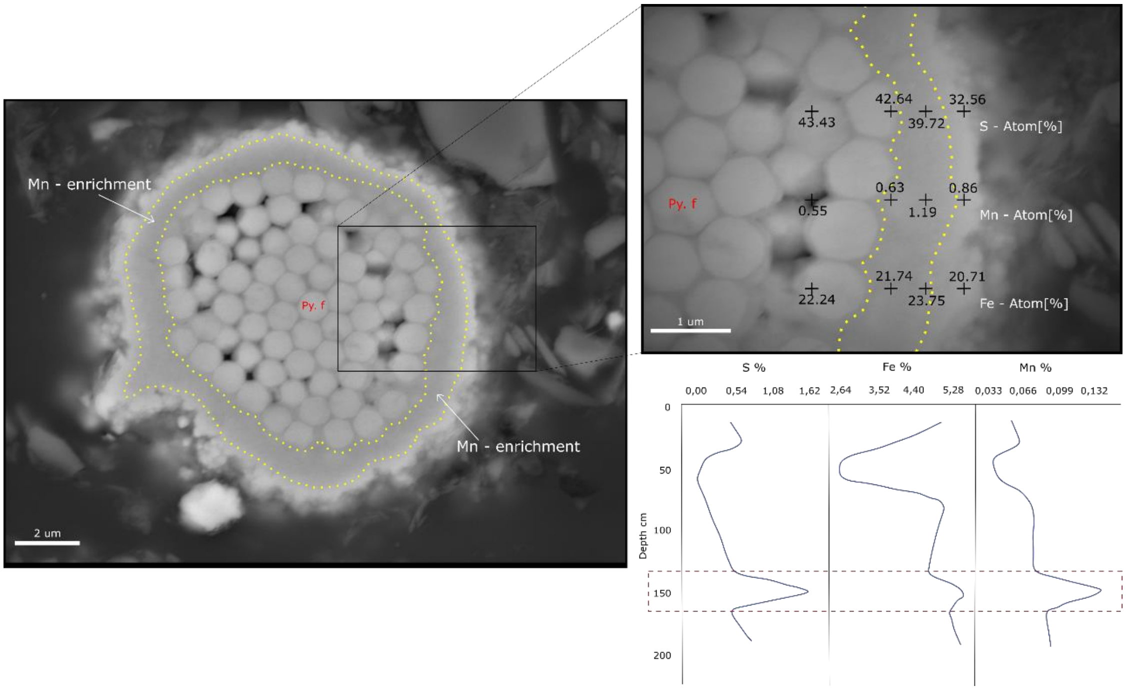

Figure 1. Backscattered electrons (BSE) SEM image showing framboidal pyrite enriched with an Mn zoning with respective increases in S, Fe, and Mn concentrations from the oxidized profile – RZ.

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Unraveling the diversity and ecological roles of viruses in acid sulfate soil of Australia

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Biography:

A second-year PhD student from The University of Melbourne. Studying soil viral ecology, including viral community diversity and ecological functions in terrestrial ecosystems.

Unravelling the diversity and ecological roles of viruses in acid sulfate soil of Australia

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Viruses are ubiquitous in the environment and contribute to important ecosystem functions, such as shaping the composition and evolution of bacterial communities, and nutrient cycling. Acid sulfate soil (ASS) affects over 17 million hectares of land across the globe. However, little is known about viral ecological impacts in ASS.

We collected 36 soil samples from Gillman of Adelaide, including 18 potential ASS samples with hypersulfidic and hyposulfidic materials (pH > 6) and 18 actual ASS samples with six organic and 12 sandy soil samples (pH < 3.5). Size-fraction metagenome (virome) and total soil metagenomes were used to investigate the viral community composition and potential biogeochemical impacts in ASS.

Viromes and total soil metagenomes yielded more than 1.68 Tb of raw data. Virome analysis recovered 13,629 viral populations (vOTU, > 10 kb), but only 257 vOTUs were identified in actual ASS, compared with 13,554 vOTUs in potential ASS. The Shannon, Simpson and Pielou's indexes of viral community in potential ASS were significantly higher than that in actual ASS ($P < 0.01$). Principal coordinate analysis (PCoA) based on the Bray-Curtis distance of vOTU read mapping coverages showed that viral community composition in potential ASS varied from that in actual ASS ($P < 0.01$). Viral communities were also separated by soil depth, soil types (sulfuric organic and sandy soil samples), and sample collection sites ($P < 0.01$), which was consistent with the results of hierarchical clustering. Mental test showed that pH was the most important factors (R=0.69) affecting viral community composition, flowed by soil water content (R=0.45), and total Mg (R=0.45).

A total of 8,515 AMGs were identified from 13,629 vOTUs by VIBRANT. The highly abundant AMGs were related to 11 categories of metabolism, with "carbohydrate metabolism" being the most abundant, followed by "metabolism of cofactors and vitamins" and "Amino acid metabolism". Those AMGs were related to carbon, sulfur, and nitrogen cycling. In particular, AMGs associated with both assimilatory sulfate reduction and dissimilatory sulfate reduction were identified, which indicated the roles of viruses in sulfur cycling.

This study illustrated the viral community diversity in both potential and actual ASS, and suggested that viruses may participate in the formation of ASS, providing novel insights into the ecological characteristics of viruses in the ASS.

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Classification of acid sulfate soils and materials in Finland and Sweden: Re-introduction of pseudoacid sulfate soil materials

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Biography:

Boman has been working his entire career (2002>) in the field of acid sulfate soils. His PhD (Åbo Akademi University, 2008) focused on sulfur dynamics in acid sulfate soils. During 2009-2012, he did a post doc/Assistant Professor session at Luleå University of Technology and since 2012 he is working at the Geological Survey of Finland. His research focuses on geochemical characterization, mapping, and classification of acid sulfate soils. Understanding the geochemical pathways involved in acid sulfate soil formation is crucial for management of these harmful soils. Boman has 20 referred publications and >40 abstracts and reports. Boman have experience of supervising students, both nationally and internationally, at all degree levels (PhD, MSc, BSc). Boman has been the Chair of the International acid sulfate soils working group since 2018.

Classification of acid sulfate soils and materials in Finland and Sweden: Re-introduction of pseudoacid sulfate soil materials

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Established international soil classification systems cannot directly be applied on acid sulfate soils (ASS) in Finland and Sweden because: **1)** there are depth requirements in some of these classification systems for certain diagnostic ASS materials which are not fulfilled in several ASS in Finland and Sweden, and **2)** there is a lack of tools for classification of acidic, and potentially acidic, soil materials that are not completely fulfilling the diagnostic pH-criteria of pH <4.0, but which may have a considerable environmental impact due to mobilisation of acidity and potentially harmful elements. The definitions, diagnostic criteria, and terminology for ASS materials set by the International Acid Sulfate Soils Working Group in 2008 (Sullivan et al., 2010) have been adopted in the Finnish-Swedish ASS classification. The ASS mappings in Finland and Sweden done by the geological surveys of Finland (GTK) and Sweden (SGU) have, however, led to an understanding of which soil properties are important to consider in ASS classification and in risk assessment, and this has resulted in slight modifications to existing ASS classification systems to fully embrace the environmental consequences from ASS present in these countries.

Classification of Finnish and Swedish ASS has previously been cumbersome using international soil classification systems such as the old versions (prior to 2015) of the WRB and the Soil Taxonomy as the typical ASS properties and diagnostic materials are commonly located too deep to fulfil the depth criteria. In the most recent version of WRB, the depth criteria are no longer an issue but there are, however, still problems to classify soil material that are containing sulfidic materials, but which are not completely fulfilling the pH-criteria for sulfuric (field-pH <4.0) and hypersulfidic materials (incubation-pH <4.0), but which may have a considerable acidifying impact on the environment (e.g. Mattbäck et al., 2017). Many soils in Finland and Sweden contain acidic soil materials in the oxidised horizon, with a pH slightly above 4.0, and where there are indications of mobilization of acidity and potentially harmful elements into water courses. Similarly, there are many soils that contain sulfidic materials in the unoxidised part of the soil and where pH may drop several units from circumneutral values to near sub-four pH-values and which also have a high acidifying potential. Using established classification systems, these types of soil materials would be classified as “non-ASS materials” even though their possible environmental impact, e.g. release of acidity and metals, may potentially be very high (e.g. Mattbäck et al., 2017). The ASS mapping in Finland and Sweden have brought to attention that these types of soil materials are quite common and therefore the prefix “pseudo” (used as “pseudoacid sulfate soil”; PsASS) has been introduced in the Finnish-Swedish ASS classification to describe a soil, or soil material, not fulfilling the ASS criteria, but which may have a considerable environmental impact due to oxidation of sulfidic material. In the surveys done by GTK and SGU, it has also been indicated that organic soil materials (>20% organic matter) need to have a lower diagnostic pH-limit for classification as ASS material. This is because organic acids may lower the soil-pH to values below 4, and therefore a pH-limit of <3.0 for classification of organic-rich ASS materials have been introduced to distinguish between a low pH caused by organic acids and a low pH caused by sulfide oxidation.

The term “pseudoacid sulfate soil” was already in the early 1960´s applied by Leen Pons to describe less acid soils (pH 4–5) in Surinam formed by oxidation of sulfidic sediments with “low” (<0.64%) pyrite concentrations and with no presence of carbonates (Pons, 1965). During the first International Acid Sulfate Soils Conference in Wageningen 1972, pseudoacid sulfate soils were defined by Brinkman and Pons (1973) as soils containing one or more horizons with the characteristic yellow mottling commonly associated with acid sulfate conditions, but which does not have a pH below 4 and does not contain free acids or more than about 60% exchangeable Al. In the Soil Classification for Surinam from 1979, the term pseudoacid sulfate soil was used for describing acid soils having a pH-KCl of >3 and <3.5 and which do not have toxic Al-concentrations (Boer, 1979). The definition of pseudoacid sulfate soils differ somewhat (e.g., different pH-thresholds) between these sources, but the common denominators are that pseudoacid sulfate soils defined in the past are: **1)** containing low sulfide concentrations, **2)** poor in carbonates, **3)** acidic but do not fulfil the diagnostic pH-criteria for ASS, and **4)** not containing toxic Al-concentrations. The term “pseudoacid sulfate soil” seem to have been lost from the ASS community since the late 1970´s but is now re-introduced in the Finnish-Swedish ASS classification and the prefix “pseudo” has been further extended to include also “pseudosulfuric materials” (field-pH of 4.0–4.5 and 3.0–3.5 for mineral and organic soil materials, respectively) and “pseudohypersulfidic materials” (incubation-pH of 4.0–4.5 and 3.0–3.5, and ≥0.5 pH drop, for mineral and organic soil materials, respectively) (Boman et al., in preparation). It has been shown that PsASS soil materials (especially fine-grained) in Finland may sometimes contain higher sulfur concentrations and acidities compared to some types of ASS materials (e.g., coarse-grained; Visuri et al., 2021); this further justifies the addition of diagnostic PsASS materials. Inclusion of diagnostic PsASS materials would minimize the risk of overlooking potentially harmful soils.

It is proposed that the Finnish-Swedish ASS classification may serve as a framework for establishing a harmonized ASS classification globally and that the new diagnostic ASS materials are included into relevant soil classification systems.

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Does the water quality of stream waters reflect the predicted occurrence of Finnish acid sulfate soils?

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Biography:

Boman has been working his entire career (2002>) in the field of acid sulfate soils. His PhD (Åbo Akademi University, 2008) focused on sulfur dynamics in acid sulfate soils. During 2009-2012, he did a post doc/Assistant Professor session at Luleå University of Technology and since 2012 he is working at the Geological Survey of Finland. His research focuses on geochemical characterization, mapping, and classification of acid sulfate soils. Understanding the geochemical pathways involved in acid sulfate soil formation is crucial for management of these harmful soils. Boman has 20 referred publications and >40 abstracts and reports. Boman have experience of supervising students, both nationally and internationally, at all degree levels (PhD, MSc, BSc). Boman has been the Chair of the International acid sulfate soils working group since 2018.

Does the water quality of stream waters reflect the predicted occurrence of Finnish acid sulfate soils?

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Acid sulfate soils (ASS) cause harmful environmental impact in the form of acidity and high concentrations of toxic elements in the recipient streams. The west coast of Finland is a hot-spot area of ASS (Edén et al., in preparation; Åström and Björklund, 1995), and many streams and rivers show a poor ecological and chemical status according to legislation and classification systems in the European Union. A predictive model of the occurrence of ASS Finland has been produced (Edén et al., in preparation). The question of this study is if the water quality in streams and rivers matches the predicted occurrence of ASS?

The occurrence of ASS in Finland has been mapped during 2009–2021 by the Geological Survey of Finland (Edén et al., in preparation). The resulting ASS map shows the probability of encountering ASS in four different probability classes: high (93.4% probability), medium (54.9% probability), low (6.5% probability), and very low (2.7% probability). The extent of ASS is calculated based on the calculated probabilities and is estimated to about 10 000 km^2 on the coastal plains of Finland (Edén et al., in preparation). A suite of streams (n=11, drainage area 10–99 km^2) and rivers (n=16, drainage area $\geq$100 km^2) in western Finland was selected for the study. The extent of ASS in the study area is estimated to 2696 km^2 which is about 20% of the total study area within the mapped area. The water courses were sampled during three occasions in autumn 2016, spring 2017, and spring 2019. The sampling periods mainly represent periods of high flow when the impact from ASS on water quality is highest (Österholm and Åström 2008). The water was analyzed for sulfur (S) concentrations (ICP-OES). The S-concentration in stream water in the area is derived from oxidation of sulfidic soil materials to sulfuric acid. The resulting high sulfate concentration is readily flushed to nearby streams. The sulfate-S is also considered a robust element not easily affected by geochemical reactions. Because there are no tides in the Gulf of Bothnia, S originating from sea water is negligible. Therefore, the S-content in streams and rivers are considered to directly reflect the load from ASS (Toivonen et al., 2013). A flow-corrected average for the S-content was calculated for each stream and river, where samples taken during higher discharges were given greater significance. The predicted share of ASS in the catchment of each stream and river was correlated against the flow-corrected S-concentration in the stream water using Spearman rank correlation (p=0.05).

A significant correlation between the predicted ASS occurrence and water quality was found for the rivers ($r_s = 0.59$), but not for streams (Fig. 1). This means that the use of water quality parameters can be a complementary tool to creating soil probability maps on a large scale. The lack of correlation for the streams may be due to differences in the ratio active/potential ASS or differences in grain sizes; it has been shown that coarse-grained ASS materials commonly contain lower S-concentrations and leach less sulfate than fine-grained ASS materials (Mattbäck et al., 2022). These factors are not considered in the current soil map but are important in the environmental risk assessment.

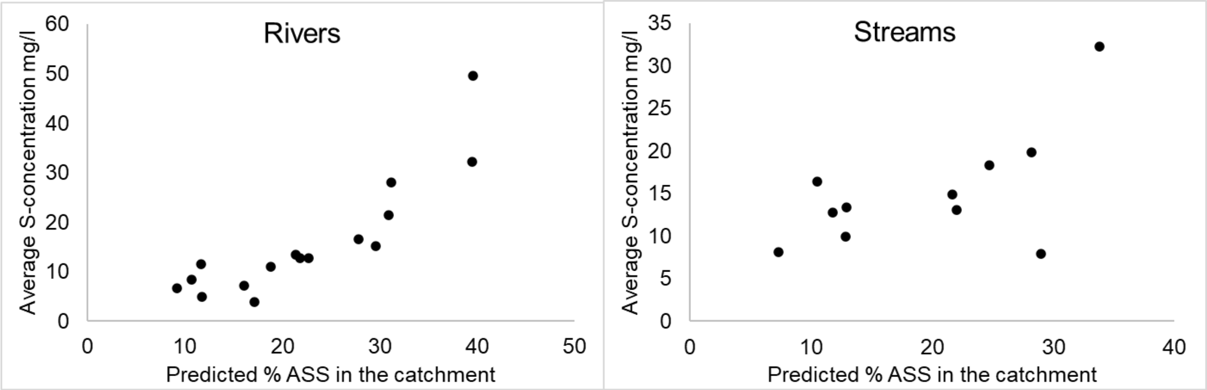

Fig. 1. Correlation between the predicted occurrence of ASS (%) and the runoff weighted average S-concentrations in rivers (left) and streams (right).

The study shows that two independent mapping methods give comparable results on a river scale whereas the weaker match for smaller streams indicates the need of not only probability maps, but also risk maps.

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Potential acid sulfate soils in Arctic regions of Finland: A first survey

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Biography:

Boman has been working his entire career (2002>) in the field of acid sulfate soils. His PhD (Åbo Akademi University, 2008) focused on sulfur dynamics in acid sulfate soils. During 2009-2012, he did a post doc/Assistant Professor session at Luleå University of Technology and since 2012 he is working at the Geological Survey of Finland. His research focuses on geochemical characterization, mapping, and classification of acid sulfate soils. Understanding the geochemical pathways involved in acid sulfate soil formation is crucial for management of these harmful soils. Boman has 20 referred publications and >40 abstracts and reports. Boman have experience of supervising students, both nationally and internationally, at all degree levels (PhD, MSc, BSc). Boman has been the Chair of the International acid sulfate soils working group since 2018.

Potential acid sulfate soils in Arctic regions of Finland: A first survey

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For the first time, the occurrence of acid sulfate soils (ASS) has been investigated in the Arctic regions of Finland. Altogether 25 sampling sites were visited during August 2021 in a 2218 km^2 large area in the surroundings of Lake Inarinjärvi and Utsjoki in Northern Finland. Part of the shores of Lake Inarinjärvi and in the surroundings of Utsjoki has previously been subaquatic (former ice lakes) and there are therefore chances of occurrences of ASS materials in this region. Occurrence of ASS can also be related to black shales which are found as outcrops or as eroded material enriched in moraines in the area. The quaternary geology of the area has been described in detail by Hirvas (1991). Basal till with a general thickness of 0-7 m is the predominant type of Quaternary deposit. Drumlin fields and other stream-lined landforms oriented by the continental ice sheet are encountered in the study area. Glaciofluvial sorted sediments (e.g., eskers, deltas, sandurs, and ice marginal formations) are fairly evenly distributed throughout the study area. Fine-grained sediments and littoral deposits are rare as much of the area is supra-aquatic and much of this material was deposited in ice-dammed glacial lakes. Marine sediments are present in river valleys and in Lake Inarinjärvi. In some regions, eolian deposits are occurring in connection with glaciofluvial formations. About 10-20% of the areas around Inari-Utsjoki is covered by peatland.

A sampling scheme (targeted spatial coverage sampling) was constructed using modelling techniques in such a way that all possible soil materials in the study areas were included and so that all the sampling sites had easy access to roads. At some planned sampling sites, soil sampling was not possible due to presence of bare bedrock, large boulders, and blocky till Where soil cores were possible to obtain, the general sampling depth was about 2-3 m, and the soil sampling was generally done by using a percussion handheld drill and soil auger. Peat samples were generally collected using a D-section corer whereas till samples were generally obtained by digging a pit with a shovel. Altogether soil samples were collected from 25 sites.

All collected soil samples were analysed at the Geological Survey of Finland (GTK, Kokkola) for incubation-pH, titratable incubation acidity (TIA), and loss on ignition (LOI). The incubation-pH method follows the procedures described in Boman et al. (in preparation), whereas TIA was performed according to the procedure described in Österholm and Nystrand (2016) and Mattbäck et al. (2017). Loss on ignition was done by combusting the dried samples for four hours at 550 ^{o}C. Selected soil samples were analysed at a commercial accredited laboratory (Eurofins Labtium Oy) for aqua regia extractable sulfur, including 30 other elements, using ICP-OES. The soil samples were classified according to the Finnish-Swedish ASS classification developed by the Geological Survey of Finland (GTK) and the Geological Survey of Sweden (SGU) (Boman et al., in preparation).

Typically, the ASS in the study area were associated with peatlands, and to some extent also to black schist areas. Of the 25 sampling sites, 14 had ASS properties; two sites contained unsorted active acid sulfate soil (AASS) materials, eight sites contained potential acid sulfate soil (PASS) materials, and four sites contained pseudoacid sulfate soil (PsASS) materials, which is a new ASS material described in Boman et al. (in preparation). One of the PASS sites, a sediment sample (subaqueous ASS material) from the bottom of Lake Inarijärvi, contained hypersulfidic material (up to 1.08% total S) in the uppermost 60 cm of the sediment. The other seven PASS were generally found in association with peatlands, where either the peat itself, or the underlying mineral soil material, contained hypersulfidic materials. The number of identified ASS is quite high but is probably to some extent the result of targeted spatial coverage sampling which was utilized in this study. No ASS like the extremely environmentally un-friendly ASS typically found within the so called Littorina Sea area in Western Finland were found. Except for the hypersulfidic sediment from Lake Inarinjärvi which contained fine-grained soil material, the mineral soil material in the ASS in this study was quite coarse-grained (typically sand and till) and had low sulfur concentrations.

Based on the TIA-results, the reduced soil material was classified into a high, medium, or a low acidifying potential (expressed as mmol H^+ / kg dry weight) according to the guidelines presented in Visuri et al. (2021). Due to differences in bulk density between various types of soil materials, and especially between peat and mineral soil materials, different thresholds were used for defining the classes of acidifying potential for peat, gyttja (LOI >20%), fine-grained, and coarse-grained soil materials. Furthermore, peat contain organic acids which also contribute to acidity, and the natural acidifying potential is therefore often very high even without a contribution of acidity from sulfide oxidation. For these reasons, peat and gyttja have higher threshold values for defining the acidifying potential compared to fine- and coarse-grained soil materials. A high acidifying potential was found at all PASS sites, and they were mainly in association with peatlands. The sulfur content varied between the sampled ASS materials and depending on the type of soil material present. Peat contained the highest sulfur concentrations (up to 6.91%) whereas mineral soil materials (mainly coarse-grained) had significantly lower sulfur concentrations (typically < 0.04%).

Although this first ASS survey in the Arctic regions of Finland did not indicate any current environmental problems associated with ASS, there are areas underlain with PASS which may develop into a real environmental threat in the future if they are disturbed for instance in infrastructure and agriculture development. It is therefore crucial to map the occurrence, as well as their possible risks, of PASS in the Arctic regions of Finland.

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28 years of managing broadacre acid suflate soils on the North Coast of NSW: what have we done and what's left to do?

Mrs Chrisy Clay[1], Mr Peter Wilson, Mr Ron Kemsley
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Biography:

Working with stakeholders to bring about change is my specialty. I've spent the past 23 years working with landowners, the NSW Sugar Cane Industry, local and state government, Universities and private industry to change how floodplain drainage and acid sulfate soils are managed.

I'm currently focused on the Richmond River estuary and floodplain, one of the most degraded coastal systems in NSW.

On any given day you will find me assessing how Council's floodgates and drains can be managed to reduce their environmental impact, garnering support from landowners, liaising with industry, monitoring water quality and casting an eye towards future challenges and opportunities.

My vision is to repair the Richmond River estuary and floodplain, so it supports sustainable agriculture, healthy aquatic habitats and abundant birds, fish and oysters.

28 years of managing broadacre acid suflate soils on the North Coast of NSW: what have we done and what's left to do?

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The large coastal floodplains that are a distinct feature of the North Coast of NSW have been historically drained for flood mitigation and to open land up for agriculture and rural settlement. Since the late 1800's successive federal, state and local governments have encouraged and funded the construction and maintenance of infrastructure that drain these floodplains.

This historic drainage has left a legacy of unintended broadacre disturbance of hundreds of thousands of hectares of acid sulfate soils (ASS). However, it was only in 1987 when the Tweed River estuary became acidified, that this widespread disturbance of ASS was first recognised. The first attempts to reduce the impact of this widespread ASS disturbance followed in 1995 and these first actions marked the start of what is now 28 years' worth of remediation effort on the North Coast of NSW.

What's happened?

Over the past 28 years, our collective ability to identify and understand ASS has improved greatly. This knowledge together with state-wide mapping paved the way in 1998 for contemporary disturbance of ASS to be regulated. Following this, the NSW Sugar Cane industry adopted best management practices and obtained self-regulation for routine farming practices that disturb ASS. The adoption of laser levelling and the associated reduction of on-farm drains reduced the acidity leaving many cane farms.

In 1998 the State Government also endorsed the NSW Acid Sulfate Soil Strategy which identified the need to manage both contemporary and historic disturbance of ASS. The remediation of historically disturbed broadacre ASS commenced initially by working with landowners willing to change how drains and floodgates were managed and operated. Floodgates were opened to allow tidal water to exchange and neutralise acidity in drains before it entered downstream waterways.

In some areas, drains were redesigned so they didn't intercept ASS, some landowners trialled retaining water on low lying areas to grow wetland plants for grazing and scalds were revegetated.

In 2007, guidelines for the remediation of broadacre ASS were published by the State Government. In some areas, private properties were purchased by State and Local Government, and full wetland restoration occurred e.g. Big Swamp in the Manning.

What's worked?

Partnerships at the local, regional and state level have been instrumental in making progress, as has working cooperatively with industry. Formal collaborations such as the NSW Acid Sulfate Soil Management Advisory Committee oversaw important developments in the assessment, management and remediation of ASS. At the local level, stakeholder partnerships continue to identify priorities, source funding and oversee remedial works.

Significant effort and resources have been spent educating landowners and addressing their barriers to adopting new management techniques. Applied and industry-based research, often conducted on farm with landowners, improved industry understanding and adoption of remediation strategies. In some locations the acquisition of private properties has allowed full wetland restoration to occur.

What hasn't worked?

At present, the remediation of historically disturbed ASS is still reliant on the willingness of private landowners. There are no statutory tools that can be used to direct historically disturbed ASS to be remediated or to change the drainage systems that continue to transport acidity and metals into downstream waterways. As a result, most remedial activities undertaken to date are small scale and cause no negative impact on the agricultural productivity of the privately owned land. While these activities can be beneficial, the outcomes have not improved water quality at a scale that is meaningful at a landscape or estuary level.

Although remediation attempts continue, they face major obstacles and limitations, particularly when agricultural productivity could be impacted. The acquisition of private properties, which so far has allowed the most successful remediation to occur, is also reliant on landowner willingness and often results in a fragmented approach. Acquisition is also reliant on the capacity of Local Government or State-based National Parks agencies to purchase the property and to undertake the long-term maintenance.

Finally, the responsibility for most key historical floodplain drainage systems has fallen to Local Government. North Coast Councils are amongst the most economically disadvantaged in the State and their capacity to make significant changes varies considerably throughout the region. Additionally, these Councils are usually the designated Flood Mitigation Authority, responsible for reducing the impact of floods, but at the same time needing to reduce the environmental impact of draining low lying land, two aims that are diametrically opposed.

What's left to do?

The challenge remains to create change at the scale required to truly reverse the impact of floodplain drainage on the exposure and mobilisation of acid sulfate soil. Over the last 28 years, change has not been possible at the scale necessary and acidity still chronically discharges into many estuaries and fish kills still regularly occur.

A long term strategy for how the lowest lying floodplain areas (which discharge the most acidity from historically disturbed acid sulfate soils) will be used into the future has not been determined. These areas which are predominantly 1mAHD and below, are mostly zoned for agricultural use and continue to be drained by historical drainage systems.

What does the future hold?

In the coming years, several changes may provide the final impetus for determining a long-term strategy for remediating the widespread historic broadacre disturbance of ASS on the North Coast of NSW.

1) It is likely that climate change and sea level rise will necessitate a review of the land uses permissible for the lowest lying floodplain areas which are high risk ASS.

2) Large areas of high-risk ASS will also undergo generational landowner change in coming years and demand to keep these areas under agricultural production may decline.

3) The wide-ranging and cumulative environmental impacts of draining the lowest lying areas on the floodplain are now recognised as are the potential benefits of restoring floodplain wetlands for downstream water quality, biodiversity and carbon capture.

It remains to be seen how these factors will guide and generate urgency for future policy development and lead to the final determination on the fate of historical floodplain drainage systems in the lowest lying areas. Whilst research is important for understanding and monitoring change, the key emphasis in the next 5 years needs to be on support for strategic land use adaptation and change.

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How the zebra rock got its stripes: the formation of hematite banding from acid-sulfate fluid-rock interactions.

Dr Andrew Coward

How the zebra rock got its stripes: the formation of hematite banding from acid-sulfate fluid-rock interactions.

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Zebra rock is a patterned Western Australian siltstone renowned for its highly unusual hematite banding, displaying a level of symmetry, regularity, and diversity of pattern morphology unique among examples of geochemical self-organisation. These remarkable rocks are restricted to a few isolated outcrops in the East Kimberley region of Western Australia, where they are mined at a small scale

Two examples of zebra rock from the East Kimberley and their associated patterns as semi-precious stones. The origin of zebra rock has been highly debated over the last century, with recent theories ranging from redoximorphic banding in an Ediacaran acid-sulfate soil (Retallack, 2021), to Liesegang banding induced by hydrothermal alteration (Kawahara et al. 2022). However, at present, no consensus has been reached, in part due to the lack of any extensive mineralogical and geochemical analysis of the rock in question. To answer this long-standing mystery, this study examined a large number of zebra rock samples using a broad range of analytical techniques, including x-ray diffraction, laser ablation, scanning and transmission electron microscopy, and x-ray fluorescence microscopy, followed by the computational modelling of specific reaction pathways in order to reproduce observed patterns.

We present the first evidence that the iron-oxide banding of zebra rock developed simultaneously with a period of aluminosilicate dissolution, clay precipitation, and fluid flow, consistent with the infiltration of an acidic fluid. This conclusion was evidenced through the hexagonal-platelet morphology of the hematite pigment and through the textural relationships between the hematite and clay phases. However, while the mineralogy of zebra rock strongly suggests interactions with acid-sulfates, the origin and temperature of the fluid could not be conclusively determined. Supporting a hydrothermal origin, a thorough analysis of zebra rock mineralogy revealed a mineral assemblage extremely consistent with advanced argillic hydrothermal alteration, wherein pyrophyillite, kaolinite, and dickite indicate minimum palaeotemperatures upwards of 120 °C and the presence of alunite and a svanbergite-woodhouseite solid solution suggests oxidising, acidic (pH <5) conditions. The low Rb/Sr ratio and relative immobility of rare earth elements in most zebra rock deposits are also consistent with an acidic hydrothermal origin. Further support was also observed in the mineralogical trends between examined outcrops, grading from alunite-type to kaolinite/dickite-type facies in a south-west direction. But despite this evidence, the acid-sulfate soil hypothesis could not be refuted and was itself supported by the large number of pyrite dissolution voids both underlying and within the patterned layer. Furthermore, the consistent compaction of reduction spheroids, dissolution voids, and pseudomorphic inclusions within the light banding of zebra rock are in agreement with near-surface supergene weathering, ruling out hypogene hydrothermal alteration.

The viability of pattern formation via Liesegang banding was tested through computational modelling of ferrous iron oxidation by oxygen under both hydrothermal, and pedogenic conditions. Through this method, banding was obtained in both environments, successfully reproducing stripe, rod, and spot pattern morphologies highly reminiscent of zebra rock, particularly with the inclusion of Ostwald ripening. Consequently, this study proposes that zebra rock banding formed by the Liesegang phenomenon, driven by the oxidation of Fe^{2+} ions during the infiltration of an Fe^{2+}-rich, acid-sulfate fluid into oxidising host sediments.

Detailed background information about the nature and properties of zebra rock and methods used can be found in Coward et al. (2023).

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Coming of age; early acid sulphate soils knowledge and ASS management

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Coming of age; early acid sulphate soils knowledge and ASS management

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Abstract: We have come a long way since the first international symposium on acid sulphate soils (ASS) in 1972. Soils that generate battery acid are no longer a curiosity. By the time of the 5th symposium at Coolangatta in 2002, they had entered the mainstream of technical knowledge. That much, we owe to the Dutch and, in particular to Leen Pons who led the first four symposia in Wageningen, Bangkok, Dakar and Ho Chi Minh City.

This was no accident. Linnaeus gave us the first description of *argilla vitriolica* from his own fieldwork in the Dutch Republic in 1735. As the world's great drainage engineers, the Dutch created what they called *katteklei* in their polders at home and, as a colonial power, in sugar cane and oil palm plantations in the East and West Indies. ASS chemistry was elucidated by van Bemmelen in 1886 and their reclamation by liming mastered in the Zuyder Zee polders in the 1930s which also saw the first detailed, predictive soil maps. The only common feature of all succeeding maps is their individuality and complexity - at any scale.

Chemistry was only the first hurdle. Tides, stinking mud, biting insects, snakes, crocodiles and fever discouraged close examination by all but the most curious so, for a long time, we were a select band but by the time of the fourth symposium, in Ho Chi Minh City in 1992, we were no longer solitary individuals but working clusters; serious attention was being given to environmental issues; and multi-national, multidisciplinary teams introduced ambitious work that was only just beginning.

One of the contingents was from Australia but the big issue wasn't acid sulphate soils: *the big issue was fish kills.* Drainage of the floodplains for cane farming was releasing iron in solution and black ooze; every time it rained, these were flushed into the streams and stole the oxygen. Everyone could see the millions of suffocated fish. Soon after, the legislature of New South Wales banned any further drainage of sulphidic soils and commissioned detailed surveys to map them out. The credit belongs to the press: hard-hitting, well-informed newspaper articles pushed politicians into action. The states and even the Commonwealth put up money for research and reclamation. We learned a lot very quickly and by the time of the 5th conference at Tweed Heads in 2002 the existence and significance of ASS was known in agriculture, fisheries and environment departments at state and Commonwealth level; and they were being discovered hundreds of miles from the coast - any wetland will do. Acid sulphate soils had come of age. Job done!

Of course, it wasn't. Twenty years on millions of fish suffocate every time it rains, and not just in the northern rivers. What have you been doing for twenty years?

The genie is out of the bottle. The only way to put it back again is to restore the original hydrology. That doesn't require a lot of research. It needs political will. There is a price to pay whether the job is done or left undone. Are you up for it?

Keynote address

Rob Fitzpatrick and I first teamed up 30 years ago to investigate acid drainage from the Ranger uranium mine. You must know that we are both fans of Sherlock Holmes, who famously remarked: *'The ideal reasoner* *would, when he had once been shown a single fact in all its bearings, deduce not only the chain of events which led up to it but, also, the results that would follow'* (Conan Doyle 1891). So, it might come as no surprise that my first encounter with acid sulphate soils was fictional.

I had entered myself for a scholarship to the University of Durham and, attempting a question on life on other planets, I supposed a life based on silicon rather than carbon with sulphur instead of oxygen as the electron sink – unaware that the sulphur sink had been exploited on this planet long before there was any oxygen in the atmosphere. But the examiners were impressed and I went on to read geography with chemistry and botany, which was the nearest thing to soil science available in the early sixties.

The striking thing about those days was how few we were. Fewer still encountered acid sulphate soils. Quite apart from the chemistry, stinking mud, snakes, crocodiles and virulent fevers discouraged all but the most curious. So, we were a select band and, mostly, Dutch. This was no accident. Linnaeus gave us the first description of *argilla vitriolica* from his fieldwork in the Dutch Republic in 1735: the world's drainage engineers created what they called *katteklei* in their polders at home and, as a colonial power, in plantations in the Indies. So it was that the chemistry was elucidated in Dutch by van Bemmelen in 1886 and reclamation was mastered in the Zuyder Zee in the 1930s, which also saw the first detailed, predictive soil maps.

I was lucky to be adopted by Leen Pons, one of a band that kept their heads down in the swamps of the Biesbosch during the German occupation and, as soon as peace was declared, emerged to survey the whole country. With extraordinary energy, Leen led the first four international symposia in Wageningen, Bangkok, Dakar and Ho Chi Minh City. He was supported by polymaths like Robert Brinkman and Nico van Breemen and the shrewd colonial administrator Harm Dost. Institutional backing came from the International Institute for Land Reclamation and Improvement (ILRI) that had been established to underpin the national recovery from the 1953 floods. These were serious people: six out of ten Dutch live at or below a rising sea level; when you drain the land, it subsides. They need to know what they are doing – and the title *engineer* carries more weight in Holland than Doctor or Professor.

The first symposium in Wageningen (Dost 1973) set a standard that has never been matched: the proceedings read like the Charles Darwin's voyage of the Beagle – reviews of all the specialist fields that were needed to piece together the acid sulphate story, crescendos of questions and answers, followed up by earnest engineers and scientists seeking ways to characterise these extraordinary soils. Sight, smell, taste, feel, field tests, microscopy, sedimentology, ecology, farmers' observations… We tried anything and everything because, in those days, laboratory methods were finicky, expensive and, more to the point, hard to interpret. I thought I was terribly technical going around with a lump of platinum soldered onto a metre long probe, connected to my pH/Eh meter; everyone, including Nico, told me that it couldn't possibly give stable readings, but it worked for me.

This was the golden age of soil survey in the service of the *Hydraulic Mission* to bring water, power and food to the developing world. Dams, drains and canals were being built in every possible place, and some impossible places, and I was hired to procure a hundred thousand acres to be irrigated from the proposed Gambia Barrage. In the wet season, the great river flows into the Atlantic but, then, it doesn't rain at all for seven months – and a tongue of tidewater licks 200km upstream. The idea was to build a barrage to hold back the tide and impound a freshwater lake to provide irrigation in the dry season; it would also save trucks travelling from Senegal to Casamance a long wait at the ferry.

This was 1979. As it happened, the whole country had just been mapped by British Dept of Overseas Surveys and the soils mapped at soil series level by the Land Resources Division (Dunsmore and Blair Rains 1976). But they hadn't ventured into the tidal areas, which were pencilled in as *mangrove soils*. LRD *had* mapped extensive areas of severely acid, red-mottled Mandori Series without realising that they were ripe, former acid sulphate soils left over from a previous higher sea level. One look was enough tell that they wouldn't be good for irrigated rice, or anything else. However, working from a powerful boat, I soon located the desired irrigable land – and had it checked out by the local witch doctor. I also looked at the sulphidic mud in the mangroves and, one night, kicking away at the rats in the boat, it occurred to me that evaporation from the reservoir, let alone irrigation, would lower the water level by several metres and generate enough sulphuric acid to kill all the fish in West Africa. I quickly gathered a few samples, established the sulphide datum using pegs painted with red lead, and headed back to Banjul to cable the top brass in London. Something like: 'Barrage unwise – Stop – Do nothing till I return – Stop – Dent'.

I was young. And, when I returned, I was well and truly carpeted; in particular by the great man in charge of the Land Resources Division. No one had even heard of acid sulphate soils so they hadn't looked for them. But my samples revealed about 12 900 ha of potential acid sulphate soil upstream of the barrage with total S contents of 2-5 per cent. If the barrage were built and operated as planned the pH of the reservoir would be about 2.3; even 50 years on, only a quarter or half of the accessible sulphur would be oxidised (Dent & Raiswell 1982). Only one man in LRD was brave enough to venture that such things might be – Peter Thomas. For his temerity, he was despatched with a five-man team to check it out. Unfortunately, it was all true; the barrage was aborted; *and no one spoke to me for years and years.*

All the world came to the next symposium, in Bangkok, in 1982. But hardly anyone had read the literature which, by then, had been graced by Nico van Breemen' s thesis *Genesis and chemistry of acid sulphate soils in Thailand* (van Breemen 1976) that covered all the bases in flawless English. With staggering self-confidence, I decided that what was needed was a comprehensive account in even plainer English which ILRI kindly published (Dent1986). Hardly anyone read that either but, by the time of the fourth symposium, in Ho Chi Minh City in 1992, we were no longer solitary individuals but working clusters; serious attention was being given to environmental issues; and multi-national, multidisciplinary teams introduced ambitious work that was only just beginning (Dent and van Mensvoort 1993).

One of the contingents was from Australia and I was lucky enough to strike up some lifelong friendships. In 1993, my good friend Bernie Powell roped me in for and the Ross McDonald Lecture Tour and corralled cane farmers, fishermen, greenies, officials and politicians in every town hall and RSL club on the East Coast to hear about the big issue. The big issue wasn't acid sulphate soils: *the big issue was fish kills.* Drainage of the floodplains for cane farming was releasing ferrous ions and black ooze; every time it rained, these were flushed into the streams and stole the oxygen. Everyone could see the millions of suffocated fish.

Chemistry isn't everyone's cup of tea, so explaining it in public was something I had to learn quickly: as for the slings and arrows aimed at any head above the parapet, I already had experience. But, soon after, the legislature of New South Wales banned any further drainage of sulphidic soils and commissioned surveys to map them out, Queensland followed, but *the credit belongs to the press:* hard-hitting newspaper articles like 'The trouble with the Tweed' (Easton 1989) alerted the public and pushed politicians into action. The states and the Commonwealth put up money for research – so we all learned a lot very quickly. By the time of the 5th International Acid Sulfate Soil Conference at Tweed Heads, in 2002, Australia had held two rumbustious national conferences (Bush 1993, Smith & Smith 1996) acid sulphate soils were common knowledge in agriculture, fisheries and environment departments; Rob Fitzpatrick was finding them hundreds of miles from the coast; Ray Isbell had written them into the national soil classification and Del Fanning had put them into the international textbooks. Acid sulphate soils had come of age. Job done!

Of course, it wasn't. Twenty years on, Australia is hosting the 9th international conference andmillions of fish are still killed every time it rains, and not just in the northern rivers. The genie is out of the bottle. The only way to put it back again is to restore the original hydrology, as we established at Trinity Inlet and as the Dutch found out a century ago – everyone in the Netherlands pays a substantial special tax to hold the line of control more or less where it is now.

Restoring the hydrology doesn't need a lot of research. It needs political will. There is a price to pay whether the job is done or left undone; involvement in the necessary campaign might not be a good career move, whatever the outcome – I should know. You can read all about the tactics of the opposition in Richard Beasley's book *Dead in the water* (Beasley 2021). On the other hand, the cane growers successfully overcame soil erosion by adopting the trash harvester, they can live with a higher water table and losing a few acres if they have to, and raising the cost of sugar would be a good thing – the medical profession would be with you.

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Improving prediction accuracy for acid sulfate soil mapping by means of variable selection

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Biography:

Virginia Estévez received her PhD in Physics in 2011 from Universidad Autónoma de Madrid (Spain). After, she was a postdoctoral researcher at Universidad del Pais Vasco (Spain) from 2012 to 2013, and at Aalto University (Finland) from 2013 to 2017. Moreover, she was a guest researcher at several universities: in 2007 at the University of Chicago in USA (4 months), in 2008 at the University of Duisburg-Essen in Germany (4 months), and in 2011 at Universität Konstanz in Germany (3 months). Her research has focused on the theoretical study of several topics in physics, mainly in spintronics and nanoelectronics. In 2018 she started working on artificial intelligence. In 2020, she obtained her Master degree of Engineering in Big Data Analytics from Arcada University of Applied Sciences (Finland). Currently, she is a postdoctoral researcher at Arcada University, where she applies machine learning to soil sciences, specifically to acid sulfate soil mapping.

Improving prediction accuracy for acid sulfate soil mapping by means of variable selection

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Acid sulfate soils are one of the most environmentally harmful soils existing in nature. This is because they produce sulfuric acid and release metals, which may cause several ecological damages. In Finland, the occurrence of this type of soil in the coastal areas constitutes one of the major environmental problems of the country. In order to reduce possible damage derived from this type of soil, it is fundamental to create occurrence maps showing their localization. Nowadays, occurrence maps can be created using machine learning techniques. This can streamline the mapping process as well as improves its accuracy. In general, the accuracy of the maps depends on two factors: the dataset and the machine learning method. Previously, different machine learning methods have been evaluated for acid sulfate soil mapping [1]. In order to improve the precision of the acid sulfate soil probability maps, in this study, we have added more environmental covariates (17 in total) to the raster dataset and applied eleven variable selection methods to select the most relevant environmental covariates for the classification and prediction of acid sulfate soils. The predictive abilities of each group of selected variables have been analyzed using Random Forest and Gradient Boosting. From the best results obtained, an acid sulfate soils occurrence map has been created. Compared with previous studies in the same area, variable selection has improved the accuracy by 15-17% for the models based on Random Forest [2]. The present study confirms the importance of variable selection for the prediction of acid sulfate soils.

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Evolution of pyrite oxidation from a 10-year kinetic leach study: Implications for mineralogical characterisations of secondary sulfate minerals

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Biography:

Dr Rong Fan leads the Diffraction, Mineralogy and Geochemistry team across Clayton and Waite sites at CSIRO Mineral Resources. He delivers X-ray diffraction and X-ray fluorescence characterisations in a wide range of mineral contexts, with emphasis on accuracy in quantitative mineral analysis and clay mineralogy. He has more than 15 years of experience in the application of innovative characterisation strategies to problems with mineralogy, geochemistry and mineral surfaces in mineral processing, acid and metalliferous drainage and mineral exploration systems. His research activities involve extensive use of X-ray diffraction and X-ray absorption spectroscopy, both bulk and microprobe, at Australian and overseas synchrotron facilities.

Evolution of pyrite oxidation from a 10-year kinetic leach study: Implications for mineralogical characterisations of secondary sulfate minerals

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Acid rock drainage (ARD) is generated when mineral sulfides, primarily pyrite (FeS_2), are exposed to weathering. Pyrite oxidation and dissolution may also result in the precipitation of secondary sulfate minerals, commonly found in weathered mine wastes, that release 'stored acidity' on subsequent dissolution. To better understand the release of this stored acidity, a kinetic leach column experiment using a synthetic pyritic (5 wt%) mine waste was conducted for a period of 524 weeks, during which treatments with alkaline solutions have been applied (Figure 1).

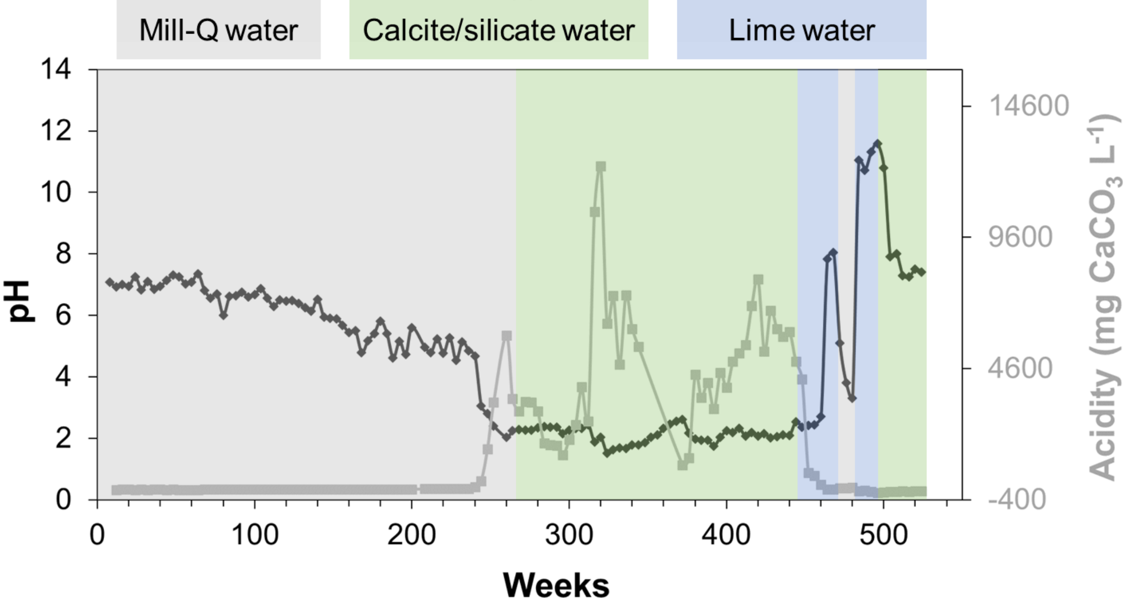

Figure 1 pH and titrated acidity profiles for the kinetic leach column leachate over 524 weeks.

An important finding is that the rate at which acidity was generated from secondary mineral dissolution was significantly greater than from pyrite oxidation after the first calcite-saturated silicate water treatment during the period from 260−440 weeks (Fan et al., 2022). This suggests that in weathered pyritic wastes, both the amount of acidity and the rate at which it is released may be dominated by acid sulfate minerals rather than residual pyrite.

Further, it was found that passivation strategies appropriate for reducing pyrite oxidation rates were not effective for reducing the rate of acid release from secondary mineralisation. Significant amounts of lime-saturated water (with high alkalinity) were required to dissolve the secondary sulfate minerals containing the stored acidity before circum-neutral conditions necessary for pyrite passivation could be achieved. It follows therefore that it is necessary to quantify the amount of stored acidity in secondary minerals so that appropriate remediation and acid management strategies can be designed and implemented to achieve long-term sustainable ARD control and mine closure.

The secondary sulfate minerals were fully characterised by sequential extraction, X-ray diffraction and spectroscopic approaches. Using the sequential extraction method developed by Li et al. (2014), multiple forms of secondary minerals, such as jarosite, schwertmannite, melanterite ($FeSO_4·7H_2O$, acid forming on dissolution) and gypsum ($CaSO_4·2H_2O$, not acid forming on dissolution), were quantified. When mineralogical techniques, i.e., quantitative X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), and X-ray absorption spectroscopy (XAS; specifically examining sulfur speciation), the evolution of mineral and elemental composition were investigated quantitatively.

Comprehensive characterisations of secondary mineralogy and associated acid generation was utilised to evaluate the long-term evolution of acid generating and neutralising phases, providing a powerful tool to examine heavily weathered ARD and acid sulfate soils.

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Historical Developments in the Understanding of Acid Sulfate Soils

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Historical Developments in the Understanding of Acid Sulfate Soils

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This abstact is for an orally delivered paper by the senior author at the 9th IASSC in recognition of his receipt of the Pons Medal of the International Acid Sulfate Soils Working Group of IUSS (International Union of Soil Science) at the 8th Conference at the University of Maryland, USA, July, 2016. The full written paper (Fanning et al., 2017), of which the oral paper presents some highlights, was published as the first paper in a special issue of Geoderma that contained papers presented at the 8th conference. It may be consulted for more information than can be conveyed in the oral presentation. The term acid sulfate soils first came into common use at the time of the first international conference/symposium at Wageningen University in 1972. Leandert J. (Leen) Pons, a chief organizer of that first symposiium noted in a lead paper for it (Pons, 1973) that these soils, by other names for them, e.g. cat clays, were recognized by Linnaeus in The Netherlands and northern Europe as early as the 18th century. Pons went on with colleagues from Wageningen and elswhere to organize and bring about and publish, through the International Land Reclamation Institute, Wageningen, the proceedings and papers of the first four symposia/conferences (Wageningen, 1972; Bangkok,Thailand, 1981; Dakar, Senegal, 1986; and Ho Chi Minh City, Vietnam, 1992).

Fig. 1 Professor Pons undertaking the 'index of squishiness' test developed by Pons and Zonneveld (1965) on a field trip during the 3rd International Acid Sulfate Soil Conference in 1986, in Guine' Bissau, West Africa

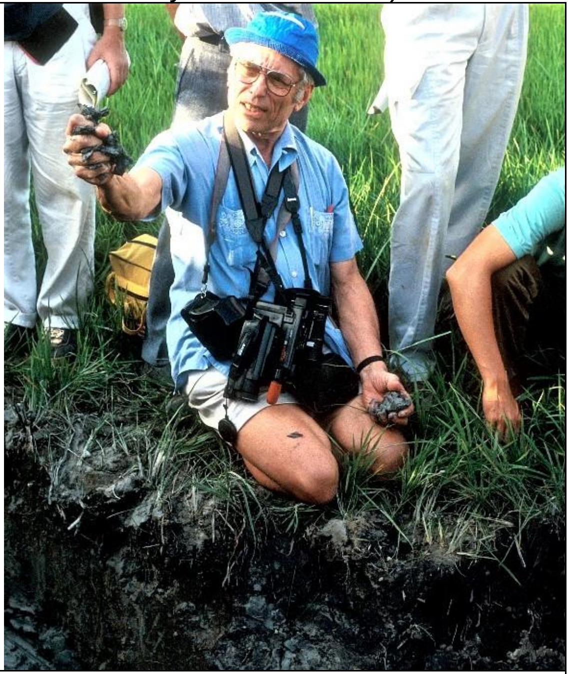

Fig. 2 Professor Pons undertaking the 'index of squishiness' test in the Mekong Delta, Vietnam in 1992 during the 4th International Acid Sulfate Soil Conference.

For his many endeavors, including efforts to get the International Acid Sulfate Soils Working Group established, Pons became recognized as the Father of the International Acid Sulfate Soils Conferences and after his death in 2008 (he was born in 1921) a book of remembrances of him with many pictures of him working with colleagues and fellows and students from various places in the world was published (Fanning, 2009), available on the web site of Wageningen University, see references. In Figure 1 he is demonstrating the *n-value* squeeze test for the degree of ripening of soft sediments/soils (i.e. 'pelagic ooze' materials) as they dewater on a field trip of the 3rd Conference in 1986, in Guine' Bissau, West Africa. Attendees on conferences field trips in which he was involved used to demand that he demonstrate this test as shown in Figure 2 during the 4th Conference in 1992. He always beamed a big smile as he did it. Some of the straps around his neck were for binoculars for viewing the birds of these environments that he loved to visit.

For teaching purposes, Fanning and Fanning (1989, chapter 10) developed and published concepts for gross processes of soil formation and change by which iron sulfide minerals form and accumulate in coastal soils and sediments by **sulfidization**, and for how these potential acid sulfate soil materials, that may qualify as *sulfidic materials* by soil taxonomic concepts, upon exposure to aerobic conditions, may undergo **sulfuricization** oxidation of sulfides and the ferrous form of Fe and hydrolysis of Fe^{3+}, to produce sulfuric acid that reacts with other minerals to produce iron "oxides", jarosite, gypsum and other minerals. These concepts were first developed based on papers by Rickard (1973), for sulfidization (he called it pyritization) and by van Breemen (1973) for sulfuricization in the proceedings of the first 1972 symposium. These concepts have become more refined with time. With sulfidization it is now recognized that much the reduction of the iron of the iron "oxides" to form iron sulfides happens by chemical reduction of the ferric form of iron by H_2S and/ HS^- in dissolved or gaseous forms, whereas the production of the H_2S and/ HS^- is by biological oxidation of organic matter using sulfate S of sea water or other sources as the oxidant.

Recently, much interest in subaqueous soils has developed, especially for coastal and deeper sea water environments. These soils or soil materials have typically been found to be strongly influenced by sulfidization and to be composed of soil taxonomic *sulfidic materials.* In the geologic past sulfidization was involved in the accumulation of sediments that have become sedimentary rocks and sediments that in many inland/upland places upon exposure to aerobic conditions have given rise to active acid sulfate soils that with time have become post-active acid sulfate soils. The "big bang" soil genesis and weathering continues at the base of the current oxidized zone of the soil-geologic column, often now at several meters below land surfaces, with deleterious effects upon ground water released or extracted from water perched at the top of the often dense unoxidized zone. Extreme droughts, e.g. Millennium Drought in Australia, can cause sometimes disastrous acid sulfate environmental effects. We will be visiting sites of such soils and landscapes in Australia on field trips during the 9th Conference.

If the time of formation of j (jarosite) present in deep post-active soils could be dated for various depths, it might be possible to determine the rate of deepening of the oxidized zone. To develop ways to do this, is a challenge for scientists of the future. Observations of some old, deep, post-active soils indicates that except for near surface horizons, where organic matter is or has been present to serve as an energy source for the reduction of the iron of the j structure, to bring it into solution, J is a very stable and long lasting mineral in soils to indicate, by its distinctive pale yellow color, those zones in soils that presently are experiencing or did experience sulfuricization at the time the j was formed at the low pH predicted by Eh/pH stability diagrams. In some post-active acid sulfate soils in Texas, USA., j is found in horizons where secondary calcite is also present, reflecting a current pH about 8, whereas the pH when the j formed likely was (often much) lower than 4. We hope those exposed to this presentation and/or the written version (Fanning, 2017) will conclude that many soils of the world, some now in interiors of continents, have been influenced by acid sulfate soil processes that need to be understood for them to be managed by means that acknowledge their properties. We have found that some Ironstone, ferricrete by another terminology, can form in very short periods of time in some active sulfuricization environments. Silica (opal-CT) cemented rock-like horizons or layers, (silcrete, duripans by Soil Taxonomy?) are found in other acid sulfate affected soils. More studies of the silicate mineralogy of acid sulfate soils are needed. Even If he can't be involved in conducting such studies himself, the senior author hopes to be on the sidelines somewhere cheering those who do. Professor Udo Schwertmann 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 or IMA (Bigham et al. 1990, 1996). Schwertmannite is a poorly crystalline iron oxyhydroxysulfate mineral, which is indicative of rapidly changing local environments and variations in redox, pH and rates of availability of S and other elements. As such, the presence of schwertmannite has been included as an acceptable indicator of acidity (pH <4) for *sulfuric materials* or the *sulfuric horizon* in several international (e.g. Soil Taxonomy and WRB) and national (e.g. Australian) soil classification systems. During the Post-Conference field trip of the 9th Conference we will be visiting the Gutheries wetland where schwertmannite was first identified in a natural soil environment (see Figure 3) and also in an acid mine drainage environment at the abandoned Brukunga pyrite mine.

(a) (b)

Fig. 3 Photographs of the Gutheries wetland in the Mt. Lofty Ranges, South Australia in: (a) July 1990 showing Peter Self (left) and Rob Fitzpatrick (right) where a thin weakly cemented reddish/orange-brown crust (2 to 5 mm) was found to contain the so-called "acid mine drainage mineral", which was originally identified by Bigham et al. (1990) in acid mine drainage (AMD) waters.
(b) August 1993 showing Professor Udo Schwertmann (right – after whom the mineral schwertmannite is named) and Rob Fitzpatrick (left) both pointing to the thin friable crust where schwertmannite was first identified in a natural soil environment (i.e. *Alfic Sodic Sulfaquent*) by Fitzpatrick and Self (1997) as opposed to an unnatural AMD environment and hence used as justification to register the "AMD mineral" as a new mineral named schwertmannite by the IMA (Bigham et al. 1996).

Examples of serious engineering acid sulfate chemical (e.g. Fanning et. al., 2004) and physical (e.g. "pyrite heave" from expansion of volume of pyrite-bearing calcareous shales upon which houses have been built in Ireland from transformation of pyrite and calcite to goethite and gypsum as cited by Rickard, 2012 and 2015) problems will be cited. The greatly increased and wide-spread and deep disturbance of earth surfaces by humans in recent (post World War II) times has brought greater awareness of acid sulfate soil issues to many people, but, so far, too little training in the curriculum of civil and other engineers and land use planners and managers about how to avoid and manage these issues.

To close the presenter hopes to sing/recite his sulfidization poem.

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Acid sulfate soil change processes during wetting-drying cycles in peaty wetlands on Norfolk Island and impact of climate change

Rob Fitzpatrick, B.P Thomas, S Philip

Acid sulfate soil change processes during wetting-drying cycles in peaty wetlands on Norfolk Island and impact of climate change

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Soil survey investigations on Norfolk Island in 1953 (Stephens and Hutton, 1954; Hutton and Stephens, 1956) did not identify and map the occurrence of acid sulfate soils (ASS). The reason for this omission was because the global existence of ASS was only recognised in 1973 by Pons (1973). However, a wide range of ASS have been identified across the Island in drainage lines with peaty wetlands (Fig. 1) based on successive field and laboratory investigations in four representative areas during: (i) 2020 following a dry period caused by drought conditions (Petheram et al. 2020), (ii) 2021 following a wet period of “just below” average rainfall and (iii) 2022 following 12 months of wet periods with above average rainfall.

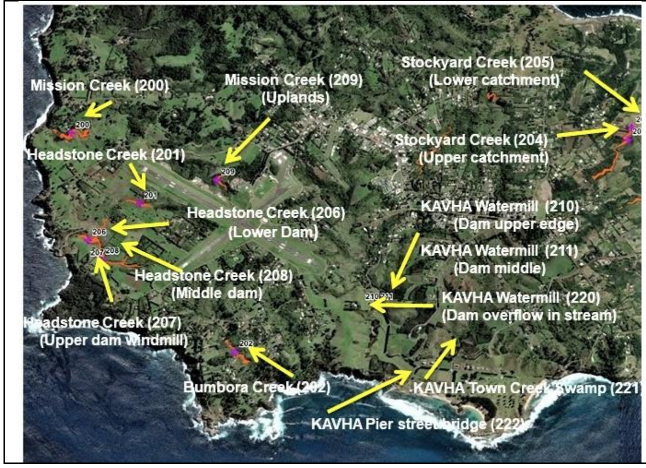

Fig. 1 Aerial photograph showing localities of the successive sampling of fourteen acid sulfate soil profiles in: (i) February 2020 after extreme drought conditions since 1970 (mostly dry), (ii) December 2021 after 18 months of just below average rainfall (partly wet and boggy) and (iii) December 2022 after 12 months above average rainfall (saturated & subaqueous).
Where KAVHA = Kingston and Arthurs Vale Historic Area

We provide illustrations (e.g. Fig. 2) of the following 4 sequential acid sulfate soil transformation processes caused by environmental (rainfall) and anthropogenic (drainage and dam building) factors:

1. Formation of Hypersulfidic organic soils (pH >4) during prolonged wet pre-drought periods (i.e. remained inundated and saturated for many thousands of years with continued accumulation of organic matter).

2. Transformation of Hypersulfidic organic soils to Sulfuric organic soils (pH<4) during prolonged dry periods. As water tables progressively receded between 1970 and 2020 the formation of Sulfuric organic soils followed the sequence:

Subaqueous hypersulfidic organic soils (inundated) → Hypersulfidic organic soils (moist to mostly waterlogged) → Sulfuric organic soils (drying) (Fig. 2). These soils have accumulations of: (i) pale-yellow Ammoniojarosite and Hydronium jarosite and (ii) brownish-yellow precipitates of schwertmannite on dry dam surfaces and on dead reeds along sides of dams.

3. Transformation of Sulfuric organic soils to Monosulfidic and/or Hypersulfidic organic soils during reflooding periods caused by high rainfall conditions (Fig. 2). Reflooding caused the reformation of Fe-monosulfides and pyrite and the formation of Subaqueous Monosulfidic organic soils (Fig. 2) and

Hypersulfidic organic soils. Monosulfidic material with gel-like consistency is common in shallow dams and contains monosulfides (FeS), which can rapidly deoxygenate water if disturbed (Fig. 2).

4.Irreversible or permanent transformation of Hypersulfidic organic soils to Sulfuric organic soils following deep excavation (>2m) and draining of wetlands (drying).

Fig. 2 Photographs of Headstone Creek dam with Sulfuric organic soils in: (i) 2020 during the drought/dry period showing overlying sulfuric material with pale yellow and brownish-yellow iron precipitates (pH 1.7) on the dry dam surface and on dead reeds along the side of dam overlying black monosulfidic material at depth and (ii) 2021 & 2022 during wet/waterlogged periods showing suspended brown coloured iron-rich precipitates in the water filled dam with Subaqueous Monosulfuric material overlying sulfuric material.

The Sulfuric organic soils, especially with acid iron-rich precipitates pose a major remediation challenge because of:

- the large volume and distribution of pyritic and acidic material
- the lack of neutralising minerals due to the dominance of organic matter (peats)
- the low pH (i.e. ranging from 1.7 to 3.5) with complex biogeochemistry and hydrology
- iron-rich precipitates (dominantly as schwertmannite and jarosites) that buffers acidity and scavenges metals between drying, rainfall and reflooding events.

The oxidation of pyrite to form sulfuric acid and the mineral jarosite in Sulfuric organic soils, due to extreme drought conditions across Norfolk Island, offer the first visible warning against much larger imminent environmental problems such as: (i) surface and ground water pollution, (ii) damage to heritage structures within the KAVHA by corrosion and dissolution of cement mortar, calcarenite building bricks used to construct the Watermill dam and bridges and (iii) strong odours from Sulfuric monosulfidic soils. Hence, we liken acid sulfate soils on Norfolk Island to the *canary-in-the-coalmine*, being the first to suffer when the environment is under stress such as impact from climate change because external drivers can render the various types of ASS either relatively stable (i.e. wetting, reflooding or reducing to form Hypersulfidic organic soils), or susceptible to rapid change (i.e. under drying or oxidising to form Sulfuric organic soils) conditions. Like *canaries-in coalmines*, the types of ASS across Norfolk Island can provide critical information about deteriorating environmental situations. A detailed understanding of ASS change processes during wetting-drying cycles has assisted advisors and landholders to easily recognise the different dominant types of ASS and to know what management actions to take if they identify these soils on their property.

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Optimization of sampling and laboratory approaches using chip-tray methods for improved assessment, classification and communication of acid sulfate soils

Rob Fitzpatrick, B.P. Thomas

Optimization of sampling and laboratory approaches using chip-tray methods for improved assessment, classification and communication of acid sulfate soils

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Chip-trays are plastic containers that are 50.5 cm long by 5.5 cm wide by 3.5 cm deep, and contain 20 compartments - or cells - that can be closed with a snap lock lid (i.e. partly air-tight) (Fig. 1). For 2 decades we have used chip-trays in a wide range of acid sulfate soil (ASS) investigations globally. They have proved essential to collect and characterise ASS for environmental risk assessment, monitoring campaigns, community volunteers in citizen science projects and mineral exploration.
Chip-trays provide improved field sampling, archival storage, and moist incubation methods to better characterise and classify ASS with sulfuric, hypersulfidic, hyposulfidic and monosulfidic materials (Isbell & NCST 2021) in a wide variety of soil types ranging from thick peats (Fig. 1), organic.material overlying black saturated monosulfidic material to heavy clays.

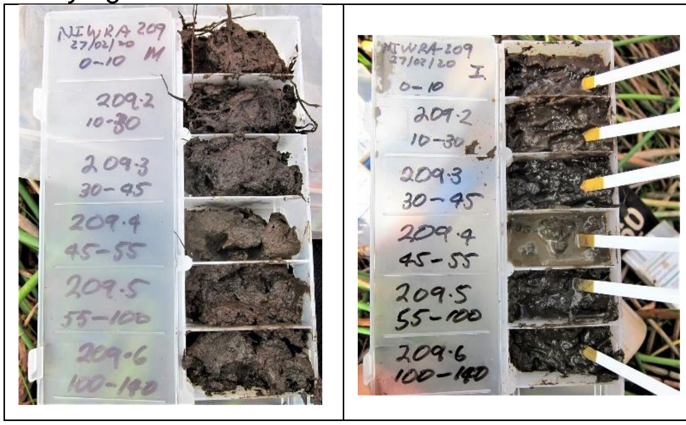

Fig. 1 Two chip-trays containing 6 sampled layers of peaty ASS with hypersulfidic material from a soil profile to a depth of 140cm from Norfolk Island (Fitzpatrick 2020) showing:
(i) Left side chip-tray filled to ¾ full with undisturbed representative materials to display the soil morphology and
(ii) Right side chip-tray filled to 1/3 full with disturbed crushed samples and moistened with distilled or deionised water for acid sulfate soil pH incubation testing ($pH_{incubation}$).

Field protocol involves soil sub-samples to be placed in two separate plastic chip-trays:
First chip-tray (Fig. 1) is used to display the morphology of representative aggregates for each sampled layer (compartments filled to ¾ full with representative, intact aggregates or peds). Salt efflorescence's and/or coatings observed in the field are also placed in chip-trays for further mineralogical analyses. The "morphology chip-trays" are stored in soil archival systems for visual reference and frequently photographed for inclusion in full profile descriptions (e.g. Fitzpatrick et al. 2017a,b).
*Second chip-tray (*Fig. 1 & 2) is used for incubation testing (pH_{INC}) in the laboratory. Compartments are filled to approximately ⅓ full with representative layers of samples that are kept moistened (not saturated) with deionised water. Chip-trays are suited to prevent excessive desiccation (i.e. samples remained moist for periods beyond 4 weeks with minimum attention). After at least 8-weeks of incubation (or in some cases more than 8 weeks) at approximately 25°C, soils are examined periodically for incubation pH and formation of minerals (e.g. jarosite) that indicate

significant acidification. Since the solution in contact with the soil in the chip-tray compartments is likely to be in equilibrium with the soil, the incubation pH of the whole soil is measured using a calibrated pH meter or Merck pH indicator strips (Merck™ strips for pH 2.5–4.5; pH 4.0–7.0; pH 6.5–10.0).

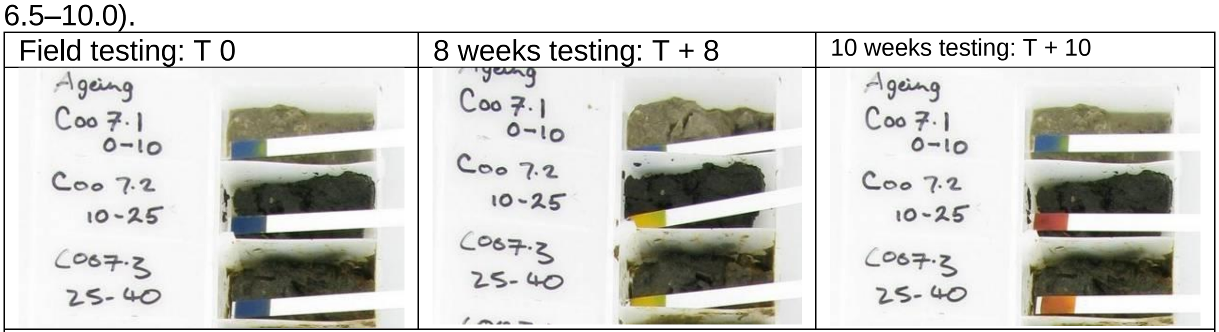

Fig. 2 **Time sequence (T 0, T +8, T +10) for a chip-tray of soils from the Coorong in South Australia undergoing incubation.** Each photograph shows soil pH as indicated by Merck pH strip colours at: (i) T 0, at sampling in the field, (ii) at T +8, after incubation for 8 weeks and (iii) at T +10, at 10 weeks. Here pH indicator strip colours indicate that most samples remain alkaline or neutral (blue colour >pH 7) with only two becoming acid after incubation for 10 weeks (red or pink colour - pH 3.9 to 4) - preferred method is to measure the pH of the whole soil using a calibrated pH meter (Fitzpatrick *et al.* 2011; 2017a; Mosley et a. 2019).

To conclude: The advantages of using chip-trays include rapid field collection and storage of moist soil samples, which offer standardised and improved incubation conditions to those previously used. Chip-tray field sampling and incubation method represents a “realistic tool” for ASS testing based on allowing the soil to “speak for itself” (Dent 1986).

The chip tray method has been adopted by Scientific Reference Panel of the Murray-Darling Basin (MDB) Acid Sulfate Soil Risk Assessment Group for use in rapid and detailed assessment of acid sulfate soil materials in the MDB (MDBA 2010).

The chip-tray method has been extensively used, tested and refined since 2007 during several investigations (e.g. Fitzpatrick et al. 2009; 2017b; 2018) and in development of ASS guidelines and handbooks (e.g. Fitzpatrick et al. 2011, 2017a; Mosley et a. 2019). Chip tray method results were assessed against conventional acid-base accounting methods.

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2

Case Study: Ellenbrook Residential Development, Perth, Western Australia 1994–2020

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Biography:

Alan Foley is an environmental consultant with RPS, with over 18 years' industry experience in Australia. His work includes coordinating ASS programs for major infrastructure and residential projects. The works include investigations and management of ASS, groundwater, surface water and dewatering effluent during and post-construction.

Case Study: Ellenbrook Residential Development, Perth, Western Australia 1994–2020

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The Ellenbrook development is located approximately 30 kms north-north east of Perth in Western Australia. It represents one of the largest master-planned communities constructed in the Perth Metropolitan Region in the past several decades and houses more than 50,000 people.

The development is located on the eastern margin of the Swan Coastal Plain, an extensive sequence of marine derived dunes, with Ellenbrook situated on the oldest and most heavily leached Bassendean Dune Formation, characterised by sandy soils underlain by Guildford Formation clays that extend from the east.

Western Australian Department of Water and Environmental Regulation (DWER) Acid Sulfate Soils (ASS) Risk Mapping identifies a “moderate to low risk of ASS within 3.0 metres of the natural soil surface, with a high to moderate risk of ASS beyond 3 m of the natural soil surface”. Pockets of high to moderate risk of ASS within 3 m of the natural soil surface occur throughout the area, typically associated with existing or former wetland areas. The classification is based on the natural geology (i.e., stratigraphic relationships between soil units) and the regional geomorphologic location forming part of an extensive interdunal wetland. Significantly a shallow unconfined aquifer exists across the region, with depths to groundwater varying between 0.5 m to 6 m over the northern portion of the development, and that this groundwater resource is at significant risk of ASS acidification impacts where ASS is disturbed.

Construction of the development, through a series of “villages”, began in the mid-1990s with RPS providing ASS and groundwater advice and management from around 2006 to the completion of ASS and groundwater commitments in 2020. The commencement of onsite ASS investigation and management was in response to new State government regulatory requirements, following the “discovery” of ASS in the Stirling region of Perth in 2002.

Early studies, focussed on the northern portion of the development, and included the drilling and testing of around 200 ASS core locations across the development to investigate the soil profile at varying depths, consistent with the proposed maximum depth of disturbance for civil works as part of the subdivisional drainage and sewer network. The site investigations and monitoring also comprised in excess of 50 groundwater monitoring bore locations used for characterising groundwater quality pre, during and post development. RPS also undertook validation of treated ASS and monitoring of dewatering effluent over various stages of development.

Soil investigations at the subject site identified a common soil profile, characteristic of highly leached Bassendean Sands with Coffee Rock (podzols) profiles, overlying dense clays of the Guildford Formation, and pockets of wetland soil units. Areas commonly identified as ASS were generally associated with the ferruginous Coffee Rock profiles containing deposits of framboidal pyritic crystals.

Groundwater quality at the site was identified to be extensively degraded (acidified) having been influenced by anthropogenic effects on shallow watertable levels such as changed vegetation cover (i.e., planting of extensive pine plantations to the north) and groundwater abstraction, that acts to drop water tables regionally and locally, potentially exposing ASS to oxidative conditions.

The environmental regulator had placed restrictions on groundwater abstraction over the site due to low pH (several pH units below management criteria), and elevated concentrations (an order to several orders of magnitude above management/guideline criteria) of:

- acidity,
- trace metals and metalloids (dissolved aluminium and iron) and
- sulfate:chloride ratio.

Key elements in the planning and delivery of the Development in addressing ASS and groundwater risks included:

- extensive upfront characterisation of soils and groundwater, defining baseline conditions and informing management approaches
- aquifer pump-testing and groundwater modelling to predict groundwater dewatering (for civil construction) rates, establish drawdown trigger-levels, and inform contractor documents
- development of Acid Sulfate Soils and Dewatering Management Plans, that are site-specific and implementable
- focus on sustainable reuse of treated ASS materials where practicable
- implementation of dewatering controls for disposal that prioritised groundwater recharge via use of settling ponds and groundwater recharge infrastructure
- dewatering effluent treated via automated lime dosing units

The implementation of these management practices changes, along with changes to groundwater abstraction across the site, has resulted in significant improvements in groundwater quality (pH >5, acidity typically <200 mg/L) and subsequent removal of groundwater abstraction restrictions.

Central to the successful delivery of environmental work programs has been the ability to transfer knowledge gained from the investigation phases into practical implementation during construction. This includes the flexibility to adapt planning and working methods based on the experience brought by the civil contractors over the life of the development, in consultation with the responsible regulatory agencies.

With ASS and groundwater commitment requirements completed for the development, the Author will share learnings gained on this long-term construction project, through the implementation of ASS and groundwater management protocols, and how these were adapted over time to reflect enhanced scientific and industry knowledge in Western Australia.

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Assessing Acidic Soils versus Acid Sulfate Soils – Some Case Studies

Mr Laurence Fox[1]
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Assessing Acidic Soils versus Acid Sulfate Soils – Some Case Studies

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A growing population and increasing urbanization in Australia, has meant that many naturally occurring acidic soils are now subject to environmental assessment for a change in landuse from rural to either residential or industrial subdivisions. When these acidic soils become surplus to requirements onsite and need to be disposed, or re-used offsite, they are subject to a waste classification. As waste they must meet stringent criteria for beneficial re-use, including pH criteria and the presence or absence of sulphidic ores.

In acidic soils the low pH can be caused by organic sulphur, organic acids, iron and aluminium hydrolysis and/or the application of fertilisers. In acid sulfate soils (ASS) the low pH can be caused by the oxidation of Reduced Inorganic Sulphur (RIS). In order to distinguish between acid soils and ASS, the practitioner needs to look for evidence of RIS (pyrite) and/or oxidation products (jarosite and possibly schwertmanite) as well as understand the physical (geology and geomorphology) and environmental setting.

Waste classification of these soils and weathered rock usually involves a range of test methods that were originally developed for coastal ASS (below about 5m AHD). Problems have arisen when laboratory results, in isolation, have been used for interpretation with acidic soils sometimes being classified as ASS and vice versa.

The objective of this paper will be to provide, via case studies, methods for assessing what is an acidic soil and what is an ASS in a rural and urban setting. The case studies will make use of laboratory data interpretation, plus review of supplementary information such as geology, ASS risk maps, topography and interpretation of field screening results. This will provide a weight of evidence approach to the assessment.

Three case studies will be presented, two from NSW and one from Tasmania, each from a variety of environmental settings, geology and topography. The case studies will present the interpretation of laboratory data, how RIS and or oxidation products were identified, plus the supplementary information used.

There are many variables and sometimes the laboratory results can lead to uncertainty and misinterpretation. The case studies show that uncertainty can be largely removed by adopting a weight of evidence approach where not only laboratory results, but also supplementary information, can be used to reach a conclusion.

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31

Acid mine drainage: source control, standard testing methodologies and a case study of unexpected non-acid drainage

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Biography:
Prof. Andrea Gerson is the Managing Director of Blue Minerals Consultancy (BMC); Hon. Prof. Fellow, Dept. Physics, Melbourne University; Hon. Prof., Research School of Earth Sciences, Australian National University and Adjunct Professor, University of Flinders. She completed a PhD at Strathclyde University (Scotland) in 1990, followed by a post-doc at King's College (London) until 1993, both focussing on n-alkane crystal structure. Prior to establishing BMC in 2015 she led the Research Group, Minerals and Materials Science and Technology at the University of South Australia. She specialises in the relationship between mineral structure, reactivity and implications for environmental impact and remediation. She now applies and develops advanced analytical techniques for direct application to industrial environmental issues. Andrea has 217 publications, over 17,450 citations and an H-index of 49.

Acid mine drainage: source control, standard testing methodologies and a case study of unexpected non-acid drainage

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Part 1: Mineral surface passivation by micro-encapsulation has become an emerging methodology for acid mine drainage (AMD) source control. Many microencapsulation and passivation approaches have been critically reviewed and, to be effective, were found to universally require the addition of chemical reactants to form the passivation or microencapsulation layer. In contrast it has been demonstrated that iron oxyhydroxide passivation layers on pyrite surfaces can be achieved and stabilised by adsorption of dissolved silicate (Fan et al., 2017) or aluminium hydroxide (Zhou et al., 2018), both of which may be available due to natural aluminosilicate mineral leaching. Under batch leach conditions, reductions of acid generation rates greater than 90% have been achieved (Schumann et al., 2009). In the study by Fan et al. (2017), upon silicate adsorption onto pyrite at pH 7.4, as compared to pH 5 and 3, the slowest dissolution rate was obtained, the opposite trend to the rates measured in the absence of silicate addition. This was demonstrated to be due to the formation of a passivating coherent and apparently amorphous iron oxyhydroxide surface layer, approximately 100 nm in thickness, into which silicate is structurally incorporated inhibiting the phase transformation from amorphous iron (oxy)hydroxide to goethite. Geochemical passivation and major AMD reduction has been demonstrated to be effective for site wastes, e.g., PT Freeport Grasberg (Indonesia); Savage River (Tasmania) where silicates were present in the associated waste rock.

The activity of iron- and sulfur-oxidising microbes can accelerate the oxidation of pyrite and the subsequent acid generation rate by up to six orders of magnitude. While some chemoautotrophic microbes can exacerbate AMD, other groups of microorganisms, such as heterotrophic bacteria, can form protective biofilms on pyrite surfaces reducing the rate of AMD generation by reducing oxidant (O2, ferric iron) availability at the mineral surface and O2 availability generally within the waters contained within the wastes. Most AMD environments are classified as oligotrophic (nutrient poor) due to their low concentrations (<20 mg L–1) of dissolved organic carbon. Supplementing these environments with an exogenous organic carbon supply is a common form of bio-stimulation used to support the growth and activities of beneficial microbial communities. It has been shown recently that the microbial populations in waste rock change dramatically with addition of biosolids and organic amendments resulting in effective AMD control (Ogbughalua et al., 2020). Such treatments are also likely to improve the competence of waste-rock for revegetation.

Part 2: The AMIRA 'ARD [acid rock drainage] Test Handbook', recognised as the Australasian standard in site usage, resulted from the AMIRA (2002) P387A Project, defines the test procedures commonly applied to AMD systems. The focus in this section of the presentation will be on the strengths and weaknesses of some of these tests: the net acid generation (NAG) test, definition of maximum potential acidity (MPA) and acid neutralisation capacity (ANC) test. The resulting values are generally used for acid base accounting (ABA) in some combination to define whether waste rock and tailings are classified as potentially acid forming (PAF), uncertain (UC) or non-acid forming (NAF). However, the application of these tests without understanding of their weaknesses can lead to erroneous classification with consequent resulting implementation of inappropriate remediation strategies. We highlight the need for in-depth mineralogical understanding of waste rock and tailings systems to enable effective characterisation testing.

Part 3: Most rock extraction sites, including mine sites and building construction sites, require a plan to assess, and mitigate if present AMD. We have demonstrated that the standardized internationally recognised ABA tests may not always be provide the correct AMD classification for commonly occurring waste rocks containing low-pyrite and -carbonate due to mineralogic assumptions inherent in their design (Gerson et al., 2019). The application of these standard ABA tests at a copper mine site in South Australia resulted in the classification of a portion of its waste material as PAF in apparent contradiction to long term field measurements. Full definition of the sulfide and silicate minerals enabled re-evaluation of the weathering reactions occurring. The overall rate of neutralisation due to silicate dissolution was found to always exceed the rate of acid generation, in agreement with field observations. Consequently, the waste rock was redefined as NAF. The methods developed represent a significant advance in AMD prediction and more strategic, cost-effective environmental planning, with potential for reclassification of wastes with similar characteristics.

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Stability of jarosite in acid sulfate paddy soil from Central Thailand

Mr Andrew R. C. Grigg[1], Dr Laurel K. ThomasArrigo[1], Dr Luiza Notini[1], Ms Katrin Schulz[1], Dr Ralf Kaegi[2], Mr Kurt Barmettler[1], Dr Worachart Wisawapipat[3], Dr Ruben Kretzschmar[1]
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Biography:
Andrew Grigg is a doctoral student in the Soil Chemistry research group at ETH Zurich (Switzerland). Andrew researches the dynamic behaviour of iron minerals in redox-active soil environments, developing new techniques using spectroscopy methods (such as Mössbauer, Raman and X-ray absorption spectroscopy) and X-ray diffraction to measure the rates and pathways of iron mineral transformations as they occur in soils. His project has specific application in the acid-sulfate rice paddies soils of central Thailand. Andrew holds a Master's of Environment Science from ETH Zurich, and bachelor degrees in Environmental Engineering from the University of New England and University of Southern Queensland.

Stability of jarosite in acid sulfate paddy soil from Central Thailand

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Jarosite ($KFe_3(SO_4)_2(OH)_6$) is a common and prominent mineral in active acid sulfate soils. Forming only under acidic conditions in the presence of elevated dissolved Fe^{3+} and SO_4^{2-}, jarosite is indicative of the oxidation of compounds containing Fe and S, such as pyrite. Jarosite regulates the cycling of trace elements, major ions, and acidity, and therefore, its stability in soils is important to understand. Furthermore, substitutions of structural Fe, K or S by other ions, for example, the substitution of Al for Fe, can affect the stability of jarosite in the environment. In managed wetland soils such as rice paddies, regular wetting and drying cycles may expose oxidised layers containing jarosite to flooding. Under flooded conditions, microbial metabolism using electron acceptors with progressively lower redox potential can leads to the reduction of Fe, driving the transformation of jarosite to other mineral phases by reductive dissolution, hydrolysis or Fe(II)-catalysed transformation. In laboratory studies of constantly mixed mineral suspensions (mixed-suspension studies), under reducing conditions, jarosite has been observed to transform to ferrihydrite, goethite and lepidocrocite.[1-3] Such mixed-suspension studies are useful to measure the comparative reactivity of minerals under specific chemical conditions. However, many complex biogeochemical processes occur in wetland soils that cannot be replicated in mixed-suspension systems. Determining the stability of minerals in soil systems requires an experimental approach that takes account of the chemical complexity, microbiological diversity, and spatial heterogeneity of the system.

In this study, we compared the transformation of jarosite minerals in a mixed-suspension system with transformation in an acid sulfate soil from a rice paddy in Central Thailand. Both the transformation of synthetic unsubstituted jarosite and synthetic aluminium-substituted jarosite (collectively: (Al-)jarosite) were studied. The mixed-suspension systems were set up using glass bottles on a shaker in an anoxic glove box atmosphere. (Al-)jarosite suspended in 50 mM MOPS buffer (pH 7.1) and 0.5 or 5 mM Fe(II) transformed completely into ferrihydrite, lepidocrocite, and goethite within eight hours. Aluminium substitution hindered jarosite transformation and favoured the formation of ferrihydrite and goethite over lepidocrocite. To test jarosite stability in soils, mesocosms containing acid sulfate soils under continuous flooding were set up in a 30°C temperature-controlled laboratory. Mesh bags made of PETE fabric (pore size of 52 µm) were used to bury (Al-)jarosite, and soil enriched with ^{57}Fe-labelled (Al-)jarosite, in the soil mesocosms. Products of mineral transformation in the mesh bags were measured by ^{57}Fe-Mössbauer spectroscopy, and X-ray diffraction where possible. In mesh bags containing pure synthetic jarosite, complete transformation of jarosite to goethite and minor amounts of ferrihydrite occurred within twelve to sixteen weeks. As in the mixed-suspension system, Al-jarosite transformed more slowly than unsubstituted jarosite, remaining only partially transformed after 16 weeks. When contact between jarosite and soil was maximised by burying mesh bags containing soil with ^{57}Fe-labelled jarosite enrichment, jarosite was completely dissolved within sixteen weeks without the formation of iron (oxyhydr)oxide products such as ferrihydrite, goethite and lepidocrocite. The results demonstrated that jarosite stability is influenced both by structural elements of the mineral (such as stabilisation by Al substitution), and the chemical complexity, microbiological diversity, and spatial heterogeneity of the reaction environment. The results offer new insight into the stability of jarosite in acid sulfate soils and highlight the importance of experiments using soil to understand jarosite mineral transformation reactions in the environment.

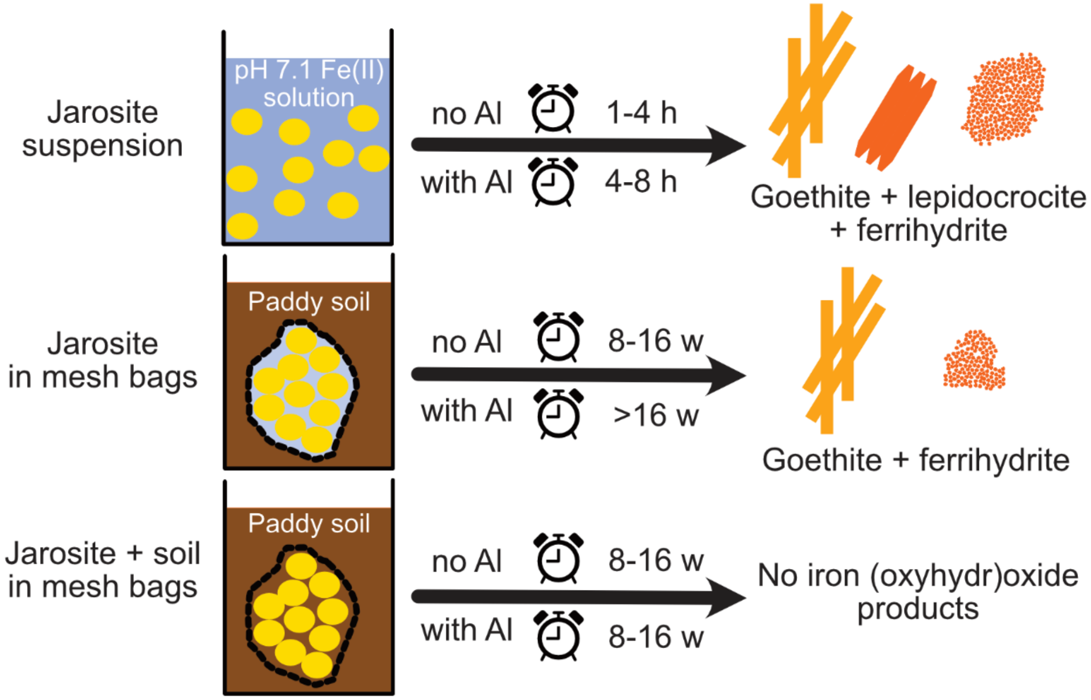

Figure 1: Jarosite (yellow dots, left hand side) transformed to different products, and at different rates, depending on the reaction medium (Fe(II) solution, paddy soil pore water or paddy soil pore water with soil contact) and presence of substituted Al.

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Interactive Effects of Nanozeolite and Ca-Humate in Alleviating Acidity and Al Toxicity of Sulfate Acid Soil from Segara Anakan Island, Indonesia

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Biography:

Name: Assoc.Prof.Dr. Eko Hanudin, Head of Magister Program in Soil Sciences, Faculty of Agriculture, Universitas Gadjah Mada. Research Interest: Soil Chemistry, Short range order (SRO) aluminosilicate, Soil Quality, Soil amendments (zeolite, biochare, humic substances), and Nutrient management,

Interactive Effects of Nanozeolite and Ca-Humate in Alleviating Acidity and Al Toxicity of Acid Sulfate Soil from Segara Anakan Island, Indonesia

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Abstract

Beside nutrient deficiency, acidy and aluminum toxicity of acid sulfate soil is a grave matter. Extremely acidic soil pH conditions and high Al saturation can disrupt the balance of nutrients in the soil and the uptake of essential nutrients by plants. This causes plant growth is not optimal. This study tried to use nano zeolite (<100 nm) and Ca-humate as amendments to address the problem of acidity and toxicity of Al. The nano zeolite preparation method follows Subramanian et al., (2015) with a physical approach, specifically using high-energy ball milling. The zeolite was crushed into nanoparticles by mashing 100 mesh size of zeolite powder with steel balls for 6 hours. This method can produce a total percentage of zeolite size that can be categorized as nanoparticles (<100 nm) which is 91.41% (Ratih et al, 2021)This study used acid sulphate soil from the "Segoro Anakan" Island, Indonesia. The pot experiment was arranged in a Completely Randomized Design (CRD) consisting of 2 treatments, namely 1). Nanozeolite with doses of 6.12 and 18 tons/ha, equal to 14, 28,42 g/pot) , 2) Ca-Humate (6.88, 8.6 and 10.32 tons/ha, equal to 16, 20,24 g/pot) with 3 replications. The same replication also used for no treatment soil as a control. The weight of the soil used per pot is 10 kg, after being treated it is incubated for 10 days to allow the amendments that have been mixed to reach a reaction equilibrium with the soil. Then each pot after incubation took a soil sample to observe changes in its chemical properties.

The results obtained from this study indicate that this soil has a clay texture and very small porosity so that it can physically inhibit the growth of plant roots. In addition, soil also has complicated chemical properties, namely very acidic soil reactivity (pH-H_2O 3.91), very high Al and Na saturation, while very low N and P. Figure 1 shows the effect of the combination of Nano-zeolite and Ca-humate on exchanged H levels, saturation of Al, available Fe and available SO4 was very fluctuating, although the dose effect was not significant, compared to the control it showed significant results in reducing the four soil chemical parameters. The use of a combination of 12 tons/ha Nanozeolite and

10.32 tons/ha Ca-humate was significantly effective in reducing the solubility of Al^{3+}, Fe^{2+}, SO_4^{2-} and pyrite respectively by 59.5, 42.7, 79.2, and 50 % , while the levels of available Ca, Mg, K and Na increased by 33.4, 14, 72.2, and 65.3%, respectively. The combination of Nanozeolite and Ca-humate is quite prospective to be used as an ameliorant to overcome the toxicity of Al and Fe, and at the same time increase the levels of macronutrients Ca, Mg and K.

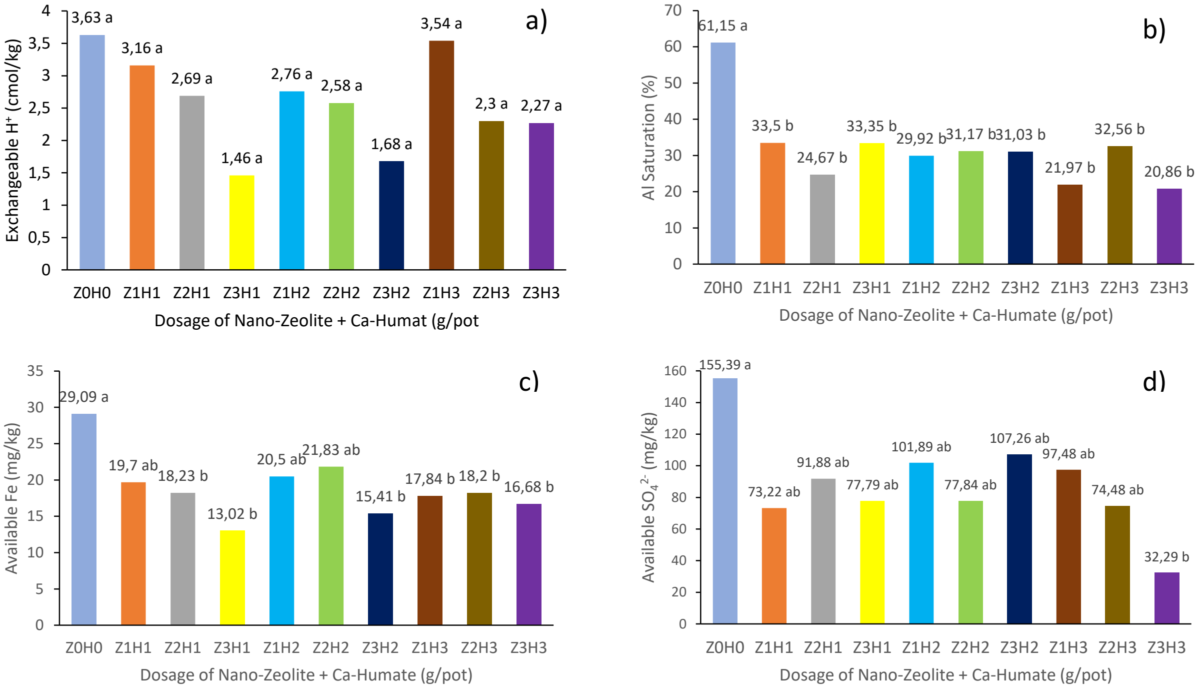

Fig.1. Effect of nano-zeolite and Ca-humate on a).Exchangeable H+, b). Al saturation, c) Available Fe and d). Available SO_4^{2-} in acid sulfate soil. ZoHo= untreated soil as a control; Z1, Z2, Z3= Nano-zeolie with dosage of 14, 28,42 g/pot, respectively; H1, H2, H3= Ca-humate with dosage of 16, 20,24 g/pot, respectively.

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Monitoring lime application and movement using mid infrared spectroscopy

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Biography:
Ruby is currently undertaking her PhD at the University of Adelaide's Waite Campus, working on a Primary Industries-led project that focuses on managing the issue of soil acidification in cropping regions around the state. Her focus is on the application of infrared spectroscopy as a management tool for this ongoing problem.

Monitoring lime application and movement using mid infrared spectroscopy

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Infrared spectroscopy is becoming increasingly widespread in soil science as a fast, accurate and cheap alternative to traditional laboratory methods for measuring and monitoring soil chemical properties. In this study, we explored the use of Mid Infrared (MIR) spectroscopy as a tool to measure the concentration of carbonates present in acidic cropping soils following the application of agricultural lime. To ensure its value in an agricultural context, we worked to develop MIR spectroscopy methods for the detection of carbonates at agriculturally relevant concentrations of <1%. MIR Partial Least Square Regression (PLSR) prediction models were developed using carbonate-specific spectral regions to predict carbonate concentrations in soil. Prediction models were tested with acidic soils collected from field trials that had been treated with various rates and sources of agricultural lime. Prediction models using specific carbonate peak regions were established and compared with models using the entire MIR spectrum to assess model performance, and a single peak models in the range of 2560–2460 cm^{-1} gave the best results (highest R^2 values and lowest RMSE values). Following this, we explored the use of this MIR–PLSR approach to monitor lime dissolution and vertical movement through soils at high spatial resolution. Soil samples were collected at 2.5cm intervals to 20cm depth at three acidic cropping sites in South Australia, with various lime treatments applied either 6 years or 1 year prior to sampling. MIR-PLSR prediction models for both soil pH and carbonate were used to measure lime dissolution and alkalinity movement and undissolved lime presence. Lime balance calculations were also performed to determine the fate of applied lime and assess efficacy of various rates of lime products applied at the surface only or via incorporation. Results indicated that movement of alkalinity at all sites was limited and that residual lime remained in the top 7.5cm of the soil profile while soils remained acidic below this depth.

Findings support the potential of MIR spectroscopy as a powerful tool to measure and monitor the effectiveness and movement of lime in acidic soils. Management implications of this novel approach may improve amelioration of soil acidity in agriculture via high throughput information about lime movement and efficacy.

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Survey of Swedish acid sulfate soils - microbiology

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Biography:

Anders Johnson is a PhD student at Linnaeus University in Kalmar, Sweden. He is investigating the microbial ecology present acid sulfate soils. His primary investigations surround the differences within the ripening layers, as well, examining the differences based on region throughout Sweden. He also has ancillary projects that explore the changes within the acid sulfate soil microbial communities during treatment methods to mitigate acidity and metals release.

Survey of Swedish acid sulfate soils - microbiology

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Acid sulfate soils are a notable source of acid and toxic metals (e.g. Ni, Al, Cd, Be, Mn, Cu, etc.) and have been implicated in massive fish kills along the Baltic Sea coastlines [1]. In Finland, there are an estimated 336,000 ha of acid sulfate soils [2] and it has been estimated that they release more toxic metals into adjacent waterways than the total of the country's industrial waste [3]. The parent sediment materials of acid sulfate soils in Sweden, and around the Baltic coastline, were deposited during the Littorina Sea stage (ca 7000 yr BP – present) [4] and due to isostatic uplift, drainage, and other anthropogenic activities have started oxidizing and converting to actual acid sulfate soils. Acid sulfate soils have long been known to occur around the northern Swedish Baltic Sea coastline and consequently, this region is where the majority of related research has taken place. However, a connected study to estimate the extent of acid sulfate soils in Sweden [5] suggested that acid sulfate soils were not limited to the northern coast of Sweden and actually extended much farther south. In this study, 20 samples of active acid sulfate soils (pH <4.0) were also collected along the entire Swedish coastline plus inland areas around the Stockholm archipelago and Lake Vänern for geochemical (metals concentrations, grain size, and pH) and microbiological analyses based upon DNA extraction, amplification of the 16S rRNA gene, and high throughput sequencing. Preliminary geochemical analysis suggested that there were limited differences between the acid sulfate soils sites based on the geographic region. In contrast, analysis of 16S rRNA gene sequencing data showed regional differences between acid sulfate soils in the north versus south of Sweden as well as the oxidized, transition, and reduced layers of each of the respective sites. Ongoing analyses are seeking to identify the under-laying mechanisms leading to the identified differences through co-application of bioinformatics and geochemical data.

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Arsenic and antimony co-sorption onto jarosite: An X-ray absorption spectroscopic study of retention mechanisms

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Biography:

Dr Niloofar Karimian is Post-doctoral Research Fellow at CSIRO. She is an environmental geochemist, interested in applied and fundamental aspects of environmental geochemistry and mineralogy. Her research explores the multi-disciplinary links between mineralogy, geochemistry, and microbiology in controlling environmental mobility and speciation of a wide range of toxic metalloids, such as antimony, arsenic, and chromium, in soil-water systems. She is interested to explore how mineral formation and evolution over time affect the environmental behavior association and bioaccessibility of impurities and contaminants in the geo-environment using a wide range of advanced analytical techniques including state of art spectroscopy techniques such as synchrotron-based X-ray Absorption Spectroscopy (XAS). In her current role at CSIRO, she is carrying out innovative research to resolve the invisible phosphorus puzzle in iron ore which is a critical step in unlocking the economic potential and reducing the carbon intensity of iron ore processing.

Arsenic and antimony co-sorption onto jarosite: An X-ray absorption spectroscopic study of retention mechanisms

NILOOFAR KARIMIAN, EDWARD BURTON

Jarosite, a common mineral in oxidising acidic environments including acid sulfate soils (ASS) mining and mineral-processing wastes (e.g., waste rock, tailings) and acid mine drainage (AMD), can strongly sorb both antimony(V) and arsenic(V). Sorption of toxic metalloids As(V) and Sb(V) to mineral surfaces is an important phenomenon that controls their mobility in soils, sediment, and aquatic systems. Previous studies have shown that Fe(III) minerals display a strong sorption affinity for both As(V) and Sb(V)[1]. Jarosite has been found to be a particularly potent host for As(V) and Sb(V) under oxidising/acidic conditions. Previous research has shown that jarosite can retain thousands to tens of thousands ppm of both metalloids[1,2]. However, little is known regarding the mechanisms that control dual sorption of Sb(V) and As(V) to jarosite. In this study, we investigated the mechanisms controlling Sb(V) and As(V) sorption to jarosite under acidic pH conditions in dual and single metalloid treatments. Jarosite was found to sorb Sb(V) to a greater extent than As(V) in both dual and single metalloid treatments. The dual presence of both As(V) and Sb(V) decreased sorption by almost 50% for each metalloid. Antimony K-edge EXAFS spectroscopy revealed that surface precipitation of an Sb(V) oxide species was the predominant sorption mechanism for Sb(V). In contrast, As K-edge EXAFS spectroscopy showed that As(V) sorption occurred via bidentate corner-sharing complexes on the jarosite surface when Sb(V) was absent or present at low loadings, or by formation of similar complexes on the Sb(V) oxide precipitate when Sb(V) was present at high loadings. Overall, our findings highlight a strong contrast in the comparative sorption of Sb(V) versus As(V) to jarosite under acidic environmental conditions.

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Variations in Fe/S speciation and trace metals mobilisation in fresh water re-flooded ASS wetlands in a highly dynamic climate

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Biography:
Dr Niloofar Karimian is Post-doctoral Research Fellow at CSIRO. She is an environmental geochemist, interested in applied and fundamental aspects of environmental geochemistry and mineralogy. Her research explores the multi-disciplinary links between mineralogy, geochemistry, and microbiology in controlling environmental mobility and speciation of a wide range of toxic metalloids, such as antimony, arsenic, and chromium, in soil-water systems. She is interested to explore how mineral formation and evolution over time affect the environmental behavior association and bioaccessibility of impurities and contaminants in the geo-environment using a wide range of advanced analytical techniques including state of art spectroscopy techniques such as synchrotron-based X-ray Absorption Spectroscopy (XAS). In her current role at CSIRO, she is carrying out innovative research to resolve the invisible phosphorus puzzle in iron ore which is a critical step in unlocking the economic potential and reducing the carbon intensity of iron ore processing.

Variations in Fe/S speciation and trace metals mobilisation in fresh water re-flooded ASS wetlands in a highly dynamic climate

NILOOFAR KARIMIAN

Fresh water re-flooding of former axid sulfate soil (ASS) wetlands is a contemporary remediation approach which generates alkalinity and leads to the reformation of various Fe(II) and RIS. In wetlands with high seasonal redox oscillations, these newly formed RIS and Fe(II) species may be vulnerable to oxidation subsequent acidity generation during future drought episodes. However, the kinetics and magnitude of acid generating reactions and competing acid neutralisation reactions during a drought episode are unknown. By breaking the dry period, first flush flooding can release substantial amounts of acidity and metals to the adjacent water bodies, prior to the establishment of reducing conditions. Therefore, obtaining a clear insight in to the geochemical conversions of these sediments during wet-dry periods is of great importance to manage these wetlands.

In this study, initially ten surface soil samples were collected from two freshwater re-flooded ASS wetlands and subjected to oxidative incubation for up to 130 days. During the oxidative incubation, soil pH decreased rapidly by ~2–3 units, whilst H^+ concentration increased. RIS species decreased over time whilst the reactive pool of Fe (III) minerals (e.g. schwertmannite) increased. Importantly, the highest rates of acidity generation occurred within the first 20 days, indicating that surface soil layers in these remediated wetlands are prone to rapid oxidation.

In the second phase of the experiment, we re-flooded selected oxidised sediments from both wetland under anerobic condition, for up to 84 days. During the early stages of the re-flooding (up to 7 days) we observed initial release of acidity and metals, followed by quite rapid (4-6 weeks) reversion to anaerobic, sulfate-reducing conditions which ameliorated acidity and sequesters Fe, S and trace metals. Given these results, management of ASS wetlands in a highly dynamic climate, could be challenging over the long term. Knowledge of the timing of redox oscillations and the associated changes in water geochemistry can be helpful to mitigate of risks to the downstream estuarine water quality.

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Coastal Acid Sulfate Soils Assessment and Management – Story of Removal of Two Rail Crossings in Victoria, Australia

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Biography:

Navjot is an Environmental Professional with technical background, competent knowledge of soil science and more than 20 years of experience. Navjot enjoys equally working with natural and problem soils concerning assessment and management. She has considerable experience in the assessment and management and/or remediation of Acid Sulfate Soils (ASS), saline and sodic soils, and contaminated soils including contamination with heavy metals, hydrocarbons, solvents, Per and Poly fluoroalkyl substances (PFAS). She has worked with a wide array of projects and clients including local and state government, the Department of Defence, transport including road and rail, industrial, energy resources including oil and gas, building and construction, etc mainly in Queensland and to a lesser extent in Western Australia, Victoria, and New South Wales.

Coastal Acid Sulfate Soils Assessment and Management – Story of Removal of Two Rail Crossings in Victoria, Australia

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In 2017, the level crossings at Edithvale Road Edithvale (Edithvale), and Station Street/Bondi Road, Bonbeach (Bonbeach), located approximately 500m west of Port Phillip Bay, were selected for removal as part of the Victorian Government's Level Crossing Removal (LRA) Programme. The programme aimed to remove 50 of most dangerous and congested level crossings in and around Melbourne to provide efficient transport networks for the community.

The Edithvale and Bonbeach Level Crossing Removal Project was guided by an Environmental Effects Statement (EES) that was referred by the Minister of Planning due to the potential for a range of significant environmental effects. The Coastal Acid Sulfate Soil (CASS) assessment was undertaken by joint venture between AECOM and GHD for the LXR Authority (LXRA). The key objective of the CASS assessment was to prevent adverse environmental and health effect from disturbing, storing or influencing the transport/movement of potential acid forming soil material within the Project area.

The proposed design to remove the level crossings included lowering the Frankston railway line beneath the existing road levels. The dimensions of the proposed excavation was approximately 1,300m in length and width ranging between 14m and 24m (including pile widths) at new station platforms at each crossing. At both of the existing level crossings, the rail track would be approximately 8m below ground level (mbgl) with a trench base to allow installation of infrastructure. The maximum proposed depth of the excavation was 15m with pile depths up to a maximum of 24m at the deepest point of the trench.

The CASS assessment was undertaken in accordance with the relevant Victorian CASS guidelines i.e., CASS BPMG, 2009 and IWRG 655.1, 2009. These publications outline four stages (Stage A through to D) during the ASS risk identification and assessment process as:

- **Stage A** - desktop review of available maps, previous investigation reports and a Project area inspection (Stage A).
- **Stage B** - detailed soil sampling program and assessment included drilling of 41 soil bores to a maximum depth of 22.5 mbgl across the length of the trench. Soil samples were collected at a 0.5 m interval at each borehole with field screening including pH field and pH oxidised, undertaken on 1045 soil samples.

- **Stage C** - based on the initial laboratory results, approximately 28% of the primary samples or 292 samples were selected for detailed Chromium Reducible Sulfur Suite (CRS suite) analysis. In addition, 22 existing groundwater bores were sampled and analysed for pH, salinity, major cations and anions, heavy metals and nutrients.
- **Stage D** - the CASS hazard assessment included reviewing the proposed design, construction, and operation methodology of the Project with respect to the existing CASS conditions to identify the management and monitoring required during the Project.

The CASS hazard mapping indicated that both sites had a 'high probability/high confidence' for CASS occurrence. The lithology observations during drilling indicated general presence of layer of fine sand overlying layer of clayey sands, silty clay and clay (including shells) followed by a layer of dense sands with occasional gravel. Laboratory data indicated the presence of Potential Acid Sulfate Soils (PASS) in most samples with net acidity exceeding the DSE 2010 criteria (0.03%S) in approximate 33% to 39% of samples collected from the central unit with a maximum net acidity of 1.58 %S at Edithvale and 1.01%S at Bonbeach. The groundwater elevation was approximately 1.0 mbgl, and the groundwater chemistry results did not indicate the presence of existing acidity at either of the level crossings.

Based on the understanding of the CASS distribution and type, along with groundwater modelling for the Project concluded that, the key 'high risk' included permanent drawdown of groundwater on the downgradient side of the trench due to installation of cut off walls across the trenches resulting in potential activation of CASS and groundwater acidification causing health and environmental impacts and impact to inground structures. Additionally, during construction, there was 'low risk' of disturbing, handling, storage, disposal or transport of CASS and any acidic groundwater.

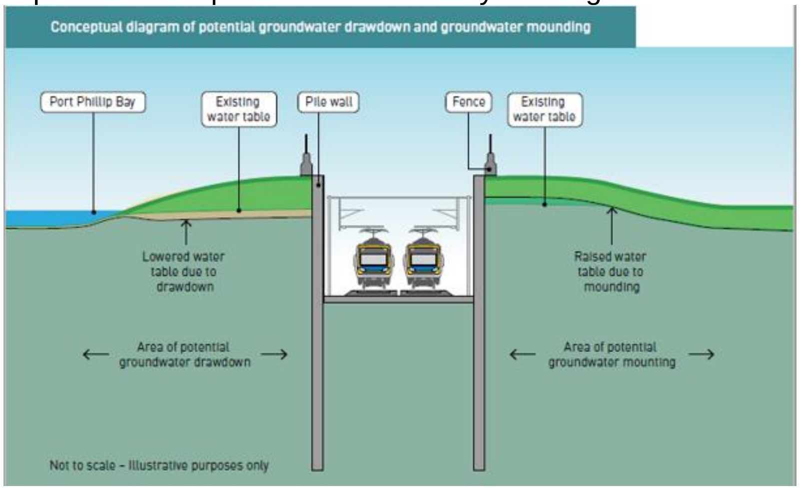

Figure 1: Conceptual Diagram of trench walls

To reduce the risks associated with groundwater drawdown and CASS activation, an engineering solution comprising installation of a passive horizontal drain around the trench pile wall to limit the magnitude and extent of mounding and drawdown was recommended at Edithvale in consultation with Groundwater modellers, geotechnical and design engineers. Such solution was not needed for Bonbeach based on modelling data. Additionally, a CASS management and monitoring plan was implemented during construction and operation to manage potential impacts from ASS.

The construction works started in 2020 with both level crossings successfully removed in November 2021.

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Importance of mineral-organic matter interactions for remediation of acid sulfate soils by submergence and organic matter addition

Dr Angelika Koelbl[1], Dr Klaus Kaiser[1], Prof Robert Mikutta[1], Dr Pauline Winkler[1], Dr Stefanie Schulz[2], Dr Franziska Bucka[3], Dr Werner Haeusler[3], Prof Ingrid Kögel-Knabner[3], Prof Rob Fitzpatrick[4], Prof Petra Marschner[4], Assoc. Prof Luke Mosley[4], Prof Aaron Thompson[5]

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Biography:

Angelika's research focuses on the amount, composition and allocation of soil organic matter under different land uses, with particular regard to changing redox conditions. In the current research project, she investigates interactions between organic matter and iron oxyhydroxysulfates / iron sulfides during remediation of acid sulfate soils.

Importance of mineral-organic matter interactions for remediation of acid sulfate soils by submergence and organic matter addition

Kölbl, A.[1,*], Kaiser, K.[1], Mikutta, R.[1], Winkler, P.[1], Schulz, S.[2], Bucka, F.[3], Häusler, W.[3], Kögel-Knabner, I.[3], Fitzpatrick, R.[4], Marschner, P.[4], Mosley, L.[4], Thompson, A.[5]

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Remediation of acid sulfate soils via re-establishment of reducing conditions requires submergence and sufficient amounts of biodegradable organic carbon (OC) to support reducing bacteria. However, biodegradable organic materials differ in suitability, and also the mineral assemblage of the soils can be important as reactive minerals sorb organic materials, thus limiting the OC availability for microbes. In addition, it is not fully understood which mineral transformations occur due to changing solution composition following submergence (e.g., dissolution of Fe oxyhydroxy sulfates due to changing pH and redox values), and if potentially newly-formed Fe-organic associations reduce the accessibility of OC for microbes. The aim of this presentation is to summarise emerging experimental evidence on the role of organic matter and the mineral-organic interplay in acid sulfate soil remediation.

In a first set of anoxic incubation experiments, we used a (mineralogically simple) sandy sulfuric subsoil with low OC concentration (~3 mg g^{-1}), allowing for studying exclusively the impact of added OM sources. We tested organic matter additions between 10% up to 200% of the native soil OC content by adding ground wheat straw. Additions of OC ≥50% of the native soil OC content and pre-adjustment of pH to values ≥5.0 were necessary to induce microbial reduction processes, which increased the pH to values ≥5.5. Additions of OC ≥100% of the native soil OC caused more rapid changes in redox and pH values, and slightly higher microbial activity, as indicated by CO_2 release. In a follow-up incubation experiment we tested if pre-adjustment of pH was not required if there is a higher OC addition. At OC additions of approx. 150% of the native soil OC content no pre-adjustment of pH was necessary for anoxic remediation of the tested sandy sulfuric soil. We concluded that addition of sufficient amounts of plant litter activates reducing bacteria, likely due to the release of readily available soluble organic matter. However, the effect of soluble organic matter from plant residues had not been tested so far. Thus, we studied the potential of water-extractable, dissolved

OC (DOC) derived from different plant species for remediation of the sandy sulfuric soil in another set of anoxic incubation experiments. The addition of DOC from wheat straw induced strong reduction and rapidly increased the pH by 2–3 units within 3 weeks of incubation under submerged conditions. Addition of DOC from litter of reed (*Phragmites australis*) gave very similar results, while DOC from mangrove litter (*Avicennia marina*) did not induce long-lasting reduction and pH increase. The addition of DOC from River Red Gum (*Eucalyptus camaldulensis*) induced neither reduction processes nor pH increase at all. The extremely low protein content probably caused the low microbial degradability of this DOM. Thus, successful remediation of sulfuric soils may much depend on the source and type of organic material applied.

In all treatments with dropping Eh (to <100mV) and concomitant pH increase (to >5.5) after OC addition and submergence, we found increased concentrations of Fe and S in the soil solutions, indicating the redox- and pH-induced dissolution of Fe oxyhydroxy sulfate phases such as jarosite. This was confirmed by Mössbauer spectroscopy and X-ray diffraction revealing jarosite losses. In turn, short range-ordered Fe^{III} oxyhydroxides were formed, most likely by Fe^{II}-catalysed transformation of jarosite. In addition, Mössbauer spectroscopy revealed Fe^{II} and Fe^{III}, likely in Fe–organic associations. No Fe^{II} sulfides were detected, suggesting that growth of sulfate-reducing bacteria is limited as long as redox conditions are governed by the Fe^{II}–Fe^{III} redox couple.

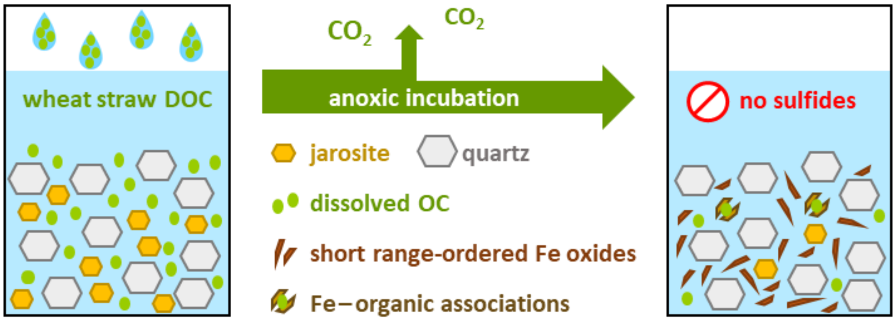

Figure 1: Mineral transformations in a sandy sulfuric soil after submergence and OC addition

In a current set of incubation experiments, we studied mineralogically more complex clayey sulfuric soils with native OC concentrations of ~15 $mg\ g^{-1}$ and found that much higher DOC additions are needed to sustain reducing conditions and pH values of >5.0. Sorption experiments showed that most of the added OC is immediately bound to the soil minerals, making it less available for microbial processes. Compared to the sandy sulfuric soils, pH values remained lower, although similarly low redox potentials were achieved. We assume that high amounts of organic acids identified in the native OC partly compensate the reduction-related proton consumption by deprotonation. Similar to the sandy sulfuric soils, increased Fe concentrations in the soil solution point at pH- and redox-induced dissolution of jarosite. Under the resulting pH and redox conditions, formation of Fe sulfides is unlikely as well.

In summary, our studies showed that remediation by submergence and addition of plant-derived DOC is possible for all sulfuric soils, with wheat straw and Phragmites litter being most suitable. Amounts of OC added may need to be adjusted depending on the mineral assemblage of the soil, in order to compensate for possible sorptive reducing of bioavailability. We suggest addition of OC at amounts that maintain redox conditions that allow for transformation from jarosite into Fe oxyhydroxides while avoiding sulfide formation. Since Fe oxyhydroxides, unlike Fe sulfides, are not prone to support renewed acidification in the case of future aeration, this result has important implications for the remediation of sulfuric soils.

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Effect of limestone amount and grain size on acid neutralization and metal release in dredged sulfide-bearing sediments: laboratory oxidation experiment

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Biography:

1st-year doctoral student in environmental geochemistry at Linnaeus University, Sweden. 5 years of experience in regional field geology and geochemistry at PGE-Cu-Ni and Au deposits in Russia

Effect of limestone amount and grain size on acid neutralization and metal release in dredged sulfide-bearing sediments: laboratory oxidation experiment

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The main goal of a laboratory oxidation experiment was to find out how additions of peat and different proportions and grain sizes of limestone can maintain a near-neutral pH and minimizethe leaching of nutrients and toxic metals from dredged sulfide-bearing sediments exposed to atmospheric oxygen. The study was conducted in Finland, where sulfide-bearing sediments are extensively dredged and used for improving farmlands, and regulations for lime additionstherefore exist but seem not to work very well. Therefore, our aim was to test in the laboratoryhow the Finnish recommendations and several other alternative lime and peat treatments workon oxidizing sulfidic sediments from the boreal region. Since there is a similar problem with sulfide-bearing sediments in Sweden, also the Swedish recommendations were tested duringthe experiment.

Dredged sediments were mixed with five different treatments:

- Agricultural limestone ($CaCO_3$) according to Finnish recommendations (10 kg/m^3)

1) Agricultural limestone ($CaCO_3$) according to Swedish recommendations (40 kg/m^3)
2) Ultra-fine grained $CaCO_3$ (C2 quality by Nordkalk) according to Finnish recommendations (10 kg/m^3)
3) Ultra-fine grained $CaCO_3$ (C2 quality by Nordkalk) according to Swedish recommendations (40 kg/m^3)
4) Combination of C2 (10 kg/m^3) and fine-grained peat (10 kg/m^3)

The difference between agricultural limestone and C2 limestone is mainly in particle size. For agricultural limestone median particle size is 3.15 mm and for C2 it is 2.5 µm. In general, methods 3 and 4 follow the recommendations of Finland and Sweden in terms of amount of limestone, the difference lies in the choice of limestone particle size. Samples that were not subjected to treatment were used as reference samples. All treatments were made intriplicates. For efficient sulfide oxidation and leaching control, boxes with sediments were irrigated once a week during the first year, and every two weeks during the second year, withone litre of ultrapure water, and the drainage water that was formed was collected at the bottom of the box. The drainage water was sampled once a month during the first year, and every two months during the second year, for pH and multielement ICP analysis. The durationof the experiment was two and a half years (December 2019 to May 2022).

The changes in water pH are presented in fig. 1. It is seen that all studied samples can be divided into three groups: acidic (reference samples), semi-acidic (Finnish recommendations),and neutral-alkaline (Swedish recommendations and all C2 treatments). As for the Finnish recommendations, the pH values showed stable near-neutral results only in the first year ofobservations, then the pH dropped sharply to values from 4 to 5. The pH results of the Swedishrecommendations and all C2 treatments varied from 7 to 8 for quite a long time, but in the 10kg treatments with both agricultural limestone and C2 limestone, the pH eventually dropped (in 1,5-2 years). In the case of applying peat and 10 kg of C2 limestone, the pH drops even more significantly (down to 5) than just adding the same amount of limestone of the same quality. Regarding the leaching of chemical elements, two trends can be distinguished that characterize the difference between the reference samples and the samples to which the treatments have been applied. The first one covers those elements that are leached tens andhundreds of times more from reference samples. These elements include for example Fe, Mn,Al, Co, Ni, and Zn. The second trend has to do with those elements that are leached out morein alkaline treatments. Among them are elements such as P, Ca, Mo, Sb, and V. Some of these elements are crucial nutrients for increasing the productivity of growing crops.

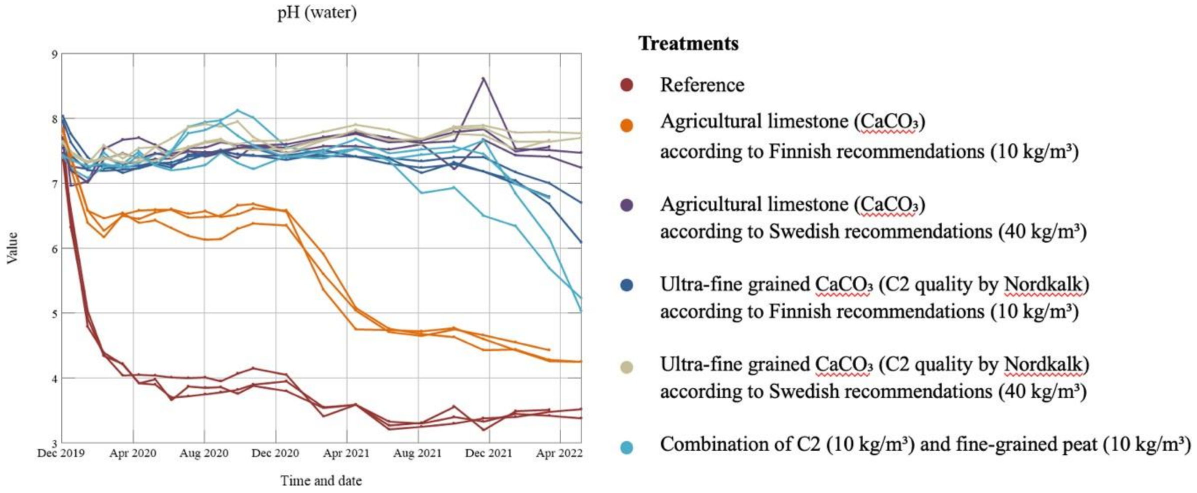

Fig. 1 Changes in water pH during the oxidation experiment

The main conclusion regarding pH is that only treatments according to the Swedish recommendation, i.e. 40 kg agricultural limestone or 40 kg C2, kept a stable near-neutral pH during the duration of the experiment. A near-neutral pH is advantageous for the assimilationof N, P, K, S, Mg, and Ca by plants. Regarding the release of metals with toxic properties, it should be stated that due to the treatments, the leaching of major metals such as Fe, Mn, andAl, as well as trace metals such as Co, Ni, Cd, and Zn, was significantly reduced. On the contrary, after applying the treatment to the sediment, the leaching of Mo, Sb, P, V, and Ca increased.

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Stabilization of sulfide-bearing clays as a new building ground

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Biography:

D.Sc Thomas Kronberg is a senior researcher at Åbo Akademi University, Turku, Finland. His research focuses on clay-based materials (raw materials, ceramics, building materials, etc.). In all research, circular economy and a resource-wise use of raw materials are present. During the last years, most work has been related to characterisation, stabilisation and neutralisation of acid sulfate soil materials. He also has 20-years' experience from industry, where he worked as production-, production development-, and environmental manager in a ceramic factory.

Stabilization of sulfide-bearing clays as a new building ground

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In a growing city, more and more areas are being used for construction, where the ground is technically challenging including clay-rich soils, contaminated soils, and dredged masses. There are also major challenges in how to utilize the surplus soil materials from construction work areas. The fine-grained soils in the coastal areas of Finland are frequently sulfide-bearing sediments, which have emerged from the former Baltic Sea due to postglacial isostatic land uplift and are today found in coastal areas up to 100 m above the current sea level. Due to anthropogenic actions, large quantities of these sulfide bearing sediments have become acid sulfate (AS) soils with a pH <4 mobilizing enormous quantities of acidity and soluble metal to the environment with the runoff water.

In this work, the aim was to find local and resource-wise solutions for stabilizing urban fine-grained sulfide-bearing soil materials and to prevent the dissolution of potentially toxic metals. This would reduce the need of mass transport and enable the safe use of dredged masses and surplus clays in the city's land and green building sites.

The clay soils were collected from different areas in the coastal city of Turku. On the day of sampling the field pH, water content, particle size and visual features were determined. To verify if the sampled clay contained sulfides, a quick oxidising test with hydrogen peroxide (pH_{FOX}, S_{FOX}) was performed (Visuri et al., 2021). The content of organic matter (LOI), titratable incubated acidity (TIA) (Österholm et al., 2016), and pH incubation was performed in the laboratory for a period of 19 weeks to simulate the natural oxidation behavior of possible existing sulfidic materials. After incubation of the clays, the amount of soluble S and potentially toxic metals (Ni, Cd, Cu, Al, etc.) was determined by ICP-OES. The total concentration of S and several metals were analysed by ICP-MS and/or ICP-AES after a digestion in aqua regia.

Stabilization recipes for the soils were systematically developed, with an emphasis on reducing the amount of cement by using industrial side streams (e.g., ash, blast furnace slag, and lime). Different levels of binders were mixed with the clays and cylindrical samples for testing compression strength were prepared. The compression strength was measured after 7, 28, and 91 days. The change in acid production potential was determined for the stabilized samples after 91 days. The effect of

stabilization on the leaching of S and potentially toxic metals was determined by measuring the solubility after 91 days. The stabilized samples were further analyzed by SEM/EDS, XRD, and TGA measurements.

The untreated sulfide-bearing clays used in this study had a high acidity (TIA >200 mmol H^+/kg) and sulfur content of 0.93%. The reference non-sulfide-bearing clays had correspondingly an acidity < 10 mmol H^+/kg and < 0.04% S. The solubility of potentially toxic metals from the incubated acid sulfide-bearing clay was enhanced (e.g., Zn 10.8 mg/kg, Cu 0.55 mg/kg and Al 113 mg/kg), whereas there was no noteworthy leaching from the non-sulfide-bearing clay. After stabilization, the pH remained neutral in the samples and thus the solubilities of potentially toxic metals were low after incubation. Thus, stabilization effectively prevents the leaching of harmful substances from potential AS soils.

The industrial side streams could successfully be utilized to stabilize clay soils. The amount of cement was reduced with all side streams used in this study. When using blast furnace slag about 2/3 of the cement content could be replaced and still receive similar long-term strength values. Thus, a significant reduction in carbon footprint, calculated as CO_2 emissions, can be achieved with these applications.

The compression strength was significantly lower in the stabilized sulfide-bearing clay samples, thus more binders are needed to achieve the same strength as in non-sulfide-bearing clays. However, water content and particle size also influence compression strength.

The results show that it is possible to stabilize and sustainably recycle acid sulfate soils, i.e., sulfide-bearing clays. The strength development and immobilization of potentially toxic metals enable their use as a building ground material.

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ASPAC Global Proficiency Testing, Acid Sulfate Soils Interlaboratory Testing Data and Analytical Methods for the National Guidelines

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ASPAC Global Proficiency Testing, Acid Sulfate Soils Interlaboratory Testing Data and Analytical Methods for the National Guidelines

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The Australasian Soil and Plant Analysis Council (ASPAC) runs through Global Proficiency, an interlaboratory testing program. It initially focused on agricultural soils and plants but has expanded into acid sulfate soils and in recently years further into soil physical methods.

Up to 15 laboratories participate in the interlaboratory acid sulfate soils testing program, with all laboratories based in Australia. The program is available to New Zealand, Indo Pacific and Asia Pacific member countries. The program includes four acid sulfate soils sourced from all areas of Australia and provided to participating laboratories on a yearly basis.

The ASPAC proficiency program is designed for laboratories to:

- assist in maintaining and increasing current levels of testing
- increase confidence in a laboratory's existing methods and results
- assist in implementing standard methods and validating new testing methods
- provide cost effective quality assurance programs to members
- indicate a laboratory's current level of proficiency to existing and prospective clients.

Assessment and interpretation of comparative analytical results over the last four years identifies some interesting trends in the understanding of analytical methods and the performance of Australian laboratories.

In 2018, the updated best practice for identification and analysis of these soils was published as the National Acid Sulfate Soils Guidance: National acid sulfate soils identification and laboratory methods manual. This manual, for which I was a contributing author, made significant progress in redefining the appropriate and most suitable analytical methods. As part of this review it also removed reliance on the perceived in-situ neutralising capacity of acid sulfate soil environments, unless the capacity of these soils to self-neutralise is validated with incubation trials.

In refining the best practice analytical methods, the Suspension Peroxide Oxidation Combined Acidity and Sulfur (SPOCAS) methodology is no longer considered an acceptable suite of techniques. The adoption of this change has been slowly recognised by industry, government authorities, consultants and laboratories. The primary analytical methods for identification are Chromium Reducible Sulfur (S_{CR}), Peroxide Oxidisable Sulfur (S_{POS}), Titratable Actual Acidity (TAA), Net Acid Soluble Sulfur (S_{NAS}) and Acid Neutralising Capacity by Back Titration (ANC_{BT}).

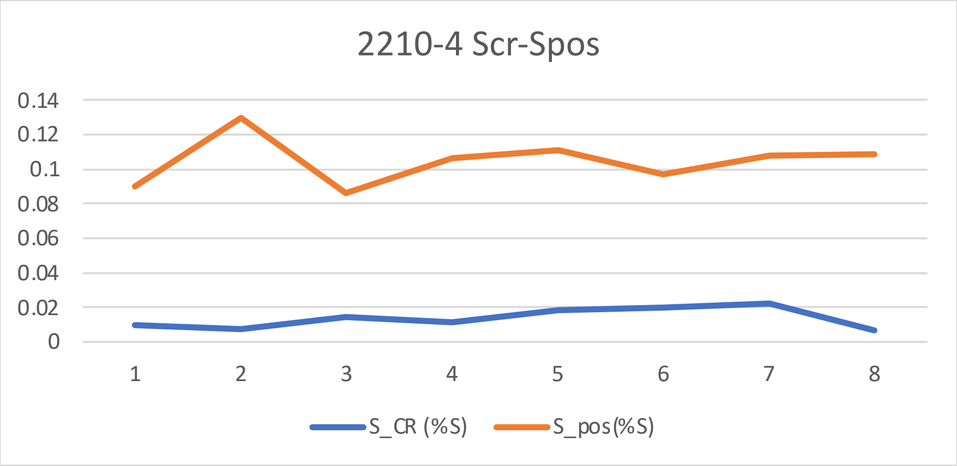
The use of S_{POS}, previously part of the SPOCAS suite, while still within the Guidance, is not recommended where total organic carbon is > 0.6% or close to the action limit. Where the S_{POS}

method is used for identification of pyritic environments, the Guidance recommends validation of 15% of samples by the S_{CR} method. This information is poorly recognised by industry.

Figure 1 below is an example soil from the 2022 inter-laboratory testing program and clearly accentuates the false acid sulfate classification concerns of using an inappropriate technique.

The S_{POS} method clearly classifies the site's soil as potential acid sulfate. This data alone, without reference to Net Acidity, indicates the site requires an acid sulfate management plan – a huge cost to the client. Whereas, Actual, Retained Acidity, or both, would be required with this S_{CR} to trigger the lowest texture dependent Net Acidity trigger of 0.03% S for management. The consistency of data between the eight laboratories that performed both methods on the interlaboratory soils is generally very good and consistent.

Figure 1- 2022 Global Proficiency Trial sample 4 S_{CR} and S_{POS} comparison



A potential concern in the interlaboratory testing program is laboratories may not achieve full pyrite recovery using the S_{CR} technique. The interlaboratory soils clearly show a significant and consistent 20% average underestimation of the %S using S_{CR} analysis.

Laboratories conducting S_{CR} should analyse pure pyrite and sand reference samples to ensure 100% sulfide recovery. The Environmental Analysis Laboratory (EAL) and researchers at Southern Cross University developed the S_{CR} technique (Sullivan et al. 2000) and with interlaboratory soils achieved a near 1:1 relationship between $\%S_{CR}$ and $\%S_{POS}$ in non-organic soils.

ASPAC was formed in 1990 with the goal of improving understanding of Australasian Laboratory methods, quality and interlaboratory consistency to reliably support analytical requirements. We have reported very significant analytical method quality improvements over these years and strive to continue to support training and industry engagement for future enhancement of laboratory quality and capabilities. Future training days and programs on acid sulfate soil analysis methods will be forthcoming.

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Iron and sulfate reduction dynamics in coastal soils undergoing seawater inundation from sea level rise

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Biography:
Emily Leyden is Research Fellow at the University of Adelaide, with research interests in soil geochemistry, coastal acid sulfate soils, geochemical and hydrological modelling, environmental resource management, and sea level rise. Her research primarily examines geochemical changes and complexities in coastal soils and landscapes due to sea water intrusion.

Iron and sulfate reduction dynamics in coastal soils undergoing seawater inundation from sea level rise

Dr. Emily Leyden

Sea level rise induced seawater inundation will begin to change the biogeochemical cycling of iron, sulfur and carbon in coastal wetland soils. A long-term () laboratory experiment, slowly inundating intact coastal soil cores with seawater from the 'bottom up', was conducted to observe how coupled iron and sulfur dynamics change in different soil types. Pore water was extracted from the 60 cm cores at 10 cm depth intervals every 90 days and destructive solid phase analyses were made at the start and end of the experiment. Iron and sulfate reduction was induced in soils with readily available TOC as anoxic conditions established, evidenced by statistically significant increases in dissolved Fe^{2+} and sulfide concentrations in porewaters, as well as simultaneous and progressive increase in the sulfur isotope (34S/32S) ratios. An increase in AVS indicated formation of metastable iron sulfide (FeS) minerals resulting from Fe^{2+} and sulfide in porewaters post inundation. This was supported by PHREEQC modelling of local mineral saturation states/indices in the system. Overall, the Fe^{2+} concentration increased to a peak at between 270-360 days, and then began decreasing at some depths, indicating slowing iron reduction, presumably because reactive iron became progressively consumed by microbially driven reductive processes. However, microbially mediated sulfate reduction continued as abundant sulfate was still available from seawater. In the absence of free Fe^{2+}, sulfide accumulated in the porewater, but only in those soils inundated the longest (> 360 days), and with greater than 5% TOC. The combined use of sulfur ($^{34}S/^{32}S$) and strontium ($^{87}Sr/^{86}Sr$) isotopes supported the observed results, and represents a new and robust technique to quantify progressive sulfate reduction and seawater mixing phenomena in coastal soils. This study gives new insights into the biogeochemical cycling of sulfur and iron in soils experiencing seawater inundation from sea level rise over longer timescales. It is likely that sulfidization (due to in-situ sulfate reduction) will begin to affect coastal wetland soils, especially in areas where TOC is high and where reactive iron depletes over time.

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How does potential and actual acidity of Acid Sulfate Soils (ASS) change over twenty years of soil storage?

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Biography:

Jeremy Manders is a Land Resources Officer with the Department of Environment and Science. He has over 20 years experience in ASS mapping throughout the state and is an author on the 2016 East Trinity Soil Remediation Report. Jeremy is a licensed driller and has travelled the state drilling holes for numerous soil and groundwater mapping and research projects - most recently for the Queensland Soil Monitoring project. He is our WH&S and Soil and Land Information database guru.

How does potential and actual acidity of Acid Sulfate Soils (ASS) change over twenty years of soil storage?

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Archived soil samples are an invaluable resource, enabling samples to be re-analysed later using improved methods, or for different analytes. Between 1996 and 2019 soil scientists from the Queensland Government collected almost 50,000 samples for multiple mapping projects throughout the state. Soils were rapidly dried at 85°C, ground to <2 mm, then placed in sealable polyethylene bags for archiving. Concurrently, split samples were finely-ground and chemically analysed. Soil samples were stored in a dark, air-conditioned facility at 24°C. As shown by Fig. 1, the vast majority these samples were collected and stored over 10 years ago.

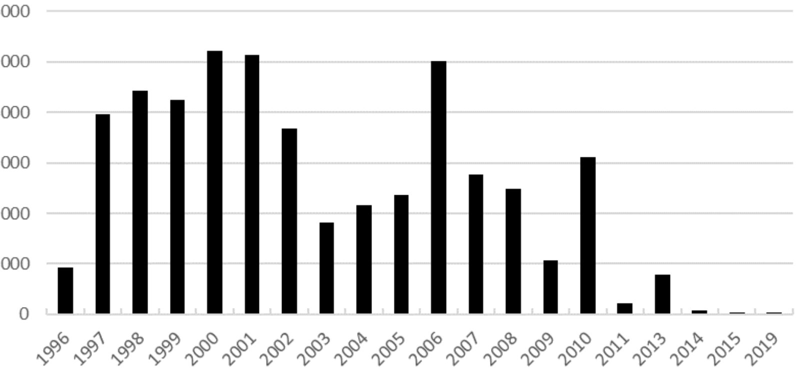

Fig. 1. Approximate number of samples stored each year from acid sulfate soil projects.

The storage conditions described above could at best be described as sub-optimal for ASS, which are susceptible to oxidation during prolonged storage. To best preserve ASS after preparation, samples should be vacuum-sealed inside gas-impermeable bags. (The DES Chemistry Centre has vacuum-sealed its Laboratory control soils and has seen no detectable changes in potential and actual acidity in soils stored for >10 years). However this procedure is too expensive and time-consuming to be applied to all samples.

The archive contains numerous samples from the East Trinity ASS remediation site (Cairns, Australia), dating back to 2001. With recent global interest in ‘blue carbon’ for climate mitigation we wondered if these archived samples could be successfully re-analysed for organic carbon, which had not originally been measured. At the same time, we were interested in exploring if any changes had occurred in the potential and actual acidities of these East Trinity soils during storage, and if any such changes might depend on initial soil properties.

A subset of 10 archived East Trinity soils spanning a representative range of textures, depositional environments, and net acidities, was selected for re-analysis (Table 1). These soils were ground to <0.5 mm, then re-analysed for actual acidity and potential sulfidic acidity according to the TAA and S_{POS} components of the SPOCAS method (Ahern *et al*. 2004). The 2001 and 2021 results are compared in Fig. 2. Total organic carbon (TOC) is also being analysed, but results were unavailable at the time of abstract submission.

Table 1. Details of samples analysed from East Trinity

Sample	Colour (Munsell)	Texture	pH Field	pH Peroxide	Sample Depth	Depositional Environment
1	Dark Greenish Grey (5GY41)	Silty Light Clay (ZLC)	6.3	5.0	0.9-1.1	Estuary Muds
2	Greenish Grey (5GY51)	Silty Light Clay (ZLC)	7.8	6.2	3.3-3.5	Estuary Muds
3	Greenish Grey (5GY51)	Silty Light Clay (ZLC)	7.0	6.6	0.8-1.0	Estuary Muds
4	Grey (N60)	Coarse Sand (KS)	5.8	3.7	1.3-1.5	Mixed Zone
5	Grey (5Y51)	Sandy Light Clay (SLC)	6.3	3.6	1.8-2.0	Mixed Zone
6	Greenish Grey (5G51)	Light Medium Clay (LMC)	7.5	1.5	12.8-13.0	Pleistocene
7	Very Dark Grey (5Y31)	Silty Light Medium (ZLMC)	7.1	1.4	0.7-0.8	Mangrove Muds
8	Dark Grey (5Y41)	Silty Light Clay (ZLC)	7.6	1.8	2.5-2.7	Mangrove Muds
9	Dark Grey (5Y41)	Silty Light Clay (ZLC)	6.8	1.2	1.3-1.5	Mangrove Muds
10	Grey (10YR51)	Silty Light Clay (ZCL)	6.5	0.8	0.2-0.3	Mangrove Muds

The original net acidity contents of soils (measured in 2001) ranged from –1.0 equiv. %S (sample #1) to >2.5 equiv. %S (sample #10) (Fig. 2).

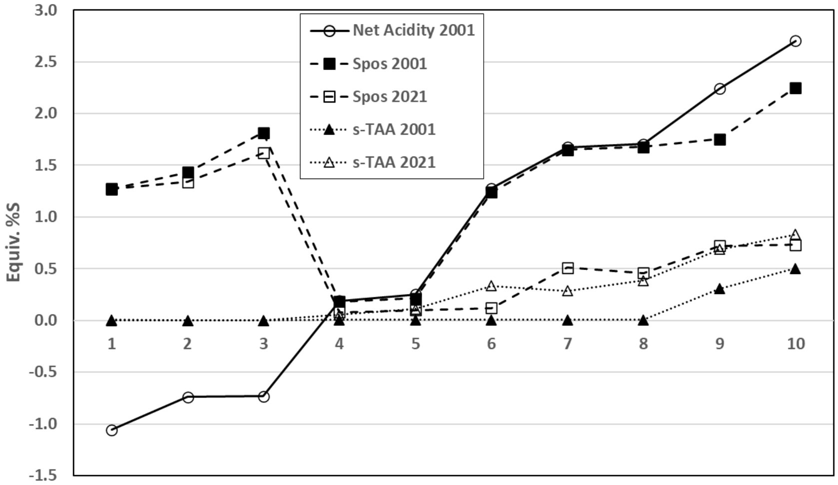

Fig. 2. S_{POS} and TAA measured in 2001, then in 2021 after storage, for 10 East Trinity soils. (The ten samples are plotted in order of increasing Net Acidity as measured in 2001).

The samples with negative net acidity (#’s 1–3) are highly sulfidic, but are self-neutralising when oxidised, due to the presence of microscopic calcitic *Foraminifera* (Chaproniere, 2002). They oxidised slowly on storage, reflected by the small change in S_{POS} over 20 years. In samples with positive net acidities, the difference between the S_{POS} measured in 2001 and 2021 was significant and became more pronounced with higher initial net acidities. The loss of potential sulfidic acidity (S_{POS}) in the samples with a positive net acidity showed a corresponding but not commensurate increase in actual acidity. This differential can be explained by the conversion of the ‘lost’ potential acidity into retained acidity (as illustrated by sample #9, where the differential of 0.656 %S is compensated for by a retained acidity (s-S_{NAS}) result of 0.668 %S measured in 2021).

These results indicate that soil storage conditions are not as critical for soils with a negative net acidity, compared to those with positive net acidities, which are susceptible to significant change under the current soil storage conditions.

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Packaging Acid Sulfate Soil (ASS) science for First Nations storytelling and ecotourism engagement

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Biography:

Michelle Martens is a Land Resources Officer with the Department of Environment and Science. She has spent the last 20 years at least knee deep in the remediation of the acid sulfate soils (ASS) at East Trinity. Michelle has become a jack-of-all-trades with expertise in ASS remediation, monitoring, education, research, and WH&S, but has yet to find a way to quickly remove the lingering stench of monosulfides.

Packaging Acid Sulfate Soil (ASS) science for First Nations storytelling and ecotourism engagement

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The Queensland Government purchased the freehold East Trinity property in 2000 and has successfully remediated the severe acid sulfate soils on the 740 ha property near Cairns, North Queensland (CRC CARE 2018). The remediated landscape is dominated by features from ASS disturbance to facilitate sugar cane production (bundwall, floodgates and drains) and subsequent remediation (water bodies, standing dead trees and monitoring stations).

The remediated landscape enables the indigenous tourism vision of the traditional custodians to be realised through their Mandingalbay Ancient Indigenous Tours (MAIT) https://mandingalbay.com.au/eco-structure/. With the first phase of their infrastructure plan in place, MAIT welcomes visitors via boat from Cairns, sharing their culture with school groups through to international tourists immersed in 'deadly dinners', hands-on country eco-tours, and multi-day camps. The rich oral tradition of the Mandingalbay Yidinji people is evident during site tours with MAIT Rangers and Guides, but the acknowledged 'elephant in the boat, bus or croc enclosure' is the lack of stories about the site's ASS history.

While storytelling is the backbone of Indigenous knowledge transfer and is still highly valued today, modern science communication relies heavily on written documents and visual aids. Packaging the ASS remediation history of East Trinity property for delivery to tourists by MAIT Guides and Rangers with no formal scientific training needs to accommodate this fundamental difference in communication style.

Initially, MAIT requested a stand-alone water quality dashboard, packaged for use on a screen at their welcome shelter and on the MAIT website. As discussions around the dashboard progressed, the ability for MAIT Rangers and Guides to interactively access historical content (e.g. photos and water quality from the early days of the ASS remediation) for specific locations on their regular tour route, became apparent.

In consultation with MAIT, and in conjunction with the DES Data Improvement and Machine Learning (DIML) team, we developed a Power BI dashboard that will deliver near real-time data from a cloud-based Microsoft Azure water quality database that can be both embedded in a website and accessed via touch screens. The dashboard displays the current water monitoring stations located on a site map, as well as the latest weather data. For each station the most recent data is displayed, along with a brief description of the parameters and units used. Selecting a water station icon allows access to a graph of the last 2 weeks of water quality data recorded at that station. The dashboard also has the capability to display historical photos showing the site in both its current and formerly acidified states, illustrating how the remediation has transformed the landscape. These images are a powerful communication tool, as well as an effective prompt for indigenous Rangers and Guides leading tours and discussions.

To complement this dashboard and to address the most immediate ASS knowledge gaps, we liaised with MAIT to develop a knowledge-transfer package relevant to local indigenous cultural traditions and tailored to their preferred on-country learning style.

The entire package is planned to build the capacity of the MAIT Rangers and will comprise:

- The interactive water quality dashboard
  - Explanations of ASS terminology, the remediation process, other ‘terms’ and parameters featured in the dashboard
  - The ASS knowledge-transfer modules to be delivered over 2 x ½ day sessions, that will include;
    - ASS fundamentals and relevance, established through an initial session of testing pH and electrical conductivity of native products provided by MAIT Rangers,
    - Simple field tests to demonstrate the ability of on-site ASS to drop the pH and dissolved oxygen,
    - Timeline of East Trinity ASS management activities, and
    - On-country ASS management talking points at locations along the usual MAIT tour route, covering neutralisation of acidity, tidal exchange, attenuation of tides, regular saltwater inundation indicators, freshwater remediation, etc.
  - Support to develop training videos, following feedback from on-country ASS management talking points, and recorded on-country at appropriate locations.

It is envisaged that once the entire package is delivered, it will be used to create contextualised stories about the ASS history of the East Trinity property, and prompt MAIT Guides and Rangers for ASS talking points on tours, which will initiate new story traditions that will embed the East Trinity ASS remediation into Mandingalbay Yidinji culture.

Acknowledgements

Mandingalbay Ancient Indigenous Tours (MAIT) for their time and engagement in this process.

DES Data Improvement and Machine Learning (DIML) team for their patience and expertise in developing a workable solution for the East Trinity water quality database and external-facing dashboard.

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Finnish Acid Sulfate Soil Land Systems

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Biography:
Stefan Mattbäck has been involved with the mapping of Finnish acid sulfate soils and the analysis related soil materials since 2010. He is employed as a researcher by the Geological Survey of Finland and does his PhD studies at the Åbo Akademi University.

Finnish Acid Sulfate Soil Land Systems

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The concept of land systems was introduced by Christian & Stewart (1953) and define areas of similar geology, soils, land cover and land use. Land systems are often used to study and describe the relationship between people and their environment (Reenberg, 2006). The term “land system” have previously been mentioned in relation with AS sulfate soils (Pons et al., 1982a; Pons et al., 1982b; Madsen & Jensen, 1988), and we intend to elaborate this further by identifying and describing AS soil land systems in Finland, based on the type of AS soil material, land cover and land use (e.g. agriculture, sand mining, peat excavation), landforms (e.g. estuaries, peat bogs, river valleys etc.), hydrology and sulfur geochemistry.

The goal of this ongoing study is to characterize the main types of AS soil materials and produce conceptual models of the AS soil land systems occurring in eight land areas (defined using the LiDAR-based preliminary ice stream lobe map of Finland produced by Putkinen et al., 2017) in the former Littorina-sea coastal area in Finland by utilizing data from the national mapping of Finnish AS soils (25 000+ observations) together with LiDAR derived covariates, geological data and land cover data to. By fulfilling this goal, we wish to improve sustainable land use planning on areas with actual or potential AS soils by information in a new way to the Finnish authorities. This study will be an important step towards developing AS soil risk maps, which complement the national AS soil probability map that show the possibility of AS soil occurrences but not the environmental risk.

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Phosphorus Availability in Acid Sulfate Soils as affected by soil water content and P addition

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Biography:
Dr Sonia Mayakaduwage is a postdoctoral fellow at the University of Adelaide. Her work focuses on nutrient availability in acid soils. She received her doctoral degree from the University of Adelaide in 2020. Her thesis explored phosphorus pools in acid sulfate soils and how they are affected by pH, soil water content, and phosphorus addition.

Phosphorus Availability in Acid Sulfate Soils as affected by soil water content and P addition

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Acid Sulfate Soils (ASS) are important for crop production because they often occur in rice paddies (Dent and Pons, 1995). Also, plants are being increasingly used for remediation of ASS (Gardner et al., 2018). The macronutrient phosphorus (P) is essential for plants as it plays a vital role in photosynthesis, respiration, enzyme reactions, and carbohydrate metabolism (Vance, 2011a). Phosphorus availability in acid soils is influenced by interactions of P and Fe-oxides which are modulated by soil water content ((Nguyen and Marschner, 2005; Wisawapipat et al., 2017). In ASS, available P is low as it can be sorbed to amorphous Fe-oxides (Haynes, 1982; Li et al., 2012). However, when the soils are flooded, the consequent lowering of the redox potential can solubilise Fe-oxides thereby releasing bound P (Shenker et al., 2005; Wisawapipat et al., 2017). In contrast, when previously flooded soils are drained and Fe-oxides are formed under aerobic conditions, the available P concentration in the soil solution can decrease due to sorption on newly formed Fe-oxides (Sah et al., 1989). Availability of P is also influenced by addition of organic materials as they can release inorganic P directly and after mineralisation of organic P (Sharpley and Moyer, 2000). Further, organic amendments influence P availability indirectly either by exchanging their organic anions with bound P from anion exchange sites, or during microbial decomposition which consumes oxygen and thereby lowers the redox potential to where Fe oxides are reduced/dissolved (Hue, 1991; Yi et al., 2012). However, little is known about the effect of P added as organic or inorganic on available P in ASS, under varying water content. Sandy ASS (pH adjusted to 5.5) was amended with 400 mg P kg^{-1} as inorganic P, manure or combinations of inorganic P and manure. Amendment treatments included inorganic P alone (100F), manure alone (100M) and P added as 50% inorganic P + 50% manure (50M/50F) as well as an unamended control. The soil was submerged for 2 weeks, then the overlying water was removed and the soil dried to maximum water-holding capacity. The soil was incubated for 4 weeks at this water content followed by submergence for 2 weeks. In the unamended control, available P were very low and not affected by soil water content. At the end of the first submergence, available P was two-fold higher in 100F than in 100M and 50M/50F. Oxalate extractable Fe was higher in 100M than 100F and remained unchanged until the end of the experiment. In the following moist incubation and after the second submergence, available P remained unchanged in 100M, but halved in 100F. Available P strongly increased in 50M/50F and was about two-fold higher than in the other two amended treatments. It can be concluded that with inorganic P addition, available P was initially very high, but then strongly decreased in the moist period due to removal of phosphate with the overlying water and to binding of P to amorphous Fe where it remained after re-submergence. With manure on the other hand, available P was lower than with 100F initially, but then remained stable. Phosphate in the overlying water was low with manure which indicates that, in contrast to inorganic P addition, the threat of P transfer into the surrounding environment is low.

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Changes in cationic plant nutrient availability during Acid Sulfate Soil pedogenesis

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Biography:

Michael Melville was appointed to academic staff at UNSW in March 1973. Retired in October 2000 but continued Honorary appointment until December 2022.

Michael has been involved in Acid Sulfate Soils research since seconded to ANU Mangrove Project out of Darwin in 1987.

Changes in cationic plant nutrient availability during Acid Sulfate Soil pedogenesis

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This presentation identifies the need for research to improve understanding of changes in cationic plant nutrient availability from pedogenesis of Acid Sulfate Soils (ASS). Our ASS research began during 1987 with Melville's involvement in the ANU Mangrove Project out of Darwin. That initiation later grew from the early 1987 massive Tweed River fish-kill.

Our initial ASS research assessed cationic potassium nutrient availability using the potassium potential determined from the potassium exchange isotherm (K^+pot) in Northern Territory ASS floodplain sediments. Marilyn Ball's 1988 ANU PhD showed that photosynthesis metabolism and growth of the grey mangrove, *Avicennia marina* depended upon nutrient potassium availability. Our measurements beneath *A. marina* on a meander loop of the Adelaide River demonstrated that variable mangrove growth was explained by a decrease in K^+pot in the floodplain sediments (Keene & Melville, 1999). Subsequently, Annabelle Keene's UNSW PhD (Keene, 2001) showed these pedogenic changes in K^+pot also occurred in ASS floodplains of the South Alligator R., Tweed R., and Botany Bay (Keene *et al*., 2004, 2008). This research showed that pedogenic acidification destroyed Illite clay in the upper sediment profile, releasing K^+ for temporary storage in Jarosite, but subsequently its removal to the estuary with rain-induced upward leaching. The decreased K^+pot measured on Robert Quirk's Tweed floodplain canefields caused him to add Potassium to his previous N&P fertilizer application regime which, together with other changes in husbandry, resulted in significantly increased yields.

The 2015/16 massive mangrove tree death on the shores of the Gulf of Carpentaria has been attributed to major El Niño drought conditions causing sea level and associated water table lowering (Duke *et al*., 2022). While a massive decrease in water availability seems likely, our hypothesis is that major ASS pedogenesis would also have occurred oxidizing pyrite in the mangrove sediments. The resultant acidification then would cause decreases in K^+pot availability. The impact of reduced K^+pot for *Avicennia marina* is well established, and it is reasonable to assume that other mangrove species and associated vegetation are also susceptible to reduced K availability. While nutrient availability measurements are well established in agricultural soil studies, they are not common with more general ecological research.

An additional area of ASS research is to use the exchange Isotherm method to measure cationic nutrient Ca, Mg, and Fe potential as a measure of their availability. These elements are part of green plant's normal nutrient requirements and they too are liable to changes by ASS acidification on minerals in estuary floodplain sediments. Our clay profile measurements also showed a proportional increase in Smectite-type clays in the oxidized ASS layers. We do not know whether such an increase was simply due to the decrease of Illite, or if new Smectite-type clay was formed during acidification. Such new clay formation would require the addition of Mg in the 2:1 clay's aluminium octahedral layer and addition of both Mg^+ and Ca^+ as charge-balancing exchangeable cations within the clay micelles.

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The importance of establishing terrestrial and aquatic plants to manage sulfuric and sulfidic soils under general soil use conditions

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Biography:
Patrick investigated the plant-based management of acid sulfate soils at the University of Adelaide under Professors Robert J. Reid and Robert W. Fitzpatrick. He is now an Associate Professor at the Department of Agriculture, PNG University of Technology, Papua New Guinea.

The importance of establishing terrestrial and aquatic plants to manage sulfuric and sulfidic soils under general soil use conditions

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Abstract

Acid sulfate soils (ASS) have been described as the ‘nastiest soils’ on earth because of their negative impacts on the surface environment. Under anaerobic soil conditions of high pH (>4) and low redox values, ASS poses no problems unless disturbed and sulfuric acid, iron, and aluminium species are produced and released. The resultant accumulation of the acid and metals has negative impacts on the receiving environment. The management of the negative impacts includes avoiding disturbance, inundation, or application of an alkaline material. Recently, research into the use of organic matter of dead plant origin to manage ASS impacts has advanced. However, the understanding of the long-term roles of live plants and the root biomass accumulation of plants adapted to growing under varying soil moisture is still being investigated. To understand the long-term roles of live plants and pH-dependent root biomass accumulation, three studies lasting twelve months were conducted using *Melaleuca armillaris* as a terrestrial plant and *Phragmites austsralis* as an aquatic plant, respectively. In the first, alkaline sandy loam soil (pH*w* 9) was mixed into sulfuric soil (pH*w* 3.7) until the neutralized sulfuric soil pHw was 6.7, and *Melaleuca* seedlings were planted. In the second and third studies, *M. armillaris* and *P. australis* were planted in both sulfuric and sulfidic soils and maintained under aerobic (75% water holding capacity) and anaerobic (flooded) soil conditions. All the studies were set up using 300 mm stormwater tubes whose bottom ends were sealed. The treatments were replicated four times and set up under glasshouse conditions in a completely randomized design manner. The 75-water holding capacity was maintained on a weight basis by weighing within the first six months and when the plants were older, 120 ml of water was added around the plants daily throughout. The anaerobic soil conditions were maintained by flooding and allowing a sufficient amount of water to the pond on the surface. All the treatments were harvested after 12 months and pH and root biomass were measured from the surface (0 - 100 mm), middle (100 – 200 mm), and deep (200 – 300 mm) soils. The results showed the neutralization obtained by mixing alkaline soil was stable without plants and deteriorated when planted. An even

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[ε] Correspondence: patrick.michael@pnguot.ac.pg distribution of root biomass was measured compared to those measured in the sulfuric soil. When *Melaleuca* was planted in aerobic sulfuric soil, the pH increased to near 7 units, whereas in the sulfidic soil lowered it to <4 units. The root biomass within the surface soil was 2 g and in the deep was variable in the two soil types. Planting *Phragmites* in both soils increased the pH under all the moisture regimes and the root biomass accumulated in the deep. Similarly, when *Phragmites* were planted in sulfidic soil, the pH ranged between 5 – 6 units, and root biomass was much bigger at the deep. The study showed the establishment of vegetation (plants) is an important strategy and the findings have implications for the management of ASS.

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The importance of establishing terrestrial and aquatic plants to manage sulfuric and sulfidic soils under varying soil moisture regimes

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Biography:

Dr. Patrick Michael has done his PhD studies on how to use organic matter of plant origin to manage acid sulfate soils at the School of Earth and Environmental Sciences, The University of Adelaide under Prof. Rob Reid and Prof. Rob Fitzpatrick. He is current teaching at the Department of Agriculture, PNG University of Technology, Papua New Guinea.

The importance of establishing terrestrial and aquatic plants to manage sulfuric and sulfidic soils under varying soil moisture regimes

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Acid sulfate soils (ASS) have been described as the 'nastiest soils' on earth because of their negative impacts on the surface environment. Under reduced and anaerobic soil conditions of high pH (>4.5) and low reduction oxidation potential (redox) values, ASS pose no problems unless disturbed and sulfuric acid, iron, and aluminium species are produced and released. The resultant accumulation of the acid ($H^{+)}$ and metals (Fe^{2+} and Al^{3+}) has a negative impact on the receiving environment. The management of the negative impacts includes avoiding disturbance, inundation, or application of an alkaline material, e.g. mineral lime. Recently, research into the use of organic matter of death plant origin to manage ASS impacts has advanced. However, the understanding of the long-term roles of live plants and the root biomass accumulation of plants adapted to growing in ASS under varying soil moisture is still being investigated. In order to understand the long-term roles of live plants growing in ASS and changes in pH-dependent root biomass accumulation, three studies lasting twelve months were conducted using *Typha* and *Phragmites austsralis* as aquatic and *Melaleuca armilllaris* and *Eucalyptus calycogona* as terrestrial plants, respectively. In the first, alkaline sandy loam soil (pH*w* 9) was mixed with sulfuric soil (pH*w* 4) until the mixed soil pHw was 6.7 and Melaleuca and Eucalyptus were planted. In the second and third, *M. armillaris* and *P. australis* were planted in both sulfuric and sulfidic soils and maintained under aerobic (75% water holding capacity) and anaerobic (flooded) soil conditions. All the studies were set up using 300 cm stormwater tubes (diameter 5 cm) whose bottom ends were tidy sealed with caps. The treatments were replicated four times and set up under greenhouse conditions in a randomized block design manner by placing the tubes in several polythene crates. The 75-water holding capacity was maintained on a weight basis by weighing initially within the first six months and when the plants were older, 120 ml of water was added around the plants on a daily basis throughout. The anaerobic soil conditions were maintained by flooding the soil and a sufficient amount of water was allowed to pond on the surface. All the treatments were harvested after 12 months and pH and root biomass were measured from four different profiles: surface (100 – 200 cm), middle (100 – 200 cm) and deep (200 – 300 cm). The results of the first study showed the neutralisation obtained by mixing alkaline soil was stable and Eucalyptus

accumulated root biomass. Planting Melaleuca in the mixed soil resulted in the loss of the neutrality obtained and the root biomass measured was small. Planting Melaleuca in aerobic sulfuric soil increased the soil pH to near 7 units, whereas in the sulfidic soil lowered it to below 4 units. The root biomass within the surface soil was 2 g and the deep was variable in both soil types. Planting Phragmites in both soils increased the soil pH under the two moisture regimes and the root biomass accumulated at the deep. Similarly, when Phragmites were planted in sulfidic soil, the pH remained unchanged, around 5 – 6 units, and root biomass was much higher at the deep. The studies showed establishment of vegetation (plants) is an important strategy and the findings have implications for management of ASS under different soil moisture regimes.

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Australian response to ASSs in regulating regional off-farm impacts is a template for measurably responding to climate change

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Australian response to ASSs in regulating regional off-farm impacts is a template for measurably responding to climate change

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The solutions for addressing landscape induced climate change need not be ground breaking. The pathway taken to address acid sulfate soils (ASS) in Australia is a template that will guide instrumental change and is the focus of this presentation. The 20 year journey ASS took from full blown outrage in 1992 to inclusion in planning scheme processes, with the release of ASS national guidelines in 2015, is laudable and instructive. This presentation will reflect on our response to ASS, lessons learned, our evolving response, and how it might be a template for measurably responding to anthropogenic climate change.

Causes of ASS are all consequences of landscape management: lowering the water table; inundation; and lowering the land (consolidation of organic soil after clearing and agricultural use). Coastal ASS, particularly former estuarine mangroves, salt water grasslands, deltas and swamp land, now used for agriculture are most vulnerable to inundation. Many researchers more qualified than I, are focusing on these areas, and there is little I can add. However, inland ASS are most effected by landscape management and it is in landscape management that a solution resides for climate change.

[*Landscape management is the coordinated care of land to ensure that landscapes can fulfil needs and aspirations in an effective and sustainable manner for present and future communities of users. Critical to landscape management is understanding and mitigating adverse impacts, such as chemical runoff, aerosols pollution, soil degradation and excess heat from land clearing etc*.]

Both inland and coastal ASSs and climate change are primarily the result in mismanagement of landscape. Based on explorer diaries it appears likely that in the great droughts, prior to European arrival, stream flow cessation of the major rivers was rare and presumably inland ASSs did not or only rarely occurred; even during prolonged droughts. Principally because the nutrients necessary to drive reducing conditions was limited to the last of the stagnant ponds during fish death and this water was quickly evaporated and thus potential ASS were rarely created. Extensive inland river sediments, riverine wetlands and lake ASS is a modern feature of poor landscape management as much as extensive coastal impacts of ASS are.

Mismanagement of the water table in catchments is known as the major problem for coastal ASS. Mismanagement of the water table exported acid, heavy metals and monosulfidic black oozes via the rivers to their neighbours. But the problem of mismanagement of landscape reducing rainfall (ie anthropogenic climate change), impacting infiltration and runoff is not understood. Several catchments are now known as being in hydrologic drought long after actual drought. What is hydrologic drought? Hydrologic droughts occur after prolonged droughts when the water table has significantly dropped below the bed of the river and the loss of organic matter in soil is so bad that dispersion and disaggregation has reduced infiltration and consequently groundwater recharge, such that it is unlikely that the water table will ever again provide basal flow to the river, or at least take a long time to do so.

Return baseline stream flow reduces the impact of both drought and floods on river catchments and reduces the opportunity for ASS to occur. Both ASS and climate change are a result of many (diffuse) sources of emission release in the landscape.

Environmental professions and laws (including planning processes) were derived throughout the developed world in the 1970s to address impacts of development from single point sources. The rise of diffuse and/or multiple impacts on landscape, from adverse impacts that individually have little to no effect but collectively have a substantial impact on our environment, requires a rethink of our laws. In Australia, responding to ASS was the first example of a state-wide, nationally coordinated, response to diffuse pollution sources. Today we are faced with another major environmental problem. A problem also substantially caused by poor landscape management, in which we are exporting adverse environmental impacts and collectively and cumulatively those impacts are leading to more frequent and significant extreme climatic events, both regionally and nationally.

It is now well accepted that increased anthropogenic emissions of greenhouse gases (GHG) is changing the Earth's climate. In particular, increased carbon dioxide, methane and nitrous oxide are causing excess heat. Rather than that heat dissipating into space, solar energy entering earth's atmosphere is converted by the Earth's surface to infra-red energy and then trapped and reflected back to the earth's surface by GHGs. This climatic effect and ASSs share a feature in common, they both are caused by offsite impacts from poor management of landscape. This talk will address landscape controls on both climate and ASSs, and how to use landscape solutions to mitigate the impacts of climate change on ASSs.

Solar energy is converted at the earth's surface into two types of heat; sensible and latent heat. Sensible heat heats the land, which during the evening releases infra-red radiation and a portion is reflected back to Earth by the atmosphere. Latent heat (on the land), evaporates water from water surfaces, vegetation and the soil. The greater the vegetative cover and the greater the organic matter in the soil, the greater the amount of latent heat. Any decrease in organic matter and/or vegetative cover increases sensible heat at the expense of latent heat. A spring water meadow has about 90 per cent latent heat, and at the other end a bare tilled paddock with low organic matter about 10 per cent. Thus, clearing forest for monoculture cropping with no cover crops, increases sensible heat by between six and nine times – a substantively greater impact than increasing GHGs by three times. Clearing forest and or savanna for monoculture, and set and forget grazing practices, regionally is more damaging than a threefold increase in greenhouse gases.

Decreasing the portion of latent heat also reduces precipitation. Between 30 and 85 per cent of precipitation is from the small water cycle, which sources rain locally. Significantly reducing latent heat crashes the small water cycle, resulting in a loss of light winter rains, mists, fogs and frequency of summer thunderstorms. This has been noticed across the world. The change in relation of the two heats, sensible and latent heat, also causes heat waves, rapid short intense floods, increased frosts and bushfires. These problems are caused by cumulative multiple and diffuse adverse impacts exported from landscape regionally – the same as ASS mismanagement. By adopting as a blueprint our experience and response to ASS, we can measurably accelerate our policy response to landscape impacted climate change.

Further Reading: Mulvey P and Mulvey F, 2021, Ground Breaking: Soil Security and Climate Change; Kerr Publishing, Melbourne.

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Kinetics and Nature of ASS Systems is Equally Important as Thermodynamics

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Kinetics and Nature of ASS Systems is Equally Important as Thermodynamics

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Oxidation of potential actual soil has traditionally focused on the chemistry of acid generation and environmental fast mechanisms of neutralisation, ignoring long terms mechanisms. Natural buffering stages are not often considered or how to promote them. Consequently, though thermodynamics are mostly well understood, the environmental controls on kinetics are less known.

The Australian Acid Sulfate Soil guidelines as part of the initial assessment do not consider any natural buffering in classification and management of acid sulfate soils. Without long “kinetics” tests (8 to 16 weeks), natural occurring acid neutralising capacity can’t be considered to neutralise oxidisable sulfides. However, agricultural lime, $CaCO_3$, the same substance as what is causing the fast natural occurring acid neutralisation capacity, is almost the only permitted treatment technology. Well known principles of kinetics cannot be applied in the initial assessment. As a result of testing taking so long (to demonstrate that kinetic principles are not inhibiting natural neutralisation), nearly all consultants and advisors recommend lime neutralisation that assumes total S (or worse the acid side of POCUS) represents the amount of acid that has to be neutralised by agricultural lime (CaCO3). Clearly over-liming occurs in almost every instance.

Recent changes in law in several states, with an emphasis on general environmental duties particularly in regard to greenhouse gas (GHG) release and efficient use of resources, means that blindly following the Australian Acid Sulfate Soil Guidelines may have you breaching state environmental laws. Kinetic testing of every sample cannot be supported, therefore consideration of Net Acid Generation Potential (NAGP) within the boundaries of general kinetic principles should be part of every initial investigation.

Precipitation of gypsum over shell and shell grit (the naturally occurring short term acid consuming mechanism) and release of stored acidity by jarosite are two mechanisms proposed in preventing acid consumption, or neutralisation and the rejection of consideration of shells and shell grit in the initial risk ranking. Acid consumption is the mechanism that consumes acidity during the ongoing release of acid as pyrite is oxidised and acid neutralisation are the mechanisms that increase the pH of the soil, after all pyrite has been oxidised.

Kinetics assesses the influences on the rate of the half equations that impacts the outcome of acid sulfate soil. What basic principles of acid consumption and acid neutralisation can be applied to the kinetics of acid sulfate soils with confidence that avoids the need of undertaken kinetic testing in every instance requires clear definition.

Permeability and proximity to macropores play a significant role in the nature and type of buffering that occurs and limits the impact of precipitation covering buffering agents.

When and why carbonate buffering is effective and dissolution and precipitation of iron minerals during maturation involves a complicated interplay with exchangeable. The removal of reactants by either drainage or ionic exchange even as the cation capacity reduces with acidity is a kinetic factor not often considered.

High permeability systems, wash away the reactants before neutralisation reactions can occur but in near closed systems (K<10^{-4} cm/sec) these reactions become very important. Most sedimentary sulfides occur in the organic rich low permeability systems and until macroporosity develops the systems are near closed. Data will be presented that shows that macroporosity typically only occurs in these systems after buffering by carbonates (i.e. all shell grit less than 0.5 mm in size is dissolved allowing ionic exchange to prevent gypsum precipitation from occurring). This does not occur in open systems.

In near closed systems, acid consumption follows a series of steps involving carbonate dissolution, sesquioxide dissolution, jarosite precipitation and finally aluminosilicate dissolution. There are different mechanisms in play that restore the pH back to neutral (neutralise) and these too vary depending on open systems and near closed systems.

Jarosite conversion to goethite thermodynamically appears to create acid. This has not been apparent in the field, and the reason again relates to Kinetics of an open and near closed system. Jarosite conversion to goethite is a slow process giving time for a series of ionic exchange and precipitation reactions to consume or "mop up" the acidity that is created. In a near closed system, precipitation of the alumino-silicates such as kaolinite and smectite also play a role that cannot occur in an open system.

Understanding the nature of the system and the kinetics involved are more essential than thermodynamics. It is now essential that the principles of kinetics, be built into a NAGP test equivalent to the mining industries Net Acid Producing Potential (NAPP), but with consideration of oxidised species of sulfur. Not to do so runs the risk of being environmentally negligent.

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EARLY INDICATIONS ON POTENTIAL ACID SULPHATE SOILS FORMATION IN THE OPAK RIVER LAGOON, BANTUL, YOGYAKARTA, INDONESIA

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Undergraduate of Soil Sicience from Universitas Gadjah Mada, Indonesia (1997)
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Doctor of Soil Science from Kyoto University, Japan (2013)

EARLY INDICATIONS ON POTENTIAL ACID SULPHATE SOILS FORMATION IN THE OPAK RIVER LAGUNA.pdf(could not be inserted)

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Mapping and geochemical characterization of Acid Sulfate Soils throughout the Swedish coastline – a cost effective and rapid approach to determine environmentally relevant features over a large area

Ms. Alexandra Nyman[1], Anders Johnson[2], Yu Changxun[1], Gustav Sohlenius[3], Mark Dopson[2], Mats Åström[1], Marina Beucher
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Biography:

Ms. Nyman is a phd student at Linneaus University in Kalmar Sweden. Her research focuses on Acid Sulfate soil research in Sweden, with prior experience in AS soil research in Finland as well. The current work focuses on close collaboration with microbiologists in order to get a better understanding of the occurences, characteristics and inter-disciplinery trends for AS soils in Sweden.

Mapping and geochemical characterization of Acid Sulfate Soils throughout the Swedish coastline – a cost effective and rapid approach to determine environmentally relevant features over a large area

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Acid sulfate soils (AS soils) are some of the nastiest soils in the world, because of their adverse effects on their surrounding environment due to their strong acidity and leaching of metals. Hence, it is important to locate and characterize the extent of AS soils development, in order to know where to manage and direct remediation activities. Acid Sulfate soils have received little attention in Sweden on a national scale, with previous research limited to local/regional areas where the presence of AS soils are known to exist. The full extent across the entire Swedish coastlines have not been the focus until now. However, as thorough mapping of all of Sweden would be a considerable and time-consuming undertaking, a rapid-fire approach was used for this study to get an overview of national trends, rather than to quantify the local areal extents. Sampling sites deemed to have the highest likelihood of hosting AS soils were chosen ahead of time, with relatively even distribution throughout the coastal plains. The presence or lack of AS soils at these sites indicate a general presence or a lack of AS soils from a larger perspective.

A total of 122 sites were sampled over two field seasons of 2020-2021. The pH was documented for each profile *in situ*, and samples for geochemistry and incubation were retrieved for all sites from the determined reduced layers. The sites immediately identified as Active AS soils were more thoroughly defined and samples retrieved from the oxidized, transition and reduced zones (when present). A total of 41 of the studied sites were active AS soils. In addition, a high number of potential acid sulfate soils were discovered after pH incubation experiments. This approach confirms that a large part of the Swedish coastal plains do have AS soils, in varying stages of development. The extent of AS soils across different areas also varied notably, and as such future research can now also focus on some of these previously unrecognized areas in terms of AS soil occurrence.

Geochemical analyzes were used to determine total and reactive (1M HCl-extractable) metal concentrations across all sampled sites. The geochemical trends within the soils were determined for the oxidized, transition, and reduced zone, when these zones were present for the active AS soils. The results overall line up with what is expected of AS soils, with several elements being leached from the oxidized zone, and occasionally enriched in the transition zone. Geographical trends in geochemistry were also considered for elements typically mobilized in AS soils. Notably, sulfur concentrations across all sampled sites follows the general occurrence of AS soil, with the sulfur values being generally higher in areas with more AS soils, and generally lower in areas with few AS soils. It then follows that there is a notable correlation observed between sulfur concentrations and pH values *in situ*. An even stronger correlation is observed between sulfur concentrations in the soils, and the pH measured after incubation of the underlying hypersulfidic material, with higher sulfur concentrations corresponding closely to lower incubation pH.

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An accelerated incubation method for the identification of acid sulfate soils

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Biography:
I received my doctoral degree in 2012 in environmental geochemistry with the focus on element speciation and behavior in metal-rich Boreal River and estuarine systems more or less influenced by acid sulfate (AS) soils whereafter I first continued as a post doc researcher at the Åbo Akademi University and now my title at the University is "project researcher". As a researcher my focus has among others been on the sulfur and metal geochemistry in Boreal environments, i.e., on the effect of land use on soil geochemistry and recipient streams and estuaries. Also, a development of identification and risk evaluation methods for AS soils in Boreal environments and management of AS soils have been on focus.

An accelerated incubation method for the identification of acid sulfate soils

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Sulfide bearing sediments occur worldwide in many coastal and inland settings and if exposed to oxidation, these sediments will develop into acid sulfate (AS) soils (pH <4) mobilizing acidity and soluble metals into watercourses with serious environmental consequences and structure/infrastructure damages. Thus, management techniques to minimize these hazards are important but rely above all on a correct identification of AS soil materials. The incubation pH method (Creeper et al. 2012) is one of the most preferred, reliable, easy-used and low-cost AS soil identification method, and simulates the natural oxidation behaviour of possible existing sulfidic materials by letting a wet soil sample oxidise in room temperature for a maximum of 19 weeks. An AS soil is identified if the amount of acidity produced during soil oxidation exceeds its acid-neutralizing capacity and thereby lowers the mineral soil pH to <4 (ΔpH >0.5). For organic-rich soil materials (LOI >20%) a lower identification limit, a pH <3 (ΔpH >0.5), is suggested as organic matters are naturally more acidic due to humic acids (Visuri et al., 2021; Nystrand et al. 2021, Hadzic et al. 2014). An identification duration of 19 weeks is, however, in many cases considered as to time-consuming and the main goal in this study was to further develop and improve the incubation method in such a manner, that the outcome would be a substantially reduced incubation time. To ensure the usability of the method, different type (e.g., grain sizes, sulfur concentrations, sample locations and sample depths) of known well homogenized sulfidic soil materials were chosen along the Finnish coastline. The intention was to increase the oxidation rate and, thus, decrease the time needed for incubation. Enhanced oxygen availability was trialed by optimising the soil sample thickness (alternatives tried were 2 mm, 5 mm and 10 mm thick samples) and by stirring the samples during the incubation three times per week. Temperature dependency on the microbiologically mediated oxidation was trialed at different temperatures (in 4 °C, 22 °C, 30 °C, 40 °C and 50 °C). In addition, trials were made to quick start the microbiologically mediated oxidation by "doping" samples with microbes from previously oxidized samples. Another quick start "doping" agent tested was ozonated water. In all trials, pH was measured three times per week. The incubation time was significantly reduced (generally by 50%) by: 1) optimising the sample thickness to 2 mm, 2) increasing the air penetration by stirring the sample, and 3) adding heat to 30 °C. Potential mineral acid sulfate soils could by that already be identified in an average of 3 weeks and potential peat samples in an average of 4 weeks. For most of the mineral soil samples an incubation time of ≤2 weeks was enough to identify AS soils, but in clay-rich material the incubation time was prolonged to 5 weeks. Conclusionary, results suggest that the accelerated incubation method enables reliable identification of AS soil materials in a maximum incubation time of 5 weeks.

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Can identification and risk assessment of acid sulfate soils be simplified?

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Can identification and risk assessment of acid sulfate soils be simplified?

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Abstract

Sulfidic sediments that form acid sulfate (AS) soils (pH < 4) upon oxidation cover millions of hectares worldwide. Under natural conditions, these sediments can be prevailed under harmless anoxic conditions as potential acid sulfate (PAS) soils but due to disturbance such as reclamation for land use, building of infrastructure or dredging they oxidize rapidly. Without sufficient natural buffering capacity, they will mobilize large quantities of acidity and soluble toxic metals such as Al, Cd and Ni to water courses, with serious consequences on water quality and ecology. As a building ground fine grained AS soils are unstable and corrosive, that needs to be taken in to account in the choice of building materials and the amount of sediment stabilizing agents such as cement.

Initially, management of AS soils requires identification of the occurrence of these soils and risk assessment of the load of acidity and metals that will be released upon oxidation from the identified soils. Ideally, the occurrence and characteristics such as the acidity and oxidation depth are included on AS soil maps. On a large catchment scale reasonably reliable "risk maps" may be utilized to reduce the amount of labour needed, by using modern modelling techniques utilizing LIDAR based elevation models, geophysics, existing soil maps etc. Another challenge may be time; e.g. during ongoing drainage or constructions works, there is a need to quickly make an assessment about the occurrence and risks associated with the soil material exposed.

Identifying AS and PAS soil materials typically involves pH measurements under field conditions and subsequent pH measurements of PAS soil material after incubation for up to 19 weeks. 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 PAS soil material (also termed hypersulfidic material). For an immediate identification, hydrogen peroxide can be used to oxidize the sample rapidly, but this method is less reliable and cannot be used for very organic soils. In the field, acid sulfate soil profiles can mostly be identified directly if the low pH in the oxidized zone is underlain by an anoxic parent sediment with a circumneutral pH that indicates that the low pH is a result of sulfide oxidation. Occurrence of jarosite in the oxidized zone and/or a distinct black colour of monosulfides in the parent sediments are useful additional indicators. The commonly used criteria of pH ≤ 4 does, however, does not include all highly hazardous oxidized sulfidic sediments; some of the most severe AS soils in terms of acid and metal leaching have a field pH up to 4.5 and need to be considered. On the contrary, for peat AS soils, a lower pH is needed to distinguish (P)AS soils from soils with

organic acidity. In Finland, a country with some of the highest peat occurrences in the world, pH ≤ 3.0 is currently used as criteria for peat AS soils.

The potential acid load of PAS/AS soils can be estimated by acid base accounting where the net acidity is obtained from the sum of potential, actual and retained (latent) 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. Leaching of metals is not generally directly considered in these methods but it can typically be assumed that they correlate well with acidity.

Detailed schemes and guidelines have been developed in order to identify and make risk assessments of PAS-/AS soil materials that typically require laboratory facilities, safety concerns as well as laboratory personnel trained for the job. While the methods are described in great detail and crucial for understanding risks associated with sulfidic sediments, they rely heavily on theoretical and operationally defined assumptions on how to quantify different acid/alkaline species and/or how to simulate the (in nature microbiologically mediated) oxidation. In addition, soil properties vary significantly both vertically and horizontally. If treated with lime or other agents corresponding to the net acidity assessed, it is uncertain to what extent that agent will be mixed in to the soil and actually react with the acidity. It can easily be argued that there are lot of unknown unknowns responsible for the net acid- and metal leaching in real field conditions as well as what environmental impact it will have in different types of catchment systems.

Given all the uncertainties, it can be questioned to what extent it is meaningful to carry out very detailed laboratory analysis? What is good enough? Would the overall benefit be greater if resources were directed in, for example, more dense sampling to account for the heterogeneity of the soils, while at the same time we would lose some accuracy and precision with simplified methods? Here we will present simplified methods for identification and risk assessment of PAS/AS soils that have been developed for soils in the Baltic Sea region in the TUNNISTUS- and HaSuRiski projects.

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Dissolution of sulfide minerals in single and mixed sulfide systems under simulated acid and metalliferous drainage conditions

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Biography:

Dr Gujie Qian is a Senior Research Fellow in Chemical Mineralogy and the Area Radiation Safety Officer within the College of Science and Engineering, Flinders University. Dr Qian specialises in sulfide geochemistry, surface and bulk analyses (including acid mine drainage-related testing), and kinetic and thermodynamic modelling, with approximately 15 years of experience in these fields. He is currently a key team member of a 5-year CRC TiME AMD project, in collaboration with six national and international sponsors from the mining industry and several government authorities and academic institutions.

Dissolution of sulfide minerals in single and mixed sulfide systems under simulated acid and metalliferous drainage conditions

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Pyrite (FeS_2) commonly coexists with other sulfide minerals such as chalcopyrite ($CuFeS_2$), galena (PbS) and sphalerite (ZnS) in acid and metalliferous drainage (AMD) environments [1, 2]. Galvanic interactions between sulfide minerals are well known [3-5]; however, their potential impacts on the formation of AMD remain unclear. Therefore, the overall aim of this work was to investigate their potential impacts on the oxidative dissolution of pyrite and acid generation rates under simulated AMD conditions.

Kinetic leach column (KLC) experiments containing single sulfide minerals and pyrite with one or two of the other sulfide minerals were carried out at realistic sulfide contents (< 5.2 wt% total sulfide for mixed sulfide KLC experiments), mimicking sulfidic waste rock conditions. Chalcopyrite was found to be the most effective sulfide in delaying decrease in leachate pH and reducing both pyrite oxidation and acid generation with up to 95% reduction in pyrite oxidation over 72 weeks. Galena had a smaller impact than chalcopyrite on pyrite oxidation, while sphalerite had the least impact with reduction of pyrite dissolution by only 26% over 72 weeks. The reductions of (cathodic) pyrite oxidation and acid generation were found not to correlate with the difference between the cathodic and anodic (chalcopyrite, galena and sphalerite) rest potentials. However, anodic dissolutions are likely dependent on the difference in rest potential between the cathode and anode, in agreement with our previous findings from mixed sulfide KLC experiments [6]. The onset of increased leachate acidity was found to correspond to the onset of increases in leachate redox potential, suggesting that monitoring of the leachate redox potential can be a useful tool for predicting acid generation behaviours of mixed sulfide AMD wastes. The results from this work are directly relevant to mine

waste storage and also confirm that galvanic interaction play a significant role in controlling the sulfide dissolution behaviours and the associated acid generation in multisulfide wastes at low sulfide contents (several wt%), with very small probabilities of direct physical contact between sulfide minerals.

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Identifying non coastal ASS and the Implications for beneficial reuse in NSW

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Biography:

Colee has 20 years' experience in project management, contamination assessment, remediation/validation, groundwater monitoring, acid sulfate soils, geotechnical engineering in NSW, ACT and Victoria. Colee has successfully managed several large scale projects including combined geotechnical / contaminated land / acid sulfate soil investigations and remediation works. The projects were in private and government sectors with clients from local government, Department of Defence, developers, rail, mining and petroleum industries.

Identifying non coastal ASS and the Implications for beneficial reuse in NSW

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Urbanisation and coastal development along the East Coast of Australia has increased considerably over the past decade and better identification and management of coastal acid sulfate soils (ASS) has meant that there have been fewer environmental incidents. Increasing development has recently encountered naturally occurring residual soils (B and C Horizons) and deeper weathered rock containing reduced inorganic sulphur (RIS) and RIS oxidation products.

These soils are sometimes referred to as upland ASS. The descriptive term preferred is non coastal ASS to help distinguish these soils, as they can be found at low elevations (below 10m AHD) and in close proximity to coastal ASS. For example, at Port Kembla NSW, both coastal and non-coastal ASS can occur below 5 m AHD.

By non coastal ASS, the authors are referring to soils and weathered rock that have been either:

- Weathered in situ from rock types that contain pyrite or other sulphides as a result of the depositional history or as secondary mineralisation such as the lower one third of the Budgong Sandstone; and / or
- Deposited as a colluvial or alluvial layer in close proximity to rock types that contain sulphides.

The objective of this paper is to highlight the incidence of these non coastal ASS in NSW through the use of case studies and point out the similarities and differences these soil types have in comparison to coastal ASS. The purpose is to raise awareness and stimulate debate around whether these soil types should be assessed and classified in the same manner as coastal ASS, even though these soils have formed under different scenarios and potentially present a different environmental risk profile with respect to acid generation.

Sampling and laboratory analysis within non coastal ASS has shown them to contain low concentrations of RIS and RIS oxidation products such as jarosite and schwertmanite. What is not fully understood is the environmental harm these soils and weathered rocks cause if disturbed, excavated and / or re-used. The pH shows these soils are acidic but little is known if, once disturbed, they will further acidify and at what rate.

The increase in development plus the willingness of regulators to re-use excavated material as much as possible has meant that treatment of these non coastal ASS, in a similar manner to coastal ASS, can have major cost implications for development. These costs are ultimately passed through to purchasers or government bodies funding developments. Other implications include less environmentally sustainable outcomes where excessive resources are spent in treatment, and in some cases lead to landfill disposal.

Three case studies will be presented from within the Sydney Basin rock sequence, as this corresponds to the major urban and regional centres within NSW. The case studies will discuss the geological and depositional history that confirms the presence of pyrite and other sulphide minerals. Soil and weathered rock types will be described, and the laboratory results presented to show the differences and similarities with coastal ASS.

The applicability of the current methods of assessment including laboratory test methods and bench testing, and the use of the coastal ASS action criteria will be discussed. In conclusion a method for better assessing non-coastal ASS will be presented, though it will be acknowledged that further research is required.

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Managing “The soils from Hell”

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Biography:
Robert Quirk has been growing sugar cane in northern NSW Australia since he left school over 60 years ago.
He has retired from many of his previous roles in agriculture which included Chairing two international not for profit companies.
He still fills the role of senior deputy chair of the Australian Cane Farmer association.
He either chairs or sits on two local Government com.
Robert became involved in acid sulphate soil research following the major fish kill in the Tweed River in 1987. Some wanted to close the local sugar cane industry. Sanity prevailed and over the next 20 year a BMP was developed with the assistance of students and researchers from UNSW, ANU ,SCU and CSIRO.
He has been an invited speaker in 35 countries on the topics of ASS remediation, GHG abatement in agriculture, carbon capture by sugar cane and climate change.

Managing “The soils from Hell”

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The Dutch “discovered” acid sulfate soils (ASS) within the wetlands and islands of the Zuiderzee, a shallow estuarine embayment of the North Sea. Through several centuries prior to C^{20}th, many wetland areas were drained and dykes installed, but severe storms and flooding ruptured early dikes and caused deaths of many thousands of people. Beginning after WWI, three main polders covering about 1500 km^2 were constructed in the Zuiderzee. The perimeter dykes controlled drainage of the sulfidic estuarine sediments from under the Zuiderzee, allowed oxidation of the contained pyrite, and the formation of ASS that needed methods for their management. These now-productive polder lands represent about 40% of The Netherland’s agricultural soils. It is worth noting that The Netherlands with its population of only a bit more than 17m, is the World’s second leading food exporter (in $$) and is the clear leader of developing sustainable agriculture. To them, all their agricultural land, particularly the polders into which great science, capital, and effort was invested, is precious and fiercely retained and protected. Still, some of the negative properties of ASS have caused some to label ASS as “the soils from Hell”.

Until the recent creation of the Australian ASS Maps, earlier CSIRO Australian Soil Maps showed zero areas of ASS, so the 1974 FAO/UNESCO Soil Map of the World showed zero Thionic Fluvisols (i.e. ASS) in Australia. At least those early Australian Soil Maps identified the NSW estuarine floodplains as a valuable soil resource but needing flood mitigation and drainage. Such floodgates and drains have been installed on many NSW estuary floodplains, particularly on the northern coast since the 1960’s. Although these estuary floodplain landscapes are ASS, the sediment is generally nutrient-rich with generally flat topography and good rainfall and climate, in many ways like the polders of The Netherlands.

Early settlers on the Tweed were told by the indigenous locals that floods caused big fish-kills, but the fish could be eaten if they were still moving. After a 1893 flood there was a massive fish-kill with river clarification such that a matchbox could be seen on the river-bottom under about 20 feet of water. The early 1987 major Tweed River flood caused another massive clarification and fish-kill event that emptied the entire estuary of all fish and most benthic organisms. While several causes were initially blamed, the Tweed Shire Council Entomologist, Clive Easton, correctly identified the cause as from acidic and metal discharge from the floodplain ASS (Easton, 1989). Clive had for many years been carefully manipulating Tweed floodplain drains so as to reduce their acidity and allow fish entry to consume the mosquito larvae that developed into a major comfort and health hazard for TSC residents and their animals.

That dreadful environmental event on the Tweed set the stage for the Australian growth of science in understanding and managing ASS. While initially the NSW sugar cane industry had been blamed, and understandably reacted in a negative way, some cane farmer individuals cooperated in understanding the science and what could be done to better manage the acidic discharges from floodplain drainage systems. The floodgate and drainage systems of the estuary floodplains did not create the ASS, such materials exist on undrained NSW floodplains (Lin *et al.* 1995), the South Alligator River floodplain (Keene et al. 2004), and most coastal floodplains of the World (Pons 2008). Measurements of acidity in northern NSW floodplains showed about 50 tonnes per hectare of existing sulfuric acid equivalent, and about 0.5 t/ha could be exported in drains from a flood event (Smith *et al*. 2003). Most of this existing acidity was likely from natural ASS pedogenesis since present sea level was established. Agricultural drainage may have contributed to this 50 t/ha, but the drains provided the conduit by which the acidity was exported to the estuaries (Kinsela and Melville 2004), so better drain management should be the target.

Scientists and Governments at all levels, and pretty much all areas of Australia, have recognized the existence of ASS and regulated their best management. Thus, Australia is probably the only nation in which there has been such an achievement. NSW now has clear guidelines and regulations for the management of ASS. The NSW Sugar Cane Industry is the only group in the State who have been given self-regulation, and they dictate to each farmer what should and can't be done with their land and drain management. Each of the 700 or so cane farmers has signed to a management regime and records his drain activities. These records can be arbitrarily assessed annually by independent observers. The improved environmental outcome from better management of ASS and their drainage is from cooperative learning between land-owners and regulators (White *et al.* 2007). Such a process needs to be followed with estuary floodplain management in the coming rise in sea level. There is a proposal in NSW to remove the floodgate and drain system from estuarine floodplains and allow the backswamp areas to become tidally or permanently flooded. Such a proposal seems to disregard the existence of existing acidity in the landscape and the positive environmental and economic achievements that have been made with the existing floodplain management by the sugar industry, for example.

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Wikipedia 2020: The Netherlands Total area:	41,543 km^2
Land area:	33,893 km^2
Agricultural Land area:	18,145 km^2
Polders area:	7,150 km^2

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Impact of Water Halinity on the Occurrence of Hypersulfidic Materials in Estuarine Tidal Marsh Soils of Chesapeake Bay (USA)

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Biography:

Dr. Martin Rabenhorst is the Ray Weil E-Nnovate Endowed Professor in Soil Science, in the Department of Environmental Science and Technology at the University of Maryland in College Park (USA) where he has served on the faculty for 40 years. His areas of expertise include: the Genesis, Morphology, and Classification of Hydromorphic Soils; Pedogenesis and Soil-Landscape Relations; Hydropedology of Non-Tidal Wetlands and Coastal Marshes; Pedogenesis and Resource Inventory of Subaqueous Soils; and Technology Development for Documenting Reducing Soil Conditions. One important thread that has been consistently woven through his research and writing efforts is Acid Sulfate Soils. Prof. Rabehorst is a Fellow of the Soil Science Society of America, and he served a Chair of the Organizing Committee for the 8th International Acid Sulfate Soils Conference held in College Park, Maryland in July 2016.

Impact of Water Halinity on the Occurrence of Hypersulfidic Materials in Estuarine Tidal Marsh Soils of Chesapeake Bay (USA)

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Introduction - Tidal marshes in the Mid-Atlantic region (USA) commonly fall into distinctive Pedogeomorphic Units (PGUs) based upon geomorphic and pedological factors. Estuarine type marshes are those formed in recent alluvial (mineral or organic) deposits along major tributaries that generally are brackish near the estuary but become progressively less saline with distance upstream. Changes in water chemistry along the course of the rivers impact biogeochemical processes. Sulfidization (sulfate reduction and accumulation of sulfide minerals) appears especially to be related to halinity gradients (i.e. sulfate availability) along the tidal streams. It has been suggested that once sulfate-S content of stream water drops below 32 mg/L (halinity < 1ppt), sulfate may begin to become limiting to sulfate reduction processes in marine sediments (Goldhaber and Kaplan 1975). Over recent decades, tidal marsh soils surrounding Chesapeake Bay, including those along the estuarine rivers, have been mapped. Soil taxa that contain hypersulfidic materials (i.e. sulfihemists and sulfaquents) are commonly described and mapped in settings where the water halinity is more than a few ppt (oligohaline, mesohaline and polyhaline). However, along sections of streams where halinity is lower, the mapped soil taxa typically do not contain hypersulfidic materials (hydraquents and haplosaprists). Hypersulfidic materials have been recognized in soil classification because of their environmental importance related to their potential to generate extreme acidity if oxidized during dredging or draining operations (Fanning 2002). Although this halinity paradigm has been applied during soil survey efforts, few data have been collected to evaluate where precisely along the halinity gradient, the boundary occurs. Therefore, the objective of this study was to examine estuarine tidal marsh soils along tributaries in Chesapeake Bay, from sites of varying halinity, to evaluate at what halinity levels hypersulfidic soil materials might be expected to occur.

Methods - During the Summer of 2021, eight pedons along a range in stream water halinity (0.10 to 8.8 ppt) were described following standard procedures (Schoeneberger, Wysocki et al. 2012), and samples were collected by pedogenic horizon, stored on ice during transport, and were then frozen until analysis. All horizons were analyzed for total C content using high-temperature dry combustion. Soils were found to be free of inorganic carbon ($CaCO_3$) as they did not effervesce when tested using 10% HCl. Thus, total C was assumed to be equal to organic C content. Electrical conductivity (EC) measurements were also recorded for stream water adjacent to sampling sites. To test for hypersulfidic materials, samples were monitored using a moist aerobic incubation (MAI) procedure (Soil Survey Staff 2022), where samples (approximately 1 cm thick) were mixed with an approximately equal volume of deionized (DI) water during an initial pH measurement. Over the course of 15 weeks, samples were allowed to dry and were periodically re-moistened using DI water. At regular intervals (weekly for the first 5 weeks and then biweekly for the duration), the pH of the samples was measured in a 1:1 mixture with DI water. Salts were observed forming on the containers adjacent to the soil, and upon completion of the moist incubation, the abundance and color of the salts was visually estimated and documented and salinity of the samples following MAI was measured. The salts were collected and X-ray diffraction (XRD) analysis was run to identify the minerals present.

Results/Conclusions - Surprisingly, all pedons had horizons (>15 cm thick within 50 cm of the soil surface) where pH dropped to < 4.0 during MAI, suggesting that they contained hypersulfidic materials. With the exception of the freshest site (with stream water halinity of 0.10 ppt), pedons from all other sites (with stream water halinity ranging from 0.15 to 8.3 ppt) had a majority of soil horizons that appear to contain hypersulfidic materials and essentially all pedons had > 50 cm of hypersulfidic materials within the upper meter. During the 15 weeks of the MAI, salt efflorescences were observed in most horizons from all pedons. Measured salinity at the end of the MAI was far greater than would be contributed from the stream halinity alone, even in samples from the freshest sites, suggesting that salts were generated from oxidation of sulfides. X-ray diffraction analysis of the salts showed that halite (derived directly from river halinity) became progressively more abundant as halinity of the adjacent river water increased. Nevertheless, in all pedons, sulfate salts (such as gypsum CaSO4•2(H2O); hexahydrite $MgSO_4 \bullet 6(H_2O)$; pickeringite $MgAl_2(SO_4)_4 \bullet 22(H_2O)$; halotrichite $FeAl_2(SO_4)_4 \bullet 22H_2O$; pentahydrite $MgSO_4 \bullet 5H_2O$) dominated the XRD patterns, confirming that oxidation of sulfides was primarily responsible for the formation of sulfate salts.

Evidence for the presence of sulfide minerals was present in pedons at halinities well below the proposed threshold of 1 ppt (Goldhaber and Kaplan 1975). While we understand the necessity for sulfate from stream water halinity for the formation of sulfide minerals in hypersulfidic materials, there seem to be additional contributing factors that may include the organic matter content of the soil horizon and the proximity of the horizon to (or distance from) the soil surface. In the freshest sites, moderate to strong reactions of the soil materials with alpha-alpha-dipyridyl indicated that there was an excess of reactive Fe, suggesting that the formation of Fe-sulfide minerals was limited by low availability of soluble sulfide, likely restricted by limited sulfate inputs. However, while sulfate may limit Fe-sulfide mineral formation and accumulation, there may still be sufficient sulfate present to form some sulfide minerals. It is postulated that sulfate inputs leading to formation of sulfide minerals in fresh marshes may be the result of periodic tidal pulses tied to unusual or extreme storm events like hurricanes.

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Measuring Pore Water Sulfide in in Benthic (Subaqueous) Soils using Indicator of Reduction In Soils (IRIS) Devices

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Measuring Pore Water Sulfide in in Benthic (Subaqueous) Soils using Indicator of Reduction In Soils (IRIS) Devices

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Soluble sulfide is known to be toxic to many plants and animals, and is especially problematic in brackish environments of the coastal zone where flora and fauna of marsh and benthic environments can be detrimentally affected (Wang and Chapman, 1999). The techniques used to measure pore water sulfide are difficult and cumbersome and typically involve some method to collect or extract pore water which is transported to the lab (sometimes implementing some process to stabilize the highly labile sulfide, such as SAOB or Zn acetate) where titration or potentiometric methods are applied for quantification. Pore water collection devices have utilized suction (sippers) or diffusion across a semipermeable membrane (peepers) and generally provide poor spatial (vertical) resolution (a few cm to 10 cm) (Marsh et al., 2005; Hesslein, 1976). A decade ago, it was demonstrated that soluble sulfide reacts with the Fe oxides on IRIS (Indicator of Reduction In Soils) devices to form gray to black monosulfide stains and coatings, the color of which is a function of both the concentration of the sulfide and the time of exposure – this permits quantification using IRIS (Rabenhorst et al., 2010). Until recently, however, the utility of the IRIS approach has been limited because the dark FeS colors fade quickly (over a period of minutes to hours) in the presence of oxygen, so obtaining high quality images for analysis was difficult. In addition, our ability to accurately quantify the sulfide on the IRIS image at a fine resolution was limited. However, as a result of technical advances, both of these difficulties have been resolved, and sulfide levels in soil pore water in emergent settings, such as tidal marshes, can be accurately and quickly quantified with high spatial resolution (Rabenhorst et al., 2023).

The challenges of working in benthic environments, however, have been even greater. Suction and membrane devices used in emergent settings like marshes are not practical for use below water. Heretofore, the most viable approach to measure pore water sulfide in submerged sediments was to collect a sample core and then to extract pore water via suction, pressure or centrifugation (often challenging), followed by analysis of the extracted pore water. This approach also typically provides poor vertical resolution. Some limited earlier work suggested the possible use of rigid IRIS tubes in benthic systems, but the newer IRIS developments permitting rapid and accurate quantification of soluble sulfide in marshes require the use of flexible IRIS films (Rabenhorst, 2018; Rabenhorst et al, 2023). Therefore, the objective of this project was to develop an approach for deploying flexible IRIS films in subaqueous soils in order to offer improved methodology for quantifying pore water sulfide in benthic/subaqueous systems.

We will report on a device developed for deploying IRIS films from a boat into subaqueous soil/sediment to a specified depth (50 cm). A line and buoy attached to each film allow retrieval of the films after a specified deployment period (5 min, 60 min, 360 min). Extracted films are retained in a shallow water bath to prevent oxidation of the Fe sulfide pigment for the couple of minutes while the lines and hardware are removed and the film is gently washed. Films are wiped dry and quickly scanned onboard using a portable scanner to capture a high quality image, being exposed to air for less than 30 s. Images can then be analyzed according to the procedure described in Rabenhorst et al, (2023). This approach has been applied in water up to 3 m deep, but could conceivably be used in deeper settings.

In the Rhode River and South River subestuaries (of Chesapeake Bay) four study sites were selected representing distinct subaqueous soil map units. Following preliminary investigations at each site to determine the appropriate deployment time, five replicate IRIS films were deployed at each site for either 60 min or 5 min using the new device. Porewater sulfide content varied dramatically between soils and also vertically (with depth) at each location. The relationship between pore water sulfide and soil properties will be discussed.

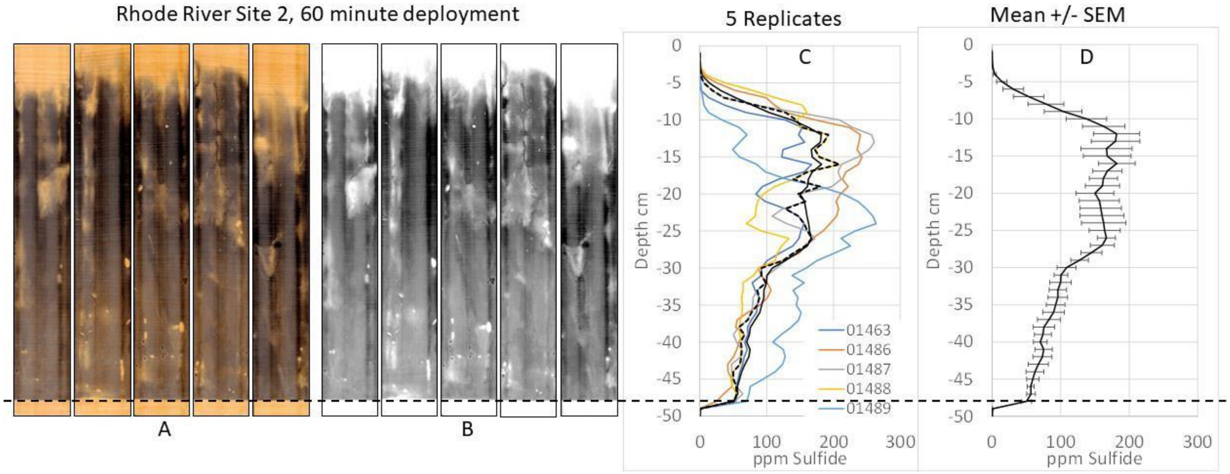

Figure 1. For an example, we present images of five replicate IRIS films collected from one of the four study locations following a 60 minute deployment. A) original color images; B) images following processing to remove color from the IRIS paint leaving grayscale that

reflects soluble sulfide concentration; C) depth function for each of the five replicate films following analysis, including mean and median; D) depth function showing mean pore water sulfide concentration with error bars at 1 cm intervals representing the standard error of the mean (SEM). Note the dashed line at the bottom represents the lower depth limit of measurement.

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The Evolving Classification of Acid Sulfate Soils

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Biography:
Dr. Martin Rabenhorst is the Ray Weil E-Nnovate Endowed Professor in Soil Science, in the Department of Environmental Science and Technology at the University of Maryland in College Park (USA) where he has served on the faculty for 40 years. His areas of expertise include: the Genesis, Morphology, and Classification of Hydromorphic Soils; Pedogenesis and Soil-Landscape Relations; Hydropedology of Non-Tidal Wetlands and Coastal Marshes; Pedogenesis and Resource Inventory of Subaqueous Soils; and Technology Development for Documenting Reducing Soil Conditions. One important thread that has been consistently woven through his research and writing efforts is Acid Sulfate Soils. Prof. Rabehorst is a Fellow of the Soil Science Society of America and he served a Chair of the Organizing Committee for the 8th International Acid Sulfate Soils Conference held in College Park, Maryland in July 2016.

The Evolving Classification of Acid Sulfate Soils

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The process of classification helps us organize knowledge and it helps us to better appreciate relationships and connections. Classification also facilitates communication, and good classification systems will be (to some degree) practical and utilitarian. While the problematic nature of acid sulfate soils has been recognized (by some) at least since the 18th century, the discipline of soil science dates back only to the late 19th century. And much of what we understand about acid sulfate soils really only began to be recognized just a little before the 1st International Acid Sulfate Soils Conference in 1972. As our modern soil classification systems emerged during the last half century, their architects knew to incorporate these difficult and unique (acid sulfate) soils. Nevertheless, as our experience and understanding of challenging soils has expanded, we have also seen corresponding changes or adaptations in the classification systems to accommodate the new knowledge. In this paper we examine the classification of acid sulfate soils through three systems used broadly around the world, and consider how these systems have evolved through time in an effort to keep pace with the state of knowledge.

After a series of "approximations" during the 50's and 60's, the 1st edition of *Soil Taxonomy* was published in the USA in 1975. Since then, every few years updated versions have been released,

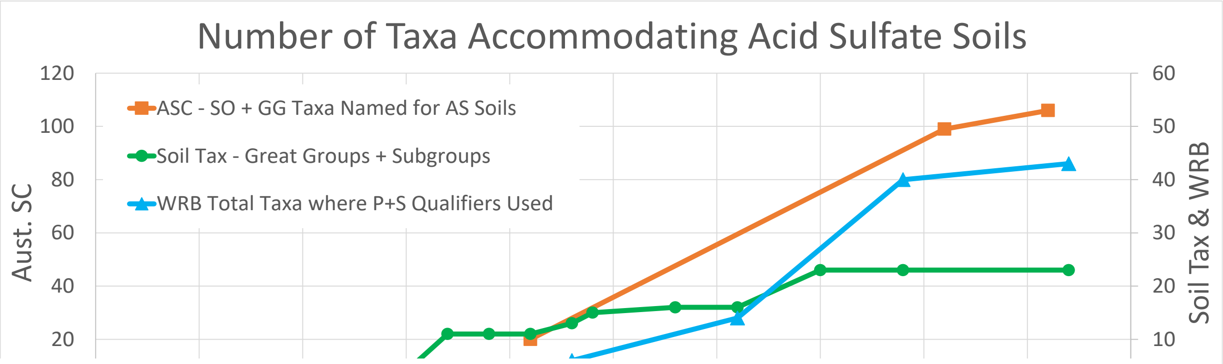

Figure 1. One important accommodation of acid sulfate soils in taxonomic systems over time is the increased number of taxa designated for such soils.

including a 2nd edition in 1999 and 13 more abbreviated "Keys", the most recent being in late 2022 (Rabenhorst, 2016; Soil Survey Staff, 2022). Initially growing out of the FAO/UNESCO *Soil Map of the World*, and under the oversight of the ISSS, the *World Reference Base (WRB) for Soil Resources* (then the IRB working group) project was initiated in the early 80s in a mammoth effort that included many collaborators worldwide. The 1st edition was released in 1998 at the 16th World Congress in Montpelier, as a guide for classifying the reference soil groups and their qualifiers (IUSS Working Group WRB, 1998). Based on information emerging from an ongoing series of meetings and field trips, subsequent editions were published in 2006 and 2014 and the most recent 4th edition was just released in 2022 (IUSS Working Group WRB, 2022). As was the case in other parts of the world, soil classification in Australia in the period leading up to the 1950s and 60s, emphasized the concept of Great Soil Groups which were included in the *Factual Key* (Northcote, 1960) and the *Handbook of Australian Soils* (Stace et al., 1968; Stephens, 1961) which was released in conjunction with the 9th World Congress in Adelaide in 1968. As the ongoing collection of additional information brought deficiencies to light, continued efforts led to the development and publication of the of the *Australian Soil Classification* in 1996 (Isbell, 1966). Continued efforts have resulted in updates in 2016 (2nd Ed) and in 2021 (3rd Ed) (Isbell, 2021).

Each of these classification systems have accommodated acid sulfate soils throughout their history and each has demonstrated distinctive changes during particular periods. As our concepts and understanding of acid sulfate soils have developed, these have become encoded (quickly or slowly) in our classifications. The acid sulfate soil concepts that have been addressed in classification systems generally fall within several groups that are listed below. Some are handled differently among systems and have remained stable while others have changed over time.

- The names and terms used to describe acid sulfate soil materials
    - The criteria by which acid sulfate soil materials are defined
    - The minimum thickness of acid sulfate materials required in order to be recognized in the system
    - The depth in the soil profile within which acid sulfate soil materials must occur in order to be recognized
    - The categorical level within the system at which acid sulfate soil properties are incorporated
    - The number of classes (taxa) within which acid sulfate soils are recognized

This paper will explore how various acid sulfate soil concepts have been addressed within these three classification systems, how these concepts have changed through time, and how changes in each system have preceded, followed or paralleled the other systems. We intend to highlight differences between systems that have existed and that may remain, and to offer perspectives on the rationale for these distinctives. We will also demonstrate the ways in which collaborations and shared knowledge have drawn parts of these systems more closely together. We may then speculate on potential future changes, or suggest areas where modifications might be beneficial.

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The geochemistry of arsenic in acid mine drainage: the role of pharmacosiderite

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Biography:
Dr Jason Reynolds is a Senior Lecturer at Western Sydney University. His research interests include soil and landscape regeneration. Jason is interested in the linking underlying soil properties to repair/improve landscapes and how these properties can be manipulated to achieve beneficial outcomes. A goal of his research is to understand the contributions of soil type to the productivity of managed and natural systems and how these systems respond in the Anthropocene. He currently works on several projects focused on the repair of degraded soils through soil structure repair.

The geochemistry of arsenic in acid mine drainage: the role of pharmacosiderite

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One of the most interesting discoveries of the well-studied Sunny Corner acid mine drainage (AMD) site in the central west of New South Wales, Australia, is the presence of pharmacosiderite. The detection of this 'rare' iron arsenate mineral by chance in the hard host-rock geology triggered several questions on its occurrence, formation, solubility and ultimately – how it influences arsenic geochemistry. Pharmacosiderite group minerals ($A\mathrm{Fe}_4(\mathrm{OH})_4(\mathrm{AsO}_4)_3\cdot n\mathrm{H}_2\mathrm{O}$) have been identified at the oxidised ores of Sunny Corner Mine This group of minerals are considered rare and are typically identified in discrete quantities such as a 3 mm seam on a quartz substrate (Hager, 2013). The synthesis of pure pharmacosiderite minerals has proven difficult and the hydronium endmember is the most elusive (Majzlan *et al.* 2019).

Only recently has the synthesis of pharmacosiderite been reported and the inference has been that this rare iron arsenate requires significant formation energies. In this work, we explore the Sunny Corner AMD site and report on the concentrations of arsenic within, we then explore low energy approaches to the formation of pharmacosiderite. We establish that although rare, the formation of hydronium pharmacosiderite is not as constrained as previously reported. These findings have implications for the understanding of the pharmacosiderite-group in the environment and provide avenues for the use of these minerals for industrial purposes. The approach has implications for the scorodite to pharmacosiderite transition process (Figure 1).

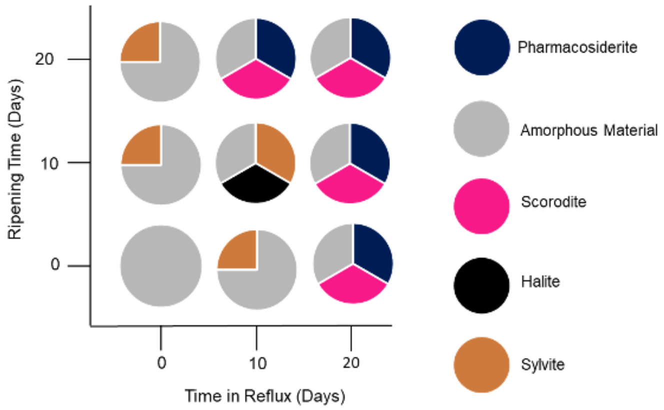

Figure 1. Relation between ripening time and reflux duration to form pharmacosiderite.

Pharmacosiderite group minerals are nonzeolitic molecular sieves which are predicted to have the capacity to remove dissolved iron and arsenic from solution. The beneficial characteristics of pharmacosiderite are attributed to ridged framework of the cubic $P\bar{4}3m$ space group which is comprised of pores and cavities within the crystal structure which are capable of selective ion exchange (Figure 2). This is beneficial for the remediation of iron, arsenic, and cation contaminants from AMD sites.

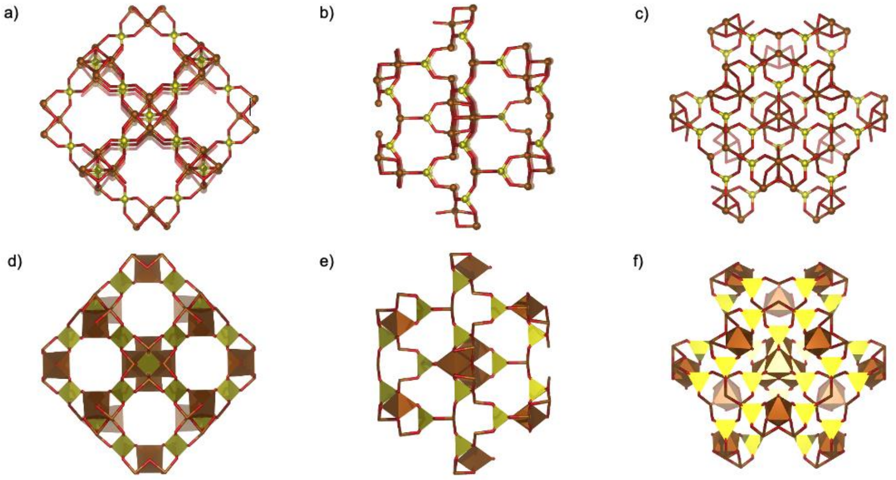

Figure 2. *Model of the crystal structure of synthesised pharmacosiderite generated using single crystal data. Views: a) and d) are face to face, b) and e) are edge to edge, and c) and f) are corner to corner. Figures e), f), and g) have been space filled for clarity where colours have been assigned to represent iron (brown), arsenic (yellow), and oxygen (red). Potassium ions are not represented as they are located within the pores and channels.*

Pharmacosiderite is resistant to radiation damage, have high selectivity, are very porous, and show potential to immobilise arsenic over geological timescales. It is these characteristics which are of interest for the removal and safe storage of fission products from contaminated ground and surface waters. The constraints of using pharmacosiderite have been the formation energies and these barriers are now removed due to the successful low energy synthesis. This achievement provides knowledge into the occurrence, formation, solubility, and geochemistry of pharmacosiderite. The results of this study forges avenues for further research and development of an industrial role for pharmacosiderite.

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Modifications to Accepted Acid Sulfate Soil Management Practices to Address External Risk Factors

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Biography:

Dr Silvana Santomartino is a Certified Professional Soil Scientist (CPSS) and Environmental Geochemist with 22 years of experience in assessing and managing Acid Sulfate Soils (ASS). She is Managing Director of PSK Environmental, a consultancy company she formed in 2013.

Silvana has been the Technical Lead and/or Project Manager on a large range of soil investigation projects including Acid Sulfate Soil (ASS), Contaminated Land (including Per- and polyfluoroalkyl substances) and Land Resources Assessments.

Silvana is a former President elect of the Queensland Branch of Soil Science Australia and was the recipient of the Australasian Land and Groundwater Association (ALGA) 2020 Annual Industry Excellence Award for "Outstanding Contribution by an Individual", and the Soil Science Australia (SSA) 2021 LJH Teakle Award for raising awareness of soil science in Australia. She has been appointed Adjunct Industry Fellow within the Australian Rivers Institute at Griffith University.

Modifications to Accepted Acid Sulfate Soil Management Practices to Address External Risk Factors

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Management and treatment of Acid Sulfate Soils (ASS) and naturally acidic non ASS in Queensland, Australia, is typically undertaken in accordance with the guidance provided in the *Queensland Acid Sulfate Soil Technical Manual: Soil Management Guidelines v4.0* (Dear et al. 2014) and the five National Acid Sulfate Soil guidance documents, released by the Department of Agriculture and Water Resources in 2018. However, in some instances, the management of these soils must depart from the accepted ASS management practices to address external factors, such as workplace health and safety, the presence of contaminants, and the sensitivity of the receiving environment. The following examples represent modified management measures adopted for specific projects based on a detailed risk assessment and following review by the relevant state or federal regulators.

During the assessment of ASS for the construction of a new 1470 m rock seawall in South East (SE) Queensland, Australia, remnant buried asbestos containing material (ACM) from the demolition of historic buildings was intercepted. Given the presence of ACM within the ASS requiring excavation, modifications of the typical treatment methodologies were undertaken to manage and minimise asbestos-related health risks associated with the handling, management, removal and disposal of ACM-contaminated ASS. Carting ACM-contaminated ASS to a lime treatment pad was not a desirable option given the potential disturbance to ACM and risk to human health. Instead, the ACM-contaminated ASS was used to form a permanent berm adjacent to the seawall, thus minimising the movement of the material. To construct the berm, the insitu surface at the berm locations were compacted prior to placement and treatment of the ASS spoil. An agricultural lime (aglime) guard layer containing double the approved application rate for a standard ASS treatment pad was placed beneath the material, serving as a 'proxy' treatment pad. Lime treatment took place in 300 mm layers. Aglime was applied at the required quantity in uniform layers thus building up the treated spoil profile without mixing the lime into the spoil. An increased factor of safety (2.0 instead of 1.5) was adopted for lime treatment. Verification testing of each 300 mm layer was completed with subsequent layers added only when verification results indicated successful lime treatment. Field pH tests were undertaken at the time of verification sampling to detect any likely failures in verification test results and to limit any risks arising from leaving the unverified material at the location while awaiting final laboratory results. A final layer of aglime was applied to the final surface. The treated ACM contaminated ASS spoil was then capped with a compacted 0.5 m thick layer of clean fill.

During a sediment assessment for drain maintenance for a series of tidal drains in SE Queensland, Per- and Polyfluoroalkyl Substances (PFAS) was detected in sediment, sediment porewater and surface water. Acid Sulfate Soils and monosulfidic black oozes (MBOs) were also present in the sediment. Given the low volumes removed during drain maintenance activities, sediments were previously excavated, lime treated during excavation and placed immediately, and permanently, on the top of the banks of the drain. The presence of both PFAS (and MBOs) in the sediment triggered the requirement to modify the standard management approach to meet the relevant guidelines, including the PFAS National Environmental Management Plan Version 2 (NEMP 2020). Temporary bunds were required to be constructed on either side of the dredge location at low tide prior to sediment removal. All sediment was taken to a lime treatment pad which was designed to include a polyethylene liner to prevent uncontrolled runoff of PFAS-impacted water to surface water receptors and groundwater. The liner was placed below a minimum 300 mm thick sacrificial clean fill layer to limit the risk of the plastic liner tearing during lime treatment. If temporary stockpiling could not be avoided, the PFAS-contaminated ASS and MBOs were placed adjacent to the drain on duct tape sealed polyethylene liner, coated with a super-saturated lime slurry and covered with impervious tarpaulin or plastic. Due to the presence of PFAS, any lime treated ASS/MBO had to be reused on the same lot, away from waterways and in an area where background PFAS levels would not increase the risk level for harm to the site or downstream receptors.

Modifications to accepted ASS management practices were also required for a road upgrade project on the Sunshine Coast in Queensland, Australia. The receiving environment included the wallum-dependent frog species which are pH-sensitive and thrive in low pH, organic-rich soft waters. Disturbance and/or treatment of ASS can negatively affect their habitat. Most of the soils investigated along the project alignment were residual soils that were naturally acidic soils and did not contain pyrite-derived acidity. A risk assessment was completed, which supported a reduced level of treatment for the reuse of acidic soils as embankment fill onsite. A basal layer of aglime was placed under soil fill zones at nominated rates (5 kg Aglime/m^2), using a reduced factor of safety of 1.2. The basal lime guard layers were repeated for each fill layer of a thickness of 1 m or part thereof (Figure 1). In addition, the fill was compacted under controlled conditions to reduce soil permeability, thus minimising infiltration and further reducing the potential for mild acid leachate.

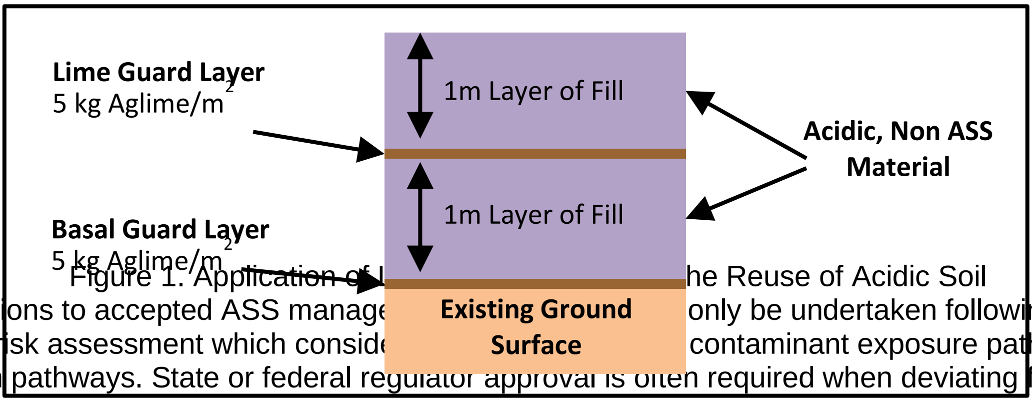

Figure 1. Application of L he Reuse of Acidic Soil

Modifications to accepted ASS manage only be undertaken following a detailed risk assessment which conside contaminant exposure pathways and migration pathways. State or federal regulator approval is often required when deviating from accepted ASS management practices.

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Corrosion of zinc-aluminium and galvanised-steel fencing in Anthropogenic sulfuric soils

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Biography:
Dr Rob Fitzpatrick's career has focused on the interface of soil science (pedology), regolith science, mineralogy, biogeochemistry, forensic science, mineral exploration and climate change. He has over 40 years experience in leading major multi-disciplinary research projects and conducted over 500 specialised soil-regolith investigations and surveys, covering a wide range of regions and climates worldwide.

Corrosion of zinc-aluminium and galvanised-steel fencing in Anthropogenic sulfuric soils

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Acid sulfate soils occur in a range of different environments in Australia and across the world. These may be naturally occurring (e.g., wetlands and mangroves) or anthropogenically sourced (e.g., acid mine drainage deposits). Acid sulfate soils are strongly corrosive towards buried infrastructure due to their high acidity and salinity (Dent, 1986). Studies addressing soil corrosivity potential risk and the prediction of infrastructure failure/suitability in different environments have predominantly been focussed on processes occurring in subsoil conditions (Arriba-Rodriguez et al., 2018). This study aimed to quantify the corrosion processes occurring in the top 10 cm of Anthropogenic sulfuric silty soils, which originated from a sulfuric acid manufacturing plant and dumped along a section of fencing on Garden Island in South Australia as shown in Figure 1.

Fig. 1 Photographs showing the condition of fencing on Garden Island (South Australia). The section of the fence, which is heavily impacted by corrosion damage is located above Anthropogenic sulfuric silty soils, which originated from a sulfuric acid manufacturing plant.

Standard zinc-aluminium fence netting and galvanised-steel fence wires were buried at two replicate field sites as shown in Figure 2 for three and nine months, to assess their suitability for use in this region.

At the time of sampling, the two soil profiles at these sites were classified as Anthropogenic sulfuric silty soils in the Australian ASS classification key Fitzpatrick (2013), Hyperthionic Spolic Technosol according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014) and Sulfuric Spolic Anthroposol in accordance with the Australian soil classification (Isbell and National Committee on Soils and Terrain, 2021).

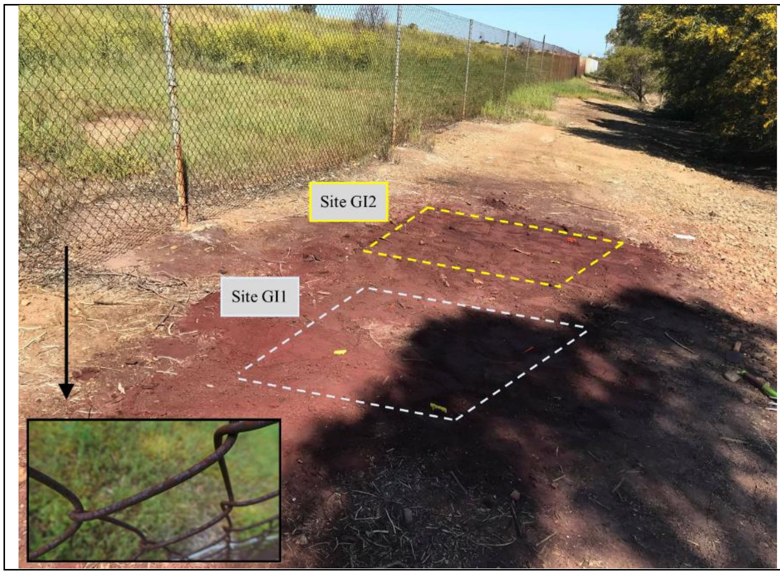

Fig. 2 Photograph of the Anthropogenic acid sulfate soil site on Garden Island. Two field sites (GI1 and GI2) were used for a nine-month fencing trial. The condition of the nearby fence is shown as an inset

Standard zinc-aluminium netting samples lost 98-100% of their protective wire coatings after only three months buried in highly acidic (pH < 2) and highly saline (11-13 dS/m) soils. Standard zinc-aluminium netting samples were completely disintegrated after nine months in contact with the Anthropogenic sulfuric silty soil. Likewise, galvanised-steel samples lost 96-97% of their zinc coatings after only three months. These results show that neither of the fencing products tested are suitable for use in these very highly corrosive soils. Further research is recommended to assess the suitability of more corrosion-resistant materials such as stainless-steel.

Both of the anthropogenic sulfuric silty soils present on Garden Island were extremely acidic (pH < 2) and highly saline (11 and 13 dS/m), and consequently were predicted to be very highly corrosive towards fencing. Standard zinc-aluminium fence netting and galvanised fence wire samples sustained significant amounts of corrosion damage after only three months buried in these soils (96-100% of zinc lost from wire coatings), which indicates that these commercial products do not provide sufficient levels of corrosion-protection for use in these highly corrosive environments. Further experimentation is recommended to ascertain the most appropriate fencing materials for use in this region, such as stainless-steel or wires with a polymer coating.

Corrosion products identified on fence samples using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy predominantly consisted of iron (up to 37%), chloride (up to 5%) and sodium (up to 21%). XRD analyses of corrosion products formed on wire surfaces are currently being processed.

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Identification and Characterisation of Corrosive Soil Properties in Coastal Acid Sulfate Soils, for the Prediction of Buried Infrastructure Deterioration Risks.

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Biography:

Andrea is an environmental scientist and PhD candidate at the University of Adelaide with a background in terrestrial ecology and soil science. Her research interest includes environmental monitoring, soil corrosion mapping, small vertebrate surveys and native species management. Andrea is passionate about science communication, community engagement/outreach and education.

Identification and Characterisation of Corrosive Soil Properties in Coastal Acid Sulfate Soils, for the Prediction of Buried Infrastructure Deterioration Risks.

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The loss of structural function of buried (or partially buried) infrastructure through soil corrosion action is a problem experienced globally (Arriba-Rodriguez et al., 2018; Wasim et al., 2018). Soil corrosivity is a term used to describe the susceptibility of buried infrastructure to degradation through electrochemical reactions with the soil environment (Arriba-Rodriguez et al., 2018; Ganiyu et al., 2018). A common engineering approach for minimising corrosion damage and infrastructure failure involves the use of corrosion preventative coatings on metal surfaces (e.g. use of zinc and aluminium in galvanised steel coatings) (Denison and Romanoff, 1952; Enning and Garrelfs, 2014). Identifying the composition of corrosion products formed when these coatings react with corrosive agents in the soil environment can provide useful insights into the nature of the corrosion processes occurring. For example, maghemite and akaganéite are corrosion products commonly formed through rapid corrosion processes in chloride-rich environments (Antunes et al., 2014; Miranda et al., 2012).

Being able to accurately characterise the unmeasurable quality of “soil corrosivity” (i.e. the corroding potential of a soil) is essential for engineers and land managers, as it can inform which materials are appropriate for use in specific soil environments and whether further corrosion control measures are needed to maximise structural integrity and longevity of buried infrastructure (Arriba-Rodriguez et al., 2018; Noor and Al-Moubaraki, 2014; Pereira et al., 2015). Corrosion research has largely been focused on understanding soil corrosion processes in subsoil environments and how these soil conditions impact underground pipelines (Bonds et al., 2005; Doyle et al., 2003), with very little research specifically targeting surface-soil corrosion processes and the influence of soil physiochemical properties on the longevity of partially buried infrastructure such as fences.

Our research aimed to identify the mineralogical and chemical composition of soil corrosion products forming on zinc aluminium fencing buried in different Coastal Acid Sulfate Soils in and around the Barker Inlet of South Australia, using scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray diffraction analysis. The types of secondary iron oxide corrosion products formed in the coastal soils varied, predominantly due to differences in soil pH and soil sulfate conditions. Gordaite, sphalerite and ferrihydrite were dominant in the hypersulfidic, sandy soil, while gordaite and schwertmannite were dominant in the sulfuric soils. The composition of the oxides on metal surfaces were compared with rates of zinc loss (a quantitative measure for fence damage) to assess their relative effectiveness in limiting fence corrosion damage in these soils. A schematic model was constructed to illustrate how the differing soil conductions and physiochemical attributes were conducive for the formation of different soil corrosion products in the short-term (3 months buried in soils) and long-term (9 months buried in soils).

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Behaviour of biogenic and geologic carbonates in disturbed sulfidic and sulfuric soil materials: particle size effects

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Biography:

Leigh is a Fellow of Soil Science Australia and recently retired as Deputy Vice-Chancellor (Research and Innovation) at the University of Canberra and. He was the Chair of the Acid Sulfate Soil Commission of the International Union of Soil Science from 2002-10 and 2014-18 and Vice Chair from 2010-14.

Leigh has been Deputy Chair of the Physics, Chemistry and Environment Panel for the Australian Research Council's College of Experts. Leigh has contributed to the development of Commonwealth and state policy both as chair and member of advisory committees for numerous state and Commonwealth government environmental agencies.

Leigh has an international reputation for his research in acid sulfate soils and their management. He has authored numerous acid sulfate soil guidelines including being lead author on four current National Guidelines covering acid sulfate soil sampling, identification, laboratory methods and management of monosulfidic black oozes (MBOs).

Behaviour of biogenic and geologic carbonates in disturbed sulfidic and sulfuric soil materials: particle size effects

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The interaction of the release of alkalinity from calcium carbonate minerals with the release of acidity from sulfide minerals in oxidizing sulfidic soil materials and sulfuric soil materials is fundamental to our understanding of both: 1) the acidity risk posed by acid sulfate soil materials, and; 2) acidity hazard management approaches that involve the addition of calcium

However, there have been few systematic studies of examining these interactions to date. For example, fundamentally important questions that remain to be answered conclusively include: What is the maximum particle size of naturally-occurring calcium carbonates (especially mollusc shells: usually aragonitic but also frequently calcitic) that is able to release alkalinity at rates sufficient to prevent acidification of oxidizing sulfidic materials? Another fundamental management question that relies on a clear understanding of this interaction is: How fine must geologic calcite be ground in order to either raise the pH of sulfuric soil materials effectively, or to prevent acidification of rapidly oxidising sulfidic materials?

In Australia, the uncertainty of the effectiveness of calcium carbonate materials (whether naturally-occurring or added) in neutralising acidifying sulfidic soil materials have resulted in assessments of the Acid Neutralising Capacity (ANC) of sulfidic materials derived from laboratory methods, being excluded from estimations of a sulfidic soil material's acidity hazard unless it can be demonstrated that the measured ANC is effective (e.g. Sullivan, et al 2018).

Here we provide an examination of the effectiveness of a range of calcium carbonate materials, each ground to nine particle size ranges, in preventing acidification of two alkaline sulfidic soil materials, and in neutralising two acidic sulfidic soil materials and one sulfuric soil material.

The approach used in this study was to incubate (1cm thick slabs incubated under field conditions) in the soil materials, with and without the addition of three different powdered calcium carbonate materials (1. geologic calcite, 2. oyster shell (predominantly calcite) and 3. cockle shell (predominantly aragonite)) in nine particle sizes: 1-2 mm, 0.5-1 mm, 250-500 μm, 180-250 μm, 125-

180 μm, 90-125 μm, 63-90 μm, 20-63 μm and < 20 μm. The pH (1:1 soil:water) was measured using a calibrated pH probe.

Figure 1 below provides some of the results of this study. These results and those of the other incubation studies (data not shown here) indicate the following:

- Ground geologic calcite should be < 0.5 mm in particle size to ensure that these materials are sufficiently reactive to prevent both the acidification (i.e. pH < 6.5) of alkaline sulfidic soil materials during oxidation, and to enable the timely remediation of both sulfuric soil materials (data not show here) and acidic sulfidic soil materials.

1. Even when uncoated, naturally-occurring mollusc shells should be < 0.5 mm in size to ensure that they are sufficiently reactive to prevent acidification (i.e. defined as pH < 6.5) occurring when alkaline sulfidic soil materials are oxidising.

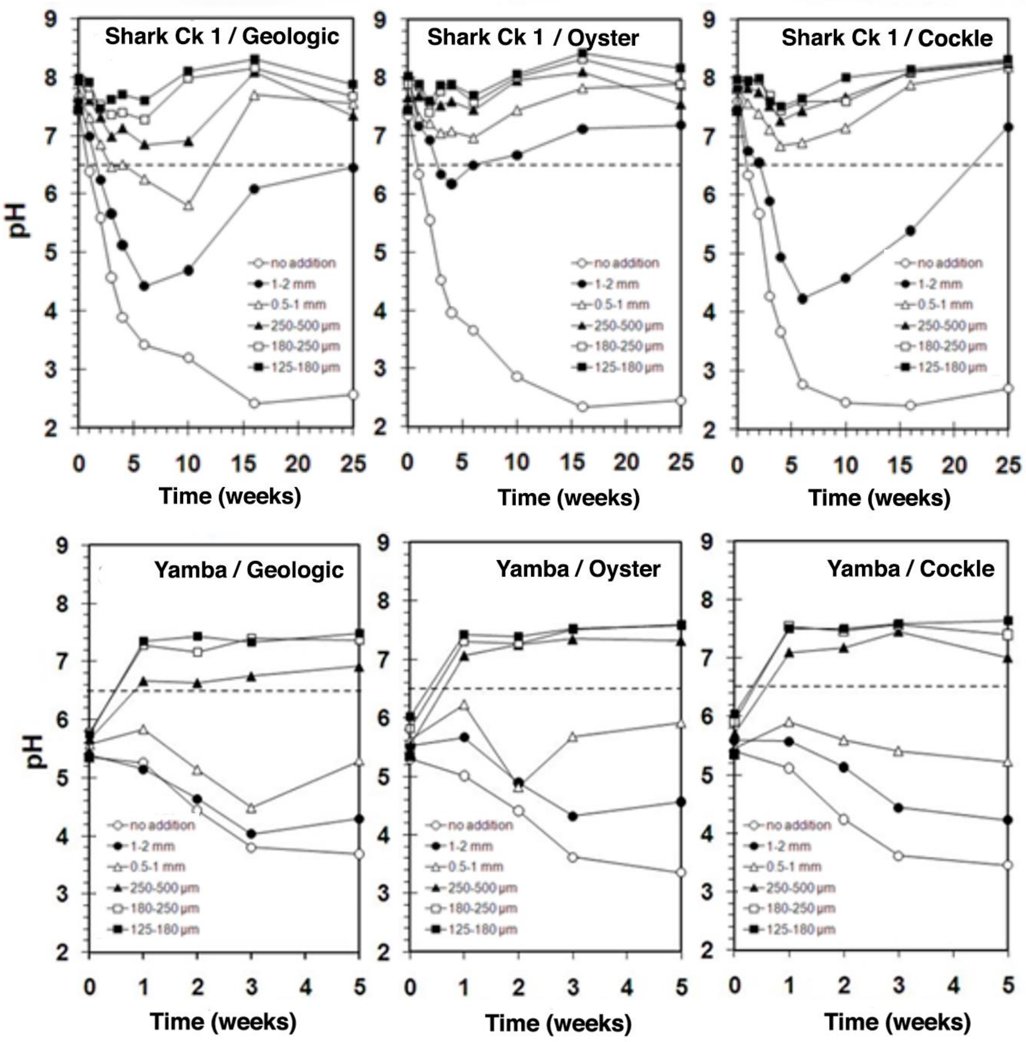

Figure 1. Changes in pH during incubation of an alkaline sulfidic soil material (Shark Creek 1) and an acidic sulfidic soil material (Yamba) using ground geologic calcite, oyster shell, and cockle shell additions at recommended application rates added in different particle size fractions. The initial pH is a triplicate mean and subsequent data points represent duplicate means.

2. Ground oyster shell material was more effective in releasing alkalinity under incubation conditions than ground cockle shell material which in turn was more effective in this regard than ground geologic calcite.

The results have important implications for the assessment of the acidity hazard of sulfidic soil materials containing calcium carbonate materials, as well as the management of such acidity hazards using additions of calcium carbonate materials. A more complete examination of the results of this study will be provided in the presentation.

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Formal Assurance of professional competence in acid sulfate soil management

Emeritus Professor Leigh Sullivan, Mr Bernie Powell, Associate Professor Vanessa Wong

Biography:

Leigh is a Fellow of Soil Science Australia and recently retired as Deputy Vice-Chancellor (Research and Innovation) at the University of Canberra and. He was the Chair of the Acid Sulfate Soil Commission of the International Union of Soil Science from 2002-10 and 2014-18 and Vice Chair from 2010-14.

Leigh has an international reputation for his research in acid sulfate soils and their management. He has authored numerous acid sulfate soil guidelines including being lead author on four current National Guidelines covering acid sulfate soil sampling, identification, laboratory methods and management of monosulfidic black oozes (MBOs).

Leigh has served as Deputy Chair of the Physics, Chemistry and Environment Panel for the Australian Research Council's College of Experts

Leigh has contributed to the development of Commonwealth and state policy both as chair and member of numerous advisory committees.

Formal assurance of professional competence in acid sulfate soil assessment and management

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The assessment of management of landscapes and sites in Australia and elsewhere that include acid sulfate soil materials, are covered by legislative instruments and a range of guidance documentation. In Australia, there is an increasing reliance on industry, rather than state and territory-based regulators, to self-manage acid sulfate soil disturbance in accordance with those legislative instruments and guidance documentation. However maintaining standards has become a nation-wide challenge.

Accordingly, Soil Science Australia aims to assist this process by ensuring that an appropriate level of professional acid sulfate soil assessment and management expertise is employed in the development and compliance assessment of Acid Sulfate Soil Assessment and Management Plans. Soil Science Australia recently commenced the establishment of an accreditation program entitled 'Registered Soil Practitioner (Acid Sulfate Soil)' as part of its larger Registered Soil Practitioner accreditation scheme. Applicants may be either professionals engaged to undertake such work, or professionals who assess compliance with the above standards. There will accordingly be two pathways to accreditation under consideration: a Consultant pathway, and; a Compliance Officer pathway.

To be successfully admitted, applicants for Registered Soil Practitioner (Acid Sulfate Soil) RSP(ASS) accreditation will need to demonstrate to Soil Science Australia that they possess a high level of technical competence in the assessment and management of acid sulfate soils.

To be eligible for RSP(ASS) accreditation, applicants must demonstrate to an Assessment Panel constituted by Soil Science Australia, that they have a minimum of 5 year's substantial work experience in the assessment and management of acid sulfate soils. In order to maintain their accreditation, accredited RSP(ASS) will be required to demonstrate their commitment to ongoing professional development and activity every 3 years. To assist progress towards accreditation, a national ASS course run by Southern Cross University is also available for less experienced practitioners.

Competencies required for Registered Soil Practitioner - Acid Sulfate Soil accreditation

Applicants must demonstrate to the RSP(ASS) Accreditation Assessment Panel that they possess at a satisfactorily high level, the following competencies:

Consultant pathway	Compliance Officer pathway
Competency #1 - Regulations and standards	
Have an understanding of the regulatory requirements and national guidance in acid sulfate soil assessment and management.	
Competency #2 – Assessment	
Have the capacity to design and undertake an appropriate soil sampling strategy utilising your knowledge of a site's geomorphology, hydrology and pedology as it applies to acid sulfate soils.	Have the capacity to assess the appropriateness of a soil sampling strategy utilising knowledge of a site's geomorphology, hydrology and pedology as it applies to acid sulfate soils.
Have the capacity to select appropriate acid sulfate soil laboratory tests and interpret the results to assess hazards arising from acid sulfate soil materials.	Have the capacity to assess the appropriateness of acid sulfate soil laboratory tests and the interpretation of theoe these results to assess hazards arising from acid sulfate soil materials.
Competence #3 – Management planning	
Have the capacity to develop effective options, as part of an acid sulfate soil management plan, to avoid or mitigate impacts arising from acid sulfate soil disturbance	Have the capacity to assess the appropriateness of options, as part of an acid sulfate soil management plan, to avoid or mitigate impacts arising from acid sulfate soil disturbance
Competence #4 – Monitoring and contingency planning	
Have the capacity to develop a monitoring plan to assess the effectiveness of strategies used as part of an acid sulfate soil management plan, to avoid or mitigate impacts arising from acid sulfate soil disturbance, including contingency plans.	Have the capacity to assess the appropriateness of a monitoring plan to assess the effectiveness of strategies used as part of an acid sulfate soil management plan, and contingency plans to avoid or mitigate impacts arising from acid sulfate soil disturbance, including closeout reports.

Assessment of competencies required for RSP(ASS) accreditation (n.b. only some aspects of the assessment measures are detailed below).

Consultant pathway	Compliance officer pathway
Applicants must provide with their application for RSP(ASS) accreditation at least two reports of comprehensive acid sulfate soil management plans	Applicants must provide with their application for RSP(ASS) accreditation at least two reviews of comprehensive acid

that they have been responsible for, that demonstrate their capacity to exercise an appropriate level of expertise, in all of the competencies required for RPS(ASS) accreditation.	sulfate soil management plans that they have been responsible for, that demonstrate their capacity to exercise an appropriate level of expertise, in all of the competencies required for RPS-ASS accreditation.
Demonstrate their competency by successfully completing an exercise in interpreting the results of acid sulfate soil laboratory tests to determine the presence and magnitude of any hazards and the calculation of lime requirement.	

1

The effect of acid sulfate soils on river water quality and fish assemblages in Finland

Dr. Tapio Sutela[1]
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Biography:

I have worked as research scientist from late 1980´s in Natural Resources Institute Finland and its predecessor Finnish Game and Fisheries Research Institute. In recent years we have studied the effects of acid sulfate soils and land-use on river water quality and biota, especially fish.

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The effect of acid sulfate soils on river water quality and fish assemblages in Finland

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In Europe, the largest acid sulfate soil areas are found in western Finland. The oxidation and weathering of these sulphide-containing sediments have taken place as a result of ditching and farmland drainage (Fältmarsch et al. 2008). As a result of dissolution and oxidation of metalsulfides, sulfuric acid is produced and metals are released (Åström and Björklund 1996). Acidic pore water rich in metals, e.g. aluminium (Al), is flushed to recipient streams especially during heavy rain periods. Percentage of acid sulfate soils in the watershed area has been found to correlate with river water acidity in western Finland. Intensified utilization of modern subsurface techniques in farmland drainage has significantly increased acidification (Österholm and Åström 2002). The primary objective of this paper was to study the effect of river water acidity and Al leached from acid sulfate soils on riverine fish assemblages.

Riverine fish assemblages in the area of acid sulfate soils in western Finland were sampled with electrofishing performed at 200 sampling sites along 35 more or less acidified rivers emptying into the Gulf of Bothnia in the Baltic Sea. The sampling sites with average area of 141 m^2 (range 30 – 1035 m^2) were fished without using escape nets. Fish were captured with an electrofishing gear using pulsed (50 Hz) DC current with usually 400–600 V voltage adjusted to water conductivity. Each sampling site was fished once by two waders, one using the anode and an assistant collecting the stunned fish with a hand net. All captured fish were identified to species and counted. Results from pH and total Al (hereafter Al) analyses of the river water in were collected from the national database, Hertta, hosted by the Finnish Environment Institute.

In acidic waters, Al is acutely toxic to fish. The lowest average pH (4.55) values and the highest average Al concentrations (7.4 mg l-1) were recorded in the river Vöyrinjoki, which appeared to be fishless. Frequency of sites with no fish was highest (59 %) in rivers with average pH < 5. Maximum number of fish species discovered by electrofishing degraded gradually from 8 in river water with a pH around 6.5 to 2 in river water with a pH below 5 (Fig.1). Acidity-sensitive species, especially grayling (*Thymallus thymallus*), brown trout (*Salmo trutta*) and Eurasian minnow (*Phoxinus*

phoxinus), were usually not found in rivers with average pH < 6 and total Al > 0.8 mg/l. Tolerant fish species, pike (*Esox lucius*) and perch (*Perca fluviatilis*), were recorded even in rivers with an average pH of 4.6 and total Al 3 mg/l. Fish-based bioassessment indicated worst ecological status in the most acidified rivers. Documented fish kills supported the concept of acidity and Al as essential drivers in fish assemblages.

Figure 1. Species richness of fish (the average number of fish species recorded in one electrofishing sample) in relation to the average pH of the river water.

Leaching of acidity and Al to rivers can be reduced by modern, controlled farmland drainage techniques. Keeping a reasonably high ground water level or re-flooding acid sulfate soils have shown to consume acidity and immobilize Al and other potentially toxic metals (Toivonen and Österholm 2011). Also development of more environmental-friendly ditching practices (more shallow ditches) has been considered advantageous (Sundström and Åström 2006). We suggest that all mitigation method available should be fully applied to reduce the damage for riverine fish and other biota in the studied areas of acid sulfate soils.

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Carbon Sequestration in Coastal Acid Sulfate Soils of Southern Australian Wetlands

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Biography:

My name is Julie Tan and I am a first-year PhD student studying environmental science at Monash University. I have a particular interest in climate change mitigation and my research project is focused on investigating carbon sequestration of coastal acid sulfate soils and the processes limiting it.

Carbon Sequestration in Coastal Acid Sulfate Soils of Southern Australian Wetlands

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The threatening consequences of anthropogenic climate change have pushed the need to establish novel and effective mitigation strategies. In recent decades more attention has turned to the use and protection of ‘blue carbon’ ecosystems as a potential strategy. In particular, wetlands containing salt marshes, mangroves and seagrass beds have been focused upon for their ability to sequester carbon 30-50 times faster than their terrestrial counterparts (Ewers Lewis et al. 2018).

It is estimated that Australia holds 9-32% of the global extent of blue carbon ecosystems which are able to sequester carbon in their soils at a rate of 3.5-5.5 Tg ha^{-1} yr^{-1} (Serrano et al. 2019). As such, more interest in blue carbon ecosystems has come from both the Australian government and research, as evidenced by the recent inclusion of blue carbon projects in the Emissions Reduction Fund (ERF) carbon credit initiative in 2022 (Clean Energy Regulator 2022).

Despite the increasing interest and popularity of investing in blue carbon ecosystems, few studies have discussed the influence of coastal acid sulfate soils (CASSs) on carbon sequestration. Although ASSs often support blue carbon ecosystems, their primary focus in the literature has been on their management against their associated hazards. To date, only one study has explored the carbon sequestration potential of two subtropical CASS wetlands in Australia (Brown et al. 2019).

The complex physical and chemical properties of ASSs open many questions about their carbon sequestration potential and processes that may influence it. In particular, the limiting role of iron in organic matter decomposition and carbon storage has been previously explored in the broader literature, but not in the context of ASSs in blue carbon ecosystems (Chen et al. 2014; Chen et al. 2020). Additionally, the importance of the role of the organic matter structure and its source on soil carbon sequestration in ASS blue carbon ecosystems has yet to be explored. To fully understand the effectiveness of blue carbon ecosystems in climate change mitigation, it is important to explore the role of ASSs that underpin them.

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Acid Sulfate Soils in the Murray Darling Basin and river regulation

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Biography:

Brett Thomas is a Research Scientist at the University of Adelaide and DBD Environmental. He has more than 15 years' experience in the environmental and contaminated land sectors providing practical solutions to a wide range of public and private sector clients. Through his career, Brett has gained extensive experience in the design and implementation of sampling and analysis plans, and data interpretation to ascertain the nature, severity and specific risks associated with site contamination. He has specific experience in understanding the biogeochemistry sites, wetlands and catchments affected by acid sulfate soil (ASS) and acidic and metalliferous drainage (AMD).

Brett has also gained experience in environmental risk management aspects of mineral exploration, mine pre-feasibility studies and closure planning required for approval under the Mining Act (Program for Environment Protection and Rehabilitation (PEPR)). Brett has authored many peer reviewed journal articles, industry reports and has presented at numerous conferences and workshops.

Acid Sulfate Soils in the Murray Darling Basin and river regulation

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Water level control by locks and weirs on the River Murray has resulted in approximately seventy-five per cent of wetlands between the South Australian border and Wellington tending to be permanently inundated with little water level fluctuation (Maschmedt, D. 2009). Floodplain areas and wetlands at higher elevations, in contrast, are now less frequently inundated than under pre-regulation conditions (DEW 2021). The transition to subaqueous (submerged) and waterlogged soils causes physical, chemical, and biological changes that may have further interactive effects on other soil properties. Some changes are cyclic and recover during the transition back to drying phases, while others result in permanent changes to soil and hydrological properties. The fluctuations between inundation and subsequent drying, associated with periodically flooded soils, are major drivers of spatial and temporal differences in acid sulfate soil properties that affect the biogeochemical processes taking place (e.g. Fitzpatrick et al. 2009; Mosley 2019; Stirling et al. 2020). River regulation has allowed accumulation of acid sulfate soil materials due to:

- Artificially stable water conditions in many wetlands for over 80 years that has resulted in considerable build-up of hyposulfidic, hypersulfidic and monosulfidic materials due to permanent waterlogging (i.e. lack of regular drying cycles to oxidise or "burn off" pyrite that has formed naturally)
  - The evaporative concentration of sulfate (a feedstock for acid sulfate soil formation) from groundwater-connected river salt loads during the period of stable pool level
  - The lack of natural scouring and seasonal flushing of wetlands
  - A plentiful supply of organic matter from aquatic vegetation
  - Fluvial processes during river regulation has undoubtedly changed cultural heritage practices on floodplains.

Near surface soils and sediments typically have the highest Reduced Inorganic Sulfur (RIS) values and it is these layers that present the highest risk of exposure, and therefore impact to surface water quality. Soil layers occurring below normally sampled depths (typically 80-100 cm) may also present an acidity hazard; however, the risk of disturbing these subsoils (e.g. during weir pool lowering or drought) and the potential for them to impact surface water quality is considerably lower, particularly under normal seasonal wetting and drying regimes. Deeper subsoils may present a higher acidity risk at the wetland scale following longer term droughts that result in significant draw-down of the water table. Construction activities or groundwater pumping are further concerns as they are activities which have the potential to disturb deeply buried acid sulfate soil materials. In clay soils, deep cracks may form to the full depth of water level drawdown, increasing oxygen penetration and RIS oxidation depth, and lateral penetration into soil peds and columns. As dry conditions persist acidity is subsoils can be moved upwards to the surface by capillary action and evapotranspiration processes, particularly in fine textured soils, and in areas influenced by groundwater mounding. Lateral seepage or discharges may occur in dried wetlands while groundwater levels remain higher than the weir pool lowering. Evapoconcentration of saline acidic seepage containing dissolved Fe and Al will concentrate soluble and retained acidity at the surface (and near surface to the capillary fringe of soil peds and columns) in the form of Fe or Al hydroxysulfate minerals and salt efflorescence, such as jarosite and natrojarosite (Fitzpatrick et al. 2017, Creeper et al. 2015, Mosley et al. 2017). Prolonged drying can potentially lead to the redistribution and accumulation of acidity and oxidation products (hazards) within a soil profile and the floodplain.

The risk of acidification in soils and water is partially determined by the substrate's proximity to the surface and its inherent acid neutralising capacity (ANC), which is determined by the content of alkaline minerals, organic matter, and clay particles in the soil environment (Fitzpatrick et al. 2009, Shand et al. 2010, Sullivan et al. 2018). The generation of sulfuric acid and formation of acidic minerals such as jarosite can thereafter prevent (or delay) the soil returning to near neutral pH during re-flooding (Mosley et al. 2017, Fitzpatrick et al. 2017, Stirling et al. 2020, Thomas et al. 2019, Ward et al. 2013). Further details on the spatial distribution of acid sulfate soil types, conceptual site models (CSMs) and management measures within regulated and natural wetlands of the River Murray are provided in (DEW 2021, Fitzpatrick 2009, Sullivan et al. 2018, Thomas et al. 2019, Mosley et al. 2019).

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Managing acid sulfate soil wetlands in a world of changing needs, values and climate

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Biography:
Nicolaas a hydrogeochemist/hydrogeologist with over 10 years' experience. He has attained a strong hydrogeological and hydrogeochemical grounding after focussing his PhD studies on groundwater-surface water tracing via chemical methods and acid sulfate soil hydrogeochemistry. Subsequently, Nicolaas has been involved in a number of acid sulfate soil and acid mine drainage projects which have added to his understanding of geochemical processes in dynamic settings.
His experience has taken place across several fields including mining, wetland management, water resource management and infrastructure support. These projects have included mapping the occurrence and severity of acid sulfate rock/soils, designing laboratory programs that characterise their response to different conditions, modelling/assessing the risk that such responses may have on different receptors, and providing management options to reduce any associated risks.

Managing acid sulfate soil wetlands in a world of changing needs, values and climate

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Big Swamp is a naturally occurring acid sulfate soil (ASS) swamp located approximately 130 km south west of Melbourne along Boundary Creek, a tributary to the Barwon River that has historically been groundwater fed. A combination of dry climate effects and groundwater extraction from the Barwon Downs Borefield has led to reductions in groundwater discharge to the creek, the drying of ASS in Big Swamp, the discharge of acid water to Boundary Creek and at least one fish kill event in the receiving Barwon River. A commitment has been made to developing and implementing a remediation plan to improve environmental outcomes for Boundary Creek and Big Swamp.
This study assesses the risk of fish kills in the Barwon River and the potential water quality outcomes associated with the currently preferred remediation strategy proposed, to augment flows through the swamp to maintain an elevated watertable and limit acid generation through sulfide oxidaiton, as well as other contingency measures being considered to mitigate the risk of fish kills in the interim.
The study was informed by a robust sampling and monitoring programme consisting of chromium reducible sulfur tests undertaken on 18 soil cores taken to ~6 m depth and monthly monitoring of groundwater acidity concentrations in 17 piezometers. Subsequently, the mass of acidity in surface water discharging from Big Swamp via Boundary Creek was compared to rainfall and runoff events as well as groundwater discharge estimates from Big Swamp given by numerical groundwater modelling of the system.
Monthly monitoring of surface water quality in Boundary Creek (physical parameters, major ions, dissolved metals and acidity) was then compared to relevant guidelines to evaluate which analytes may yield the greatest risk to fish kill events in the Barwon River. Mixing between discharge water from Boundary Creek and the Barwon River was then simulated in PHREEQC to represent seasonal ranges in mixing ratios and evaluate the timing of fish kill risks in the Barwon River. These results were then compared to observed fish kill events and low pH events to assess the real risk. The size and nature of potential treatment facilities required to reduce these risks was also assessed via PHREEQC simulations using NaOH to achieve nominated water quality end points.

The conceptual hydrogeochemical model indicates that the greatest store of acidity in Big Swamp appears to be soil acidity, however the timing of acidic discharge in water from the swamp was inconsistent with rainfall/runoff events, indicating that runoff from the upper profile is not the primary mechanism of acidity discharge from the swamp. Pore water acidity in the unsaturated zone represents a minor store of acidity and leaching of soil moisture from the unsaturated zone appears to be a negligible process for acidity mobilisation. Groundwater acidity stored in the shallow alluvial aquifer represents the second largest store of acidity in Big Swamp and modelling suggests that this is the primary mechanism by which acidity is discharged into Boundary Creek.

Comparison of surface water monitoring in Boundary Creek downstream of Big Swamp indicates that pH, iron (Fe) and aluminium (Al) pose the greatest ecological risk to the Barwon River, including the greatest risk of fish kills via respiratory failure via low pH conditions and high Al concentrations. Simulations via the modelling package PHREEQC and comparison of flows in Boundary Creek to those in the Barwon River suggest that under typical conditions, ecological risks to the Barwon River are highest during May and June, when discharge from the creek contains higher concentrations of H+, Fe and Al and flows from the creek begin to increase. However, the only recorded fish kill event in the Barwon River occurred in June 2016, when flows in Boundary Creek represented ≥40% of flows in the Barwon River. While similar events have occurred in the Boundary Creek – Barwon River system historically, this event was unique as it was preceded by an 8 month period of flow cessation in Boundary Creek (compared to other events with ≤4 months of flow cessation), indicating that it is the accumulation of acidity in mineral salts in Big Swamp during extended periods of flow cessation combined with a high proportion of flows from Boundary Creek that yield the greatest risk of fish kill events.

Calibration results for a PHREEQC mixing model developed to predict water quality changes in Boundary Creek in response to flow augmentation have been presented and demonstrate a good calibration between the modelled and observed concentration of acidity in Boundary Creek downstream of Big Swamp, with an R^2 value of 0.97. Other parameters of significance with respect to ASS and acidity concentrations including pH, SO_4 and Fe exhibited good calibration with R^2 values of 0.88, 0.95 and 0.98, respectively, indicating that the model provides a good hydrogeochemical representation of the system. The model is also consistent with the relative contribution of groundwater from different regions of the swamp predicted by the numerical groundwater-surface water model. The predicted change in acidity concentrations in Boundary Creek resulting from remediation indicate an increase in acidity concentrations. This is attributed to an increases in the volume of groundwater discharge from Big Swamp, primarily from the western portion of the swamp where concentrations of acidity in groundwater are higher.

Based on these predictions and the relative stores of acidity given by hydrogeochemical conceptual site model developed, while the remediation strategy proposed may result in an increase in the initial concentration of acidity in Boundary Creek, it may also reduce the duration of remediation by a factor of two thirds.

The study provides an illustrative example of how competing drivers such as groundwater resource demands and drier climate can lead environmental impacts associated with acid sulfate soils. It shows that by combining the use of static soil analysis, temporal groundwater and surface water chemistry and flow monitoring with numerical groundwater monitoring and PHREEQC, the major mechanisms of acidification can be identified, and the risk of fish kill events occurring evaluated. By doing so, the requirements of potential interim measures to mitigate these risks can be determined and the duration and potential short-term impact of long-term remediation via flow augmentation evaluated. As the world shifts towards a drier climate and water demand increases, it is becoming more critical than ever that approaches such as this be at the disposal of water managers, such that they have the information necessary to weigh up the competing societal, cultural and environmental needs of water during their decision making.

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The effects of soil ripening on saturated hydraulic conductivity in cultivated acid sulfate soils in Finland

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Biography:

Dr Seija Virtanen is executive director of Drainage Foundation sr in Finland. She received her Master of Sciences (Tech) degree in Water Resources Engineering from the Helsinki University of Technology, and Doctor of Sciences (Agriculture and Forestry) degree from the University of Helsinki. Her area of specialization is acid sulfate soils.

The effects of soil ripening on saturated hydraulic conductivity in cultivated acid sulfate soils in Finland

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Cultivation of acid sulfate soils cause environmental hazards in their recipient waters worldwide. In Finland, acid sulfate (AS) soils have been in cultivation since the 19th century, and currently about 41% of AS soils in the coastal area are under cultivation, which has weakened the ecological status of many rivers in that area (Westberg et al. 2012). However, the fields are highly productive, and therefore sustainable water management measures have been sought to minimize environmental loadings by field experiments and measurements. The global climate change with extreme weather conditions will exacerbate acid loadings. Future loadings can only be estimated with simulation models which take into account climate scenarios, as well as changes in soil properties. Ripening of AS soils is fast compared to other soil types (Dent 1986), and changes in soil properties have effects on water flow and acid loading from these soils. In this study, our aim was to elucidate the effects of soil texture and structure on saturated hydraulic conductivity (K_{sat}) by comparing the vertical and horizontal K_{sat} of ripe and unripe soil horizons between two soil profiles of different soil texture.

Material and methods

Undisturbed soil cores were sampled vertically and horizontally from six horizons and from four locations (N=133) in the Patoniitty field (60° 13.4’ N, 25° 0’ E) in 2007-2008 and from five horizons and one location (N=21) in the Söderfjärden field (63° 0.1896'N, 21° 35.4747'E) in 2020. K_{sat} was measured with constant and falling-head methods (m1-09.02, Eijkelkamp, The Netherlands). Both study fields have been subsurface drained since the 1950’s, and they are both in poldered area, but the texture of the soils is different. The subsoil in Patoniitty is clay or silty clay (Virtanen et al. 2014) and the subsoil of Söderfjärden is silty clay loam (Österholm et al., 2015).

Results

In Patoniitty, the K_{sat} values were log normally distributed, and therefore the medians of K_{sat} values were examined. The vertically measured K_{sat} values decreased with depth varying from 22.63 cm h^{-1} to less than 0.001 cm h^{-1}. The horizontally measured K_{sat} values were lower than the vertically measured ones, medians varying from 6.8 cm h^{-1} to less than 0.001 cm h^{-1}. A decrease with depth was not as clear in the horizontally measured values. In the structural horizons (above 100 cm depth) the median K_{sat} values were multifold higher than in massive soil horizons (below 130 cm depth).

However, two values > 0,001 cm h^{-1} were measured due to pipestems just below 130 cm. In Söderfjärden, both the highest horizontal and vertical K_{sat} values were measured in horizons directly above and below the subsurface drain depth (1.1 m) with very coarse prismatic structure. Overall, the K_{sat} values in the Söderfjärden field were lower than in the Patoniitty field (Fig. 1)

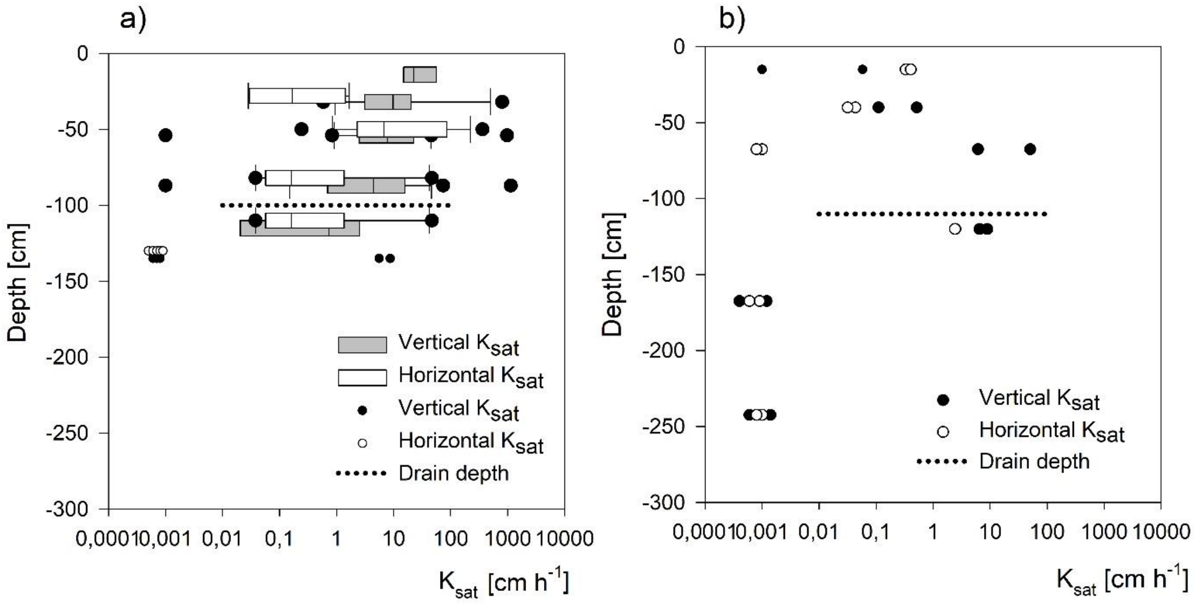

Figure 1. Saturated hydraulic conductivity (K_{sat}) a) in the Patoniitty soil horizons and b) in the Söderfjärden soil horizons. The dotted lines mean the depth of drainpipes in the fields.

Discussion and conclusion

According to the K_{sat} measurements, the ripening and soil structure formation in AS soils may result in markedly higher K_{sat} values than would be expected based only on the soil texture. In addition, the higher, measured K_{sat} values for the clay soil, as compared to the loam soil, highlight the marked importance of soil ripening on a soil's ability to convey water. Therefore, the changes in soil hydraulic properties should be considered in simulation models, especially in estimating the long-term evolution of hydrological and geochemical state of AS soils.

Acknowledgements

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Acid sulfate soils in temperate coastal vegetation communities

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Biography:

I am a research master at the School of Earth, Atmosphere and Environment, Monash University. My research area is assessing coastal acid sulfate soil environments in temperate Australia.

Acid sulfate soils in temperate coastal vegetation communities

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1. Objective of the study

Acid sulfate soils (ASS) are soils and sediments containing oxidisable or already oxidised metal sulfides (Fitzpatrick et al., 2016). The study aims to assess the acidification risks in temperate coastal vegetation communities (mangrove, saltmarsh and tea tree environments). There have been few ASS investigations in temperate coastal vegetation environments. Therefore, this research will assess the physical and chemical properties of soils sampled from Rhyll and Corner Inlet, Victoria, southern Australia and determine the potential formation of acid sulfate soils in these vegetation communities.

2. Study methodology

Soils were sampled from two sites, Rhyll (Figure 1) and Corner Inlet in mangrove (MG1 and MG2), saltmarsh (SM1 and SM2) and tea tree (TT1 and TT2) environments.

The soil samples were analysed for soil colour (with a Munsell soil colour chart), soil pH and electrical conductivity (EC), soil moisture (oven-dried for 24 hours at 105°C), particle size distribution, soluble cations, soil organic carbon and total nitrogen, reduced inorganic sulfur, titratable actual acidity (based on method 20B1 from Rayment and Lyons (2011b)), and acid neutralising capacity (based on method 20H1 from Rayment and Lyons (2011b)).

3. Results

Preliminary results from soils sampled from Rhyll are shown in Figure 3. Soil samples from the tea tree site have lower soil water content and are less saline than the mangrove and saltmarsh sites because of infrequent inundation by seawater. The tea tree sites are the most acidic of the three sites. Soil organic carbon and total nitrogen both show a decreasing trend as the sampling depth increases.

4. Conclusions

In coastal areas of Australia where mangroves, saltmarsh and tea-tree vegetation communities are found, tea-tree dominated communities are usually located at the highest elevations, while salt marsh and mangrove communities are found at lower elevations. Fluctuations in sea levels lead to seawater inundation of coastal swamp vegetation, which is likely to form potential ASS when the sea level rises. There are some studies on the soil characteristics of these three vegetation communities. However, the relationship between soil properties in the three types of plant communities and ASS formation is less well-known. In addition, limited information about ASS characteristics and formation exists in coastal tea-tree environments. This study will address this knowledge gap.

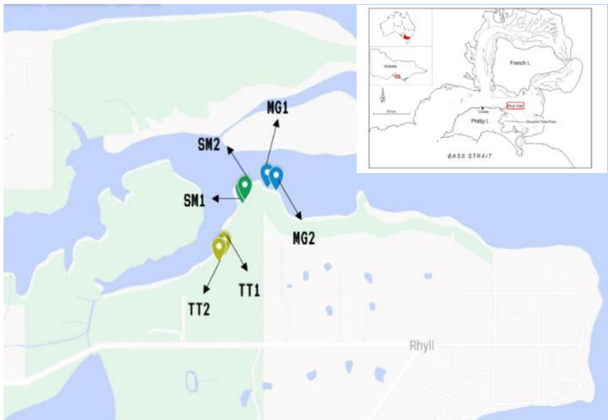

Fig 1. Sampling sites in Rhyll.

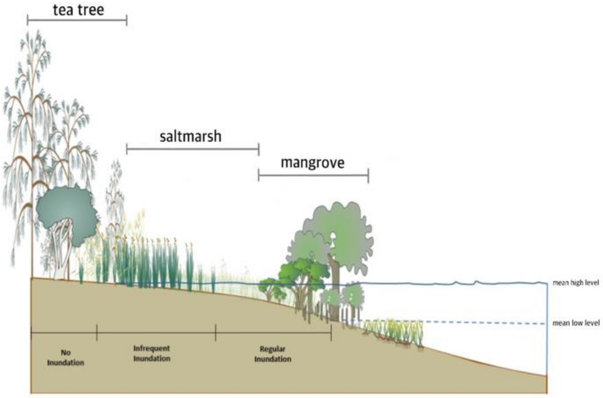

Fig 2. Modified from: Northam, K. J. (2016). Influence of entrance regime on vegetation profiles and carbon storage in south-eastern New South Wales ICOLLs.

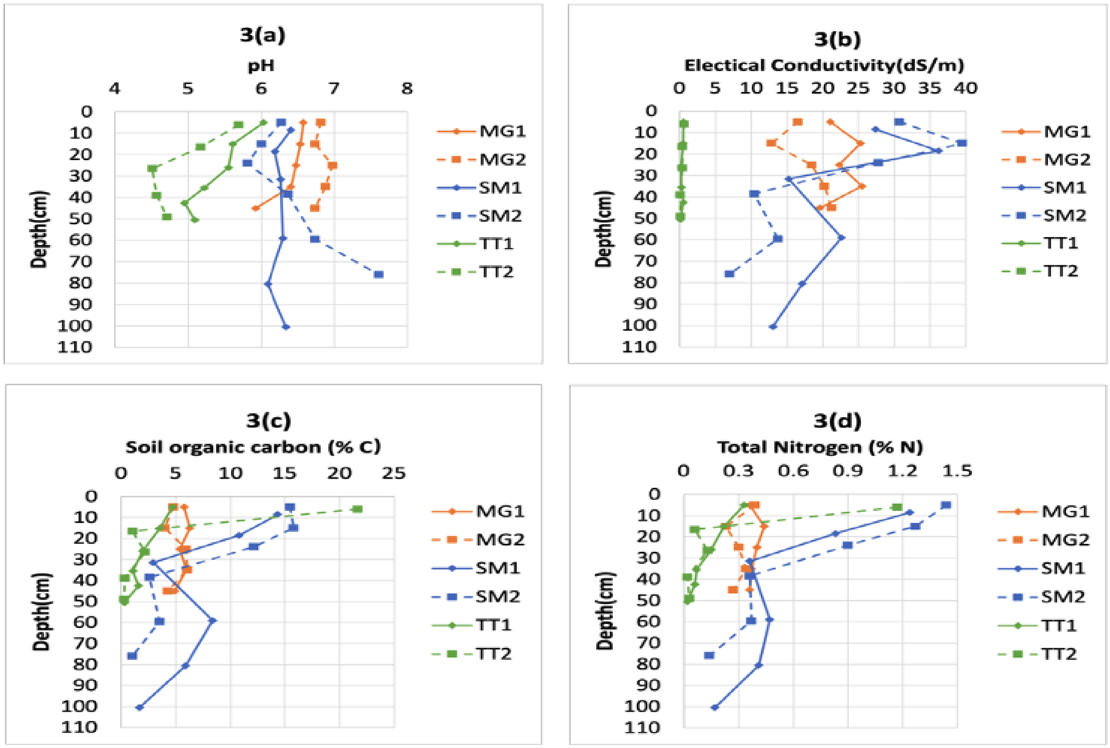

Fig 3. Preliminary results from soils sampled from Rhyll. namely 3(a) pH for a 1: 5 soil: water extract, 3(b) electrical conductivity (EC) for a 1: 5 soil: water extract, 3(c) soil organic C (SOC) and 3(d) total N, of the soil profiles in the mangrove site 1 (MG1), mangrove site 2 (MG2), saltmarsh site 1 (SM1), saltmarsh site 2 (SM2), tea tree site 1 (TT1) and tea tree site 2 (TT2) sites.

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PALEO-HYDROGEOMORPHOLOGICAL PROCESS INDENTIFICATION OF PEATLANDS ACID SULFATE SOILS USING GIS AND REMOTE SENSING APPROACHES

Dr. Wirastuti Widyatmanti

Widyatmanti _ Abstract Paleogeomorphology ASSoils Peatland.pdf (could not be inserted)

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Changes in Acid Sulfate Soils Training Delivered by Queensland Government

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Biography:

Kristie Williams has worked in the ASS field for Queensland government for more than 20 years. During that time she was one of the lead authors of the "Queensland Acid Sulfate Soil Technical Manual: Soil Management Guidelines", and she contributed to writing and implementing State Government regulations and policies about ASS. Kristie has written numerous technical reports/conference proceedings/fact sheets about ASS, assessed loads of development applications (ranging from small trenches to massive canal estates and dredging operations), and delivered numerous ASS workshops and training to a large variety of stakeholders. Kristie is a Land Resource Officer with the Queensland Department of Resources, currently based in Toowoomba on the Darling Downs (with ASS nowhere in sight!). She was previously based in Brisbane where lots of ASS can be found.

Changes in Acid Sulfate Soils Training Delivered by Queensland Government

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The Queensland Government has been involved in writing and delivering ASS training to a huge variety of stakeholders for more than two decades.

Initially, ASS training was delivered by staff from the Queensland Government group “QASSIT” (Queensland Acid Sulfate Soils Investigation Team), funded through the National Landcare Program. This was an intensive, planned program which originally focused on education and raising awareness, before evolving into targeted courses focusing on specific topics e.g. management, legislation, interpreting laboratory results, ASS mapping etc. From 2000 to 2005 alone, more than 250 workshops, seminars and conferences were delivered to industry, consultants, Queensland government agencies, interstate government agencies, local government agencies and environmental organisations (reaching a conservatively estimated audience of 5500 people). The QASSIT training ranged from 1 hour presentations to 4-day workshops. This training program continued until 2008.

Due to a change in government priorities, from 2008 to 2018 only minimal ASS training was delivered, on an ad hoc basis.

In early 2018 a local government in south-east Queensland approached the Queensland Government to deliver ASS training. This kicked off a renewed training program focused exclusively on local governments, delivered as a hybrid of presentations, hands on field tests, discussions and case studies over one day. From 2018 to the end of 2022, training was delivered to 15 local governments throughout Queensland.

Fortunately, three Queensland Government officers have remained in an ASS training role from pre-2000 to now, which offers a unique perspective to comment on the differences that have arisen in this area over time. For example:

- The training is more interactive — they teach us and share what they have learnt (this applied knowledge is then shared with other local governments in turn). Participants present local case studies e.g. Gold Coast City Council doing water treatment plant pipelines through a national park where they re-invented the definition of a confined workspace, while using automatic water quality monitoring and automatic dosing.

- The audience is much more mixed — training is delivered to many local government sections at once (e.g. planning, environmental assessment, operational works, construction etc) with a broad range of knowledge about ASS (ranging from never having heard about ASS to those who deal with it on a weekly basis).
- Presenter skill sets are more wide-ranging — a concerted effort has been made to include consultants with practical experience as well as government regulators to deliver the training.
- There has been a huge change of staff/staff turnover/loss of corporate knowledge — interestingly, we have come across only one local government officer who has remained in this field from 20 years ago to now.
- Training is demand driven and free — local government officers approach us and organise the venue, advertising, logistics and catering. We come along and throw chocolates at them to encourage interaction (one of the main consistencies over the years is that our aim has not improved!).
- One incredibly pleasing aspect is that we've been able to see the principles from the *Soil Management Guidelines* (Dear *et al*. 2014) in practice e.g. councils setting up permanent treatment pads for ASS due to maintenance dredging of canals.

Because of the renewed focus on ASS training, additional workshops have also been delivered to other State Government agencies involved in compliance, coastal assessment, fisheries and utilities during the past two years (Department of Environment and Science, Queensland Parks and Wildlife Service, Department of Fisheries). The Queensland Government training differs to that offered by other institutions as it is a shorter, more tailored product.

It has become apparent that teaching people about the fundamental science of ASS should continue, and more importantly, this teaching has to be repeated over the years because of staff turnover, people leaving jobs, generational change etc. While some consultants deliver ASS training to their staff and others, it is not sufficient. University graduates do not graduate with adequate knowledge about this field, and professional bodies are not teaching this information. Without regular ASS training programs, the end result is a huge loss of knowledge, which ultimately leads to inappropriate assessment and management of ASS.

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Acid sulfate soil characteristics in a large embayment under different vegetation types in southern Australia

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Biography:

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Acid sulfate soil characteristics in a large embayment under different vegetation types in southern Australia

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Coastal vegetation communities are important ecosystems which support high floristic diversity, provide important habitat for migratory birds, and protect terrestrial environments from high sea level events. Vegetation zonation in low-energy embayments in southern Australia is typically characterised by mangroves (*Avicennia marina*) in the lowest elevation regions which are subjected to diurnal tidal inundation, with saltmarsh communities found in areas of slightly higher elevation which are only inundated at spring tides or during storm events. Behind the saltmarsh at higher elevations, there can be a zone dominated by Swamp Paperbark (*Melaleuca ericifolia*).

Due to regular inundation, either currently or during the Holocene marine transgression (Bird 1986), and an abundance of organic matter, these environments are likely to host acid sulfate soils (ASS). However, few studies have characterised ASS in coastal environments in southern Australia. This study identified the acid sulfate soil characteristics of key sites in Western Port Bay, a tide-dominated embayment in southern Australia located approximately 75 km south-east of Melbourne, Australia.

Mangrove, saltmarsh and tea tree communities were sampled at five sites around Western Port Bay (Figure 1) and analysed for net acidity (including titratable actual acidity (TAA), reduced inorganic sulfur (RIS), acid neutralising capacity (ANC)), organic carbon, total nitrogen and particle size distribution.

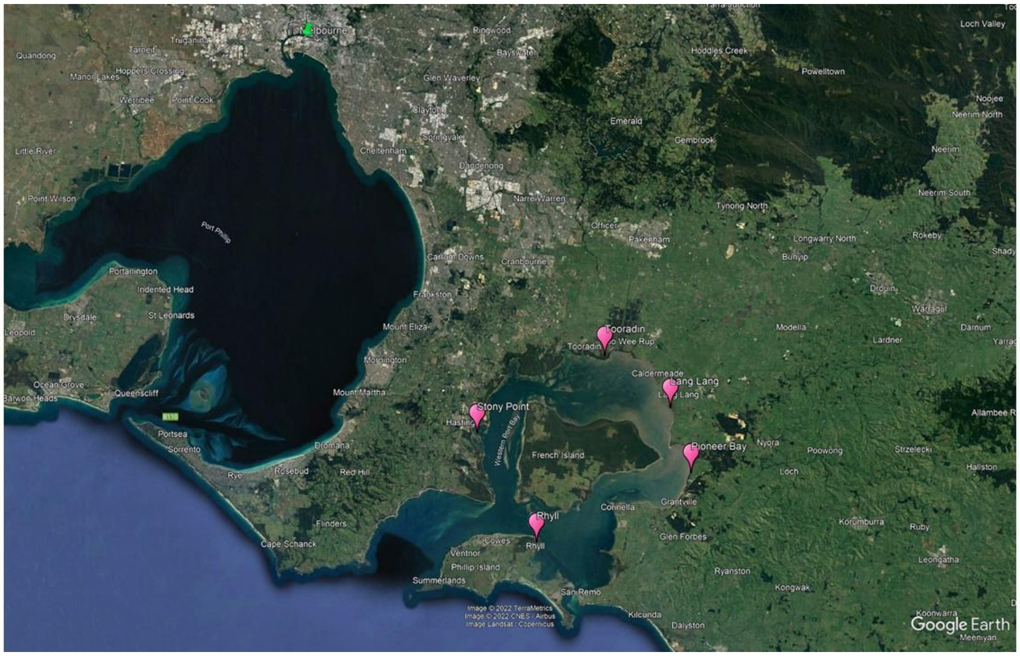

Figure 1. Sampling locations in Western Port Bay relative to Melbourne, Victoria, Australia

Reduced inorganic sulfur (RIS) concentrations were determined as the sum of acid volatile sulfide (AVS), which estimates monosulfides, and chromium reducible sulfur (CRS), which estimates pyrite. RIS was generally highest in the mangrove sites, however, net acidity was generally negative due to the high ANC supplied by seawater and additional shell material. Salt marsh sites generally had TAA and RIS concentrations, with lower ANC leading to higher net acidity concentrations.

The tea tree environments, however, had the highest net acidities (eg. Figure 2). These tea tree environments had very high TAA concentrations due to the accumulation of organic matter which can be a source of organic acids during decomposition, with soil organic carbon (SOC) content of > 30% in some sites with lower RIS concentrations. The RIS concentrations were largely dominated by CRS. These sites also had negligible ANC due to their higher elevation locations such that these sites are infrequently inundated by seawater.

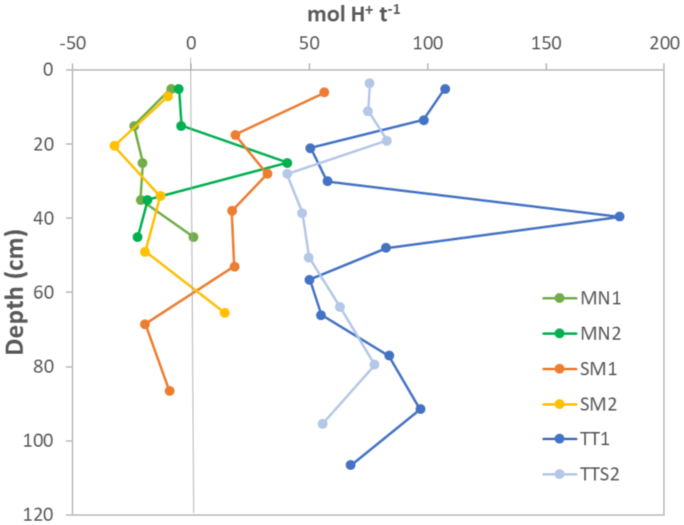

Figure 2. Net acidity from mangrove (MN1 and MN2), saltmarsh (SM1 and SM2) and tea tree (TT1 and TT2) sites from Stony Point.

The tea tree environments present an acidification risk due to the limited buffering capacity, which can impact on water and soil quality and surrounding infrastructure due to its higher elevation position and proximity to agricultural land and urban areas. The high accumulation of organic matter in these environments can also lead to the formation of new sulfidic materials with prolonged inundation by seawater, which can increase acidification risk.

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Effect of inundation and lime amendments on greenhouse gas emissions from acid sulfate soils

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Biography:

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Effect of inundation and lime amendments on greenhouse gas emissions from acid sulfate soils

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Acid sulfate soils (ASS) usually contain large amounts of organic matter which can be potential sources of greenhouse gas emissions (GHGs), such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) when decomposed. Predicted sea level fluctuations and sea level rise with climate change will affect inundation of coastal soils, including coastal acid sulfate soils (CASS) but the studies of effects of sea level variation on GHGs in ASS are not clear. Many CASS are used for agricultural production, and lime is frequently added to the soil to neutralise the acidity generated from ASS. However, the effect lime on GHG emissions is also unclear is ASS.

In our research, we identified the effect of inundation with brackish water on GHGs from CASS sites which supported four different vegetation types (*Leptospermum lanigerum,Apium gravedens, Phragmites australis* and *Paspalum distichum*) which were located on the Aire River estuarine floodplain in southern Australia. Soil cores were incubated under dry, flooded, and alternating wet-dry treatments of 14-d for a total of 54 days in controlled conditions at a constant temperature of 23℃. For the lime amendment study, soils (one ASS and one non-ASS) were sampled from the research farm of the University of Helsinki which is located on the Gulf of Finland and separated into horizons for analysis. The soils were homogenised and 10 mL of either 0.125M and 0.25M $CaCO_3$ was added as suspension.

GHG (N_2O and CO_2) measurements were measured weekly during an oxic phase of 56 days, and followed by an anoxic phase of 72 hour. Soils were maintained a 70% water-filled pore space for the oxic incubation. For the anoxic incubation, GHG emissions were measured in the presence of C_2H_2 and the headspace was replaced with N_2 to achieve strictly anaerobic conditions to determine total denitrification

The results from the inundation incubation indicate that soil organic carbon and total nitrogen concentrations were ordered *as P. distichum* > *P. australis* > *Apium gravedens* > *L. lanigerum*. The wet-dry treatment significantly decreased cumulative CH_4 emissions compared to that under the flooded treatment. *Phragmites australis* had the highest cumulative CH_4 emissions which occurred under the flooded treatment due to the high organic matter and high stem density. The highest CO_2 flux was found during the dry period of each wet-dry treatment (>200 mg CO_2 m^{-2} h^{-1}) as aerobic conditions promoted the activity and respiration of microbes as well as increasing aerobic respiration and decomposition of organic matter in soils. The highest N_2O flux was found during the dry period of each wet-dry cycle as drainage of water can increase oxygen penetration into the soil, influencing microbial processes, promoting the nitrification process and therefore, enhance N_2O emissions. Paspalum distichum had a relatively higher N_2O flux due to the highest total nitrogen and organic carbon concentrations, suggesting high organic matter loading which could be metabolized by nitrifiers and denitrifiers in the soil. In general, the main controlling factors for the GHG emissions from CASS were water table levels, soil organic carbon and total nitrogen ((Xu *et al.* 2021).

In the liming study, liming to pH ≥ 7 decreased oxic N_2O production in the Ap1, Bg1, BC horizons of AS soil, but not that in the the C horizon. Liming lowered anoxic N_2O production in the Ap1 and Bg1 horizons and the $N_2O/(N2O+N_2)$ ratio in all horizons compared with unlimed ASS. Higher total carbon and nitrogen contents in ASS corresponded with higher cumulative oxic N_2O production in all horizons, and higher CO_2 production in the Bg1, BC and C horizons, in all treatments. Overall, liming reduced the proportion of N_2O of all GHGs in most soil horizons under oxic and anoxic conditions. Liming can reduce the total GHG production based on as CO_2 equivalents under oxic and anoxic conditions only in the Ap1 horizon of both ASS and non-ASS. The results suggest that liming of subsoils would not effectively mitigate GHG emissions in the field due to concurrently increased CO_2 production and denitrification (Xu *et al.* 2023).

The two incubations determined that ASS can be substantial sources of GHG emissions, which are altered under varying seawater inundation scenarios and with management actions such as lime additions.

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Effect of organic matter addition on cadmium and arsenic mobility in paddy soil

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Effect of organic matter addition on cadmium and arsenic mobility in paddy soil

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Adding organic matter (OM) into soil to stimulate iron and sulfate reduction and pH increase after flooding is a method for the remediation of acid sulfate soils, and this method may be also useful for the remediation of paddy soils contaminated by heavy metals. We studied the effect of adding OM (rice straw), iron oxide (hematite), or sulfate (gypsum) on the mobility of cadmium (Cd) and arsenic (As) in a paddy soil after flooding and subsequent drying. Compared to the control and adding iron oxide or sulfate, adding OM stimulated microbial iron reduction and pH increase, and therefore effectively promoted Cd immobilization in the soil after flooding. Compared to the control, adding OM increased As release in the first four weeks of flooding, but this impact disappeared when the flooding was extended to eight weeks. After drying, in the soil with added OM, pH remained higher and therefore Cd mobility was lower and As mobility was higher compared to other three treatments. The results showed that straw incorporation may be an effective way to remediate Cd-contaminated paddy soils. To remediate As-contaminated paddy soils, adding iron oxide or sulfate may be useful, and straw incorporation should be accompanied by extended flooding (e.g., 8 weeks) to avoid As mobilization. The information may be also useful for the management of acid sulfate soils, especially those containing high concentrations of toxic metals.

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