



7th International Acid Sulfate Soil Conference in Vaasa, Finland 2012

Towards Harmony between Land Use and the Environment

Proceedings volume



GTK

Peter Österholm, Markku Yli-Halla & Peter Edén (eds.)

**7th International Acid Sulfate Soil Conference
Vaasa, Finland 2012
Towards Harmony between Land Use and the Environment**

Proceedings volume

Edited by

Peter Österholm, Markku Yli-Halla and Peter Edén



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Front cover: Acid sulfate soil landscape from Söderfjärden, western Finland.
Photo: Rainer Rosendahl, ProAgria ÖSL

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PREFACE

This volume contains papers presented during the 7th International Acid Sulfate Soil Conference (IASSC) in Vaasa, Finland. The conference consisted of three days of scientific sessions with oral and poster presentations, a mid-conference whole-day field tour and a two-day post-conference excursion in the Vaasa region.

Acid sulfate soils (ASS), also referred to as the “nastiest soils in the world”, are soils that contain or have contained metal sulfides that oxidize under aerobic conditions and, subsequently, typically produce very severe acidity and metal pollution. In Finland, for example, the discharge of several metals to water courses from ASS is greater than that from the entire Finnish industry, and due to the acidity these metals largely occur in a soluble toxic form.

Acid sulfate soils cover extensive areas, particularly in coastal areas of South-East Asia, the Caribbean, Western Africa, Australia and around the Baltic Sea. These soils are widely used for a variety of agricultural purposes, including rice production in the tropics, sugarcane in Australia and cereal production in Finland. Previously, management issues on ASS were mostly concerned with maximizing agricultural productivity and preventing crop failure due to the severe soil acidity. While these are still crucial issues in many areas, such problems have, particularly in industrialized countries, largely been solved, and ASS have been turned into some of the most productive farmlands. However, due to growing environmental awareness, including political goals such as the Water Framework Directive of the European Union, the focus in recent decades has shifted to reducing the environmental damage caused by ASS. Attention has also been directed to reducing environmental damage from other types of land use on ASS, such as forestry, the building of infrastructure, and the increasing pressure on urban development in coastal areas. Acid sulfate soils not only affect recipient water courses; due to their unique physico-chemical characteristics, they pose significant engineering problems due to severe consolidation and corrosion of infrastructure. More recently, emissions of greenhouse gases from ASS have emerged as a new research area.

As a summary, ASS are heavily exploited for a wide variety of purposes in different parts of the world, often causing serious environmental damage. Much still remains to be done in order to find management solutions for sustainable land use. The presentations in the 7th IASSC, representing authors from five con-

tinents, reflect the broad scope of issues that are related to ASS, including biogeochemical soil processes, soil mapping and characterization, environmental effects and management issues in a changing climate. As a solid scientific understanding of the problem is not alone enough to find sustainable management solutions, a half-day session during the conference was dedicated to presentations and discussion on the stakeholder perspective (land owners, politicians, authorities and the general public). As the ultimate goal of most ASS research and this conference is to find environmentally sustainable solutions, the overall title for the conference is “Towards Harmony between Land Use and the Environment”.

The 7th IASSC has been jointly organized by the Geological Survey of Finland (GTK) and the Working Group of Acid Sulfate Soils of the International Union of Soil Sciences (ASS WG). Previous international conferences on AS soils have been held in Wageningen, the Netherlands 1972; Bangkok, Thailand 1981; Dakar, Senegal 1986; Ho Chi Minh City, Vietnam 1992; Tweed Heads, Australia 2002; Guangzhou, China 2008.

Keywords (GeoRef Thesaurus, AGI): acid sulfate soils, sulfides, metals, pH, environmental effects, land use, environmental management, symposia

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MORPHOLOGICAL CHARACTERISTICS AND CLASSIFICATION OF MANGROVE SWAMP SOILS IN CROSS RIVER STATE ESTUARY, SOUTHEAST NIGERIA

by

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Mangrove swamp soils of Cross River estuary were studied regarding their characteristics. The soils are derived from fluvio-marine deposits and are in an environment with a peraquic moisture regime. Gleyzation is a dominant pedogenic process, as the soils have a chroma of less than 2 and a hue of 5Y – 5B (Munsell colour chart) in most of the horizons. They occur on a flat topography and possess fibric or sapric organic materials with a massive structure under wet condition. The soils are characterized by high organic carbon contents (42.2–117.6 g kg⁻¹), low pH values (2.0–4.8), high electrical conductivity values (0.87–58.02 dS m⁻¹), and an appreciable clay content (108.0–574.0 g kg⁻¹). The texture of the soils ranges from sandy loam to clay. According to the USDA *Soil Taxonomy*, the soils have been classified as *Typic Sulfaquent* or *Typic Hydraquent* and Thionic Fluvisols in the FAO/UNESCO soil legend.

CHARACTERISTICS, USES AND MANAGEMENT OF POTENTIAL ACID SULFATE SOILS FOR RICE PRODUCTION IN THE NIGER DELTA REGION OF NIGERIA

by

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Potential acid sulfate soils vegetated by mangroves are widespread, with a total estimate of 973,000 hectares in the Niger Delta region of Nigeria. The soils occur along the coastline, mouths of creeks and rivers where they are inundated with salt and brackish water in the coastal low-lying Niger Delta of Nigeria. The

Table 1: Various uses of potential acid sulfate soils in Niger Delta region of Nigeria

(i) Agriculture	Growing of rice: About 610,000 ha are suitable for general agriculture and rice cropping in the Niger Delta after reclamation. Burma Rice Farm Project at Okoroma/Tereke Local Government Area, Bayelsa State. About 50 hectares have been used for rice cultivation.
(ii) Forestry	Mangrove trees are used as timber, fuel wood, poles, tannins and dyes
(iii) Culture fishery (a) Culture of fin-fish	Function as nurseries for some crustaceans and finfish. Shellfish – oysters, periwinkles, crabs, crayfish, and mudfish are harvested from the swamps. Building of ponds for brackish water fish culture, e.g. a joint FAO/Federal Fisheries Project at Buruma, Rivers State started in 1963. Brackish water fish ponds at Ikot Abasi, Akwa Ibom State, yield about 1000 kg of mullet, tilapia and tarpon (Moses, 1985). Brackish water fish ponds at Bonny, Oron and many coastal towns. In the Philippines, 166,000 ha have been converted to fish ponds for milkfish (<i>Chanos chanos</i>), mullet (<i>Mugil cephalus</i>) and shrimp (<i>Panaeus monodon</i>). Cultural of edible crabs (Moses, 1985). Practiced in South East Asia, Philippines and Taiwan (Tomlinson, 1986).
(b) Culture of shrimps and crabs	Culture of oysters is common in Sierra Leone, Brazil and Malaysia (Moses, 1985).
(iv) Protection of coastlines	Protect and prevent excessive shifting of coastlines
(v) Sewage treatment	Used as garbage dumps and local sewage disposal units. Seen at watersides in Port Harcourt, Brass, Buguma, Bonny, Ikot Abasi, Ibeno, Calabar, Iking and other coastal cities with mangroves. Oil-producing companies (Shell, Agip, Elf) at flow stations dispose of their garbage in the mangrove swamps.
(vi) Oil well, flow stations and oil pipelines	Many oil wells operated by oil-producing companies are located in the swamp environment. Oil pipelines that link many flow stations and the oil terminals are buried in the swamp soils (Akpan-Idiok, 2002).

soils are useful in coastline stabilization, forestry, fisheries (culture of finfish, shrimps and crabs) and sewage treatment, and serve as base for oil wells, flow stations and oil/gas pipelines (Table 1).

Under wet/field conditions, the soils are near neutral or alkaline (pH 6.6–7.9), but under drained or aerated conditions, they are extremely acidic (pH 2.9–4.0) due to the oxidation of ferrous iron (Fe) in sulfides. This produces ferric iron, which precipitates as iron (hydro) oxides in the process, producing protons and sulfate for the formation of sulfuric acid, which acidifies the soils. The soils contain sulfidic materials or have the potential to form sulfuric acid when exposed to oxygen in the air in amounts that have an effect on the main soil characteristics.

The morphological attributes of the soils (Table 2) include colour variation from black, very dark grey, dark olive grey, dark reddish brown, dark brown to grey; fibric, sapric and hemic rootlets; periwinkles and crabs on the soils; many coarse/medium and fine pores; and a nearly flat topography and emission of H₂S on disturbance of the soil (Table 2). The soils are also characterized as follows: texture (sandy loam – clay loam – silty loam); sand (94–551 g kg⁻¹); silt (260–547 g kg⁻¹) and clay (103–398 g kg⁻¹); soil pH (2.9–4.0), electrical conductivity (9.10–30.7 dSm⁻¹), or-

Table 2: Selected morphological characteristics of the potential acid sulfate soils

Horizon	Depth	Matrix colour	Texture	Structure	Roots	Other features
P1 – Bakassi: Typic Sulfaquent (USDA) Thionic Fluvisol (FAO-UNESCO)						
Ag	0 – 20	5Y 2.5/1, b	cl	0	m, sap	Periwinkles, crabs, emitted H ₂ S
C1g	20 – 40	5Y 2.5/1, b	cl	0	m, sap	Many pores, emitted H ₂ S
C2g	40 – 60	5Y 3/1, vdg	cl	0	m, sap	Medium pores, emitted H ₂ S
C3g	60 – 80	5Y 3/2, dog	cl	0	m, sap	Fine pores, emitted H ₂ S
C4g	80 – 100	5Y 3/2, dog	cl	0	m, sap	Fine pores, emitted H ₂ S
P2 – Mbo: Typic Sulfaquent (USDA) Thionic Fluvisol (FAO-UNESCO)						
Ag	0 – 20	5Y 4/1, dg	sl	0	m, fip	Periwinkles, many pores, emitted H ₂ S
C1g						
C2g	20 – 40	5Y 3/1, vdg	sl	0	m, fip	Many pores, emitted H ₂ S
C3g	40 – 60	5Y 4/1, dg	scl	0	m, fip	Many pores, emitted H ₂ S
C4g	60 – 80	5Y 4/1, dg	cl	0	m, fip	Many pores, emitted H ₂ S
	80 – 100	5Y 4/1, dg	cl	0	m, fip	Many pores, emitted H ₂ S
P3 – Buguma: Typic Sulfihemist (USDA) Thionic Fluvisol (FAO-UNESCO)						
Ag	0 – 20	10 YR 3/1, vdg	sil	0	m, hem	Periwinkles, crabs, emitted H ₂ S
C1g	20 – 40	10 YR 2/1, b	sicl	0	m, sap	Many pores, emitted H ₂ S
C2g	40 – 60	10 YR 3/1, vdg	sicl	0	m, sap	Many pores, emitted H ₂ S
C3g	60 – 80	10 YR 3/1 vdg	sicl	0	m, sap	Many pores, emitted H ₂ S
C4g	80 – 100	10 YR 3/1 vdg	sicl	0	m, sap	Many pores, emitted H ₂ S
P4 – Degema: Typic Sulfaquent (USDA) Thionic Fluvisol (FAO-UNESCO)						
Ag	0 – 20	7.5YR 3/2, db	ls	1mg	m, fip	Crabs, emitted H ₂ S
C1g	20 – 40	2.5Y 5/1, g	sl	1msbk	m, sap	Many pores, emitted H ₂ S
C2g	40 – 60	2.5Y 5/1, g	sl	1msk	m, sap	Many pores, emitted H ₂ S
C3g	60 – 80	2.5Y 5/1, g	sl	0	m, sap	Many pores, emitted H ₂ S
C4g	80 – 100	2.5Y 5/1, g	sl	0	m, sap	Many pores, emitted H ₂ S

Colour: b = black, vdg = very dark grey, dog = dark olive grey, dg = dark grey, drb = dark reddish brown, db = dark brown, g = grey

Structure: 0 = massive (structureless), 1msk = weak medium subangular blocky 1mg = weak medium granular structure

Texture: ls = loamy sand, cl = clay loam, sil = silty loam, sicl = silty clay loam, c = clay

Roots: m, fip = many fibric root materials, m, sap = many sapric root materials, m, hem = many hemic root materials

Ag = Gleyed A horizon, C1g – C4g = Gleyed C undeveloped horizons

ganic carbon (31–222 g kg⁻¹), nitrogen (2.2–16.0 g kg⁻¹), available P (3–9 mg kg⁻¹); cation exchange capacity (30.1–58.8 cmol kg⁻¹), base saturation (84–95%) and soluble sulfate (0.002–0.007%). The high silt/clay ratios (0.97–3.51), exceeding the separating index of 0.15, qualify the soils for classification as “young alluvium”, being materials deposited by tidal floods in the mangrove swamps. According to the criteria of the USDA Soil Taxonomy, the pedons at Bakassi, Mbo and Degema were classified as Typic Sulfaquent, while the pedon at Buguma fitted Typic Sulfihemist. The equivalent FAO-UNESCO unit was Thionic Fluvisol for the four pedons.

The management techniques of the soil for rice cultivation aim at alleviating the problems of salinity, acidity, a low water table, toxic substances and pyrite oxidation associated with potential acid sulfate soils vegetated by mangroves. Under wet/field conditions, the soils are used in the cultivation of saline-tolerant varieties of rice such as ROC 5, DA 29, CK 73 and WAR bred by the West African Rice Development Association (WARDA) with headquarters located at Sierra Leone. Other rice varieties of lowland ecology such as FARO 52 (WITA4) FARO 37, FARO 15, have thrived well on the mangrove swamp soil in the Burma Rice Farm Project. The success of the pilot Burma Rice Farm Project located at Okoroma/Tereke Local Government Area of Bayelsa State has awakened the interest of farmers and investors in using the potential acid sulfate soils for rice cultivation. This will ensure food security, a reduction in the importation of rice and earning of foreign exchange for Nigeria.

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IDENTIFICATION AND CLASSIFICATION OF ACID SULFATE SOILS IN NORTHERN SWEDEN

by

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BACKGROUND

Substantial areas of Sweden are covered by sulfide-rich sediments that consequently form potential acid sulfate soils if they are subjected to oxidation, e.g. by drainage of the water table. Acid sulfate soil is a term used for soils that contain highly acidic horizons or layers, typically with a pH of 4 or less. Originally, these soils were deposited as sediments in the Littorina Sea around 7500–2500 years BP, but due to isostatic uplift the sediments have since emerged. When oxidised, the sulfidic sediments develop into acid sulfate soils that have been shown to negatively affect the aquatic environment of some watercourses. Observed effects include the deterioration of water quality in streams through acidification and leaching of heavy metals, sometimes leading to sudden mass deaths among fish (Erixon 2009). Earlier studies have shown that sulfidic sediments are commonly situated in areas rich in clay and silt that have been uplifted during the last 4000 years (Sohlenius et al. 2007). To prevent acid sulfate soils from having a negative effect on aquatic environments due to incautious human activity, the Geological Survey of Sweden (SGU) is collecting and assessing data to gain a better understanding of where these deposits are located.

In 2011, a field study was conducted along the northern coasts of Sweden to investigate potential acid sulfate soils. Soil samples were collected, subjected to oxidation and classified based on their acidity. The aim of the study was to assess whether shoreline displacement data could be used alongside maps of unconsolidated deposits in order to identify risk areas for acid sulfate soils.

METHODOLOGY

Fifty-five soil samples were collected by hand driven boring (the range of depth was 0.1–3 metres below ground level) from 17 sites in the counties of Västerbotten and Västernorrland in northern Sweden. The sampling sites were selected based on SGUs maps of unconsolidated deposits and shoreline displacement data. Locales of interest were fields with lowered groundwater tables, ditches and fens. Soil samples were described in field based on particle size, the content of organic material, colour, and geomorphology. Other relevant traits were the presence of rust streaks and visible sulfide and/or jarosite minerals.

Samples were thereafter submitted for pH testing in a lab. A Hamilton (340i) pH/Conductivity Pocket Meter was used to measure pH directly from the soils. Tests were executed in sequence over a period of 4 months (September 2011–December 2011). During this phase the samples were subjected to oxidation and the rate of acidification could thus be measured. Chemical analyses were performed with ICP-OES to establish the contents of sulphur (S), nitrogen (N), copper (Cu), iron (Fe) and manganese (Mn). The carbon (C) content was analysed with LECO CNS 2000 after combustion. Lastly, the soils were classified into four groups based on acidity, namely:

- Class I, pH < 3.5 very problematic sulfate soil
- Class II, pH < 4 problematic sulfate soil
- Class III, pH < 4.5 potentially problematic sulfate soil
- Class IV, pH > 4.5 sulfate soil with no risk

The methodology used for pH measurements and classification of acid sulfate soils is similar to that used by the Geological Survey of Finland (GTK), i.e. samples were oxidised and pH was measured at regular intervals over a period of time. However, unlike the GTKs system of classification, this study has not taken into account the depth at which sulfidic material lies as a parameter for problematic sulfate soils.

CONCLUSIONS

The results of this study suggest that the method of combining maps of unconsolidated deposits and shoreline displacement information, in order to identify areas with potential acid sulfate soils, is reasonably efficient. Around 50% (29 out of 55) of the sampled soils had pH levels below 4.5 after oxidation, and were thus classified as potentially problematic to very problematic sulfate soils. The topsoil samples were typically characterised by low initial pH values, probably because the top sediments were already oxidized at the time of sampling (Fig. 1). At some sites, sulfide-rich soils could be identified in field either by their black colour originating from iron monosulfide (FeS), vertical cracks covered by iron hydroxides and sometimes the occurrence of the yellow mineral jarosite.

After oxidation, the total concentration of S displayed a correlation with measured pH levels, indicating that samples with a pH below 4.5 also had the most elevated S concentrations. The total concentration of S for all samples range between 37–10 968 mg/kg, whereas very problematic sulfate soils (Class I) had total S concentrations exceeding 1 490 mg/kg. Interestingly, the relationship between organic C and S was inconsistent. This indicates that SGUs maps of unconsolidated deposits alone are insufficient for identifying potentially acid soils, but alongside shoreline displacement data the maps are reasonably functional.

Further investigations on sulfidic material and acid sulfate soils are needed and studies will continue during 2012. Additional field studies will be conducted and data from excavations and drilling operations will be gathered from external sources, such as the Swedish Transport Administration (TRV).

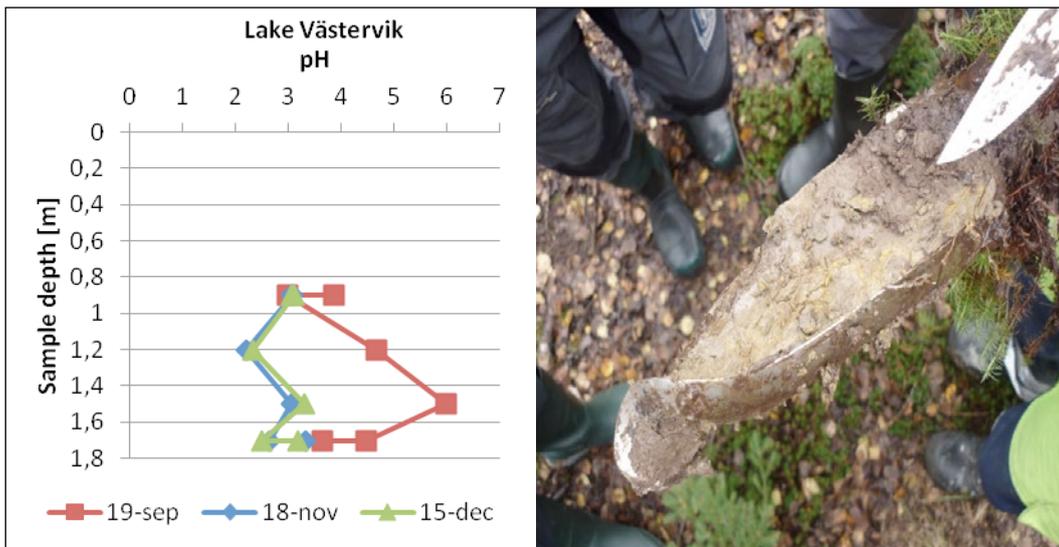


Fig.1. An example of a very problematic acid sulfate soil (Class I) taken from a drained former lake. The three curves represent pH measurements on different dates. At all depths pH is below 3.5 after oxidation. The yellow colour is probably due to the occurrence of jarosite in the oxidised sediments.

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EXCAVATION PRACTICES IN SULFIDE CLAY AREAS, IN PROJECT HIGHWAY NO. 8 SEPÄNKYLÄ BYPASS VAASA-MUSTASAARI

by

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This paper describes the challenges posed by the sulfide clays that had to be met during the improvement work on Highway No. 8 located in the vicinity of the city of Vaasa in the north-west part of Finland. The new Vaasa bypass road was planned to cross large areas of clay. Road construction in such conditions is only possible either due to extensive mass exchange, mass stabilization or a combination of columns and mass stabilization. Mass exchange and the excavation of sulfide clays from the anaerobic environment under the groundwater level and moving them to aerobic conditions is not recommended without prior treatment such as stabilization.

This paper presents various alternatives to a large mass-exchange operation on Highway 8 and the Vaasa bypass road.

While designing the details of the project (Ramboll and Skanska), the sulfide clay problem was taken into consideration and the final solutions were created in such a way that allowed the sulfide clay to be left on-site, and mass exchange to therefore be avoided almost entirely. The solutions include such procedures as column stabilization, mass stabilization and stabilizing berms.

The pH of the soil samples had a crucial role in the compressive strength of the samples. Test results showed that when the same amount of binder was used, the strength of the samples originating from bigger depth was considerably higher than of the samples originating from the layers closer to the surface. The lower the pH of a soil sample, the poorer the strength.

The stabilization works in the area will mainly be carried out using commercial binders. However, for the purpose of pH adjusting, the results indicate that this can be obtained not only with commercial binders but also by using fly ash only. In the case of the necessity for mass exchange, the clays need to be processed before landfilling. Therefore, the use of fly ash would give significant financial savings in processing costs.

There are plans to launch pilot work in late summer/early autumn, in order to test stabilization performed with the use of fly ash only. If sufficient strengths are not achieved, the masses treated with fly ash can be safely utilised for landscaping purposes designed for this project in the landfill surroundings.

MANAGING ACID SULFATE SOIL RISKS AND IMPACTS IN THE LOWER LAKES OF THE MURRAY-DARLING BASIN, AUSTRALIA, DURING EXTREME DROUGHT

by

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The Lower Lakes at the terminus of Australia's Murray-Darling Basin (over one million km²) comprise part of the Coorong and Lakes Alexandrina and Albert wetland, a site of international importance designated in 1985 under the Ramsar Convention. The water level is managed to approximately +0.75 m above sea level (Australian Height Datum; AHD) via a series of barrages that separate the lakes from the Murray mouth and Coorong lagoon (Fig. 1). The site has unique biodiversity existing within a rural, national park, traditional owner and coastal township setting.

Between 2006 and 2010, southern Australia experienced its worse drought on record. Drought conditions combined with water resource allocations throughout the Basin caused the water level in Lake Alexandrina to drop in early 2009 to its lowest level of -1.0 m AHD (Fig. 1). Initial hydrodynamic modeling of the lakes indicated that exposure of acid sulfate soils (ASS) would lead to acidification hot spots, particularly in the shallow Lake Albert, Currency Creek and Finnis River areas. As a consequence, in 2008 the Murray-Darling Basin Ministerial Council released a *Real Time Management Strategy to Avoid Lake Acidification* (RTMS). The RTMS included the monitoring of pH (and alkalinity) and water levels, bunding of Lake Albert across the Narrung Narrows and pumping of water from Lake Alexandrina to maintain the water level in Lake Albert above -0.5 m AHD. If alkalinity or water level management triggers were met in either lake, minimum quantities of seawater were to be introduced through the barrages, subject to approvals under the Australian Government's Environment Protection and Biodiversity Conservation (EPBC) Act 1991 and other legislative requirements. At the time, seawater was considered a viable management option in other coastal regions, although key concerns were raised about its use in this Ramsar-listed environment.

The consequences of such low water levels and the exposure of vast areas of ASS (up to 20,000 hectares) around the lakes to communities in the region were numerous, with water availability and quality, health issues for people and livestock, dust storms, sulfuric odors, ecological degradation, and potential fish

kills being major concerns. The iconic nature of Coorong and Lower Lakes is recognized throughout Australia, as well as the importance of the Murray River in supplying water to South Australia's capital city, Adelaide, and other regions. In response to this unprecedented situation, the South Australian Government initiated a Lower Lakes ASS research program (DENR 2010) as part of a *Coorong, Lower Lakes and Murray Mouth (CLLMM) Long Term Plan* (DEH 2010) to answer management questions concerning the extent and severity of waterbody acidification and metal release. The program confirmed an extensive and considerable long-term ASS hazard, and that whole-lake acidification risks were particularly high for Lake Albert if pumping were not continued. It also found that owing to the amount of ASS already exposed, the introduction of seawater to the lakes could increase the acidification risk in the short term due to acidic cation exchange from exposed sediments. Hydrodynamic modeling further assessed the ecological consequences of managing water levels. A key driver of ecological change was salinity, regardless of acidification, as without sufficient freshwater inflows, net evaporation and the salinity level would eventually cause severe degradation.

Rewetting of the lakes over winter (May–August) in 2009 caused some of the accumulated acidity from exposed ASS to be mobilized, resulting in acidification of surface waters in hot spots around the margins. Rather than introduce seawater, a staged approach to managing these hot spots, especially in the Goolwa channel region, was implemented. Limestone barriers were placed at strategic locations in the tributaries to intercept inflowing water, over 1,000 tons of ultrafine limestone was dosed directly into acidic waters, and temporary regulators were constructed near Clayton and across Currency Creek with water pumped from Lake Alexandrina to raise water levels. Throughout the lake margins, large swathes of exposed ASS were vegetated using bevy cereal rye to reduce soil erosion, maintain soil moisture and increase sulfate-reducing bacterial activity through carbon addition. The combination of these actions, together with intensive water quality monitoring, community-based awareness actions and continued pumping of water into Lake Albert, kept immediate acidity issues to a minimum. The site was also better prepared for summer (Jan–March) 2010, when water levels again dropped from -0.7 m AHD to -0.9 m AHD in Lake Alexandrina (and from -0.3 to -0.5 m AHD in Lake Albert).

Planning for the next phase of acidity risks shifted when substantial rain fell across the Darling River catchment in Queensland in early 2010, and then throughout the Murray River catchment. Within six months, Lake Alexandrina had risen more than 1.5 m to predrought levels, and by September high inflows had breached the bund across the Narrung Narrows and the temporary regulator across Goolwa Channel. These new circumstances brought about a different set of risks, particularly regarding metal mobilization and monosulfidic formation, and a large blackwater (deoxygenation) event upstream delivered low oxygen and low alkalinity water. Refilling of the lakes also caused a highly acidic waterbody to form in Boggy Lake in northern Lake Alexandrina, which required a further 1,000 tons of ultrafine limestone to neutralize both soil and water. Targeted research and monitoring currently continues into these ecosystem risks and potential management options to mitigate them.

Since mid-2010, water levels have been managed between 0.5 and 0.8 m AHD, with intentional lowering via the barrages to reduce high salinities (greater than 6,000 $\mu\text{S cm}^{-1}$ (EC)) that have accumulated in Lake Albert. Very high salinities (up to 100 g/L; approximately 118,500 $\mu\text{S cm}^{-1}$) have also accumulated in the Southern Coorong. In both cases, salinity loads have proven difficult to reduce, impacting on the recovery of the ecosystem as a whole. Surface water acidity in the Lower Lakes is now mostly absent, although soil and groundwater acidity still remains in the zone underlying previously exposed ASS. In terms of recovery and mitigation, sulfate reduction and bioremediation have been occurring,

and the bund and temporary regulators have been or will be removed in line with legislative requirements.

A key outcome of the program is a greater understanding of environmental thresholds and management triggers, which has been used to influence national policies. However, the prevention of future localized or widespread acidification will require the provision of sufficient freshwater inflows to the Lower Lakes. Australia is developing a Murray Darling Basin Plan (MDBA 2011) that intends to return water to the environment while catering for human needs. While this is being finalized, the South Australian Government, with assistance from the Australian Government's Water for the Future initiative, will continue to implement management actions that promote resilience and healthy ecosystem functioning for this iconic region.

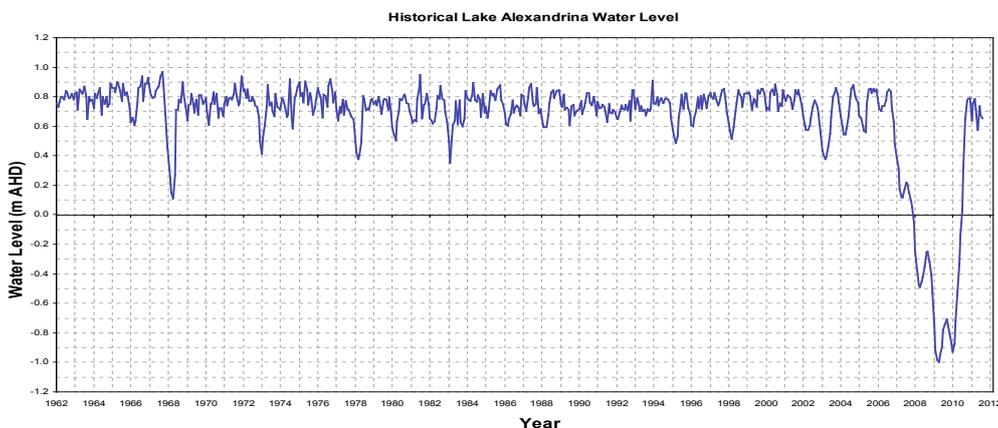
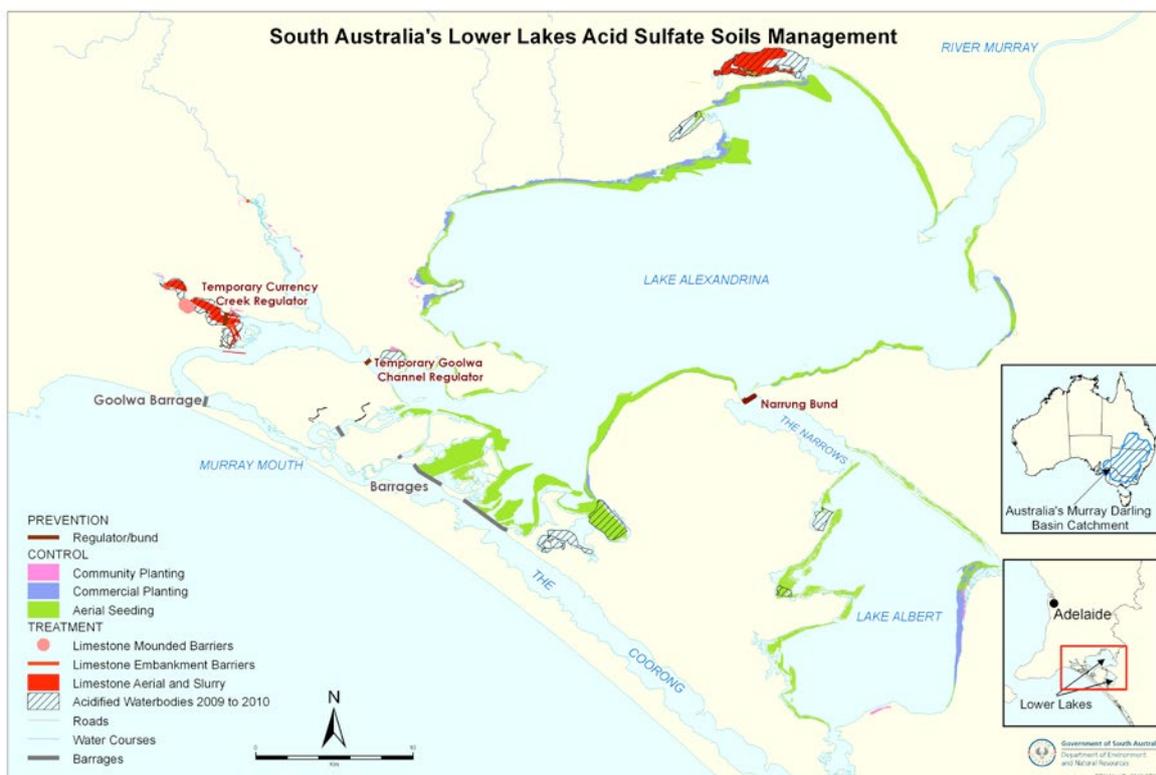


Fig. 1. The Lower Lakes, showing barrages separating the Coorong; areas of waterbody acidification (hatched), and ASS prevention, control and treatment actions in 2009–10 (upper); and the water level for Lake Alexandrina (lower).

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ARTIFICIAL NEURAL NETWORK FOR ACID SULFATE SOIL MAPPING: APPLICATION TO SIRPPUJOKI RIVER CATCHMENT, SOUTH-WESTERN FINLAND

by

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Finland has the largest occurrences of acid sulfate soils (AS soils) in Europe (in the order of 1000 km² or more). These soils leach considerable amounts of metals into watercourses, bringing even more metals than the whole of Finnish industry (Sundström et al. 2002) and causing severe ecological damage. Small hot spot areas affect large areas of coastal waters. Therefore, mapping of risk areas is essential to target strategic locations for mitigation. A cooperation network conducted by the Geological Survey of Finland has been established in order to create a nationwide AS soil map. The mapping programme started in 2010 within the framework of the EU-Life+ foundation in a project entitled Climate Change Adaptation Tools for Environmental Risk Mitigation of Acid Sulfate Soils (CATERMASS). Conventional mapping being expensive and time-consuming, spatial modelling techniques were implemented within Geographic Information Systems (GIS) in order to define and narrow down the areas of interest. Among the diverse spatial modelling techniques, an Artificial Neural Network (ANN) method was selected, as it provides very good pattern recognition and classification tools with the ability to generalize from imprecise input data (Porwal et al. 2003). The primary aim of this study was to evaluate the predictive classification abilities of an ANN for mapping AS soils. The Sirppujoki catchment (460 km²) located in south-western Finland was selected as the study area. This study was also conducted within the framework of the VALUE doctoral programme, which focuses on integrated catchment and water resources management.

An ANN called Radial Basis Functional Link Nets or RBFLN (Looney 1997, 2002) was applied in order to create probability maps for AS soil occurrences along the Finnish coastline. This method involved the use of aerogeophysical, Quaternary geology and elevation data. Aerogeophysical and Quaternary geology data layers were provided by the Geological Survey of Finland, and the digital elevation model by the National Land Survey of Finland. The RBFLN also required known AS soil occurrences, as well as non-AS soil sites. The AS soil occurrences corresponded to soil profiles containing sulfides within 3 m depth (i.e. when the profiles comprised an oxidized acidic layer as well as the underlying transition and reduced sulfidic horizons and/or when the pH decreased by 0.5 units to a value less than or equal to 4.0 after incubation). The points were divided into two sets: training and validation points. During the first stage, the neural network was trained: this basically involved associating the different data layers with

the training points (i.e. known AS and non-AS soil sites) and learning to classify these points accurately. In the second stage, the neural network classified all the unknown sites of the study area according to what it had been learning previously. This classification led to the creation of a probability map with four categories, from a very high to very low probability of AS soil occurrence. The accuracy of this map was then assessed using the validation points: the more validation points the neural network correctly classified, the more accurate was the probability map.

Using the RBFLN method, different probability maps were generated. For the best probability map (Fig. 1), the combined very high and high probability areas covered 23% of the study area and contained 94% of the validation points corresponding to AS soil occurrences. The combined low and very low probability areas covered the remaining 77% of the study area and contained all the validation points corresponding to non-AS soil sites. As these results were consistent with previous studies and verified by expert assessment, the RBFLN method demonstrated reliable and robust predictive classification abilities by generating accurate probability maps for AS soils in this study area. This method allows the creation of valid and comparable maps, and represents a powerful development within the AS soil mapping process, making it faster and more efficient. Consequently, we recommend RBFLN modelling, finalized by an expert assessment, for AS soil mapping.

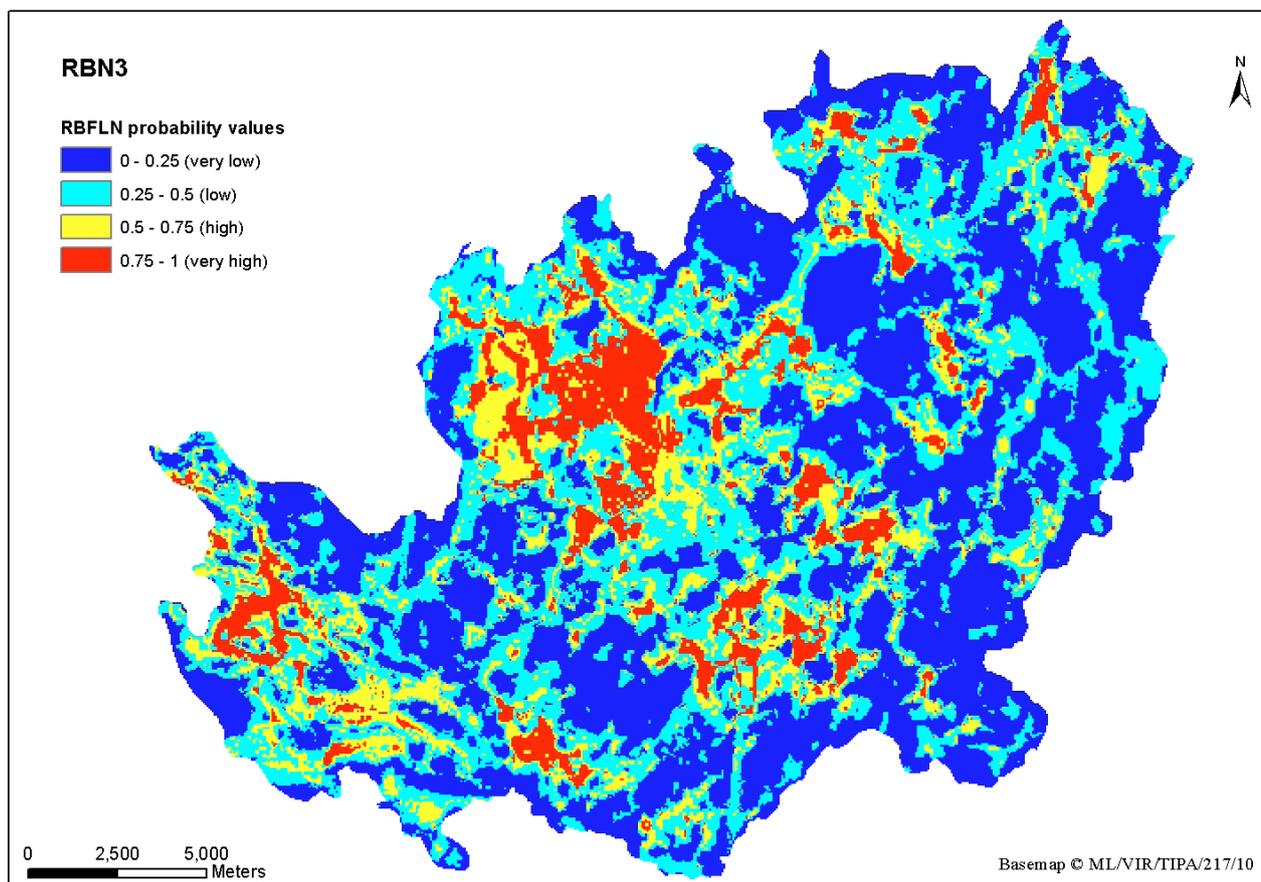


Fig. 1. Probability map created with the RBFLN method.

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CAN ZN ISOTOPES BE USED FOR TRACING ACID SULFATE SOIL DISCHARGE?

by

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The use of a Neptune multicollector ICP-MS (ThermoFinnigan) in this study has enabled high precision measurements of Zn isotopic ratios in Finnish acid sulfate (AS) soil landscapes (including AS soils, ditch sediments, estuarine sediments, and AS soil runoff).

The study sites are located within typical AS soil areas in western Finland and include Korsholm, Söderfjärden, Rintala, Vassor (including Vassor Bay), and the Vörå River Estuary. The above-mentioned locations include AS soil materials from Korsholm, Söderfjärden, Rintala, and Vassor, and sites receiving AS soil runoff. These non-AS soils include sulfide-rich ditch sediments from Vassor and sulfide-rich estuarine sediments from Vassor Bay and Vörå River estuary. In all AS soils, Zn was heavily depleted in the oxidized zone, whereas the AS soil runoff was highly enriched in Zn. At the sites receiving AS soil runoff (ditch and estuary), Zn was enriched in the upper parts.

At all AS soil sites, the measured $\delta^{66}\text{Zn}$ values ($\pm 1\sigma$) were generally negative and ranged from $(-0.49 \pm 0.01)\text{‰}$ to $(-0.01 \pm 0.03)\text{‰}$ at Rintala, from $(-0.36 \pm 0.02)\text{‰}$ to $(-0.15 \pm 0.02)\text{‰}$ at Vassor, from $(-0.33 \pm 0.02)\text{‰}$ to $(-0.09 \pm 0.01)\text{‰}$ at Korsholm and from $(-0.28 \pm 0.03)\text{‰}$ to $(-0.05 \pm 0.04)\text{‰}$ at Söderfjärden. At Rintala and Vassor, there was a slight upward decrease in $\delta^{66}\text{Zn}$ values in the AS soils. This implies that the leaching (mobile) Zn fraction should be enriched in the heavy isotope. This was indeed shown in the AS soil runoff at both locations, where the $\delta^{66}\text{Zn}$ values were positive with $(0.25 \pm 0.07)\text{‰}$ and $(0.26 \pm 0.05)\text{‰}$ at Rintala and Vassor, respectively. Possibly, this isotopically heavy mobile Zn fraction has previously been adsorbed on oxides and hydroxides (Pokrovsky et al. 2005) and/or is associated with iron sulfides and is now being released due to the acidic conditions. Some of this isotopically heavy Zn is most likely (re?) scavenged by iron sulfides (re)forming in the top of the ditch sediments, as indicated by the elevated Zn concentration (data shown in Boman et al. 2010) and occurrence of positive $\delta^{66}\text{Zn}$ values [$(0.05 \pm 0.01)\text{‰}$] in the upper parts. Nordmyr et al. (2008) showed that sediments several km out in the Vörå River estuary were enriched in Zn derived from AS soils in the Vörå River catchment. In this study, positive $\delta^{66}\text{Zn}$ values were found in the upper parts of the sediments in the Vörå River estuary. Therefore, despite the lack of isotopic Zn data from AS soils and runoff from the Vörå River catchment, these positive $\delta^{66}\text{Zn}$ values are suggested to be due to the incorporation of isotopically heavy Zn derived from

AS soils. Thus, the Zn isotopic data from Rintala, Vassor, and the Vörå River estuary suggests that Zn derived from AS soils is enriched in the heavy isotope. If this is correct, Zn isotopes can possibly be used in tracing AS soil discharge. Zn isotopes have already been used to trace metal loads from mine wastes (Borrok et al. 2009), and it is therefore not unlikely that AS soil discharge can also be traced in a similar manner. However, in contrast to the AS soils at Rintala and Vassor, the AS soils at Korsholm and Söderfjärden showed a general upward enrichment of the heavy Zn isotope. This implies that the leaching (mobile) Zn fraction at these locations could be isotopically light. Unfortunately, water samples were not collected and analyzed for Zn isotopes at these sites, and this could therefore not be checked. As a consequence, more detailed studies on Zn isotope distribution in AS soil landscapes are needed to conclude whether Zn isotopes are suitable for tracing AS soil discharge.

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BEHAVIOUR OF IRON, ALUMINIUM AND OTHER SELECTED METALS FOLLOWING THE REWETTING OF INLAND ACID SULFATE SOILS CONTAINING SULFURIC MATERIAL

by

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In this study, *in situ* equilibrium dialysis samplers, commonly known as peepers (Fig. 1a), were used to determine high resolution depth profiles of pore water chemistry and to assess the mobilisation and transport of dissolved constituents in previously dried Inland Acid Sulfate Soils (IASS) containing sulfuric material.

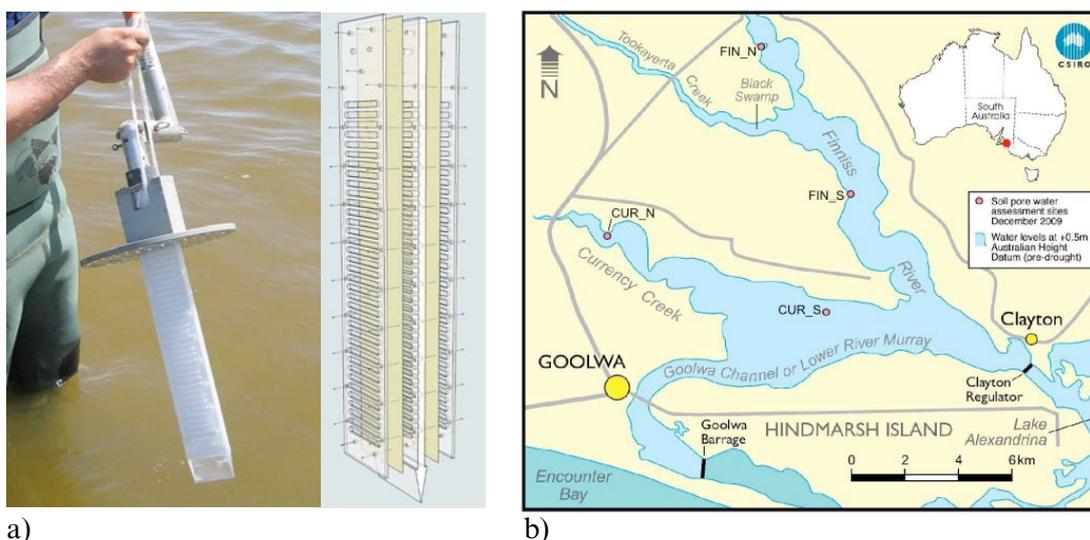


Fig. 1. (a) Photo showing specialised peeper installation apparatus with peeper ready to be deployed and diagram of peepers used in this study. The polysulfone membrane is coloured yellow in diagram for clarity (usual colour is white). (b) Locality map showing the 4 sites where peepers were installed.

Peepers are multi-chambered samplers typically constructed of a plastic such as Perspex, in which each chamber is filled with deoxygenated and deionised water. Each chamber is then sealed with a permeable inert polysulfone membrane (pore size ca. 0.45 mm). Once installed, dissolved pore water constituents diffuse across the membrane until equilibrium is reached. Typically, equilibrium is reached in around 2 weeks for Hesslein-style peepers, similar to those used in this study (Hesslein 1976, Teasdale et al. 1995), after which the peepers can be removed and the chamber contents analysed for the required parameters.

The Finnis River and Currency Creek tributaries, located to the west of Lake Alexandrina in the lower reaches of the River Murray in South Australia, experienced low water levels due to severe drought conditions. Water levels in the Finnis River and Currency Creek tributaries were at their lowest in 2007 and 2008, and during this period contained approximately 2000 ha of sulfuric soils (Fitzpatrick et al., 2011). Due to large areas of acidified IASS and the continued lowering of water levels, a water regulator was installed to raise the water levels in the Finnis River and Currency Creek and prevent further areas of IASS being exposed. Subsequent rainfall and the pumping of water from Lake Alexandrina into the tributaries led to the rewetting of the Finnis River and Currency Creek in September 2009. The rewetting of the tributaries provided a unique opportunity to study the changing properties and recovery of IASS containing sulfuric material following a rewetting event.

Peepers were installed at 4 rewetted sites in the Finnis River and Currency Creek tributaries (2 in each tributary) that were known to contain sulfuric material (Fig. 1b). Peepers were first installed at all 4 sites in January 2010, 5 months after the initial rewetting. They were then re-installed in August 2011, 24 months after the initial rewetting. Soil pore waters were analysed for pH, EC, acidity or alkalinity, and major and trace elements. Soil pore water analyses were also supported by measurements of soil pH, pH following incubation, soil Eh, and acid base accounting (Fitzpatrick et al. 2011).

At all sites, much of the profile remained acidic after 24 months of subaqueous conditions. Following 5 months of inundation, ≤ 5 cm of the uppermost sediment was partially neutralised to $\text{pH} > 4$. Below this, soil classified as sulfuric material prior to the rewetting event remained sulfuric and unaffected by rewetting. After 24 months of subaqueous conditions, an improvement of an additional 1–3 pH units in the uppermost 5 to 10 cm of the soil profile occurred at some sites. Below 10cm, an increase of <1 pH unit was typically observed.

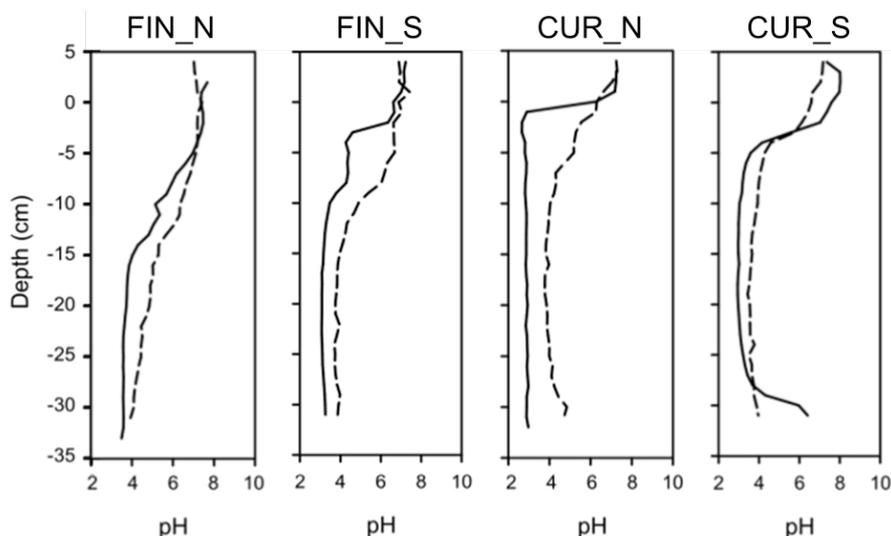


Fig. 2. Soil pore water pH profiles. Solid line = first sampling (5 months after rewetting). Dashed line = second sampling (24 months after rewetting).

Over time there has been an improvement in soil pore water quality, although many solutes still exceeded ANZECC guideline values (ANZECC/ARMCANZ 2000) after 24 months of subaqueous conditions. After 5 months of subaqueous conditions, ANZECC guideline trigger values were exceeded for Al, As, B, Cd, Cr, Cu, Mg, Ni, Pb, and Zn, with most being exceeded at all sites and over the majority of the depth-profile, including the top 5 cm. Twenty-four months after the initial rewetting event, a reduction in concentration to below ANZECC guideline trigger values has been observed at some sites for Al, As, Cd, Cr, Cu, Ni Pb, and Zn.

The detailed *in situ* sampling has demonstrated that the timescales involved for the recovery (i.e. neutralisation or removal of acidity and the re-establishment of reducing conditions) of rewetted IASS containing sulfuric material can exceed 24 months. Currently, geochemical modelling tools are being used to develop conceptual models of soil behaviour following the rewetting of an IASS containing sulfuric material.

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DEFINITION AND CLASSIFICATION OF FINNISH ACID SULFATE SOILS

by

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Systematic mapping and classification of acid sulfate soils (ASS) started in Finland in 2009, with the Geological Survey of Finland (GTK) as the responsible partner and in co-operation with Åbo Akademi University and the University of Helsinki. The first year mainly focused on method development. In the first stage of the mapping process we used airborne geophysical data together with other databases of GTK (soil maps, bedrock geological maps, peat-bottom soil information and topographic data, including LIDAR surveys) to delineate areas with potential for ASS. This data set has excluded about half of the area, while the other half is considered to potentially have ASS and is being mapped. Profiles for detailed lithological observations and sampling, as well as reconnaissance probe drillings, are being carried out to 3 m depth. On the basis of observations, measurements and analyses, we are carrying out classification and preparing maps and reports, which are available to the public via GTK's web pages (Edén et al. 2012).

During the mapping process we have also established a definition of Finnish Acid Sulfate Soils and developed a (risk) classification system for them. Both differ considerably from the internationally used ones (WRB and Soil Taxonomy). The alternative approach in Finland is a result of the different characteristics of ASS and process of formation in the Boreal environment, and of observed/measured qualities leading to harmful impacts on the environment.

DEFINITION OF ACID SULFATE SOILS IN FINLAND

Acid sulfate soils are soils with an elevated content of sulfur and consisting of an oxidized acid horizon (actual acid sulfate soil) and/or a non-oxidized (reduced) sulfide-bearing horizon (potential acid sulfate soil). Acid sulfate soils are usually gyttja-containing fine-grained soils (clay or silt).

Actual Acid Sulfate Soil (AASS):

- Field pH < 4.0 as a result of oxidation of sulfides and measured directly from the sample of oxidized minerogenic sediment or gyttja (not peat).
- If pH is 4.0–4.4 and there is no observation of underlying sulfide, further determinations are required (incubation or sulfur content).

Potential Acid Sulfate Soil (PASS):

- Sulfur in the form of sulfides (reduced, not oxidized)
- Typically pH > 6.0
- S_(tot) ≥ 0.2%
- Incubated pH ≤ 4.0 and drop of more than 0.5 units compared to field pH

RISK CLASSIFICATION OF FINNISH ACID SULFATE SOILS

The mapping/observation depth is 3 m. The classification is based on two/three parameters:

- Starting depth of the sulfidic horizon = PASS
- Minimum field pH
- Sulfur content (if analyzed)

Sulfides occur

CLASS 1	STARTING DEPTH OF PASS (m)
1	0–1.0
2	1.0–1.5
3	1.5–2.0
4	2.0–3.0
5	Sulfides entirely oxidized
6	No sulfides at 0–3 m depth

Field pH_{min}

CLASS 2	Minimum pH (0-3 m depth)
A	< 3.5
B	3.5 – 3.9
C	4.0 – 4.4
D	≥ 4.5

Sulfur (complement)

COMPLEMENT	Total S content (%)*
I	S _(tot) ≥ 1.0%
II	0.6% ≤ S _(tot) < 1.0%
III	0.2% ≤ S _(tot) < 0.6%
IV	S _(tot) < 0.2%

*Given as the mean for the uppermost 40 cm of the sulfidic (PASS) horizon

Classification for a site/sample is given in this form: **starting depth of sulfides / pH_{min} / S_(tot)**
 (e.g., 2 / A / II)

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MAPPING ACID SULFATE SOILS IN FINLAND: METHODS AND RESULTS

by

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Acid sulfate soils (ASS) have been estimated to cover approximately 100,000–150,000 ha along the west coast of Finland (Yli-Halla et al. 1998), being the largest occurrences in Europe. Sulfide-bearing fine-grained sediments were deposited in the sea between Finland and Sweden after the latest continental ice sheet had melted about 10,000 years ago. In places, the formation of such sediments is still going on today. The rapid isostatic land uplift (more than 200 m after the ice melted, currently up to 8 mm/year) after the retreat of the continental ice sheet has lifted these sediments above sea level. These so-called “gyttja-containing” soils are very suitable for agricultural purposes. However, most of them are low-lying and moist, and artificial drainage is therefore required prior to farming. Modern subsurface drainage, forest drainage, peat mining, dredging and intensified building activities, in particular, expose thick layers of the sediments to oxygen, leading to increased leaching of acidity and metals and the deterioration of streams, rivers and estuaries.

The harmful consequences of ASS in Finland have been known for decades, but due to the sporadic occurrences, diffuse knowledge and the lack of responsible organisation, no serious steps to reduce the harmful nature of these soils have been made. Sporadic, local mapping projects were carried out in the 1950s (Purokoski 1959) and 1970s (Erviö 1975), and several by Palko and co-workers (Palko 1994). They were all conducted using a wide variety of methods and criteria. The first estimation of the extent of ASS in Finland was made by Puustinen et al. (1994). Based on a wide-spaced sampling, they concluded that there are approximately 336,000 ha of ASS in Finland. These occur below the upper limit of the Litorina Sea, which is presently about 40–100 m above sea level, making up a land area of about 5 million ha. Yli-Halla et al. (1999) later used international criteria for the same data, ending up with 60,000–130,000 ha.

However, during the last ten years, unforeseen developments have occurred. Severe fish kills in 2006–2007 and the EU **Water Framework Directive** (a legislative instrument adopted to restore ground and surface waters (rivers, lakes and coastal waters) in Europe to a “Good Status” by 2015) have brought about extensive cooperation, and work has commenced during the last few years to localise ASS and find methods to prevent or reduce their harmful effects. The Geological Survey of Finland (GTK) created a national network of actors to

commence work on ASS. The Ministry of the Environment and the Ministry of Agriculture and Forestry (2011) developed a National Strategy for Acid Sulfate Soils, and ASS are also included in the Programme for Implementation of River Basin Management Plans 2010–2015 (Ministry of the Environment 2011). All agencies recommend the commencement of immediate ASS mapping of the whole coastal area using uniform and internationally valid methods.

Systematic mapping and classification of ASS started in Finland in 2009 with GTK as the responsible partner, together with Åbo Akademi University and the University of Helsinki. The first year consisted mainly of method development. At the beginning of the mapping process we used airborne geophysical data together with other databases of GTK (soil maps, bedrock geological maps, peat-bottom soil information and topographic data, including LIDAR surveys). This data set excludes about half of the area, while the other half is considered to potentially have ASS and is being mapped. Profiles for detailed observations and sampling, as well as reconnaissance probe drillings, are being carried out to 3 m depth. On the basis of observations, measurements and analyses, we are classifying ASS, and compiling ASS maps and reports, which are being made available to the public via GTK's web pages.

During the mapping process we have also established a definition of Finnish Acid Sulfate Soils and have developed a (risk) classification system for them (Edén et al. 2012). Both differ considerably from the internationally accepted ones (WRB and Soil Taxonomy). The alternative approach in Finland is a result of the different way in which ASS have formed and evolved in the Boreal environment and the observed/measured qualities leading to harmful impacts on the environment.

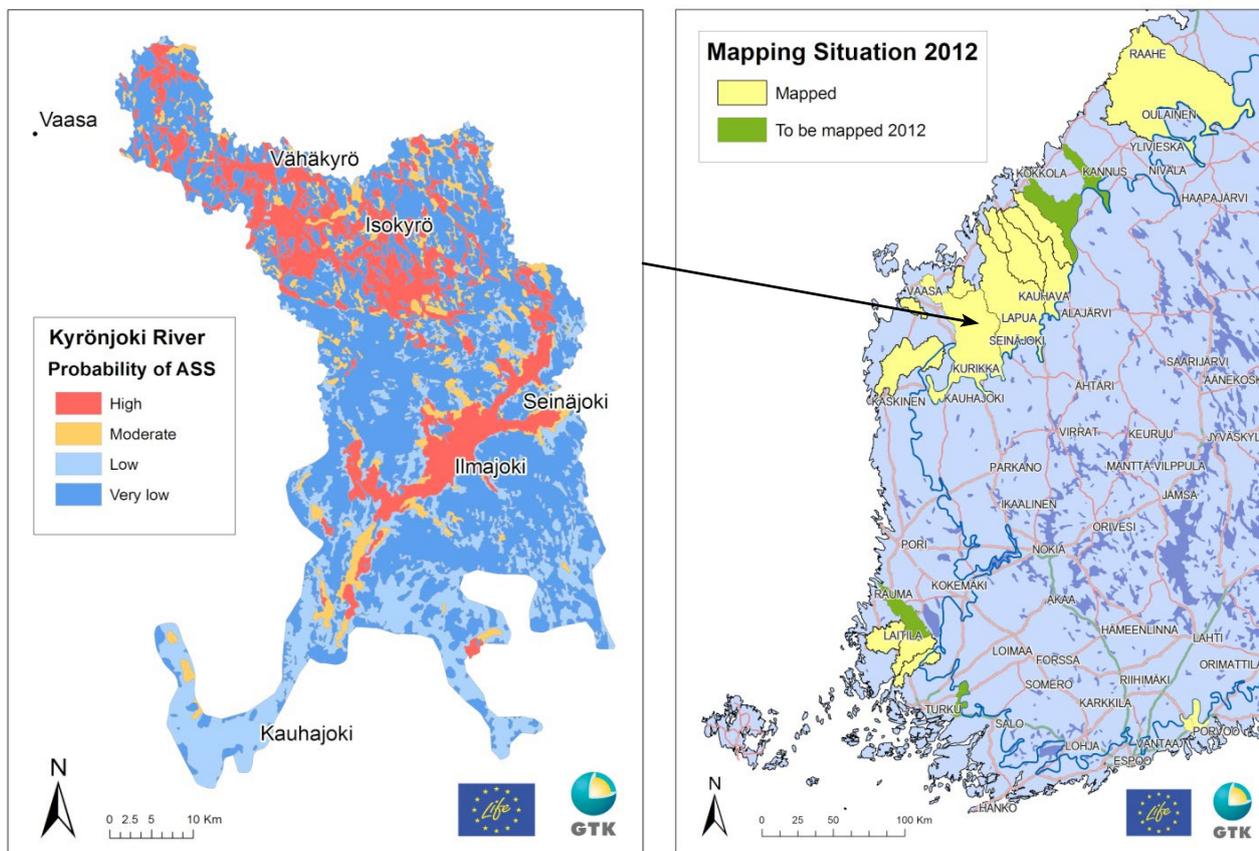


Fig. 1. A. Map showing the probability of occurrence of ASS in the River Kyrönjoki catchment, western Finland. B. Mapping situation on 31.12.2011. The dark-blue line is the upper limit of the Litorina sea, below which the majority of Finnish ASS occur.

The observations, measurements and analyses have also been used to produce:

- Probability maps (incl. individual profile data) of integrated catchment areas at the scale 1:250 000;
- Reports for the same areas;
- Guides for the identification of ASS and their environments.
- The results will be available to the public on GTK's web pages. The main users will be:
 - Authorities at governmental, regional and local levels;
 - Agriculture and forestry (organisations and farmers);
 - Ditching companies;
 - Peat-mining and earthworks companies;
 - Consultants.

The described mapping and classification are part of the following two projects: (i) a LIFE+ project (the EU's Financial Instrument for the Environment) and (ii) an ERDF project (the EU's European Regional Development Fund). Both projects will end in 2012. After this, GTK will complete the general-scale mapping by the end of 2015 according to an agreement with the Ministry of Employment and the Economy.

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UTILIZATION OF AN ACID SULFATE SOIL IN MALAYSIA FOR RICE CULTIVATION

by

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Acid sulfate soils are abundant in Malaysia, occurring almost exclusively along the coastal plains (Shamshuddin & Auxtero, 1991; Shamshuddin et al. 1995; Muhrizal et al. 2006; Enio et al. 2011). Acid sulfate soils are dominated by pyrite (FeS₂), and high acidity (soil pH < 3.5) is produced when these pyrite-laden soils in the coastal plains are opened up for crop production or otherwise. This leads to the release of high amounts of Al into the soil environment (Shamshuddin et al. 2004a), affecting crop oil palm growth (Auxtero & Shamshuddin, 1991), cocoa production (Shamshuddin et al. 2004b) and killing plants and aquatic life in the surrounding areas. The area covered by these soils is estimated to be almost 0.5 million ha in Peninsular Malaysia.

Rice feeds roughly half the planet's population, and approximately three quarters of a billion of the world's poorest people depend on the staple to survive (Zeigler 2007). The rice yield must be improved by 43% in 30 years from 2000 to meet the demands of population growth in the world (Cassman 1999). The government of Malaysia realizes that it needs to increase the self-sufficiency level (SSL) in rice production from 73% to 86% for food security reasons. Rice production can be increased by expanding the area planted with rice, by increasing the yield per unit area or by a combination of the two. With little expansion in area and slowing yield increases, growth in rice production has fallen below the growth in demand as the population has continued to increase. This allows farmers to increase their rice production on land that is predominantly unreliable. Expanding rice-growing areas into previously uncultivated areas is considered a last option, and this must be done with great care. It must be sustainable, negative environmental consequences must be avoided, and it must be socially acceptable and to the benefit of rice farmers and consumers.

Acidity is released in high amounts when pyrite-bearing soils in the coastal plains of Malaysia are drained for development, either for agriculture or otherwise. The so-called acid sulfate soils are characterized by low pH and high exchangeable Al, which affect rice growth. Rice root growth is inhibited by Al³⁺ and Fe²⁺ toxicities. The critical Al concentration for rice growth is 15 µM (Elisa Azura et al. 2011). About 3000 ha of an acid sulfate soil in Merbok, Kedah, have been cultivated with rice since 1964 (Ting et al. 1993), but the yield is far below the national average of 3.8 t/ha.

There are several approaches that could be used to ameliorate acid sulfate soil infertility. Liming seems to be a common practice to ameliorate this soil for rice cultivation. Therefore, a field trial was conducted with the objective of increasing the rice yield on an acid sulfate soil under rain-fed conditions in Merbok,

Kedah, Malaysia (Fig. 1), using various lime sources. The soil was treated with ground magnesium limestone, hydrated lime and liquid lime at the specified rate. Rice variety MR 219 was tested, which is the most common variety grown in Malaysia at present. The results showed that soil pH was < 3.5 and exchangeable Al was very high throughout the soil depth. Water pH in the rice field before treatment was 3.7, while the Al concentration was 878 μM . Rice plants grown under these conditions would suffer from H^+ and Al^{3+} stress, hence affecting their growth and eventually the yield. The results showed that the application of 4 t GML/ha gave a reasonably good yield of 3.5 t/ha, the best among the treatments.

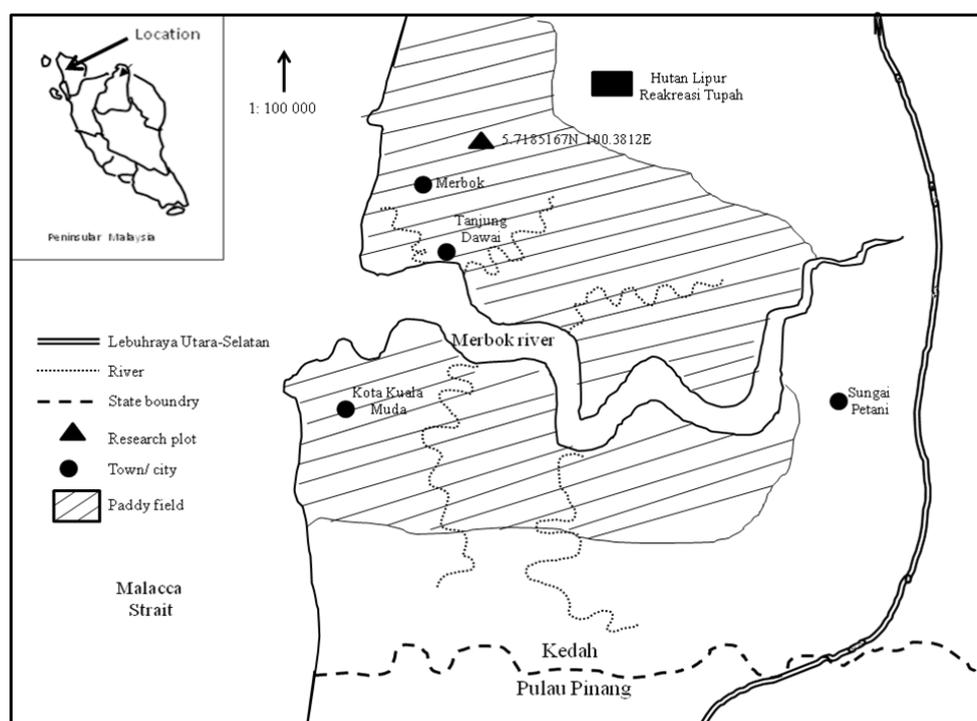


Fig. 1. Map indicating Merbok, Kedah, where the field trial was carried out.

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SOIL PROPERTIES AND CARBON DIOXIDE EMISSION FROM SULFIHEMISTS IN THE KELANTAN PLAINS, PENINSULAR MALAYSIA

by

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Organic soils that have a sulfuric horizon in their profiles can also be classified as acid sulfate soils. The peaty materials in these soils are known to emit carbon dioxide (CO₂) into the atmosphere at a rate depending on their properties. A study was conducted to determine the soil properties and the emission of CO₂ from soils having peaty materials underlain by pyrite-bearing mineral deposits (FeS₂) in the Kelantan Plains, Peninsular Malaysia (Fig. 1). Selected properties of the soils were determined and the implications of drainage and land-use type for the emission of CO₂ as well as the related factors were evaluated.

Soil pH was determined in water using a soil-to-solution ratio of 1:2.5, while electrical conductivity (EC) measurement was carried out using saturated paste. The cation exchange capacity (CEC) was determined with 1 M NH₄OAc solution buffered at pH 7 (Soil Survey Laboratory Staff, 1992). The basic cations (Ca, Mg, K and Na) in the NH₄OAc solution were determined by atomic absorption spectrophotometry (AAS). Exchangeable Al was extracted by 1 M KCl and the Al in the solution was determined by AAS. Total carbon (TC) was analyzed by the dry combustion method using a CNS analyzer. For the soils under study, calcium carbonate (CaCO₃) was absent, so the value of carbon obtained with the CNS analyzer was close if not equivalent to organic carbon (OC). Total N was determined by the Kjeldahl method (Bremner and Mulvaney, 1982) and available P by the method of Bray and Kurtz (1945). The soils for texture analysis were treated with hydrogen peroxide to remove the organic matter. The particle-size distribution was then determined by successive sedimentation (Soil Survey Laboratory Staff, 1992). The clay fraction from the mechanical analysis was kept for mineralogical analysis. The clay treatments were Mg, Mg-glycol, K and K with heat treatment at 550 °C. These treatments were necessary in order to identify smectite, vermiculite and/or mica-mixed layers in the sample. The minerals in the clay fraction were identified by XRD analysis using a Philips PW3440/60 X'Pert Pro diffractometer. Soil samples from the sulfidic layer were studied under a scanning electron microscope (SEM).

The soil CO₂ flux was measured by a closed chamber technique using an LI-8100 automated soil CO₂ flux system. The measurements were taken within a one-year period and carried out randomly at specified intervals at three sites in order to evaluate the temporal trend. Before inserting the soil chamber column, the soil surface where measurements were taken from was cleared of plant litter. At each vegetation site, three replicate measurements were carried out, and the

PVC soil column (10 cm diameter, 10 cm height) was inserted 4 cm from the soil surface approximately an hour before measurement to stabilize the accumulation of the gas. The measurements were carried out during the daytime, from 7 am until 12 pm, in order to determine the highest flux of the day. The annual gas emissions were calculated by integrating the monthly gas fluxes with the duration of their measurement. Soil temperature was recorded at every measurement point and the topsoil was sampled with a core ring to obtain the value of bulk density. The temporal and annual CO₂ emissions from the soils were subsequently measured.

The soils are acidic with a topsoil pH of 4.3 or less. Pyrite was detected in the sediments below the peaty materials, and the oxidation of this pyrite is partly responsible for the increase in soil acidity. The emission of CO₂ differed significantly among the land-use types, and seasonal variation was also observed. The highest measured annual CO₂ emission of 3.1 kg C m⁻²yr⁻¹ was found in drained forest of gelam species (*Melulueca leucadendron*), which was significantly higher ($p < 0.05$) than that of the oil palm (*Elaeis guineensis*) with an emission of 2.0 kg C m⁻² yr⁻¹ or rubber sites (*Hevea brasiliensis*) with an emission of 1.7 kg C m⁻²yr⁻¹. Based on the regression analyses, positive significant correlations were found between the flux of CO₂ and the soil microbial biomass C at the oil palm ($r = 0.864$) and rubber sites ($r = 0.849$). The emissions also significantly varied from site to site. The differences in CO₂ flux among the studied ecosystems suggest that land use affects the emission of CO₂ from the soils. Planting oil palm and rubber on these soils does not necessarily result in significant CO₂ emission to the atmosphere during the early stages of growth.

GROWTH OF REED CANARY GRASS IN HIGH MOISTURE ACID SULFATE SOILS

by

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The suitability of acid sulfate (AS) soils for perennial energy cropping was examined in 2008–2011. The aim was to provide information on the responses of reed canary grass (*Phalaris arundinacea* L.) to raised water levels, considered a management option for these problematic soils. Undisturbed field acid sulfate soils were taken into lysimeters made of large core PVC tubes equipped with ground water level control and measurement instruments. Reed canary grass (RCG) was planted in these soils. Two treatments, a high water content (HWC, 20 cm below the soil surface) and low water content (LWC, 70 cm below the soil surface, considered normal for acid sulfate soils) were considered, and there were 4 replicates for each. Tiller height, net photosynthesis and above-ground biomass at harvest were measured and Al, Fe, K, Si and S were analysed using ICP-OES.

A high water table in AS soils affected the growth, biomass quantity and quality of RCG. Tillers growing in HWC lysimeters were taller than those of the LWC lysimeters. The soil conditions greatly influenced the element composition of the harvested dry biomass. As can be seen in Figure 1, tillers in HWC lysimeters were 30% and 23% taller than those in LWC lysimeters ($P = 0.003$, $P = 0.002$) in September 2009 and 2010, respectively. Net photosynthesis was higher in LWC grasses, although the difference was only significant in 2009 ($P = 0.04$). In Table 1, spring 2009 dry matter yields were almost the same in both treat-

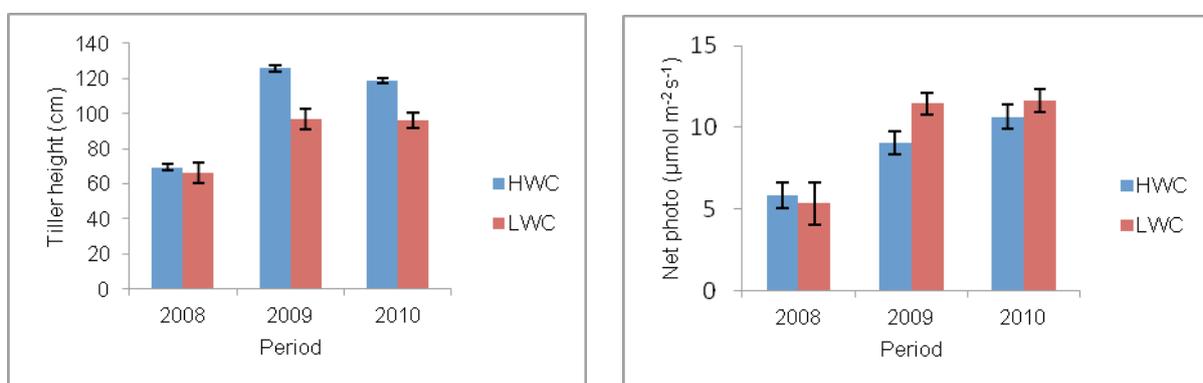


Fig. 1. Tiller height and net photosynthesis of reed canary grass grown in acid sulfate soils with low and high water contents. Error bars show standard errors of means.

Table 1. Biomass yield and element composition of reed canary grass grown in low and high water table acid sulfate soil in lysimeters.

Year/ Treatment	Biomass yield(t/ha)	Al (mg/kg)	Fe (mg/kg)	K (mg/kg)	S (mg/kg)	Si (mg/kg)
2009						
HWC	11.3	24.8	75.5	8106	1928	281
LWC	11.3	28.8	67.6	9448	1823	221
P-value	ns	ns	ns	*	ns	ns
2010						
HWC	20.1	7.3	48.5	7476	1861	386
LWC	14.1	12.1	44.3	12122	2313	504
P-value	**	ns	ns	ns	ns	ns
2011						
HWC	16.0	11.2	55.3	7564	2128	355
LWC	11.7	20.8	78.0	12258	2641	366
P-value	**	*	ns	**	*	ns

* P < 0.05; ** P < 0.01; ns (non-significance) P > 0.05

ments, but in 2010 and 2011, respectively, HWC grasses yielded 43% and 37% more than LWC (P = 0.001 in both years). Dry matter harvested in the spring of both 2010 and 2011 contained more Al, K, S and Si in the LWC treatment than in HWC treatment, whereas the concentration of Fe was higher in HWC treatment in 2009 and 2010.

It was concluded that reed canary grass, an established bioenergy crop, grows well in acid sulfate soils and can perform better when the water table is raised to reduce acidity and prevent environmental hazards. This could serve as a management option and a solution to the problems cause by acid sulfate soils, and at the same time reduce the controversy surrounding the use of bioenergy crops on arable land.

LEACHING TEST FOR THE CHARACTERIZATION OF SULFUR-RICH SOILS

by

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BACKGROUND

Sulfur-rich soils are found along the length of Sweden's east coast and in the Mälaren Valley. These soils were formed as sediments in the anaerobic and brackish conditions of the Littorina Sea. In 1965, Fromm classified and described actual acid sulfate soil (AASS) as "Alunsoil" in maps. In Sweden, the commonly accepted geotechnical term for "potential acid sulfate soil" (PASS) is "sulfide soil". In 2011, the term "sulfate soil" was brought into the geotechnical classification system and is used to identify AASS.

The primary focus on sulfide soils has traditionally been on the mechanical aspects of the soils, as they have a poor bearing capacity and are prone to settling. It has only been in the last two decades that the problems associated with acidification have been investigated. Interest was awakened in Northern Sweden as a result of several large infrastructure projects producing large quantities of sulfide soils that were left exposed to the elements without consideration for potential future environmental impacts. Towards the end of the 1990s, research was undertaken by Luleå University of Technology and MRM Konsult AB to develop a method to characterize the potential for acidification posed by sulfide soils undergoing oxidation. The method developed as a result of the academic and laboratory collaboration is described in this paper.

MRM LEACHING TEST

Many leaching tests are used to characterize ASS, but these tend to be time consuming and are not suitable for end-users in the construction industry, where time pressures are generally very demanding. The standard test for the characterization of waste (SS-EN 124573) is not a suitable option for the characterization of ASS, as this test is essentially an anaerobic leaching test that does not adequately simulate the oxidation of ASS. The MRM Leaching Test aims to simulate the wetting-drying cycles that an excavated ASS might undergo and produce reliable results within a time period suitable for the construction industry.

The MRM leaching test consists of an initial anaerobic leaching test where fresh samples are mixed with deionised water at a liquid/solid ratio of 5:1. After 30 minutes, the pH, conductivity, and redox potential of the soil sludge are measured. This provides an insight into the properties of the soil sample in field conditions. A subsample of the soil is cut into thin slices and allowed to air dry

for 24 hours. The air-dried sample (25 g) leached with 75 g of deionised water (L/S = 3). Once the leachate has stopped dripping through the filter paper, the pH, conductivity, and redox potential are measured and the amount of leachate collected is recorded. The soil sample is then oven-dried overnight and the leaching step is repeated at least 10 times or until the pH has stabilized. In addition, a subsample is sent to a certified analytical laboratory for analysis of iron and total sulfur. In general, the entire procedure takes 10 working days, depending on the acidification rate of the soil.

Pousette (2007) developed a simplified model for interpreting the results of the MRM Leaching Test in which the actual acidification and potential acidification are plotted against the acidification rate (Fig.1a). This model is endorsed by the Swedish Transport Authority. Unlike other leaching tests, the acidification rate is based on the number of aerobic leaching steps, rather than the L/S ratio. The reason for this is that tests have shown that the cycle of wetting and drying has a much more significant effect on the final pH measured rather than the total amount of water that has leached through a particular volume of soil.

When a sulfide soil is exposed to the elements, it will be subjected to wetting and drying. It is during the drying phase that the soil contracts and forms cracks at the surface. These surface cracks allow the oxidation front to expand rapidly from the surface and give rise to preferential flow when the soil is next subjected to wetting. Only a relatively small amount of water is therefore needed to produce acid leachate. This makes the use of L/S ratios less relevant in the context of modeling the acidification potential of sulfide soils, as only a limited volume of the exposed soil actually experiences wetting and drying in any one cycle.

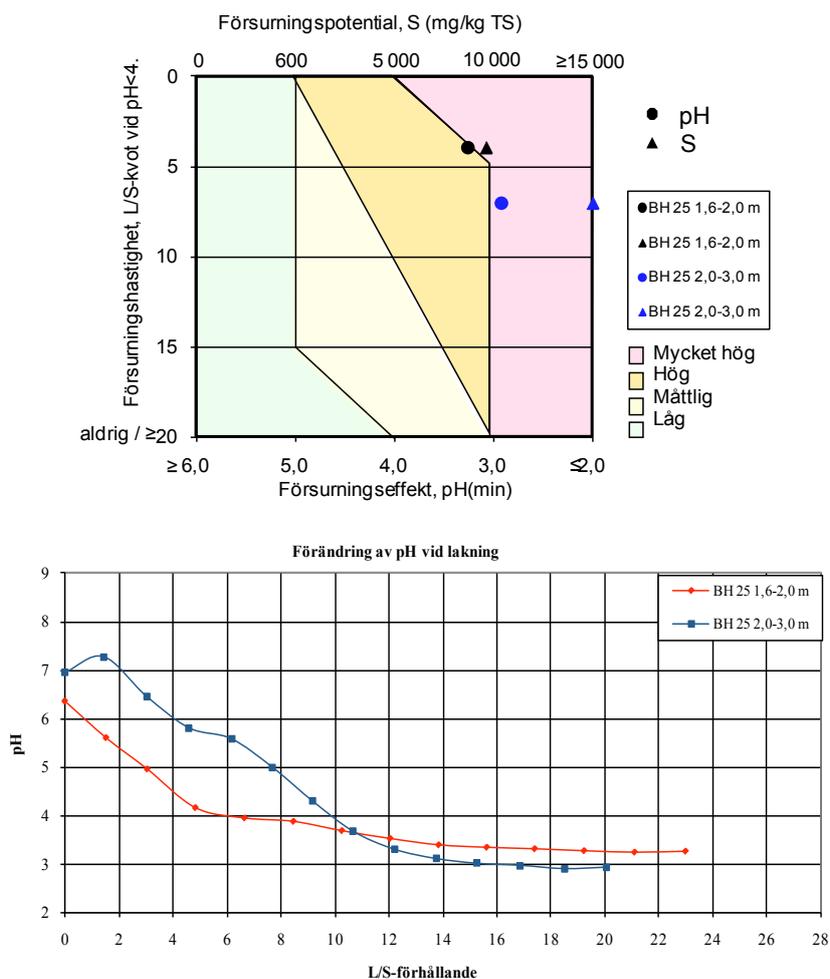


Fig. 1. Leaching tests for two sulfide soil samples with a different time response for acidification

In Figures 1a and 1b results from a test with two different samples are shown. In the simplified conceptual model, the acidification rate is shown on the y-axis as the number of aerobic leaching steps required to reach pH 4. On the upper x-axis, the potential acidification (\blacktriangle) is shown as the total concentration of S (mg/kg). On the lower x-axis, the actual acidification (\bullet) is shown as a pH value.

As can be seen from Figure 1a (right), both samples reach a pH below 4, but one after an L/S ratio of 5 and the other at an L/S ratio of 10. A better way to describe the acidification response is by the number of leaching cycles, and for these samples it takes 4 and 7 cycles, respectively, to reach pH 4. In Figure 1b (left), the acidification speed is shown where the scale equals the number of leaching steps when pH dips below 4. The acidification potential (total sulfur content) is shown on the top scale and the acidification effects on the bottom scale. The diagram can be interpreted as follows. The triangles show the *acidification potential* and the more to the right in the figure the higher acidification potential. The dots (pH) also show on the bottom scale that the *acidification effect* is higher the further to the right the dots are situated. *The acidification speed* is a relative measure. If the number of leaching steps is low before pH 4 is reached, the acidification speed is high. Consequently, the lower to the left, the lower the acidification effect, and it also takes longer to reach the minimum pH. Up in the right-hand corner, the acidification effect is high and the acidification speed is high.

The diagram is divided into four different fields for this simplified evaluation, from right to left indicating a very high down to a low acidification effect.

The reason for not using L/S ratios in characterizing the soil is that during quite a short time with changing weather conditions the soil can dry very rapidly, and then a short shower will leach through cracks with contact only with a small amount of soil. This very short contact is enough to produce an acid leachate. In this case, the L/S ratio means nothing, as the contact between the water and the soil is not a volume but a crack.

This method has been used for several hundreds of samples with a large variety of properties. Tests on dry crusts from sulfide soils (sulfate soil) have shown that pH 4 often is reached in the first or second aerobic leaching cycle. On the other hand, in tests performed on schist rock, pH < 4 is reached after 25–30 leaching cycles (or L/S ratios between 50 and 55).

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RETHINKING SULFIDIZATION AND THE ROLE OF HYDROGEN SULFIDE

by

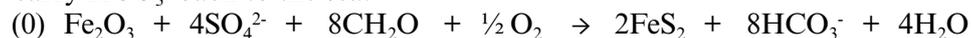
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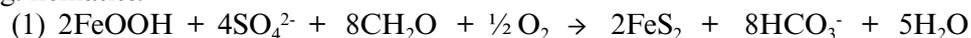
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For almost as long as acid sulfate (AS) soils have been recognized, there has been interest in the origin of sulfide minerals in them. This subject was impressively addressed at the first International AS Soil Conference by Rickard (8), who used the terms sulfidation and pyritization. Fanning and Fanning (2) introduced the term sulfidization for a gross soil-forming process that was envisioned (e.g. 2, Fig. 10.1) to take place in anaerobic tidal marsh soils, forming pyrite, FeS₂, by the reduction of S of SO₄²⁻ (from sea water) and Fe³⁺ of iron oxides (in sediments) as organic matter (OM) was oxidized to bicarbonate. Tidal flushing (as suggested by 6) was envisioned to enhance the supply of SO₄²⁻ into the soils and to carry HCO₃⁻ back to the sea.



Reaction (rxn) (0) is a traditional overall sulfidization rxn, after Pons et al. (6), utilized by Fanning and Fanning (2, page 71), who showed balanced electron transfers in the rxn and the forms (solid, aqueous, dissolved gas, and liquid) of the various reactants and products. The iron source is shown as an iron oxide, e.g. hematite.



Rxn (1) repeats rxn (0), but the iron source is shown as FeOOH, e.g. goethite or lepidocrocite, instead of Fe₂O₃; this rxn is obtained from rxn (0) by adding 1 mole of water to each side to convert Fe₂O₃ to 2FeOOH on the left side. Rxns 0 and 1 envision that both the Fe³⁺ of FeOOH and the S⁶⁺ of SO₄²⁻ are reduced by serving as electron acceptors during the oxidation of the carbon of the organic matter (OM). OM is represented as CH₂O, in which the C has an oxidation state of 0. The implication is that these rxns are greatly accelerated as energy is derived from them by microbes such as *Desulfovibrio desulfuricans*.

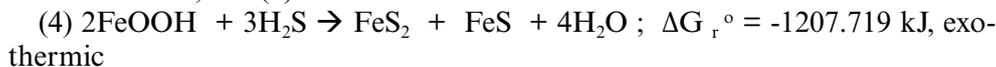
Because of some dissatisfaction with rxns (0) and (1), particularly the employment of oxygen as a reactant in environments such as tidal marsh and sub-aqueous soils, which are considered highly anaerobic, some alternative rxns and explanations are set forth below. We suggest that hydrogen sulfide is produced microbially, but that the reduction of Fe³⁺ takes place chemically as the sulfide of H₂S is oxidized to disulfide; however, H₂S does not show up in the alternative overall rxn (6).



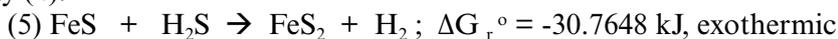
Rxn (2) shows the reduction of sulfate S to produce the sulfide of H_2S as C of OM is oxidized to produce bicarbonate, which is likely to be microbially mediated in tidal marshes and subaqueous soils.



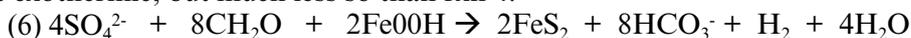
Rxn (3) is simply rxn (2) multiplied by 4. Rxn (3) facilitates balancing when rxns (3), (4), and (5) are added together to produce the alternative overall sulfidization reaction, rxn (6).



Rxn (4) shows the reduction of two moles of Fe^{3+} as FeOOH by 2 moles of S^{2-} to produce one mole of FeS_2 (has disulfide, S_2^{2-}) and one mole of FeS , in which the sulfide has not been oxidized. This rxn is predicted to be highly exothermic by its ΔG_r° , or standard Gibbs free energy of reaction, determined from the standard free energy of formation values of reactants and products from Lindsay (4).



Rxn 5 shows oxidation of the S^{2-} of FeS and H_2S to the S_2^{2-} of FeS_2 (e.g. pyrite) as 2H^+ of H_2S are reduced to produce 1 mole of H_2 . This rxn is predicted to be exothermic, but much less so than rxn 4.



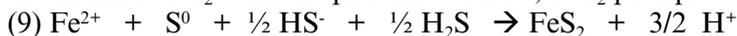
The addition of rxns 3, 4, and 5 gives rxn (6), an alternative overall sulfidization rxn. Co-authors BRJ and MCR are skeptical of rxns 5 and 6 that generate H_2 , but are also skeptical of rxns 1 and 2 employing O_2 . BRJ hypothesizes that reaction (7) may govern the FeS -to- FeS_2 transformation process:



which is an exothermic rxn that converts less stable FeS to more stable, but more slowly formed, FeS_2 . This rxn requires both S^0 and S^{2-} as S sources and reactants to increase the ratio of S:Fe from 1 to 2 in transforming the mono- to the disulfide mineral. It can result from the addition of rxn (8) governing FeS dissolution,



to the reverse dismutation reaction (rxn. 9), in which S^0 is reduced to S_2^{2-} as S^{2-} is oxidized to S_2^{2-} . In the presence of Fe^{2+} , FeS_2 precipitates.



The rest of this abstract provides observations (Fig. 1) and references to support what we interpret as evidence of the important role of H_2S or HS^- , with which H_2S is in equilibrium ($\text{H}_2\text{S} \leftrightarrow \text{HS}^- + \text{H}^+$), in chemically converting iron oxides and/or oxyhydroxides to iron sulfides and ultimately to pyrite in tidal marsh and coastal subaqueous soils. We believe the H_2S is produced microbially from aqueous SO_4^{2-} , which is readily available throughout seawater-affected soils. However, iron oxides (the term generally used here for both true oxides and oxyhydroxides) from sediments or other terrestrial sources, with which the H_2S reacts, are more localized in the coastal soils (see Fig. 1 of ref. 3 for more of our thoughts). Some observations to support these statements are provided in Figure 1.

Bohn et al. (1) found rapid blackening of iron oxide-containing soil materials contained in tubes as H_2S under low (atmospheric) pressure was passed through the (moist) soil materials. The materials returned to their original color when H_2S was no longer applied and the materials were exposed to air, after which elemental S was detected in them by X-ray diffraction (XRD). Repeated H_2S exposure caused re-blackening. Similar rapid blackening and fading to the original color has been noted with IRIS tubes (Fig. 1A), although exposure for 4 days, until the iron oxides were fully converted to Fe sulfides, caused the black material to detach from the tubes (3). In these experiments, only Fe monosulfides were noted to form rapidly, but for the reduction of the Fe of Fe oxides by H_2S , some

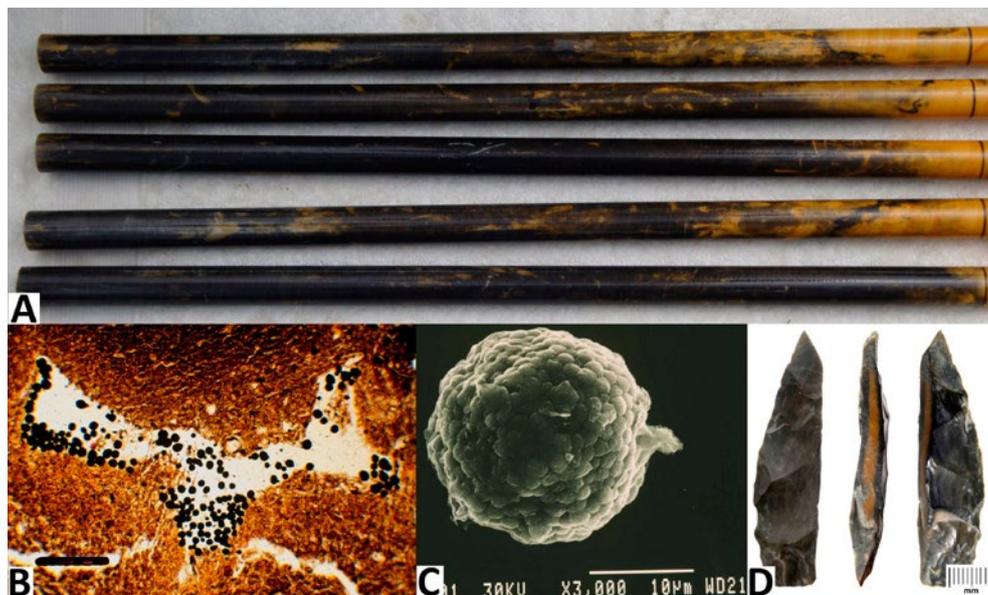


Fig. 1. A. IRIS (indicators of reduction in soils) tubes (white polyvinyl chloride (PVC), 50 cm long and 2.1 cm outer diameter) painted with iron oxides (goethite and ferrihydrite) of the color shown on the right (top) end of the tubes, blackened by the formation of iron sulfides hypothesized to occur by reaction (4) after insertion for only 5 minutes into a tidal marsh soil, a Sulfihemist according to Soil Taxonomy. B. Micrograph of a thin section under plane light showing black pyrite framboids that formed within a pore of iron oxide-rich (52 g/kg as Fe) soil material following its burial in the Oe horizon of tidal marsh soil for 2 years; see Rabenhorst (7) and Fanning et al. (3) for more details; scale bar is 0.1 mm. C. Scanning electron micrograph of framboid, like those in C; scale bar is 10 μ m. D. A section of Fig. 8 from Lowery and Wagner (5) showing a cross-section of an artifact deliberately broken after collection that was blackened on the outer part, but not in the interior, by iron oxides converted to pyrite, after natural burial under tidal marsh soil by sea level rise. The blackening by authigenic pyrite, the color of which does not fade upon exposure, occurred over several centuries. The total length of the scale is 1 cm.

of the S from the H_2S must oxidize, and pyrite is noted to form upon longer exposure (Figs 1 B, C, D). The pyrite may initially be too fine to detect by XRD.

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A MODERN SOIL-LANDSCAPE CHARACTERIZATION APPROACH TO RECONSTRUCTING AND PREDICTING PEDOGENIC PATHWAYS OF INLAND ACID SULFATE SOILS

by

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Improved understanding and prediction of inland acid sulfate soil (IASS) change and pedogenesis are critical to many changes in land management (extensive vegetation clearing and excavation of drainage channels) and waterways (building of locks, barrages and weirs). In addition to long-term monitoring for quantifying soil changes, the development of comprehensive conceptual pedogenic models to describe complex IASS systems is important. To determine the degree of external and internal factors that control the pedogenic pathways of evolution models for IASS, the following 3-stage approach is adopted:

1. Cross-sections of soil-landscapes are constructed in the form of conceptual soil-regolith hydro-toposequence models to aid in understanding the spatial and temporal heterogeneity of IASS materials (sulfuric, hypersulfidic, hypsulfidic and monosulfidic; Sullivan et al. 2010) and features (e.g. cracks or salt efflorescences) in layers, horizons and deep regolith (Fig. 1).
2. Subtypes of IASS (e.g. sulfuric clayey soil) are assigned using the simplified Soil Identification Key (Fitzpatrick *et al.* 2009a,b) to display the spatial and temporal heterogeneity of IASS subtypes (Fig. 1).
3. Dominant pedogenic processes are assigned to sequential hydro-toposequence models (Fig. 1) and summary tables (e.g. Table 1) using 3 concepts: (a) extrinsic and intrinsic pedogenic thresholds (Muhs 1984) [*The pedogenic threshold is a value, unique to a particular soil system, beyond which the system adjusts or changes, not just in rate but also in soil type. In an extrinsic pedogenic threshold, an external factor changes progressively, which triggers abrupt, fast or slow pedogenic changes. This is usually caused by climatic, geomorphic or human-made changes. In contrast, intrinsic pedogenic thresholds occur when a system changes without a change in the external variable*]; (b) pedogenic rates (e.g. dynamic balance of thickness; Johnson & Watson-Stegner, 1987); and (c) acid sulfate soil processes (e.g. sulfidization).

Fig. 1. Predictive soil-regolith models for the Finnis River system illustrating: (a) wetting and flushing (upper panel) and partial drying (second panel) cycles during pre-European development (5,000 BC to 1880s); (b) modification of water levels by barrage installations causing the build-up of sulfides under continuous subaqueous ASS conditions from 1930s-2006 [panel (i)] followed by progressive drying [panels (ii) and (iii)] and a rewetting phase in May 2009 [panel (iv)], which resulted in acidic pools and flowing water (pH 3.3, to 4) in the cracks and cattle pugs (pH 0.5 to 0.8); and finally post-drought flooding, resulting in the sequential transformation of jarosite to sulfide under subaqueous conditions after at least 3 years.

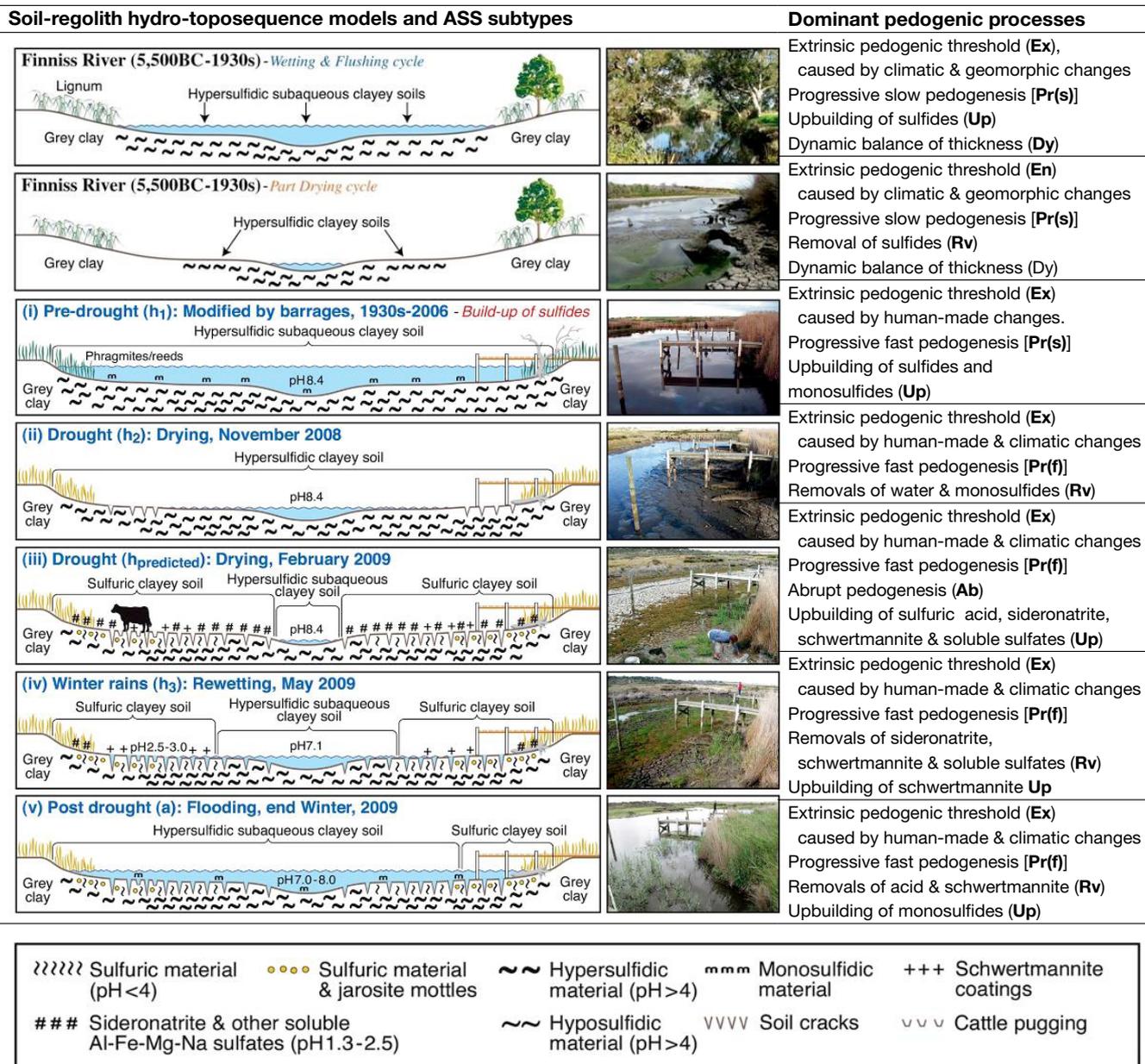


Table 1. Summary of temporal and spatial variations and changes in ASS subtypes at Wally's Landing, illustrating the dominant pedogenic process; cells bordered in blue indicate subaqueous conditions (from Baker et al. 2011)

	Pre-drought Winter 2007 (h ₁)	Drought Summer 2008 (h ₂)	Drought Summer 2009 (h ₃)	Drought End winter 2009 (a)	Drought End summer 2010 (b)	Post- drought Summer 2011 (c)	Post- drought Winter 2011 (d)
¹ Classification & ² Acid hazard	Hyper- sulfidic subaque- ous clay (H)	Hyper- sulfidic subaque- ous clay (H)	Sulfuric clay (H)	Sulfuric* subaque- ous clay (H)	Sulfuric* subaque- ous clay (H)	Hyper- sulfidic subaque- ous clay (H)	Hypo- sulfidic subaque- ous clay (M)
Dominant water and ASS process	UW & Sulfide	LW & Sulfide	LW & Sulfuric	RF &Sulfuric	RW & Sulfuric	RW & Sulfide	UW & Sulfide
³ Threshold Pedogenic Rate	Ex Pr(f) & Up	Ex Pr(f) & Rv	Ex Ab & Up	Ex Pr(f), Rv & Up	Ex Pr(f), Rv & Up	Ex Pr(f), Rv & Up	Ex Pr(f), Rv & Up
¹ Classification – Acid Sulfate Soil subtype classification ² Acid hazard – Acidification hazard: H = High; M = medium; L = Low; VL = Very Low LW – Lowering water level regime to expose soil to air due to drought conditions and water evaporation UW – Unchanged water regime, which had not yet evaporated to expose soil to air RW – Rising water level regime to inundate and saturate soils by reflooding (e.g. due to pumping, regulator installation, river flow and groundwater) RF – Rain fall rewetting and natural reflood- ing to inundate and saturate soils ³ Ex- Extrinsic pedogenic threshold ³ In - Intrinsic pedogenic threshold Dy - Dynamic balance of thickness Dp - deepening Rv - removals Up - upbuilding				Sulfuric – Sulfuricization - oxidation of py- rite in hypersulfidic material due to onset of aero- bic conditions to form sulfuric material Sulfuric* – As above with acidic minerals and/ or salt efflorescences noted (i.e. measurable RA) Sulfide – Sulfidization due to sulfide accu- mulation to form hypersulfidic material Monosulfide – Monosulfidization due to mono- sulfide accumulation to form monosulfidic material Leach – Leaching of acid from soil by winter rain fall Sulfuric subaqueous with overlying circa neu- tral water pH >4: = font coloured blue or default Sulfuric subaqueous soil with overly- ing acid water pH <4: = font coloured red Where h ₁ to h ₃ = historical samplings; (a) – (b) sam- pling conducted between 2009 to 2011 Pr(s) - Progressive pedogenesis (slow: rela- tive to previous window) Pr(f) - Progressive pedogenesis (fast rela- tive to previous window) Ab - Abrupt pedogenesis (relative to previous window) Re - Regressive pedogenesis St - Static pedogenesis			

Case study (Fig. 1, Table 1). Following stabilization of sea level to about its present position 5,500BC, the Finniss River cycled between natural wetting and flushing, and partial drying conditions in response to seasonal and climatic cycles occurring in the upper Murray-Darling Basin and its own catchment (Fig. 1; upper 2 panels). The build-up of sulfidic material in the Finniss River was thus regularly kept in check by oxidation and removal during scouring floods (Baker et al. 2011; Fitzpatrick et al. 2009a,b). During the extreme drought of 2007 to 2009, the partial drying of the Finniss River caused the hypersulfidic subaqueous clays to transform to sulfuric clays. On rewetting, sulfuric subaqueous clays were formed in 2009. Prolonged inundation encouraged sulfate reduction and caused the formation of hypersulfidic subaqueous clays in summer 2011 and hyposulfidic subaqueous clays in winter 2011 (Table 1).

In summary, soil-regolith hydro-toposequence models, in combination with summary tables and ASS maps (e.g. Baker *et al.* 2011; Fitzpatrick *et al.* 2009a,b), provide a detailed understanding of 2D, 3D and 4D (predictive) ASS soil-landscape features along representative transects, which illustrates the complex sequential vertical and lateral changes in pedogenic processes as well as the mineralogical, hydrological and biogeochemical interactions that occur across creek, river and lake hydro-toposequences.

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ENVIRONMENTAL IMPACT OF AN ASS LANDFILL ON THE CHEMICAL PROPERTIES OF A RECIPIENT RIVER

by

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A number of landfills containing acid sulfate soil have been established along the length of the newly constructed Kalix-Haparanda railway. A monthly sampling programme has been implemented to monitor potential environmental impacts on the chemical quality of rivers and groundwater as a result of the railway construction. This paper focuses on the chemical changes in water quality that have occurred as a consequence of landfilling ASS in an area draining directly into a nearby river.

The landfill in question was constructed in the summer of 2009 and consists of a 5385 m² area with uneven topography that generally slopes in a southerly direction towards the railway. Prior to the landfill, the area was covered in high grass, but very little vegetation now grows there. The landfill consists of unconsolidated fill material (0.5 to 3 m in thickness) capping a layer of ASS (0.5 to 3 m in thickness) overlying glacial till or peat. Deep cracks are clearly visible across the site, and the southwest section appears to consist of uncovered ASS. An oxidation front has been recorded in the ASS at depths of approximately 0.5 m. A drainage ditch runs along the western section of the site and marks the boundary with the forest. A further drainage ditch was built along the southern boundary of the landfill in April 2010 (*Photo 1a*). Because of the risk posed by the poor water quality in the ditch, a submerged weir was placed at the mouth of the ditch in June 2010 (*Photo 1b*).



a)



b)

Photo 1: Drainage ditch emptying into Naartijoki in May 2010 (a) and June (b).

In May 2010, field measurements (electrical conductivity, pH, and water temperature) were taken along several points of the drainage ditches and upstream and downstream of the railway bridge at Naartijoki (Fig. 1). The results demonstrated a significant drop in pH and a significant increase in electrical conductivity downstream of the railway bridge, a phenomenon that had not previously been recorded at this location. Field measurements in the following month revealed a similar pattern, despite the damming of the southern drainage ditch.

The chemical parameters of both the western drainage ditch and Naartijoki have been monitored since spring 2009, prior to the construction of the landfill. The pH of the western drainage ditch downstream of the landfill has remained relatively steady (2.9 to 3.8) over the course of the monitoring period. However, since July 2009 (initial construction of the landfill), metal concentrations in the ditch have increased significantly. The most dramatic increase was seen in the monthly aluminium concentrations, which increased from an average of 1.98 mg/l in the spring of 2009 to a maximum of 90.8 mg/l in the spring of 2011 (Fig. 2). At its peak, the southern drainage ditch running parallel to the railway was emptying water into Naartijoki with an Al concentration of 36.5 mg/l. However, the concentration has steadily decreased over time since the installation of the submerged weir. Prior to the construction of the southern drainage ditch, the aluminium concentrations upstream and downstream of the railway bridge were relatively similar, but the concentration of aluminium downstream (0.35 mg/l) remained elevated compared to upstream (0.25 mg/l) over the summer of 2010 (Fig. 3). By the end of 2011, the upstream concentration was equal to the downstream concentration and reflected the decreasing concentrations of the southern drainage ditch.

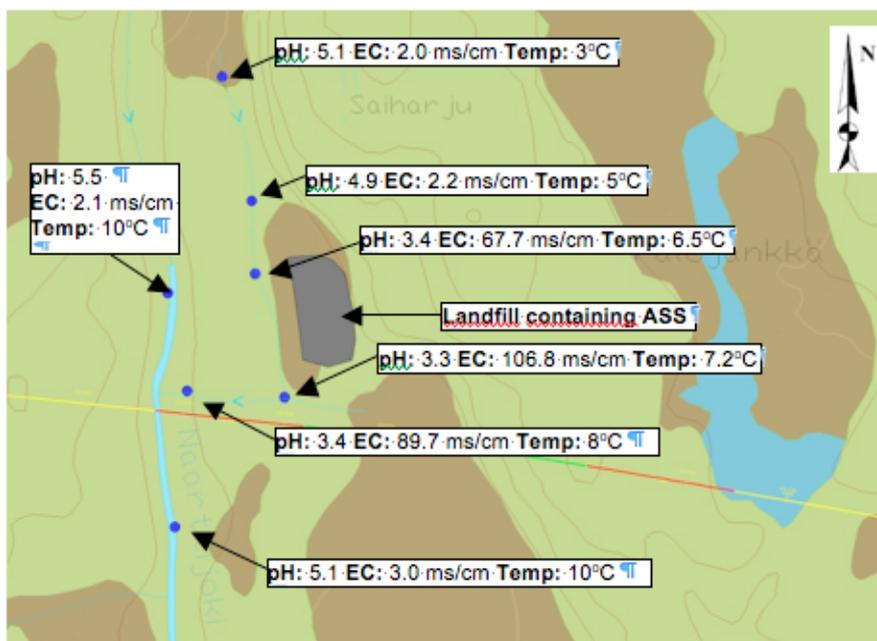


Fig. 1. Field measurements made in May 2010 along different points of the drainage ditch and in Naartijoki.

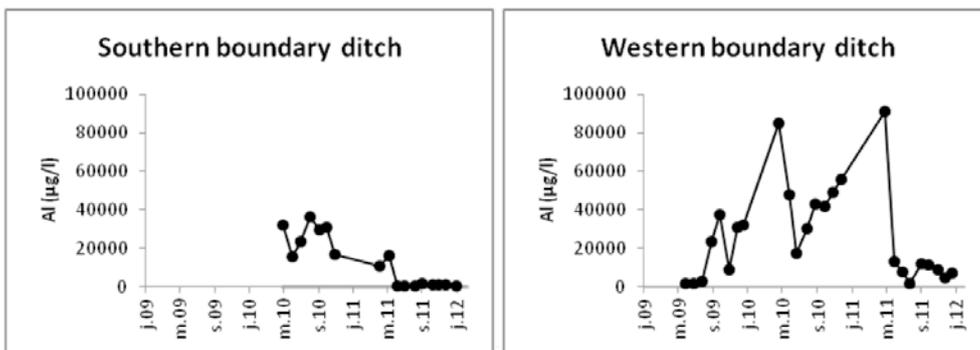


Fig. 2. Monthly aluminium concentration in the southern and western ditches.

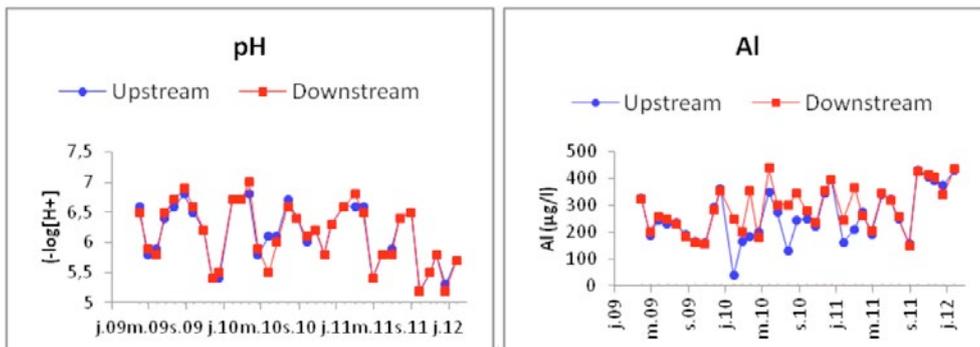


Fig 3. Monthly pH and Al concentrations upstream and downstream of the railway bridge at Naartijoki.

This study emphasizes the importance of the effective capping of excavated ASS. In this case, inadequate capping with unconsolidated fill contributed to a dramatic increase in metal concentrations, particularly Al, of the drainage ditches around the landfill. Because the affected water initially drained directly into the nearby river, a small, but significant change to the chemical quality of Naartijoki was detected, despite the large differences in water flow between the river and the ditch. By reducing the flow of the drainage ditch into the river, it was possible to prevent further changes to the river quality. Ideally, ASS containing landfills should not be constructed near waterways, but when this is unavoidable, greater attention must be paid to the drainage of the landfill site, as even small ditches can affect the water chemistry of larger water bodies.

LARVAL CRASH IN A COASTAL BURBOT (*LOTA LOTA* L.) STOCK CAUSED BY ACID SULFATE RUNOFF IN AN EMBANKED ARCHIPELAGO AND ESTUARY AREA IN THE BALTIC SEA

by

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Runoff from acid sulfate (AS) soils caused mass kills of fish in several estuaries in the Baltic Sea in autumn 2006. In an embanked archipelago, an estuary of four rivers (Lake Larsmo-Öja), the most numerous dead fish were cyprinides, e.g. bream (*Abramis brama* L.), roach (*Rutilus rutilus*) and stocked pike-perch (*Stizostedion lucioperca*). Adults of the winter-spawning burbot (*Lota lota* L.) probably avoided the most acidic period by not yet having migrated from the sea to the spawning areas in the lake. Spawning takes place in February, and after spawning the burbot migrates back to the sea (Hudd and Lehtonen 1987). Even though the debate and discussion have focused on the extreme acidic event in autumn 2006, studies have shown that the streams and rivers discharging into the lake carry very acidic and metal-rich water on a yearly basis (Palko and Alasaarela 1988, Toivonen and Österholm 2011, Toivonen and Österholm unpublished results). In the nearby estuary of the River Kyrönjoki, Hudd and Kjellman (2002) have shown that spring acidification has caused a frequent failure of burbot reproduction, which, in turn, has caused the stocks to collapse. This study examined the role of springtime acidic discharge on the reproduction success of burbot in Lake Larsmo-Öja.

Burbot larvae were sampled from an optimal large spread habitat in the lake in May during seven years (2005–2012, with 2010 missing). The critical period for reproduction success used in this study began with the spawning peak (set at February 25th) and ended at the last larval samplings (May 15th). The probability of capturing any larvae per unit effort was used as an index of abundance (hit rate), and correlated against corresponding data on water quality in the main river (River Esse) and from the recipient Lake Larsmo-Öja. Because the catchment of the River Esse constitutes almost 50% of the lake catchment, the river is expected to have a significant effect on the temporal water quality in the lake.

As seen from the significant correlation between the median pH and hit rate, water quality regarding the impact of AS soils during the critical period for recruitment is an important explanatory variable in the abundance of burbot larvae (River Esse: $r_s = 0.83$, $p = 0.05$, Fig. 1; and Lake Larsmo-Öja: $r_s = 0.70$, $p = 0.09$, data not shown). In spring 2006, the hit rate was as high as 62%, which is explained by the highest median pH during the study period in both the River

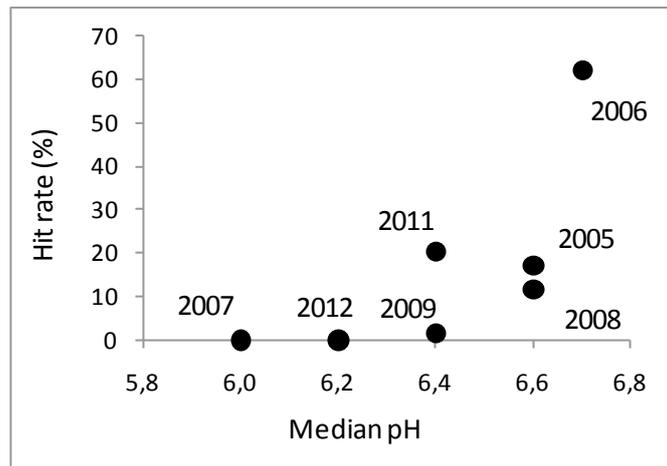


Fig. 1. Median pH in the River Esse during the reproduction period of burbot vs. the hit rate of burbot larvae.

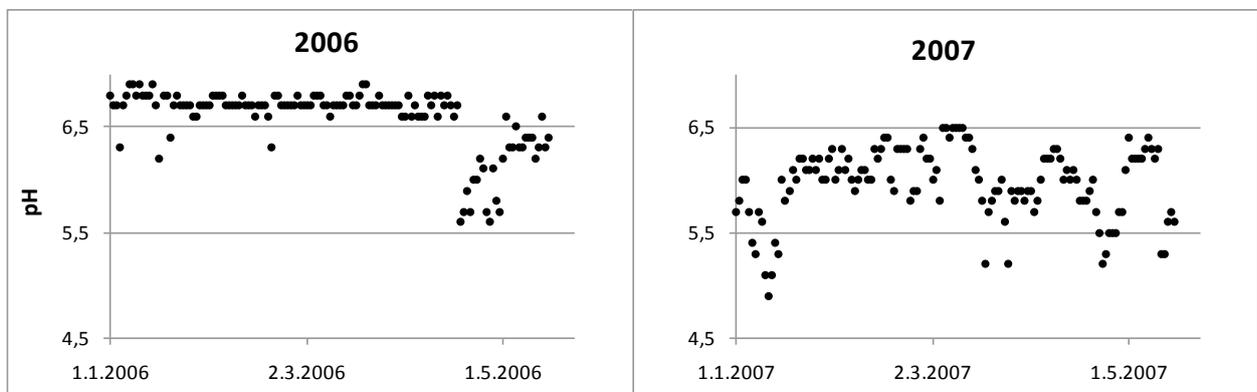


Fig. 2. The pH in the River Esse immediately before and during the spawning period with the highest and lowest median pH values in 2006 and 2007, respectively.

Esse (Fig. 1) and Lake Larsmo-Öja as a whole (data not shown). In contrast, the acidic surge during the following spawning season (Fig. 2), most likely caused the total absence of larvae in spring 2007, also indicated by the lowest median pH during the study period (Fig. 1).

The results show that the water quality variations due to runoff from AS soils have a profound effect on the annual production of offspring of the burbot stock in the Lake Larsmo-Öja system. Acidic events occurring during the development of eggs and larvae may cause the loss of entire year classes (Hudd et al. 1986), even though mass kills of adult fish are absent. Therefore, yearly monitoring of the fish larvae community is important in understanding the full consequences of the effects of runoff from AS soils.

ACKNOWLEDGEMENTS

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ARSENIC CYCLING IN AREAS WITH SULFIDIC METASEDIMENTS, N. SWEDEN

by

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In Västerbotten County in Northern Sweden, an area of about 3 000 km² is underlain by black sulfidic metasediments that could be looked upon as “fossil” acid sulfate soils of Precambrian age. The metasediments contain 0.5–1% S, mostly in the form of pyrite but with minor amounts of arsenopyrite and sphalerite (Svensson 1980). The metasediments are mixed into the till (Lax & Selinus 2005). The sulfides are oxidized on weathering of the till releasing metals, among them a pronounced amount of arsenic. The arsenic is adsorbed in the B horizon of the podzolic soils (Gustafsson & Jacks 1995). In wetlands, with reducing conditions, iron and arsenic are remobilised, but when the groundwater discharges into ditches and streams, iron precipitates and arsenic is re-adsorbed onto the ferric coatings of sand and gravel. Ferric precipitates may contain up to 0.5% As, while sandy sediments may show as much as 500 mg/kg of As. Elevated

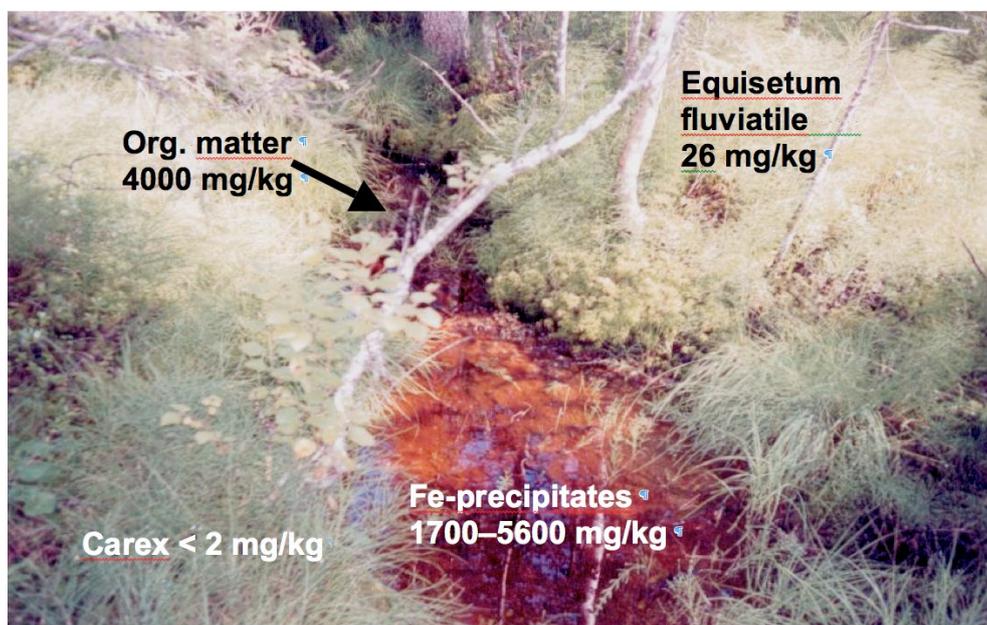


Fig. 1. A forest ditch in wetland with ferrous groundwater discharge.

amounts of zinc are also found in both the surface water and in stream sediments. Lakes in sulfidic metasediment areas show an elevated arsenic content of up to 20 mg/l in water and 0.2% As in sediments. Separation of arsenic and other metals into particle and molecular sizes reveals that most of the arsenic is found in the particulate and colloidal matter and likely to have a rather low bioavailability. Speciation of arsenic into As(V) and As(III) is difficult in surface water and the results are doubtful, but it would be reasonable to assume that the bulk is in the form of As(V) and is then adsorbed onto ferric particles and colloids (Sracek et al. 2003).

Land use has pronounced effects on metal transfer. Forest drainage has been intense in periods with subsidies. As much as 400 km of drainage ditches have been excavated in an area of 36 km² (Miskovsky et al. 2012). This has notably increased zinc transport, while most of the arsenic has found a sink in the ditches and streams. When the ditches are gradually obstructed by the growth of mosses, raising the groundwater level, arsenic and iron are mobilised and transported a little further downstream.

Our investigation has aimed at assessing the environmental risk of arsenic cycling in the metasediment areas. One risk considered is exposure of grazing and browsing wild animals to arsenic. It has been found that only *Equisetum* spp. have elevated contents of arsenic, being up to around 30 mg/kg dry weight. These species comprise a small fraction of the diet of elks, amounting to less than 4% (Johansson et al. 1994), and should not be a considerable risk. Leaves of *Salix* spp. showed elevated contents of zinc (up to 450 mg/g dry weight) and cadmium (up to 3.2 mg/kg dry weight). The other risk taken into consideration is the accumulation of metals in fish. However, this has also not been found to be very serious. Most of the arsenic in the analysed fish is in an organic form as MMA, DMA and arsenobetaine, and consequently has low toxicity (Slejkovec et al. 2004).

Table 1. Speciation of arsenic in Lake Nyängstjärnen and Lake Kyrktjärnen.

Sample	Nyängstjärnen		Kyrktjärnen	
	As mg/l	Fe mg/l	As mg/l	Fe mg/l
Unfiltered	8.2	2452	20.4	129
Filtered 0.2 mm	5.2	1340	17.2	84
Filtered As(III)	3.1	621	3.4	37
Dialysis 10 kD	3.2	325	11.1	11
Dialysis 1 kD	2.1	49	6.0	11

In lake water there is a good correlation between arsenic and iron, as illustrated in two lakes in Table 1. Nyängstjärnen is a brown water lake, while Kyrktjärnen is more of a clear water lake. The speciation of As(III) is one used for groundwater, while the outcome for surface water is quite doubtful. The association of arsenic with ferric precipitates is likely to result in a low bioavailability of arsenic and may explain the low contents of inorganic arsenic in aquatic biota. Moreover, detoxification of the arsenic and conversion to organic species in macroinvertebrates and fish may be contributing factors. Thus, in spite of the considerable amounts of arsenic mobilised in the redox cycling from soils to lakes, this does not seem to constitute a health risk to either wild animals or humans. What has been found to be a risk is elevated arsenic in some wells, with concentrations as high as 350 mg/l.

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ECOTOXICOLOGICAL RISK ASSESSMENT OF OSTROBOTHNIAN RIVER ESTUARIES AFFECTED BY ACIDITY AND METALS LEACHED FROM ACID SULFATE SOILS

by

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Finland has the largest area of acid sulfate soils (ASS) in Europe (Roos & Åström 2005). The drainage of AAS for agriculture and other land use activities enhances the oxidation of sulfide layers and the consequent formation of sulfuric acid and leaching of metals. Acid runoff and high concentrations of dissolved metals have deteriorated the ecological status of water bodies for centuries along the Western coast of Finland. While the effects of ASS on river ecosystems are well known, knowledge of their impacts in estuaries is scarce. This study is part of a CATERMASS project aiming to specify and mitigate the environmental risks of ASS under a changing climate. Here, we characterize the ecotoxicological risks in 14 Ostrobothnian river estuaries affected by an ASS hotspot area based on their exposure and ecological effect profiles.

Surface sediment samples (0–3 cm) were collected during summer and autumn in 2010 from the 14 locations. Surface water pH, total organic carbon concentrations, conductivity and concentrations of metals (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Si, Pb and Zn) were derived from monitoring results (HERTTA database of the Finnish Environment Institute). Sediment metal concentrations were determined by ICP-MS technique after microwave digestion with HNO₃. As an approximation of the sediment organic matter content (SOM) we used the loss on ignition (LOI) at 800 °C. Standardized acute and chronic toxicity tests (kinetic luminescent bacteria test ISO 21338 and Chironomid toxicity test OECD 218, respectively) with modifications were carried out with the ASS-affected estuary sediments. The luminescent bacteria were exposed to sediment extracts at concentrations ranging from 0.1% to 50%. Laboratory-reared *Chironomus riparius* larvae were exposed for 28 days in 3–5 replicates, and the number of emerging adults, the emergence time and proportion of 4th instar larvae with head capsule mentum deformities were measured. We used two synthetic control sediments (OECD 218) to encompass the minimum and maximum SOM levels. The LOI of the sediments varied from 4.5% to 24%, the mean value being 15%. Metal concentrations (mg/kg dry weight) in the ASS-affected estuary sediment were elevated (Table 1).

The ASS estuary sediment extracts were toxic to the luminescent *Vibrio fischeri*. EC₅₀ values at 30 min ranged between 0.03–9.4% (95% CL: 0.02–16.4), while

Table 1. Metal concentrations of sediments (mg/kg dw) and loss on ignition (LOI %).

Estuary	Distance from estuary (km)	Sediment metal concentration, mg/kg dw											LOI %
		Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	
Lestijoki		9572	10.4	0.23	8.0	21.2	9.0	20364	252	11.3	5.5	71	4.5
Perhonjoki		9656	9.5	0.35	10.7	81.6	12.2	23615	330	11.5	7.5	101	7.0
Ähtävänjoki		26571	15.5	0.76	44.4	40.2	24.1	52574	1492	42.9	17.1	230	18.3
Lapuanjoki		25986	11.9	0.46	17.8	36.1	26.1	38116	507	28.4	9.9	147	17.5
Vöyrinjoki		43872	8.1	0.59	22.9	39.7	50.5	34293	885	45.5	11.1	173	22.3
Kyrönjoki	1	25586	8.3	0.27	23.0	48.9	19.9	34950	444	36.4	10.2	146	7.3
Kyrönjoki	2	30605	9.3	0.66	31.3	49.3	35.5	35967	596	53.2	10.8	210	12.0
Kyrönjoki	3	35552	27.2	0.72	58.8	53.3	35.7	41133	4193	64.5	14.0	315	14.7
Laihianjoki		59900	10.2	0.92	74.3	47.1	63.1	38355	788	130.5	13.9	461	18.3
Maalahdenjoki	1	30526	5.3	0.48	15.4	39.1	37.1	28015	302	38.4	10.2	123	18.2
Maalahdenjoki	2	18284	3.8	0.36	11.0	26.6	22.3	17855	472	23.5	6.8	78	10.7
Maalahdenjoki	3	40189	14.1	1.67	121.9	44.5	44.2	38360	4008	125.6	16.9	500	19.6
Närpiönjoki		46827	10.1	0.94	33.7	62.4	59.2	38619	546	81.0	15.7	248	24.0
Lapväärtinjoki		30480	7.1	0.96	33.7	52.3	27.4	35934	533	51.2	14.8	235	15.5

1 = nearest sample point to the estuary; 3 = furthest sample point towards the sea

the reference toxicant Zn showed normal bacterial activity at 2.8–8.0 mg Zn/L (95% CL: 2.5–10.2). Correlation analysis indicated some association between individual metal concentrations and bacterial toxicity (EC_{50} values): Al: -0.26; As: -0.17; Cd: -0.26; Co: -0.38*; Cr: -0.28; Cu: -0.25; Fe: -0.48**; Mn: -0.31; Ni: -0.27; Pb: -0.46**; Zn: -0.32* (significant correlations at probability levels 0.05 and 0.01 indicated with * and **, respectively). Normalization to SOM diminished the correlations, indicating that SOM affects metal bioaccumulation dynamics and toxicity in ASS-affected sediments. Normalization of metal concentrations to a standard sediment containing 10% of SOM (as LOI) and 25% of clay on a dw basis (YM 2004) revealed that 6 of the estuary sediments had negligible metal pollution levels, 8 were elevated, and 3 of the sediments were clearly contaminated according to the YM (2004) criteria at the time of our sediment sampling. As an example (Fig. 1). Ni concentrations exceeded the level 2 limit of 60 mg/kg standard sediment in River Laihianjoki, River Maalahdenjoki (furthest sample point) and River Närpiönjoki, and 4 other rivers could be suspected to be potentially contaminated with Ni, as they exceeded the level 1 limit of 45 mg/kg standard sediment (YM 2004).

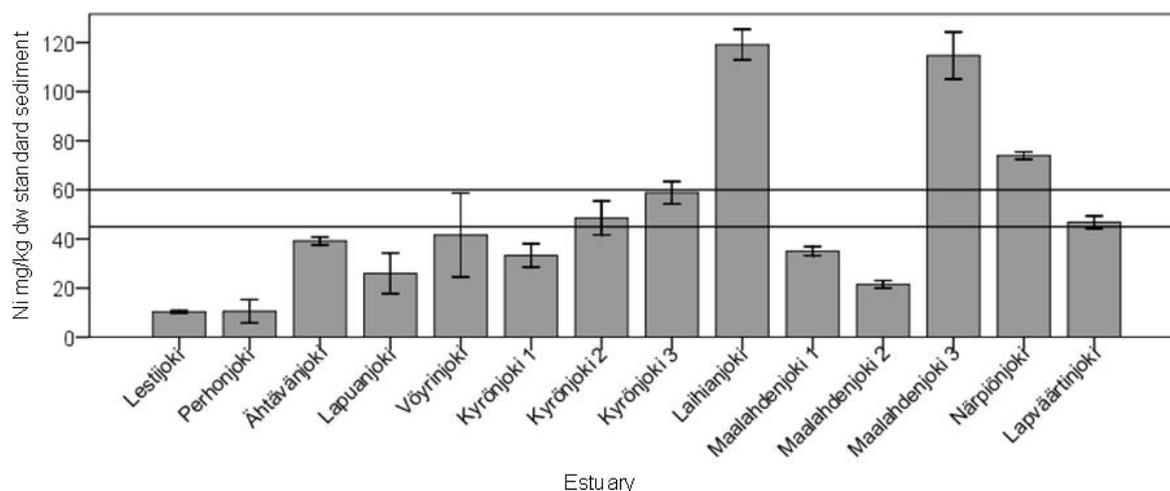


Fig. 1. Ni standard sediment concentrations (mean ± SD) (YM 2004) in the estuary sediments.

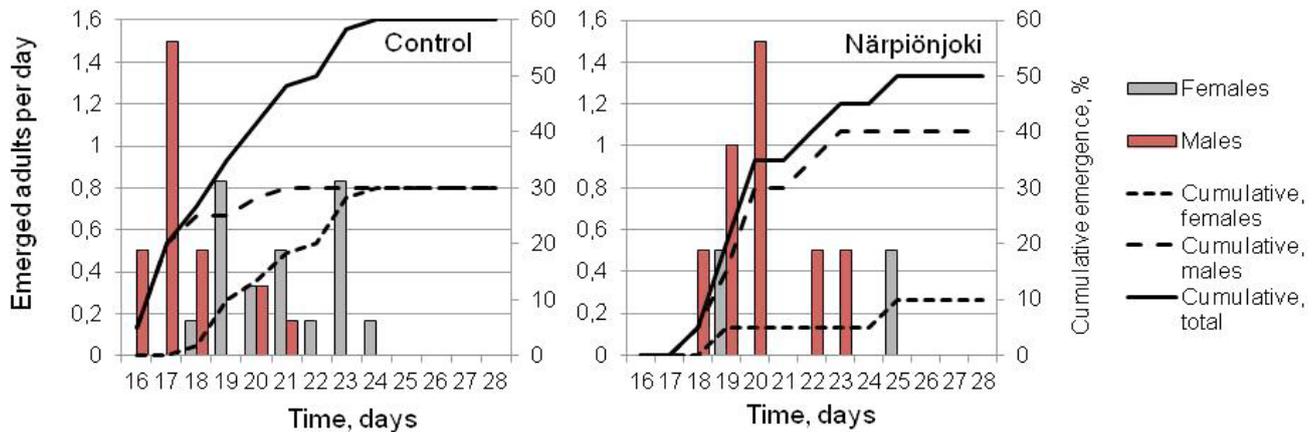


Fig. 2. Cumulative (%) and mean daily (individuals/d) emergency of *C. riparius* in the control sediment and the ASS-affected River Närpiönjoki estuary sediment.

Although the sediments indicated toxicity to bioluminescent bacteria, both the incidence of *C. riparius* mentum deformity and toxicity results mostly showed no differences between test and control sediments. However, in R. Närpiönjoki sediment, for instance, lowered the sex-specific and total cumulative emergence of adults as well as delayed emergence was observed in comparison to the control sediment (Fig. 2).

Estuary water resembles river water at high discharge. The preliminary river water Cd and Ni concentration comparisons with environmental quality standards (EQs) indicated that Cd and Ni concentrations were exceeded in 2010 in R. Kyrönjoki, and the Cd concentration was exceeded in R. Maalahdenjoki, while the concurrent pH minima in the estuaries were 5.0 and 4.3, respectively. Chironomids are able to survive in challenging conditions. *C. riparius* is considered as an opportunistic species, because its response to various toxicants is dependent on the quantity and quality of food available (De Haas et al. 2002). Thus, the species can act as a transmitter of contaminants from sediments into aquatic food webs and in this way to species likely to be more sensitive to the contaminants. We will compare the toxicity results with ecotoxicity data for aquatic concentrations of selected metals from the USEPA ECOTOX database (2012). Predicted no-effect concentrations (PNECs) will be generated and ecotoxicological risk characterization of ASS-affected estuarine sediments will be based on the multiples lines of evidence approach.

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MODELLING THE EFFICIENCY OF DRAINAGE PRACTICES AT PRESENT AND FUTURE CLIMATE SCENARIOS ON ACID SULFATE SOILS IN FINLAND

by

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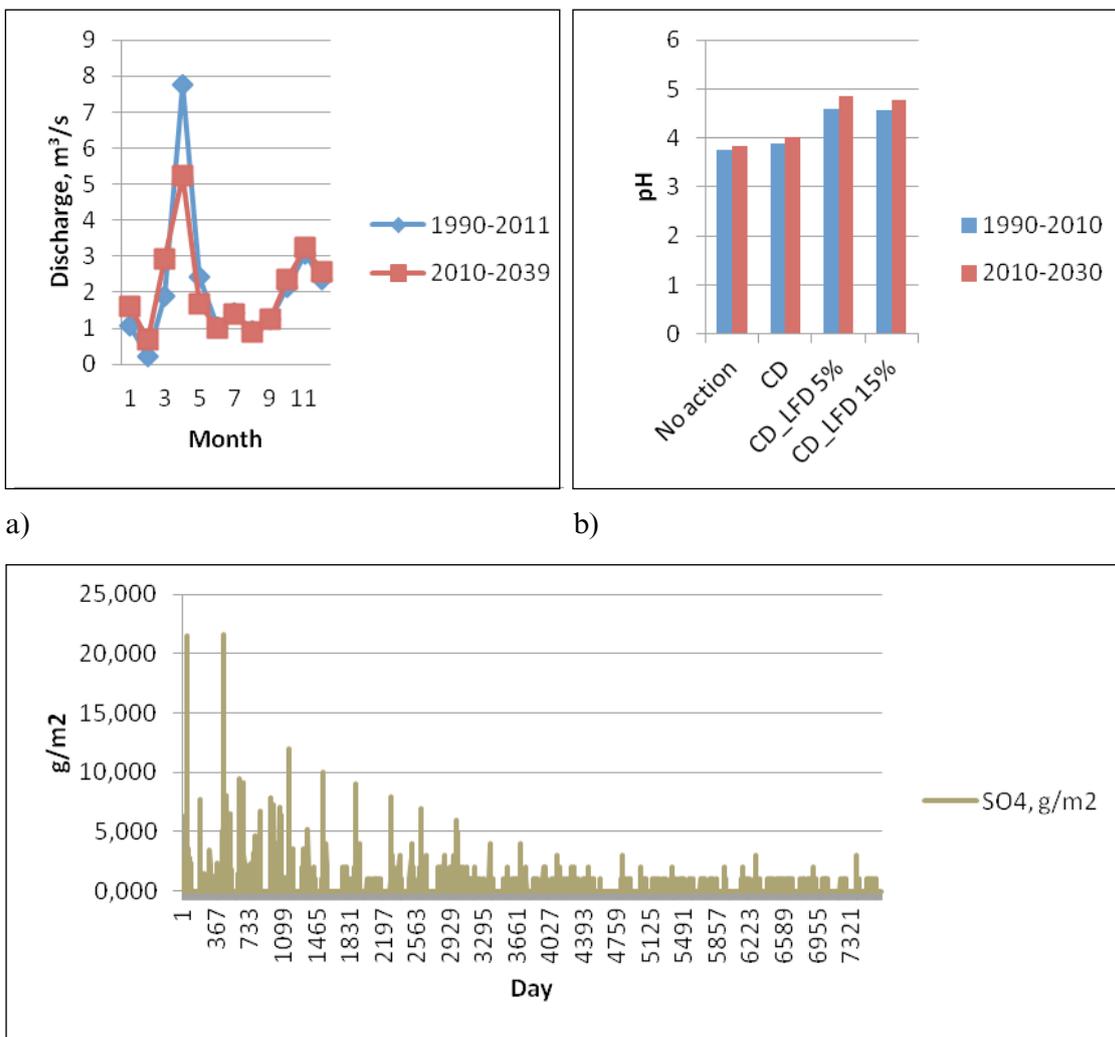
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On the coastal plains of western Finland, a large number of streams are periodically severely acidified and loaded with toxic metals because of extensive leaching of acidic sulfate (AS) soils. According to current knowledge, the leaching of acid water may be abated by applying the following measures: control drainage (CD), lime-filter drains (LFD) and a controlled drainage system with additional pumping of water during dry periods (CDP). Groundwater measurements have shown that the target level of a controlled drainage system cannot be reached during dry seasons without pumping extra water.

The ionic-flow model HAPSU was developed in the 1990s to simulate SO₄, H⁺, Fe and Al leaching from runoff areas with AS soils and non-acid soils in boreal conditions (Hutka et al. 1996). The model takes into account the boreal winter with freezing and melting, as well as the transport equations for heat, water, dissolved elements, oxygen and carbon dioxide in the soil column. The chemical part of the model includes reactions such as cation exchange, oxidation, reduction, precipitation, dissolution and weathering. Originally, the model solely consisted of normal drainage practices and lime-filter drains, and two new routines have therefore been included in order to simulate controlled drainage as well as the pumping of additional water into the drains. Controlled drainage is included in the model by reduction of the groundwater parameters and the pumping of extra water by increasing precipitation.

In this study the modified HAPSU model was used to compare the long-term effect of the different water protection measures (CD, LDC and CDP) on water quality in the Rintala area of western Finland. Long-term simulations were carried out by utilizing the temperature and precipitation data calculated for the period 2010–2039 with the average of 19 climate scenarios. According to these simulations, by the end of this century the annual mean temperature and precipitation in Finland are estimated to increase by 3–7 °C and 13–26%, respectively. The largest increases are estimated to occur during the winter period. For example, the hydrological cycle might change, since snowfall is predicted to decrease and summer and autumn rains to conversely increase. The runoff from AS soils is also most likely to change. It has been observed that the acidity of discharge water starts to increase after heavy rains, and the quality of water is most severely affected when a dry summer is followed by a rainy autumn or heavy spring flood.



c) Fig. 1. Monthly discharge averages simulated for the Seinäsuu site for the periods 1990–2010 and 2010–2039 (a). Average water pH with different water protection practices simulated for the periods 1990–2010 and 2010–2039 (b) and simulated leaching of SO₄ (g m⁻²) during the 21-year simulation period (c) from the runoff area of Isojoki.

In this study, the performance of the model was also tested using data from a lysimeter experiment on AS soils. In this experiment, AS soil monoliths (*Sulfic Cryaquepts*), which included oxidized sulfuric B horizons and a reduced sulfidic C horizon, were subjected to two water management treatments: normal drainage and waterlogging of the soil. The response of the soil redox status as well as the concentrations of aluminium (Al) and iron (Fe) in the different treatments were analyzed from pore water during the experimental period 2008–2010 and in the soil profile before and after the experiment. The chemical part of the HAP-SU model was verified against this data.

Our simulation showed that the CD method had only a minor effect on the simulated pH of discharge water during the two periods, 2000–2010 and 2010–2039. The efficiency was improved when the LFD method was used simultaneously with the CD method (Fig. 1a), and in the long-term simulations the effect strengthened slightly. With the CDP method, the groundwater level can also be kept high during dry periods by pumping extra water into the drains, and the results will probably be even better. The simulated leaching of SO₄ from the AS soil area showed a decreasing pattern during the 21-year period. The leaching of SO₄ settled at a constant value after approximately 10 years of leaching (Fig. 1c). The lysimeter experiment provided evidence of the importance of microbiological

catalysis in redox processes. The chemical part of HAPSU only takes account of the chemical reduction of Fe and ignores the microbial catalyst. Therefore, the soil response to the elevated water table might be slighter than it is in reality.

Based on earlier studies, the HAPSU model needs further improvement, especially regarding the chemical processes and the validity of the drainage practices. Model scenario runs give fresh perspectives on the future, but when judging the model output, one has to keep in mind that model simulation might give unexpected results and the uncertainty can therefore be quite high.

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SEA BOTTOM SEDIMENTS DEVELOPING INTO FUTURE SOILS AT OLKILUOTO, A SPENT NUCLEAR FUEL REPOSITORY SITE

by

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In Finland, the Olkiluoto Island on the western coast has been selected as a repository site for spent nuclear fuel. Due to the shallow sea areas around the island, the post-glacial crustal rebound (“land uplift”; at present around 6 mm/y) is going to significantly change the landscape in the relatively near future (Haapanen et al. 2009). During the next thousands of years, the present bays will narrow and form future lakes and their catchment areas. The effects of this terrain development are important factors in the long-term safety assessment for the repository, especially in the biosphere assessment (e.g. Hjerpe et al. 2010) addressing the radiation exposure of people, plants and animals in scenarios of radionuclide release.

In this biosphere assessment, the existence of acid sulfur-rich soils needs to be taken into account, as they will affect the transport of the possibly released radionuclides in the surface environment. In addition, to maintain favourable groundwater conditions for the waste canisters, it needs to be shown that the buffering capacity of the overburden and the bedrock is sufficient to prevent the transport of sulfur compounds to the deep groundwater.

Large areas of naturally occurring sulfide-bearing sediments have been deposited under reducing conditions on the bottom of the current Baltic Sea during the Holocene epoch, and due to rapid post-glacial rebound, a large proportion of these sediments have been raised above the current sea level (up to about 60 m a.s.l.), but below the highest level of the ancient Littorina Sea. Sulfur-containing sediments are also being deposited at present, especially in coastal bays and river estuaries, from where they could eventually rise to form acid sulfate soils. As these sediments are associated with certain sulfide-rich deposition conditions and, as fine-grained sediment, are prone to deposition or erosion in different conditions, information on shoreline displacement and changes in the physical exposure of the bottom is essential when predicting the future soil types.

In the sea area around the Olkiluoto Island, the stratigraphy of the unconsolidated sediment layers and the topography of the rock surface have been mapped by acoustic-seismic soundings covering in total about 300 km² (Rantataro 2001, 2002, Rantataro & Kaskela 2009). The geological units distinguished from these data are: Precambrian rock and Jotnian sandstone; till; glacio-acoustic mixed sediment; glacial clay; Ancyclus clay; Littorina clay (Fig. 1); sand and gravel, recent mud; and gaseous “bubble pulse effect” sediments. The fine-grained sediments, potential acid sulfate soils, are mainly located in the rock basins and

sheltered and shallow areas.

The geochemistry of ten fine-grained surface sea sediment cores (<50 cm) was studied by Lahdenperä & Keskinen (2011). The samples were dried using a cold-drying technique (ISO 16720) and sieved to the <2 mm fraction. The pH was determined using 0.01 M CaCl₂ extraction. The pH varied significantly between the different sampling sites. Sediments that become very acidic (pH < 4) upon oxidation were found in the western offshore area and in the sheltered Olkiluodonvesi Bay; in the Eurajoensalmi Bay the pH was slightly higher. The total sulfur concentration varied from 0.75 g/kg to 16.7 g/kg, the aluminium concentration from 44.6 g/kg to 65.2 g/kg and the iron concentration from 24.7 g/kg to 52.3 g/kg (all in dry weight). Total concentrations of arsenic, cobalt, copper, chromium, nickel, zinc and vanadium exceeded background values in most of the sediments. The distribution pattern of these high element concentrations is closely linked to that of organic matter.

Sedimentary iron sulfides are by far the most important sources producing future acid sulfide soils. Thus, it is important to analyse plausible millennial-scale scenarios on the future surface environment at Olkiluoto resulting from the post-glacial rebound, the subsequent development of the ecosystems and different forms of land usage. The description of the present conditions of the surface systems forms the basis for assessing the evolution of, for example, the topography, overburden, hydrology, flora and fauna within the climate conditions (Ikonen et al. 2008, Haapanen et al. 2009).

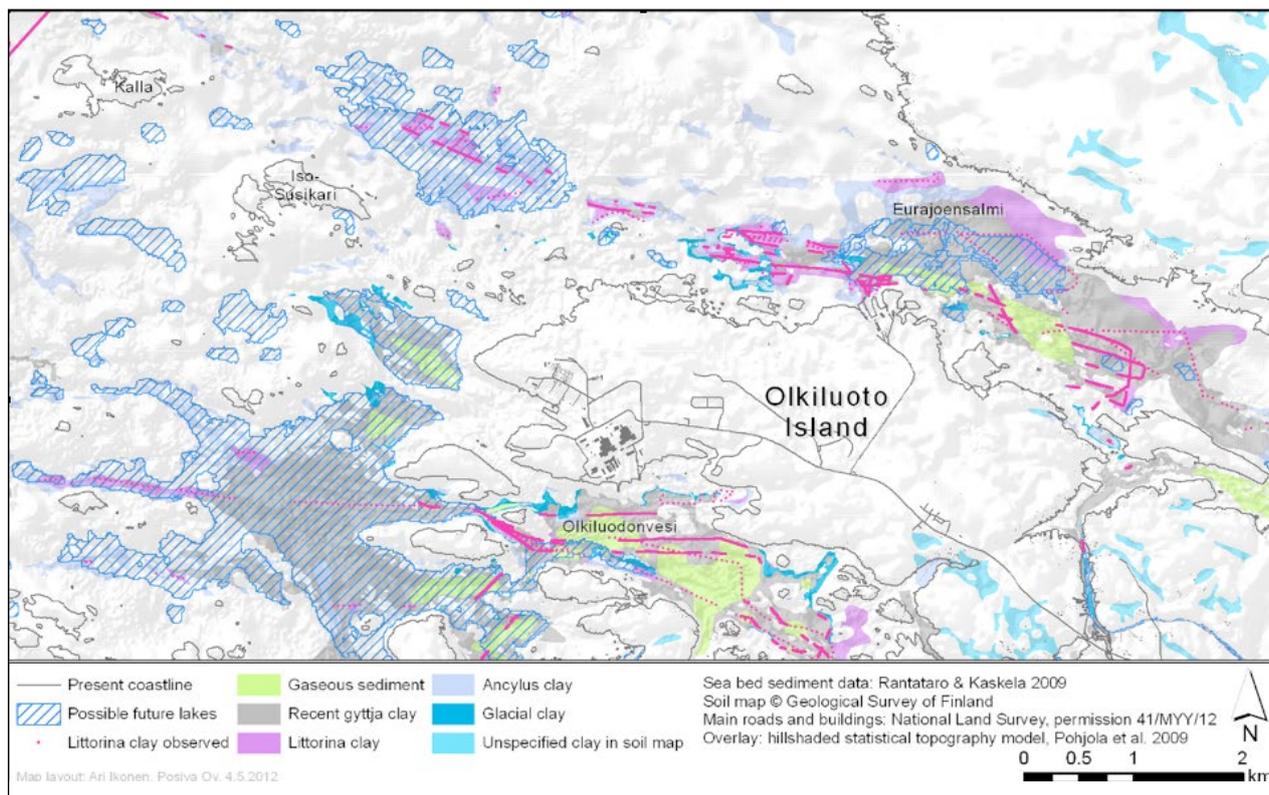


Fig. 1. Clayey Quaternary surface sediments of the sea floor and overburden in the Olkiluoto area. The possible future lakes are presented in blue raster. Observed locations of Littorina sediments within the acoustic-seismic sounding points, also where overlaid by other sediment types, are presented in violet.

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TASMANIAN ACID SULFATE SOILS INFORMATION (TASSI) PROJECT

by

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Tasmania is the southernmost island state of Australia. It has a temperate maritime climate and is located at 42 degrees south, 147 degrees east. In 2009, a major Natural Heritage Trust funded project was completed by the Tasmanian Government Department of Primary Industries, Parks, Water and Environment (DPIPWE), in partnership with the three Tasmanian Natural Resource Management (NRM) Regional Bodies. This project pioneered a new way of conducting predictive mapping of areas with the capacity to contain Potential Acid Sulfate Soils (PASS) and formally identified areas with the potential to contain these materials in Tasmania at a more detailed scale than previous work by Gurung (2001).

The outputs and data delivery system developed by this project have significantly helped to raise awareness of the acid sulfate soil (ASS) issue in Tasmania, whilst also providing management guidance to stakeholder groups. The project outputs closely align with 3 of the 4 objectives identified by the Australian National Strategy for the Management of Coastal Acid Sulfate Soils (National Working Party on Acid Sulfate Soils, 2000) to: 1) identify and define ASS areas, 2) avoid the disturbance of ASS and 3) minimise the extent of disturbance where disturbance is unavoidable.

The overall project objectives were to produce management guidelines for the management of acid sulfate soils in Tasmania, a predictive ASS map using GIS modelling techniques, a range of information products that target stakeholder groups and an information delivery system designed to make this information freely available and easy to access. A spatial model was created to develop the ASS probability maps, using best available spatial data at a range of scales.

This model effectively identified landforms with a likelihood of containing PASS in coastal, subaqueous and inland environments. Field calibration/validation and map unit classification were undertaken to National standards (Fitzpatrick et al. 2008), and occurred in parallel to the model development. Sampling was undertaken according to nationally accepted sampling standards (Ahern 1998) and full soil descriptions were recorded at each site according to McDonald et al. (1990). ASS soil field tests, acid based accounting and metal analysis were conducted by National Association of Testing Authorities (NATA) accredited laboratories.

This mapping processes identified >700,000 ha of land with the potential to contain PASS. Of this 91,500 ha has been classified as having a “high” probability and will require careful and preventative management to avoid disturbance into the future. Over 50% of this figure is found below the high water mark in

sub-tidal wetlands and intertidal flats. Fortunately, most of the high probability land above the high water mark in Tasmania has not been highly disturbed, but development pressure continues to increase from urban, industrial and agricultural intensification, especially in the coastal areas.

In order to assist stakeholders, a new web page was added to the DPIPWE website (www.dpipwe.tas.gov.au/acidsulfatesoils) to house the outputs of the project and information targeted towards stakeholder groups to assist them to better identify and manage ASS. The Acid Sulfate Soil probability map spatial information (Figure 1) is held on the publicly accessible Land Information System Tasmania (LIST) www.thelist.tas.gov.au. This system is accessible to all

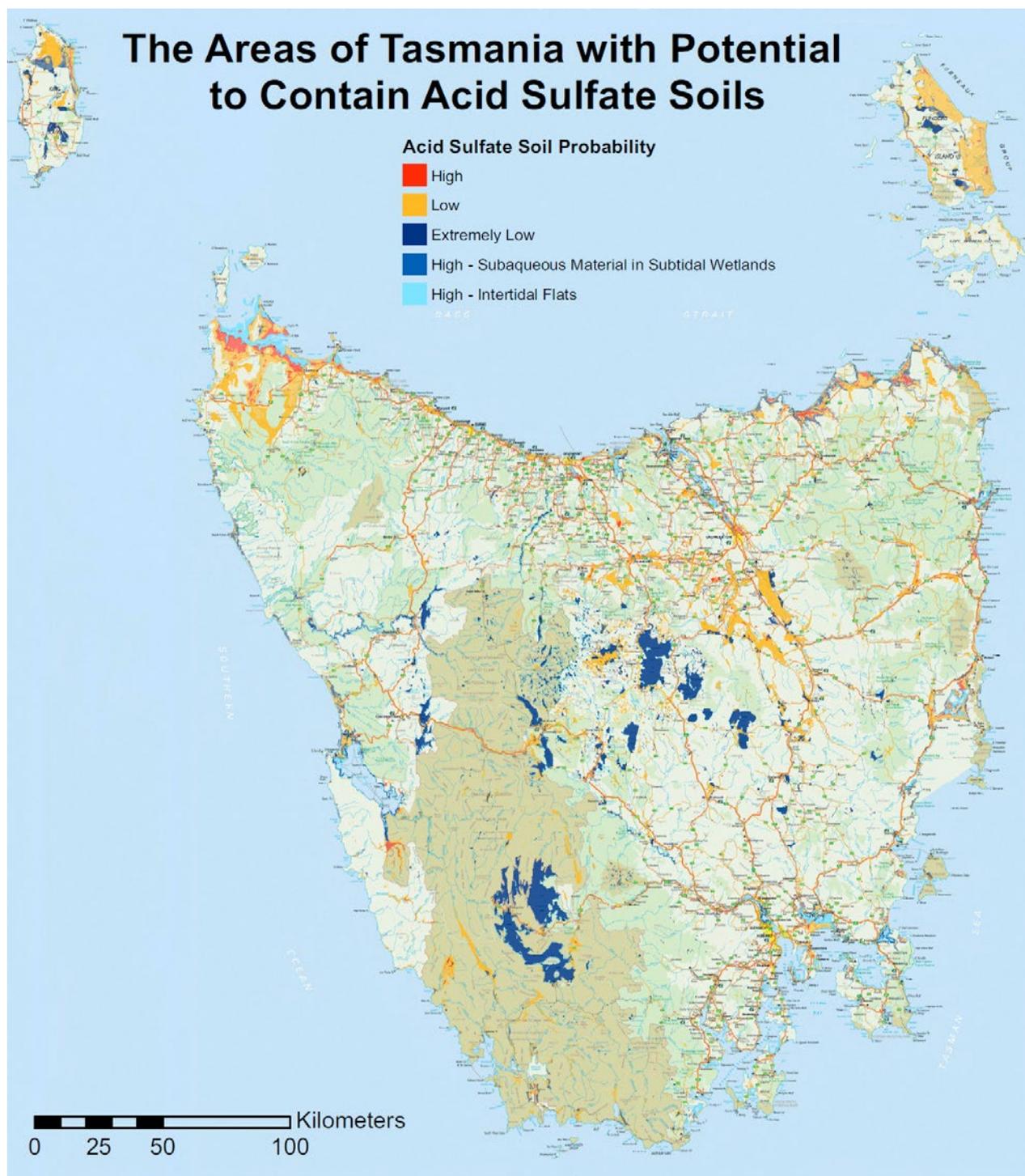


Figure 1. Areas with the potential to contain acid sulfate soils in Tasmania

stakeholder groups. It includes functionality such as viewing site information, interrogation of the ASS mapping layers, and combining maps with other spatial datasets on www.thelist.tas.gov.au. Here, ASS information may be combined with other data sets or even overlaid onto Google Earth imagery. This information is also available in digital form free of charge for organisations wishing to incorporate it within their GIS systems

The TASSI Project's information products have proven to be an invaluable data source and tool for councils, planners, engineers, consultants and other associated stakeholders and have raised the awareness of the ASS issue within these stakeholder groups so that ASS management is now increasingly being addressed in land management, strategic planning and planning schemes. This increased uptake and implementation of ASS information has highlighted the benefits of making spatial and management information accessible via an on-line data delivery system. A key lesson from this process has been the importance of asking stakeholders at the outset of the project and determining what information they need and how they want to access it. This process has led to strong usage levels of the web information.

Whilst undertaken wholly by the DPIPWE, this project has been made possible through strong support from the three Tasmanian regional NRM organisations, Cradle Coast NRM, NRM North and NRM South, and with financial support via the National Heritage Trust from the Australian Government. Technical advice and guidance were also received through the National Committee for Acid Sulfate Soils (NatCASS) and laboratory work was conducted by Southern Cross University Laboratories (EAL) and Analytical Services Tasmania. Kind assistance was also received from land managers and farmers, who provided access to their land during the field survey period.

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A NEW 1D BIOGEOCHEMICAL MODEL FRAMEWORK FOR ASSESSING AND MANAGING ACID SULFATE SOIL RISKS

by

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BACKGROUND

The biogeochemistry of acid sulfate soils is complex, involving oxygen transport into the sediment (required to oxidise pyrite), kinetically controlled reactions (e.g. pyrite oxidation, dissolved iron reactions), secondary acidification effects (e.g. acidic mineral formation, metal solubilisation), transport processes (e.g. leaching, diffusion to surface and ground water), and acid neutralisation reactions (e.g. sulfate reduction, carbonate dissolution). Currently, no single model is available that can adequately simulate all the potential processes influencing the biogeochemistry of acid sulfate soils. However, some models have been developed for oxidation and leaching processes of pyrite in mining contexts (Wunderly et al. 1996). The Simulation Model for Acid Sulfate Soils (SMASS) developed by Bronswijk and Groenenberg (1992) incorporates most relevant processes, but does not include many potentially important and more recently researched aspects (e.g. ion binding to dissolved and solid organic matter, clays and oxides). Recently, a multilayer model (SMARTml) has been developed to simulate acidification and the transport of nutrients and heavy metals in soil that includes these processes (Bonten et al. 2011). By coupling the SMASS acid sulfate soil model functionality to the SMARTml biogeochemical functionality, a powerful tool could be developed to simulate the biogeochemistry of acid sulfate soils and improve risk assessment and the management of their impacts.

The aims of this study were to: (a) describe the development of a new one-dimensional (1D) biogeochemical model framework for acid sulfate soils and (b) apply the model to simulate acid generation and drainage processes in an agricultural area in the Lower Murray River region of South Australia.

MODEL DEVELOPMENT

An outline of the model framework is presented in Figure 1.

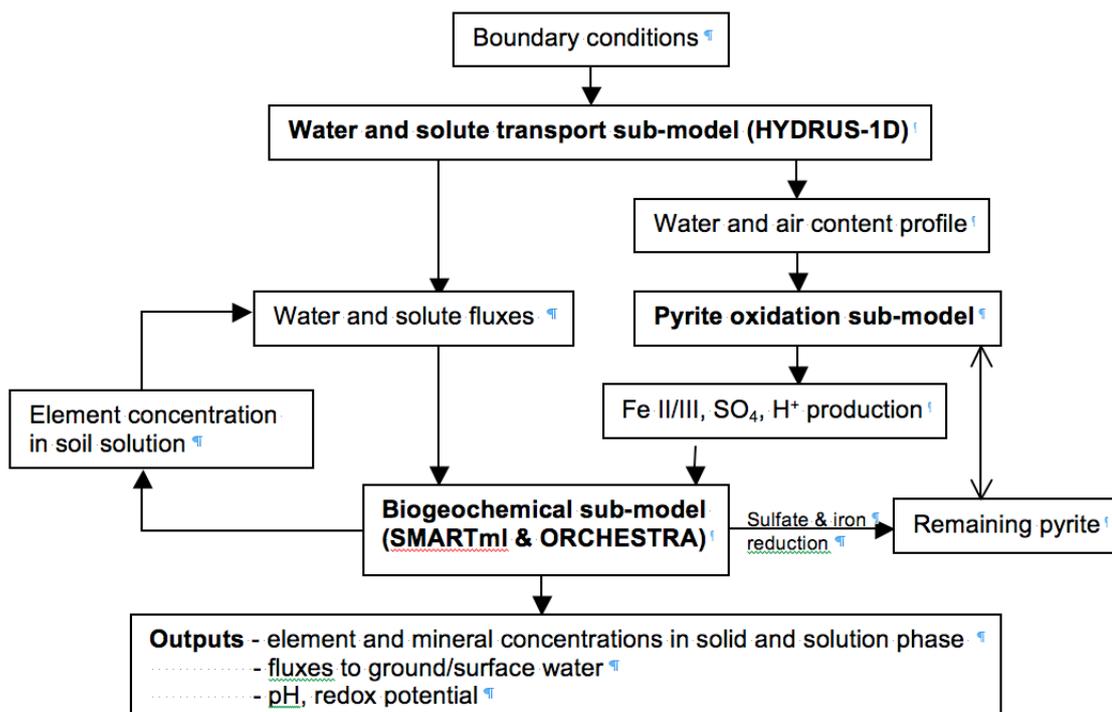


Fig. 1. Model framework

The following sub-models were coupled together (independently) to create a 1D model framework for simulating acid sulfate soil biogeochemical reactions and transport processes:

Water and transport sub-model - The widely used and supported model for water and solute flows in variably saturated media, HYDRUS 1D (Simunek et al. 2008), was used to provide moisture content and fluxes at various depths/ compartments in the soil profile. HYDRUS's graphical user interface enables schematisation of the soil profile, and the defining of different top and bottom boundary conditions (e.g. meteorological, irrigation, variable or constant pressure heads/fluxes, seepage faces, horizontal drains) and hydraulic properties.

Pyrite oxidation sub-model - The air content profile (= porosity - water content) in each soil compartment was calculated and the methods of Bronswijk and Groenenberg (1992) used to compute oxygen diffusion coefficients, oxygen consumption values (from pyrite oxidation and organic matter decomposition), rates of pyrite oxidation (also dependent on pyrite crystal size), and the concentration of pyrite oxidation products (Fe II/III, SO₄, H⁺) in each soil compartment. Oxidation and precipitation of monosulfides, FeS, can also be assessed if required.

Biogeochemical sub-model - The coupled SMARTml-ORCHESTRA models (see Bonten et al. 2011) were used to simulate the biogeochemistry of the soil profile subsequent to pyrite oxidation. First, the production/consumption terms for the non-equilibrium processes (such as iron and sulfate reduction) were calculated. The total concentrations of each chemical component were calculated in the soil compartments by summing the production/consumption terms, the inflow/outflow fluxes from the water and solute transport sub-model, and the total amounts from the previous time step. From these total concentrations, the equilibrium concentrations in the soil solution, the composition of the exchange complex, and the amount of mineral precipitates were computed for each compartment.

The coupled model utilises a daily time step, and multi-year simulations can readily be performed. The model is very flexible and capable of simulating a

wide range of acid sulfate soil issues and management scenarios (e.g. different irrigation or drainage regimes, addition of lime to soil).

MODEL APPLICATION EXAMPLE

Drought conditions and low inflows from 2006–2010 in the Murray-Darling system in Australia led to unprecedented low water levels in the lower reaches of the river. This resulted in groundwater tables falling under the adjacent agricultural areas (Lower Murray Reclaimed Irrigation Area, LMRIA). The heavy clay soils subsequently dried and cracked, resulting in pyrite oxidation in the sub-soil. The return of river and groundwater levels in late 2010 resulted in the appearance of acid drainage across an area of 3300 ha and resultant river water quality risks. There was a critical need to better quantify and model the biogeochemical processes in the LMRIA subsoils so that risk management could be improved. The new model described above was applied to simulate the pyrite oxidation processes, the mobilisation of acidic cations (H^+ , Al III, Mn II, Fe II/III), trace elements (e.g. As, Ni, Zn) and nutrients, and neutralisation (sulfate reduction) at a trial site.

ACKNOWLEDGEMENTS

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ELEVATED SULFATE AND TRACE ELEMENT CONCENTRATIONS IN SOIL SOLUTION OF AN ACID SULFATE FOREST SOIL

by

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Among 7 spruce-dominated forest sites belonging to the Finnish permanent monitoring programme of the EU-Forest Focus-FutMon / pan-European ICP forests Level II network (Merilä et al. 2007), the chemical properties of one site located in western Finland (Uusikaarlepyy) reflect the formation of an acid sulfate (AS) soil (Lindroos et al. 2007). The soil is largely composed of fine-textured material that is relatively poorly sorted.

Soil solution samples were collected during 1997–2010 at 4-week intervals during the snow-free period using zero-tension lysimeters at depths of 5, 20, and 40 cm (5 replicates at each depth). Soil solution samples were filtered through a 0.45 µm membrane filter, and Al, Fe, and Ni concentrations were determined by ICP/IRIS. SO₄²⁻-S was analyzed by ion chromatography. The pH was measured from an unfiltered subsample.

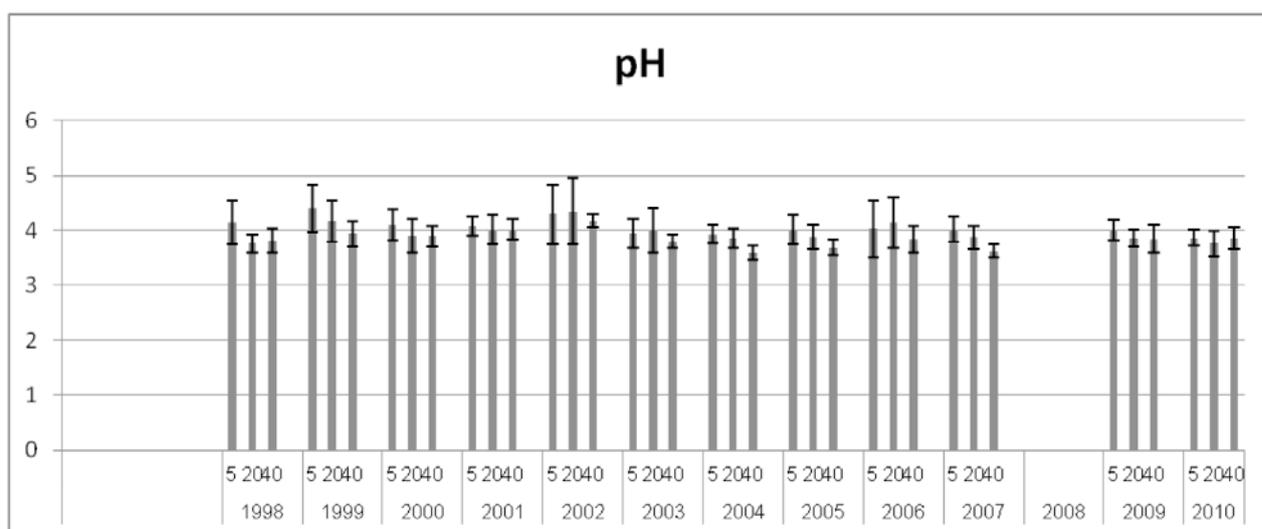


Fig. 1. Temporal trend in annual mean pH values in soil percolation water at 5, 20 and 40 cm depths of a spruce site on acid sulfate soil. Bars indicate the standard deviation.

We found clearly lower pH values, and higher concentrations of SO_4^{2-} -S and trace elements in soil solution of the AS site compared to the other spruce sites. The annual mean SO_4^{2-} -S concentrations ranged from 1.3 to 717 mg L⁻¹. There appears to have been a weak decreasing trend in mean pH values during the monitoring period (Fig. 1). In contrast to all other sites, the pH value decreased with depth, i.e. the lowest values were found at 40 cm depth and not at 5 cm (just below the organic layer), as is the case in 'normal' upland forest soils. The SO_4^{2-} -S concentrations showed the opposite trend: they tended to increase over time. According to our results, Norway spruce appears to tolerate extremely low pH and elevated concentrations of metals in the soil solution. The high volume growth of the tree stand indicates the high fertility of the AS site.

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PYRITE OXIDATION AND INHIBITION BY CERTAIN CHEMICALS IN RELATION TO THE PROBLEM OF ACIDITY GENERATION IN ACID SULFATE SOILS

by

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Pyrite is one of the main components of acid sulfide soils, and its oxidation (together with the oxidation of other iron sulfides) generates sulfuric acid. Aqueous oxidation of pyrite is an electrochemical process (1, 2), similar to the process of the corrosion of metals, and as in the case of metal corrosion it might be prevented by the application of inhibitors. It is generally believed that inhibitors act on metals by forming protective overlayers that reduce the rate of metal dissolution and/or the rate of reduction of the corrosion depolarizer (3). Many papers concerning the possible prevention of pyrite oxidation by the application of inhibitors have appeared in the literature (see (4) and references therein).

The aim of the present work was to find suitable inhibitors to prevent the aqueous oxidation of pyrite that might be used in the prevention of sulfuric acid formation in acid sulfide soils. The following compounds were tested as possible pyrite oxidation inhibitors: sodium dodecylsulfate, sodium oleate, n-octanol, dodecyltrimethyl ammonium chloride, 2-mercaptobenzothiazole (MBT), bis(2-ethylhexyl) phosphate sodium salt, phosphoric acid and humic acid sodium salt. However, it must be noted that the application of the inhibitors in field experiments is a subtle problem due to the danger of possible environmental contamination. Most of the above-listed compounds were investigated as model substances to obtain knowledge on the mechanism of the process, rather than as possible reagents to be applied in practice.

Three types of measurements were performed. The kinetics of the reaction of the reduction of Fe³⁺ ions at the surface of pyrite was investigated by measuring the exchange current density of the reaction:



at the surface of pyrite electrodes by electrochemical impedance spectroscopy (EIS). This reaction is very fast (see Fig. 1), does not depend on the properties of pyrite sample (presence of impurities, conductivity type etc.) and may be used to estimate the surface coverage of a pyrite electrode by adsorbed molecules (4). Note also that reaction (1) occurs at the pyrite surface during the aqueous

oxidation of pyrite, because the trivalent iron ion, not oxygen, is the main oxidation agent in this process (1, 2). The charge transfer resistance for reaction (1), which is inversely proportional to the reaction rate, was measured using EIS in an equimolar solution of trivalent iron and divalent iron sulfates for several pyrite electrodes conditioned in the solutions of potential inhibitors, and compared to the values obtained for the non-treated electrodes. Additional information was obtained from the simultaneously measured specific capacitance of the surface of the electrodes, which also reflects the coverage of the electrode surface by adsorbed molecules.

In another series of experiments, powdered pyrite samples were leached in aerated sulfuric acid solutions containing inhibitors of different concentrations during predetermined time periods, and the concentration of leached iron was measured. The results were compared to those for leaching in pure sulfuric acid solutions.

In the third series of experiments, powdered pyrite samples were treated in solutions of inhibitors during a predetermined period of time and then leached in aerated sulfuric acid solutions. The results were compared to those from the leaching of non-treated samples.

Keeping in mind the objections concerning the possible contamination of the environment by the applied substances, two inhibitors may be recommended: sodium oleate and humic acid sodium salt. However, the mechanisms of their action are probably different. The results of the experiments suggests that the contact of pyrite with aerated solutions of sodium oleate leads to the formation of a layer of insoluble iron oleate at the surface, whereas the action of humic acid probably consists of the complexing of trivalent iron ions by functionalities present in the structure of humic acid molecule.

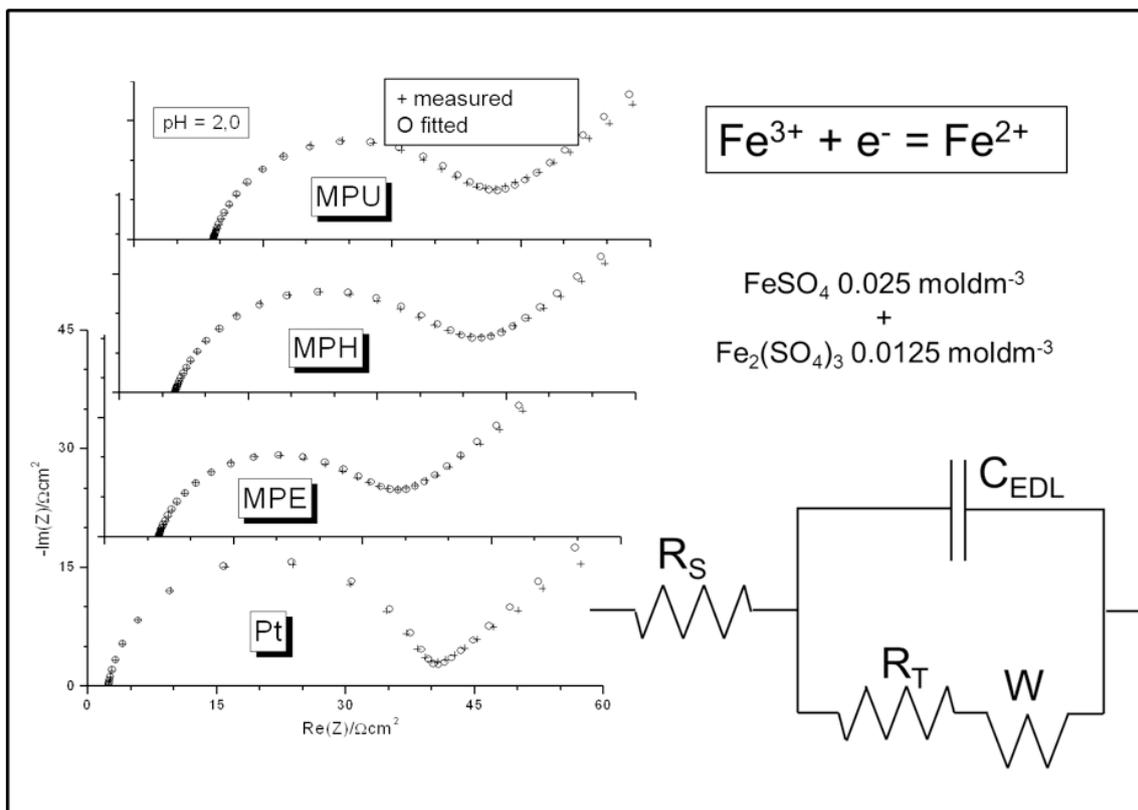


Fig. 1. Impedance spectra of three electrodes made of different mineral pyrites and a platinum electrode in an equimolar solution containing Fe^{2+} and Fe^{3+} ions. The diameter of the so-called polarization semicircle is inversely proportional to the reaction rate constant of reaction 1. Equivalent electrical circuit applied in the interpretation of the data is also shown in the figure. Note that reaction (1) occurs at approximately the same rate on pyrite electrodes as on platinum electrodes.

The inhibiting action of phosphates in the oxidation of pyrite postulated in the literature (5, 6) was not confirmed in our experiments. This may be ascribed to the fact that the application of phosphates requires strong previous oxidation of the pyrite surface, because the inhibiting action of phosphates consists of the formation of a layer of insoluble iron (III) phosphate in the reaction between the oxidation products of the pyrite surface and phosphate ions from solution. Note that Mauric and Lottermoser (7) also reported that the application of phosphates on a larger scale led to only limited successes.

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METAL SPECIATION IN AN EXTREME ACIDIC BOREAL RIVER SYSTEM

by

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The bioavailability of metals and their potential for environmental pollution depends not only on the total concentrations but also on their chemical form. Consequently, knowledge of aqueous metal speciation is essential in investigating potential metal toxicity and mobility. Aquatic metal species may be divided into three groups: particles ($>0.45 \mu\text{m}$), colloids ($0.45 \mu\text{m} - 1 \text{kDa}$) and the dissolved form ($<1 \text{kDa}$). The dissolved form is the most mobile and available to biota and is generally the most toxic fraction. Colloids (e.g. Fe and Mn oxides, Al silicates, clays and organic matter) are also increasingly recognized for their good adsorption capacity and can thus play a major role in regulating the concentrations of many potentially toxic elements. The metals associated with larger particles ($>0.7 \mu\text{m}$) are, however, progressively concentrated in the sediments and are generally not available to the biota. Although there is now fairly extensive knowledge of overall metal concentrations in rivers in Finland (e.g. Lahermo et al., 1996), including the rivers and streams severely affected by acid sulfate (AS) soils (e.g. Roos and Åström, 2005), little is known about the chemical form and size distribution of these metals. Such information is of importance when estimating ecotoxicological effects in metal-enriched waters. Thus, utilising filtration techniques and speciation modelling, the overall aim of this study was to examine the size distribution and species of major and trace elements in a Boreal river system (i.e. Vörå river in W Finland) that is heavily polluted by AS soils and discharges large quantities of potentially toxic metals to the Gulf of Bothnia (Nordmyr et al., 2008).

Water sampling was carried out in May 2006 from the River Vörå (upper, middle and lower reaches) and from 3 brooks and 7 low-order streams in the drainage area two weeks after the spring high-water flow peak. Prior to chemical analysis, the particulate and colloidal fractions were separated from the dissolved fractions by conventional filtration ($0.45 \mu\text{m}$) and frontal ultrafiltration (1kDa), respectively. Ultrafiltrations were performed with Amicon 8400 ultrafiltration equipment under nitrogen pressure (2.5 bar) using a concentration factor of 6. In addition, the geochemical modelling program Visual MINTEQ was used to predict the formation of free ions and complexes in these acidic streams.

The most important finding of this study is that the very large amounts of metals known to be released from AS soils (including Al, Ca, Cd, Co, Cu, Mg, Mn, Na, Ni, Si and U) occur and can prevail mainly in toxic forms throughout acidic river systems, as free ions and/or sulphate complexes (Fig. 1). This has serious effects on the biota, and dissolved Al (also partly complexed with sulfate; Fig. 1) in particular can be expected to have acute effects on fish and other

organisms. In our study area, only the relatively forested upstream area (higher pH and contents of OC) had significant amounts of less bio-available elements (including Al, Cu, Ni and U) due to complexation with the more abundantly occurring colloidal OC in the upstream area. It is, however, notable that some

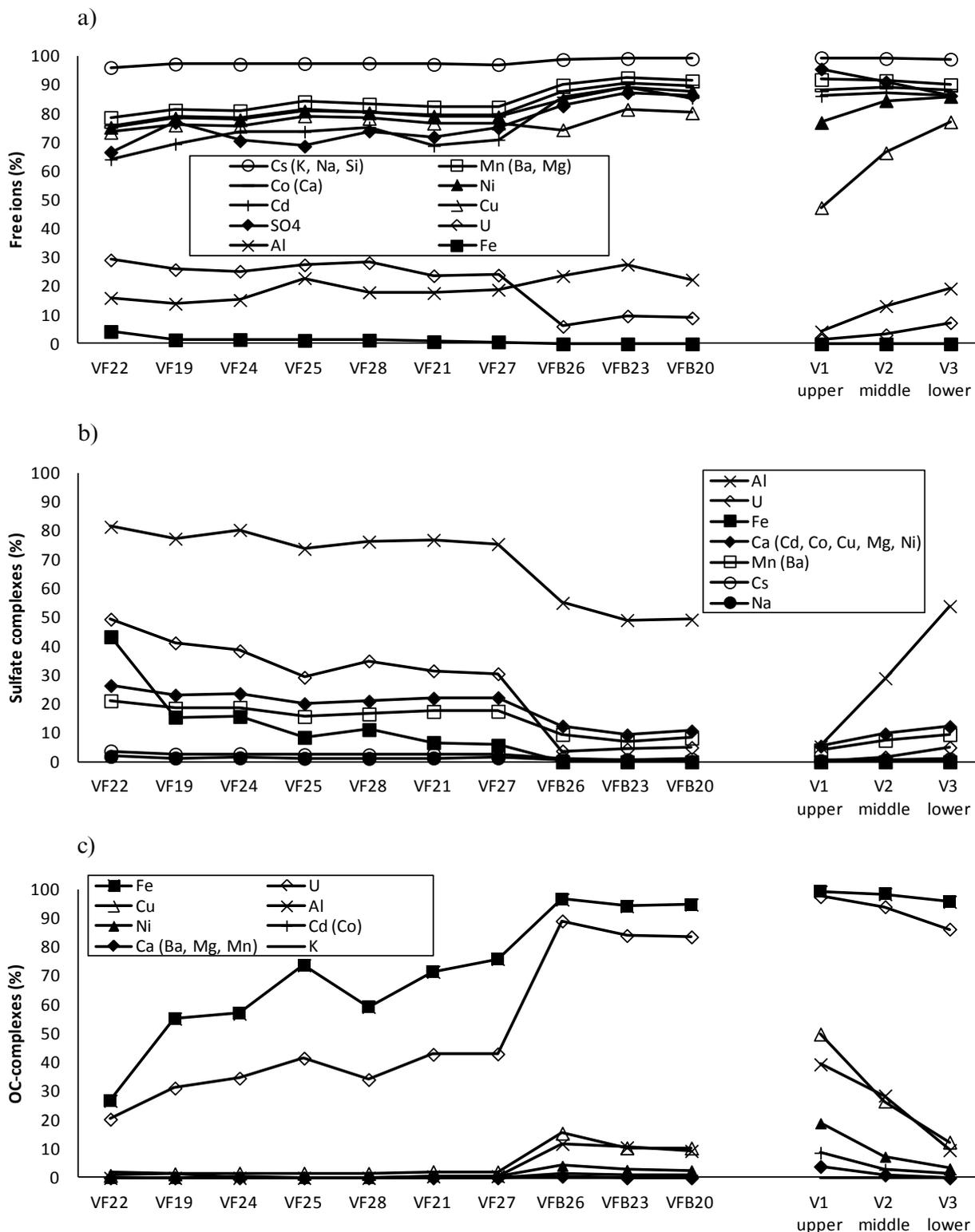


Fig. 1. Free ions (A) and element complexes with sulfate (B) and organic carbon (C) modelled with Visual MINTEQ in the low-order streams (VF) and brooks (VFB) of the River Vörå, and in the River Vörå (V). The streams and brooks are arranged from the lowest (left) to the highest (right) pH (pH 3.3–4.4). As the predicted results for some elements were very similar, only one representative element is shown for these element groups (elements not shown are in parentheses).

of the colloidal/particulate metals were most likely associated with metal bearing phyllosilicates eroded from clay soils. Moreover, the mobilisation of Fe and As was limited and As was predicted to be associated with Fe oxides, indicating a considerable influence of Fe oxides on the mobilization/immobilization processes of As. Elements will ultimately be precipitated in the recipient estuary, where the acidic metal-rich river water will gradually be diluted/neutralised with brackish seawater in the Gulf of Bothnia. According to speciation modelling, such a pH rise will first cause the precipitation of Al, Cu and U together with organic matters closest to the river mouth, in line with previous sediment studies from the estuary (Nordmyr et al., 2008).

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FIFTEEN YEARS OF MAPPING, CHARACTERIZING AND REMEDIATING ACID SULFATE SOILS IN VIRGINIA, UNITED STATES

by

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In the state of Virginia, United States, problems associated with sulfide oxidation following land disturbance have historically been associated with coal mining. It was not until the 1990s that attention was called to sulfide-related problems in other parts of the state. Recognition of problematic sulfide-bearing materials was driven by the detrimental effects of acid rock drainage at several road sites across the state. In 1997, funded by the Virginia Department of Transportation, a comprehensive study was initiated to map and characterize sulfide-bearing materials associated with road corridors in Virginia. Over a four-year period, problematic materials were identified and correlated with the state geological map to produce a state-wide sulfide hazard risk map (Fig. 1). This map illustrates the extent of sulfide-bearing geological formations across the state, and provides characterization of acid producing potentials based on peroxide

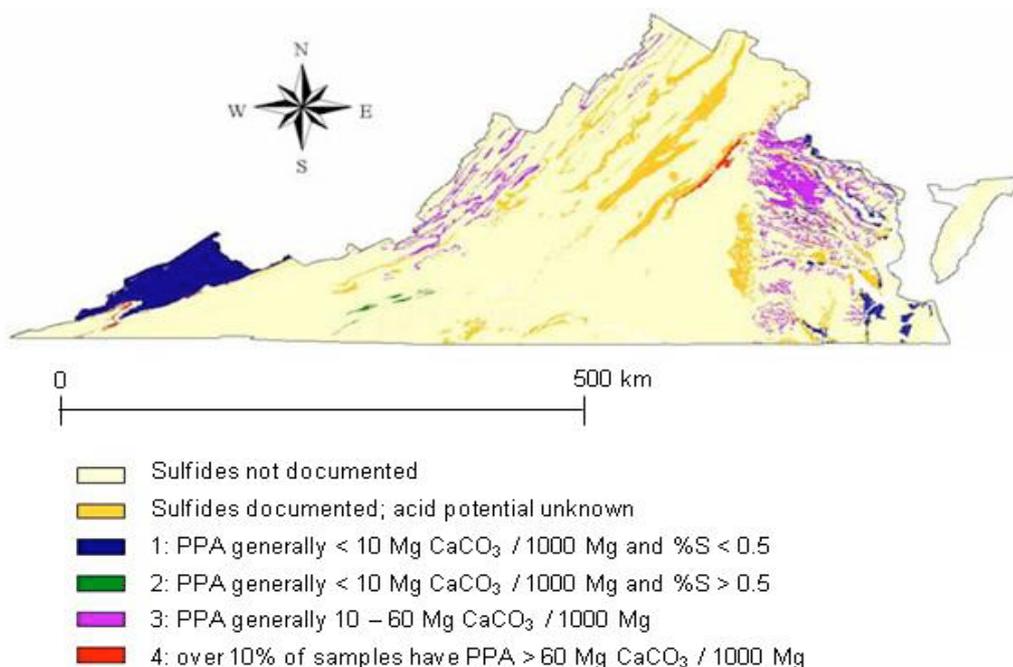


Fig. 1. Sulfide hazard risk map for the state of Virginia, United States

potential acidity (PPA) and total S, but it is not intended for site-specific planning. Since the state map is based solely on surficial geology it does not address issues such as the depth of weathering within a formation (i.e. natural oxidation of a “high-risk” unit) or geological changes with depth (i.e. a “low-risk” area may be underlain by “high-risk” materials).

Over the course of the initial study, it became increasingly evident that while sulfide-bearing materials are found in a variety of geological settings across Virginia, the majority of problems were occurring in the Coastal Plain province in eastern Virginia due to increased demand for commercial and residential development, and the ever-deepening nature of road cuts. To assist with site-specific planning, a study was completed to attempt to predict the depth to sulfidic sediments based on landscape variables such as elevation, slope, surficial geology and distance to streams. Although we could not develop a model to accurately and precisely predict the depth to sulfidic sediments, we were successful in predicting the likelihood of encountering sulfidic sediments within a specified exca-

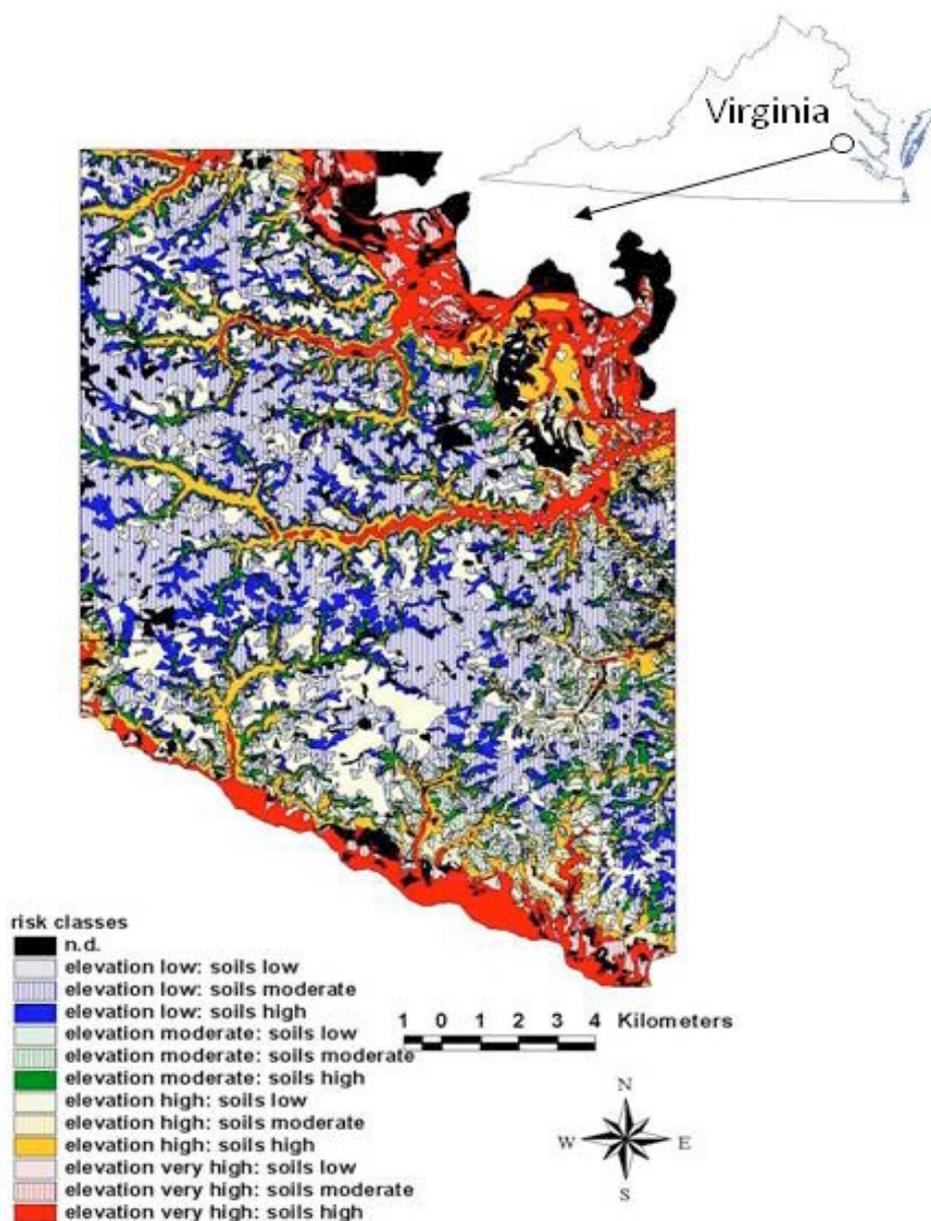


Fig. 2. Risk of encountering sulfidic sediments within a depth of 9 m based on elevation and mapped soil type for a study area near Mechanicsville, VA, United States.

vation depth based on topography and soil type (Fig. 2).

In 2001, our focus shifted to the reclamation of acid sulfate soils in the Coastal Plain as developers increasingly excavated into *sulfidic materials* with little or no understanding of how to identify or properly handle these materials. The most significant exposure was at Stafford Regional Airport in northeast Virginia, with over 150 ha of disturbance in sulfide-bearing Tertiary marine sediments. This site was successfully reclaimed with the incorporation of lime-stabilized biosolids. Smaller sites identified in several housing developments in the same region have been remediated in a similar manner with the use of lime, fertilizers and organic amendments.

Over the past 10 years, significant efforts have been made to educate engineers, developers and public officials about the significant problems associated with the exposure of *sulfidic materials*. The development of active acid sulfate soils in several housing developments, and subsequent public outcry, resulted in the establishment of regulations to test for potential acid sulfate soil materials for new construction in Stafford County (2006) and the City of Fredericksburg (2007). To date, these are the only regulations concerning *sulfidic materials* and acid sulfate soils within the state of Virginia.

STUDY OF A SULFIDE SOIL DEPOSIT AT A ROAD CONSTRUCTION IN SUNDERBYN, NEAR LULEÅ IN THE NORTH OF SWEDEN

by

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In 2004, a level separated intersection was planned on road 97 in Sunderbyn, which included the excavation of 22 000 m³ of sulfide soil (silty sulfide clay). At that time, no regulations or guidelines existed in Sweden on how to manage sulfide soil masses in order to minimise environmental problems related to acidification effects. The solution accepted by the Environmental Authorities was to deposit the sulfide soil along the main road, cover it with soil, and set up an extensive control program to follow up the effects on the environment. The control programme and evaluation of the results was executed by Luleå University of Technology (LTU). The need for guidelines resulted in a project to write a handbook as an aid for developers and consultants to: (1) perform appropriate investigations and analyses to assess and classify the acidifying properties of sulfide soil and (2) show possible management solutions for this type of soil. The project was financed by the Swedish Transport Administration and the handbook was published in 2007 (Pousette, 2007 and Pousette et al. 2008). When compiling guidelines for the handbook, results and experiences from the sulfide soil deposit at Sunderbyn were considered.

Excavation for the intersection in Sunderbyn was mainly carried out during the winter of 2005. The maximum depth of the excavation was 7 m. The soil profile in the area consists of about 2 m dry crust, and below that a 4 m thick layer of sulfide soil overlaying a silty soil. The original groundwater level was about 3 m below the ground surface. The groundwater level had to be lowered, and therefore a pump station was installed, to keep the groundwater level under the new road embankment. The sulfide soil was disposed of along the road in two heaps (460 x 20 x 2.5 m³ and 200 x 20 x 2.5 m³; Fig. 1). The aim was that the

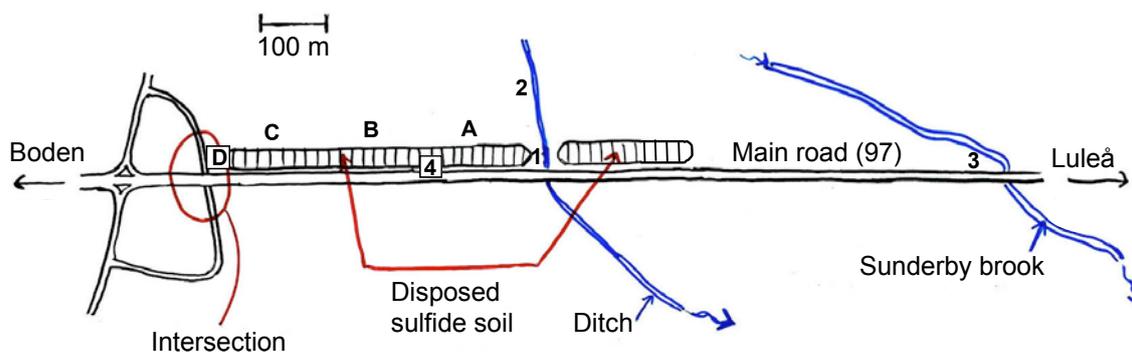


Fig. 1. Map of the area over which the sulfide soil was disposed, including sampling points.

Table 1. Properties and classification of disposed sulfide soil.

Soil cover	Part A 0.3–0.6 m		Part B 0.3–0.6 m		Part C 0–0.3 m	
	Mean value, span	No. of sam- ples	Mean value, span	No. of sam- ples	Mean value, span	No. of sam- ples
ρ , t/m ³	1.50 (1.40–1.60)	9	1.55 (1.48–1.73)	9	1.62 (1.61–1.65)	3
$w = m_w/m_s$, %	78 (62–87)	9	74 (62–93)	9	62 (60–65)	3
τ_{tu} , kPa	17 (11–20)	9	20 (8–28)	9	14 (11–20)	3
Fe, %	3.4 (2.9–3.8)	6	3.9 (3.4–4.7)	6	2.8 (2.0–3.9)	6
S, %	1.1 (0.6–1.5)	6	1.7 (0.7–3.3)	6	0.6 (0.09–1.7)	6
pH min	3.05 (2.8–3.2)	4	2.95 (2.9–3.0)	4	3.5 (3.2–3.95)	4
No. of leaching steps until pH < 4	4 (1–5)	4	3 (3–4)	4	6 (4–9)	4
Classification	highly/very highly acidifying		very highly acidifying		highly acidifying	

heaps should blend into the landscape. Table 1 shows properties of the excavated sulfide soil in different parts of the larger heap. To assess the acidification properties of the soil, the classification system proposed in the handbook was used. It comprises cyclic aerobic leaching tests according to a methodology developed by MRM Konsult AB (Pousette 2007 and Pousette et al. 2008) and analysis of the total sulfur content. From the cyclic leaching tests, the number of aerobic leaching steps until pH is below 4, and the pH minimum value reached in the tests, are used to classify the soil. The excavated soil was classified as highly to very highly acidifying.

The control program included: (1) analyses of surface water from four points (1–4 in Fig. 1), (2) measurement of pore pressure from four points at different levels (A–D in Fig. 1), (3) analyses of groundwater samples from four points at different levels (A–D), (4) analyses of leaching water collected in lysimeters installed under the soil cover and at the bottom of the disposed sulfide soil, and (5) auger drilling at 24 points to study how the oxidation front went downwards in the disposed soil. The water samples were analysed for pH, conductivity, redox potential and metals. The control programme was carried out during five years (2005–2009), with more frequent sampling during the first two years. Results from the measurements are compiled and evaluated in annually-published reports (Pousette, 2006–2010). To follow up long-term effects, more sampling is planned in the future.

The excavation and covering of the heaps was mainly conducted during the winter to take advantage of the strengthening effect of frost action. The sulfide soil had a rather low shear strength and there were problems with the low bearing capacity when piling up and covering the soil. This was especially the case for the last excavated soil (piled up in section C), where the excavation was carried out in the summer. Problems with the bearing capacity made it difficult to obtain the desired thickness of the topsoil cover. The aim was to have different thickness in sections A, B and C of the heap (Fig. 1). Auger drilling, after the covering was finished, showed that the thickness of the top cover varied from 0–0.6 m, with the thinnest cover for section C. After two years the vegetation cover on the heaps was very sparse. In autumn 2007 a thin layer (10 cm) of manmade topsoil was laid out over the heaps and grass was seeded.

Auger drilling was conducted once a year to study how the oxidation front went downwards in the disposed soil. After five years (autumn 2009) the oxidation front was located about 1 m (0.7–1.2 m) under the surface. During five years the descent of the oxidation front was highest in section C, with the thinnest top cover, and here the descent was higher in the two first years. The descent of the oxidation front has tended to slow down.

The surface water in the area is affected by natural seasonal variation in drainage water from the oxidation of sulfide soil into streams. The area is surrounded by farmland and overgrown meadow. At sampling point 2, located in a ditch upstream from the deposit, the lowest pH value (3.1) was measured. During spring and summer the pH was low, and in winter, when the water was covered with ice, the pH was around 7. At sampling point 1, where the ditch upstream from the deposit and the ditch along the deposit run together, the lowest pH measured was slightly higher, 3.8. The analyses revealed a clear correlation between pH and the content of Al, Co, Ni, Zn and Mn, with a low pH generating a higher content of these compounds. As an example, at a low pH (around 3) the content of Al was about 50 mg/l and at a pH of around 7 it was about 1 mg/l. The same correlation could be seen for the groundwater and the leachate samples.

The soil in the area has low permeability (about 10^{-9} m/s), and to be able to measure pore pressure and collect groundwater samples a closed piezometer system (BAT) was used. The variation in the groundwater level in the area during a single year was about 1 m. The sampling levels nearest the lowest groundwater level showed effects from the oxidation of sulfide soil. At the upper sampling level in point D, located at the end of the heap near the excavated area (Fig. 1), a pH between 3.5 and 4.2 was measured, the content of Al was 50–200 mg/l, and of total sulfur 400–1000 mg/l. One metre and more beneath the lowest groundwater level the pH was between 7 and 8, the Al content 0.01–1 mg/l, and the sulfur content 1–200 mg/l.

One conclusion from the study is that if sulfide soil is disposed of above ground, the location of the disposal site is important. The ground in Sunderbyn consists of sulfide soil and the environment is already affected by and adapted to the seasonal variation in drainage water from the oxidation of sulfide soil into streams. Therefore, additional acidification effects on the environment from the disposed sulfide soil were not detected in the control programme performed over five years.

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IMPLEMENTING A NATIONAL STRATEGY TO MANAGE ACID SULFATE SOILS: THE AUSTRALIAN EXPERIENCE.

by

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The late 1980s and early 1990s were characterised by a number of extensive fish kills and disease outbreaks in the northern rivers of New South Wales. At the same time the construction of canal estates, marinas and tourist development was expanding rapidly along the Australian coastline. For the first time it was recognized that the clearing and draining of wetlands as well as urban development on coastal lowlands were disturbing acid sulfate soils, leading to environmental, fisheries and engineering impacts and social disharmony. The media were regularly reporting the problems, which elevated the issue to the political sphere. While the New South Wales government implemented some response measures, it was recognized that there was an even larger national problem to address.

In 1998, the Australian Standing Committee on Agriculture and Resource Management (SCARM) instructed a National Working Party of stakeholders to prepare a national strategy on the management and use of acid sulfate soil (ASS) in consultation with industry and community interests.

The Working Party had to consider:

- The implication of existing practices in the absence of policies or strategies to control development.
- Economic, social, environmental, and technical issues requiring a national approach for their resolution.
- Roles and responsibilities of various levels of government and the community, and areas for cooperation.
- Resources required for implementation; and Australian ASS research requirements.

In 2000 the National Strategy for the Management of Coastal Acid Sulfate Soils was endorsed by the Australian government (National Working Party on Acid Sulfate Soils, 2000). It established four principal objectives:

1. Identify and define coastal ASS in Australia
2. Avoid disturbance of coastal ASS
3. Mitigate impacts when ASS disturbance is unavoidable

4. Rehabilitate disturbed ASS and acid drainage

The strategy identified the wide range of impacts arising from ASS disturbance, the roles of government, industry and the community, and most importantly set out a blueprint for the strategy to achieve its objectives.

Many stakeholders felt that it was important and urgent to maintain the political and community momentum by establishing a committee to facilitate and oversee implementation of the National Strategy objectives. This was supported by Australian, State and Territory governments and led to the formation of the National Committee for the Management of Coastal Acid Sulfate Soils (NatCASS), which continues today.

NatCASS membership comprises representatives of relevant Federal and state/territory agencies, research institutions and affected industries (fisheries, urban development and farmers). It meets twice a year, with hosting of meetings being shared across different states and territories on a rotating basis. It receives no ongoing dedicated government funding, and travel and meeting expenses are covered by the member institutions. It represents a nationwide commitment, but current economic conditions are straining the capacity of some representatives to attend every meeting.

Australia is a continent and the tyranny of distance makes the implementation of national strategies difficult. When NatCASS commenced, only the states of New South Wales and Queensland had policies or regulations that addressed ASS management. The state agencies of Western Australia and Tasmania did not attend meetings in the first year, as they did not recognize ASS as a problem. It was apparent that there were many challenges facing NatCASS to demonstrate that ASS were a national problem that needed a coordinated response at national, state and local levels. In 2008, it was decided to expand the role of the committee to include inland acid sulfate soils, which rose to national prominence following protracted drought conditions across south-eastern Australia.

NatCASS successfully provides a forum for communication and the rapid exchange of information between states, the Australian Government, industry and the community. Committee meetings have facilitated the delivery of many national, state and local ASS activities and policies that have contributed to National Strategy objectives. Examples of major achievements (including inland ASS) are provided below:

1. *Identify and define coastal ASS in Australia*

- The establishment of the web-accessible National Atlas of Acid Sulfate Soils (Fitzpatrick et al., 2010)
- The mapping of ASS and associated website delivery in Tasmania (Moreton et al., 2012)
- The mapping and characterisation of ASS in the Lower lakes of the River Murray (Fitzpatrick et al., 2008) and an Inland ASS risk assessment of wetlands in the Murray- Darling Basin (Kingham et al., 2012)

2. *Avoid disturbance of coastal ASS*

- The establishment of planning policies and regulations that aim to minimise the disturbance of ASS in all states and the Northern Territory.

3. *Mitigate impacts when ASS disturbance is unavoidable*

- The establishment of planning and environmental conditions, policies and regulations that aim to minimise the disturbance of ASS in all states and the Northern Territory.
- The establishment of national training workshops for the management of ASS in all states and the Northern Territory.
- The wider establishment of state guidelines for the management of ASS in Western Australia (<http://www.dec.wa.gov.au/content/view/2864/1653/>), and Tasmania (<http://www.dpiw.tas.gov.au/inter.nsf/Attachments/SWEN->

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- The establishment of various steering committees of experts to guide projects of risk assessment and management guidelines
 - Expert members on NatCASS freely give advice to local ASS managers at field trips associated with each meeting and inspire further action
 - Funding of the national ASS newsletter – ASSAY (currently produced quarterly).
4. *Rehabilitate disturbed ASS and acid drainage*
- Facilitation of R&D partnerships between research institutions and state governments to understand biogeochemical processes and assess the effectiveness of rehabilitation strategies

NatCASS has been an essential instrument in coordinating and improving the management of acid sulfate soils in Australia and in minimizing the adverse impacts of acid water discharges on development and aquatic ecosystems. NatCASS plans to continue to expand on its existing achievements and widen its membership to include local government and planning institutions, as well as facilitate the establishment of national guidelines.

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INTEGRATED MANAGEMENT OF ACID SULFATE SOILS IMPROVES DRAINAGE, WATER QUALITY, SUGARCANE YIELDS AND CUTS INPUTS

by

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Keywords: Acid sulfate soils, dissolved metals, toxic drainage, improved sugarcane management, increased yields

A major fish kill in Tweed River in 1987 due to toxic drainage from acid sulfate soils (ASS) under floodplain sugarcane fields caused widespread furore that threatened to close the NSW sugar industry. Individual cane growers and the industry overcame their initial denial of responsibility and, together with Tweed Shire Council, took ownership of the problem and sought solutions. Growers at McLeod's Creek encouraged collaborative research to better understand the hydrology and chemistry of ASS, and to develop techniques for their better management. The NSW Government followed and encouraged research and developed policies for better ASS management that are being followed by other States in Australia. The McLeod's Creek research showed that while natural processes prior to European settlement created a large store of existing acidity in the floodplain ASS, the artificial drainage systems provided the conduit for its increased export to estuaries. Also, the exported acidity was sourced from very close to existing field drains, and most acidity was exported in the form of dissolved metals. Laser levelling, infilling of many field drains, and the strategic application of agricultural lime have therefore been widely adopted. The focus of ASS management adopted by all in the NSW industry has been to minimise creation of new acidity and export of existing floodplain acidity, and to treat any export in the drainage system. With these and other integrated management techniques we estimate that acidity export has been reduced by up to 80% from that which existed in 1987. As well as improved environmental outcomes, sugarcane productivity and soil health have improved. The collaborative approach adopted here provides a template for the sustainable management of coastal environments.



Fig. 1. An aerial view of the McLeods Creek catchment showing the extensive sugar cane fields in the catchment (source: Google Earth).

The presentation will update the conference on the progress and unexpected benefits that have occurred in the last five years. These will include:

- the accumulation of organic carbon in the soil, from almost zero to between 5–6%, through the retention of residue following green cane harvesting,
- the reduction of chemical inputs, while increasing productivity, and
- the reduction in emissions of nitrous oxide following nutrient inputs.

The increase in soil biota has reduced some of the worst and most damaging soil pests and fungal diseases affecting the sugar industry.

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GUIDELINES FOR MITIGATION OF THE NEGATIVE EFFECTS OF ACID SULFATE SOILS UNTIL 2020 – A FINNISH NATIONAL STRATEGY

by

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In 2011, the Ministry of Agriculture and Forestry and the Ministry of the Environment agreed on a Finnish National Strategy for Acid Sulfate Soils (AS soils). This strategy was prepared in broad cooperation and it includes the central goals and policy instruments for diminishing the negative effects of AS soils as effectively as possible.

The vision until year 2020 is that “The special needs due to AS soils are included in legislation and subsidies, so that the risks caused by AS soils are taken into account in the zoning and land-use regulation and also in the requirements for actions and agricultural subsidies. Operators in areas with AS soils are well aware of the special characteristics of the land and the cost-effective actions required. Actions for diminishing the negative effects of AS soils are effective; the influence of actions is verified and can be allocated to the problem areas based on reliable information from geological surveys.”

The strategy summarizes the policy actions needed as follows:

- AS soils are to be taken into account when legislation is being developed;
- It is to be ensured that AS soils and their effects are included in national and regional programmes and guidelines;
- Diminishing of the negative effects of AS soils will be accelerated as the subsidy systems of agriculture, forestry, drainage and the reallocation of land are developed;
- Guidelines and recommendations are to be completed, so that guidelines for identification and preventive actions to avoid negative effects of AS soils are concrete;
- Studies, information and guidance concerning AS soils are to be strengthened;
- Mapping of AS soils should be sufficient and GIS-based data is to be collected and made available to the public;
- Research is to be carried out concerning the negative effects of AS soils on fisheries, water supply and sewerage, recreational use, agriculture, forestry and peat production;
- AS soils are to be taken into account in land use, planning and in civil engineering works;

- Mitigation of the negative effects of AS soils is to be enhanced and new methods of controlling the effects are to be developed.

The Ministry of Agriculture and Forestry and the Ministry of the Environment are responsible for the implementation of the strategy together with regional councils, municipalities, research institutes and advisory organizations. Local and regional authorities and operators are responsible for following the guidelines of the strategy when implementing concrete actions. The implementation of the strategy will be continuously followed up through a steering process by competent authorities, general planning of water resource management and independent reports.

THE RISÖFLADAN EXPERIMENTAL FIELD FOR CHEMICAL PRECISION TREATMENT OF ACID SULFATE SOILS

by

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This paper presents the experimental field that has been constructed as an integral part of the PRECIKEM (Chemical precision treatment of acid sulfate soils to prevent acid formation) project. This three-year project was launched in late 2010 by Novia University of Applied Sciences, Vaasa University of Applied Sciences, YA! Vocational Education and Training and Åbo Akademi University. The field was planned and its construction was supervised by Pro Agria, the Rural Advisory Centre of Ostrobothnia. The field was constructed by a local entrepreneur, Nybacks Gräv. The ultimate goal of the project is to find and demonstrate applicable management techniques that enable sustainable agriculture on Ostrobothnian acid sulfate soil farmlands while reducing the acid and metal load received by nearby natural waters. Large-scale experiments, based on laboratory-scale experiments, with oxidation-inhibiting chemicals mixed into irrigation water are going to be performed using the Risöfladan Experimental Field in 2012 and 2013.

The field is situated on Risöfladan, an area that not long ago still was part of the nearby sea. Risöfladan was drained and dried in the 1950s by surrounding the area with embankments and by pumping excess water into the nearby Toby å/Laihianjoki river. The area was taken into agricultural use by its owner, the Agricultural School of Korsholm (a predecessor to YA! Vocational Education and Training). The area is still drained by pumps and the ground surface is about 0.5 metres below sea level. Altogether, 9.58 hectares of the Risöfladan area is used for the experimental field. A new drainage system tailored for the project experiments was built on the experimental field in the spring of 2011. A map of the experimental field is presented in Fig. 1.

The experimental field is divided into nine 1-hectare subfields, each with its own drainage system. Each system consists of subsurface drain pipes, a collector pipe and a control well. The average depth for the subsurface drain pipes is

1.2–1.3 m. Each subsurface drain pipe is equipped with a flush pipe that is used for cleaning the drain pipes as well as for remote visual inspection of the drain pipes using an endoscopic video system. Every subfield is surrounded by a plastic sheet that extends from about 0.4 m below the surface down to about 1.9 m. This sheet provides hydraulic insulation between the subfields and between the subfields and the ditches. The only exception is subfield 2, where the plastic sheet between the subfield and the ditch was not installed, in order to provide information about the extent of the natural by-pass flow from the field. In order to also be able to control the water levels in the ditches surrounding the field, dams have been constructed in three places and mobile pumps can be used to drain the ditches and thereby control the groundwater table.

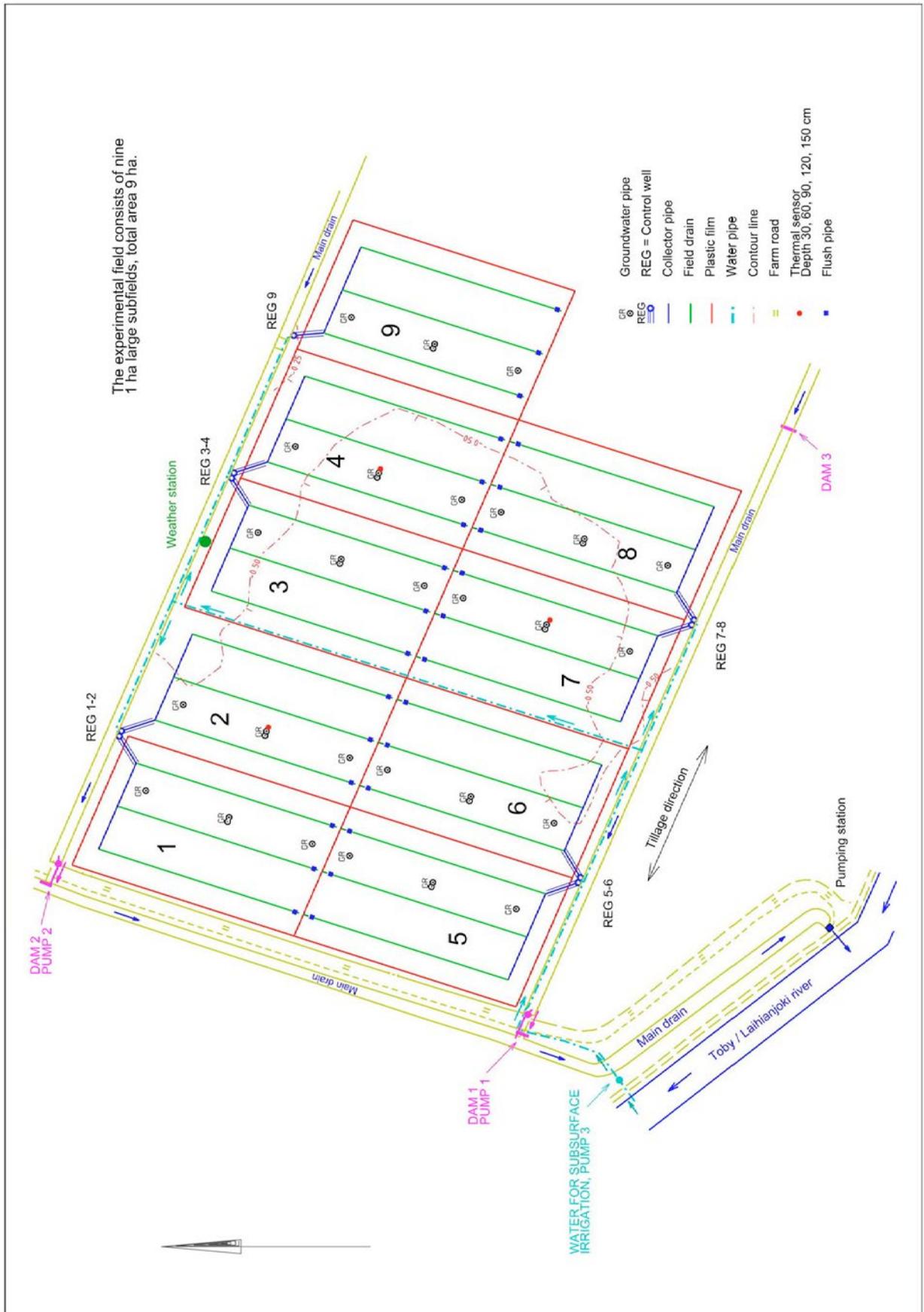
Subsurface irrigation is an important part of the experimental setup. A water pipe has been installed from the Toby å/Laihianjoki river to the experimental field in such a way that every subfield can be reached. By pumping river water into the control wells, the subfields are irrigated from below.

In order to be able to follow the groundwater level, three groundwater pipes have been installed in each subfield. Each of these groundwater pipes reaches down to a depth of 2.5 m below the surface. A liquid level float connected to a rod that is visible above the pipe is used in these groundwater pipes for quick and easy visual observation of the groundwater level. In one of these pipes per subfield, automatic logging of the groundwater level is also used. A fourth groundwater pipe per subfield is shallower and allows for specific sampling of groundwater down to 1.3 metres. A weather station logging temperatures, wind speeds and directions, humidity, and precipitation has also been installed in the field. Furthermore, soil temperatures at depths of 0.3, 0.6, 0.9, 1.2 and 1.5 m below the surface are being followed at four points.

ACKNOWLEDGEMENTS

The PRECIKEM project is funded by the European Agricultural Fund for Rural Development via the Rural Development Programme for Mainland Finland 2007-2013. This programme is administrated by the Centre for Economic Development, Transport and the Environment in Ostrobothnia. Co-funding is provided by the Field Drainage Association, Maa- ja vesitekniikan tuki, the Central Union of Agricultural Producers and Forest Owners (both by the Foundation of this organization as well as the regional chapter in South Ostrobothnia), and Österbottens Svenska Producentförbund. The investments needed in the drainage system, field monitoring equipment, pumps, etc., are funded by the Oiva Kuusisto Säätiö, Aktiastiftelsen i Vasa, and K.H. Renlunds stiftelse. Aid and support in the construction of the field, as well as in performing experiments, are provided by KWH Pipe and Nordkalk companies. All funding, aid and support is gratefully acknowledged. We would also like to express our deep gratitude to Professor Mats Åström and Environment Councilor Pertti Sevola for their continuing support of, and interest in, the PRECIKEM project.

Fig.1. The Risöfladán Experimental Field.



PEATLAND FORESTRY AND SULFIDE-BEARING SEDIMENTS – HOW TO AVOID ACID SURGES?

by

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Extensive drainage of acid sulfate (AS) soils for agriculture and forestry causes widespread environmental problems in several watercourses in Western Finland. A large proportion of the rivers in the western coastal area are classified as being in a moderate or poor ecological state due to high concentrations of metals and acidity derived from AS soils. It has been estimated that metal leakage from Finnish AS soils is up to 10–100 times higher than the effluent discharges from the entire Finnish industry (Sundström et al. 2002). The most obvious effects of increased acidity are fish kills, which can in some cases be extensive after summer droughts. Thus, there is an urgent need for sustainable and cost-effective methods to prevent acidification and avoid ecological damage in rivers. The most effective way to prevent the acidification of watercourses is to maintain sulfides in a reduced state in the soil by controlling the decrease in the groundwater (GW) level. In peatland forestry areas, the drainage depth should not reach the sulfide mineral soils beneath the peat layers.

Most studies related to the management of AS soils have concentrated on the effects and potential prevention methods of the acid load in agriculture. This study focused on AS soils and peatland forestry drainage. The study was conducted during 2010 and 2011 in the Luohuanjoki river basin (area 352 km²) in north-western Finland, which is one of the tributaries of the River Siikajoki, and has problems with acidity leaching from AS soils. Three peatland forestry sites were selected for study based on mapping of the potential location of sulfide-bearing sediments via geophysical maps (aerogeophysical mapping of resistivity) and soil sampling (Fig. 1).

Firstly, the actual effects of peatland forestry on runoff water quality were studied by using both manual and automated measurement data for both the groundwater and main ditch in each area. Soil samples were taken for analysis of both the pH and total sulfur concentrations in the soil profiles of each site. Secondly, the potential effects were estimated using the DRAINMOD model. Different simulations were run for the scenarios of different ditching depths, spacings and weather conditions. Climatological data (e.g. temperature, precipitation, evaporation) from nearest weather station were used as input data in DRAINMOD. In addition, soil data (e.g. hydraulic conductivity, infiltration) and drainage data (e.g. depth and space of ditches) were used at each site.

The thickness of the peat layer was 80 cm, 160 cm and 90 cm at sites 1, 2 and 3, respectively. Immediately below the peat layer, the total sulfur concentration increased and was above 1% at sites 1 and 2. The mean GW level was 55, 46 and 42 cm below ground at sites 1, 2 and 3, respectively. Thus no significant oxidation of sulfide minerals in soil during growing seasons 2010–2011 was observed.

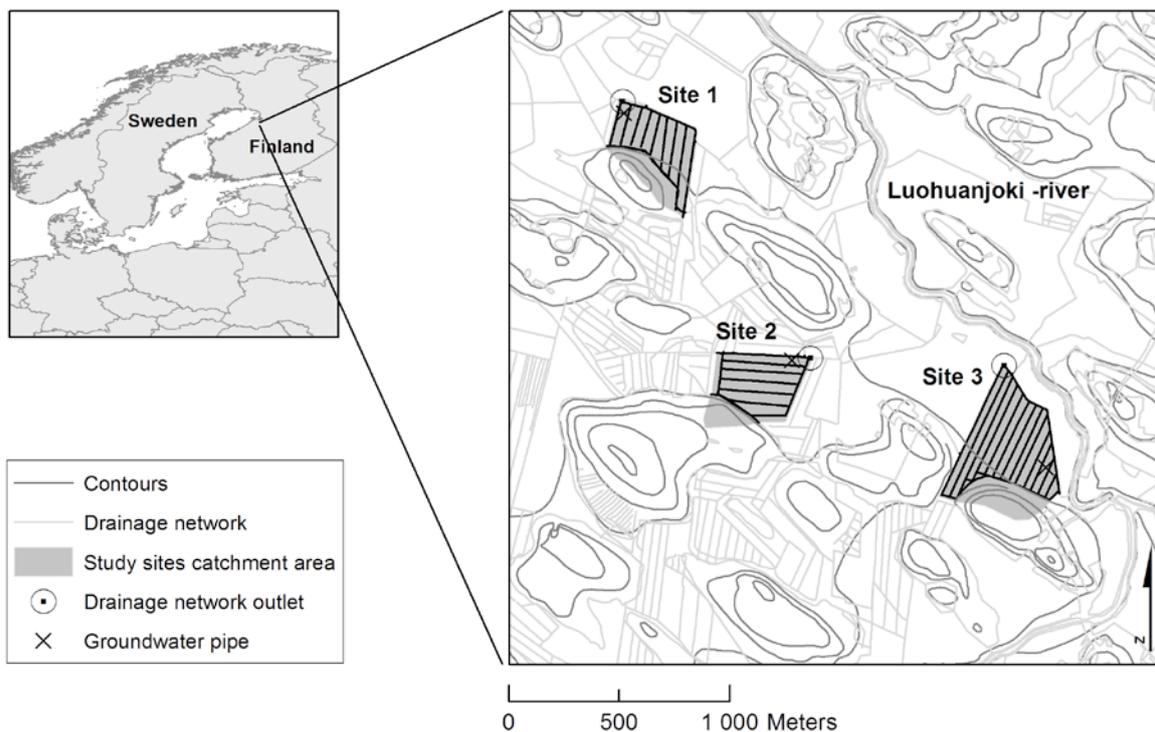


Fig. 1. Location of the study areas. © Maanmittauslaitos permission no. 7/MML/09.

This can also be seen in pH measurements in groundwater, in which the mean pH varied between 5.5–6.8, and never decreased below 4. In the main ditch, the minimum pH was 4.4, 4.8 and 5.5 at sites 1, 2 and 3, respectively, during high runoff in autumn. However, there was a significant negative correlation between the TOC concentration and pH, but not between SO_4^{2-} and pH, which also indicates that the acidity was derived from humic acids of peat rather than sulfide oxidation. Simulated GW levels fitted well the observed values in 2010 ($R^2 = 0.51\text{--}0.63$) and 2011 ($R^2 = 0.50\text{--}0.71$). According to the simulations, the depth of the GW level was highly dependent on the ditching depth and the distance between ditches. For example, at site 1, if the distance between ditches was less than 30 m and the ditching depth over 120 cm, there was a dramatic decline in the GW level into the mineral soil. This enables the oxidation of sulfides and potential leaching of metals. With the current drainage of site 1 (ditching depth 100 cm and space between ditches 40 m), there was no observed decline in the simulated GW level into the mineral soil. However, according to the simulation, during the dry summer of 2006, the GW level dropped into the mineral soil, which enabled the oxidation of sulfides. The results highlight that ditch depth has a major effect on sulfide oxidation processes, and a shallow ditch depth during maintenance draining is therefore recommended.

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ASSESSING THE ORIGIN OF THE ACIDITY IN A HUMIC BOREAL RIVER DRAINING PEATLANDS AND SULFIDE-BEARING SOIL MATERIALS

by

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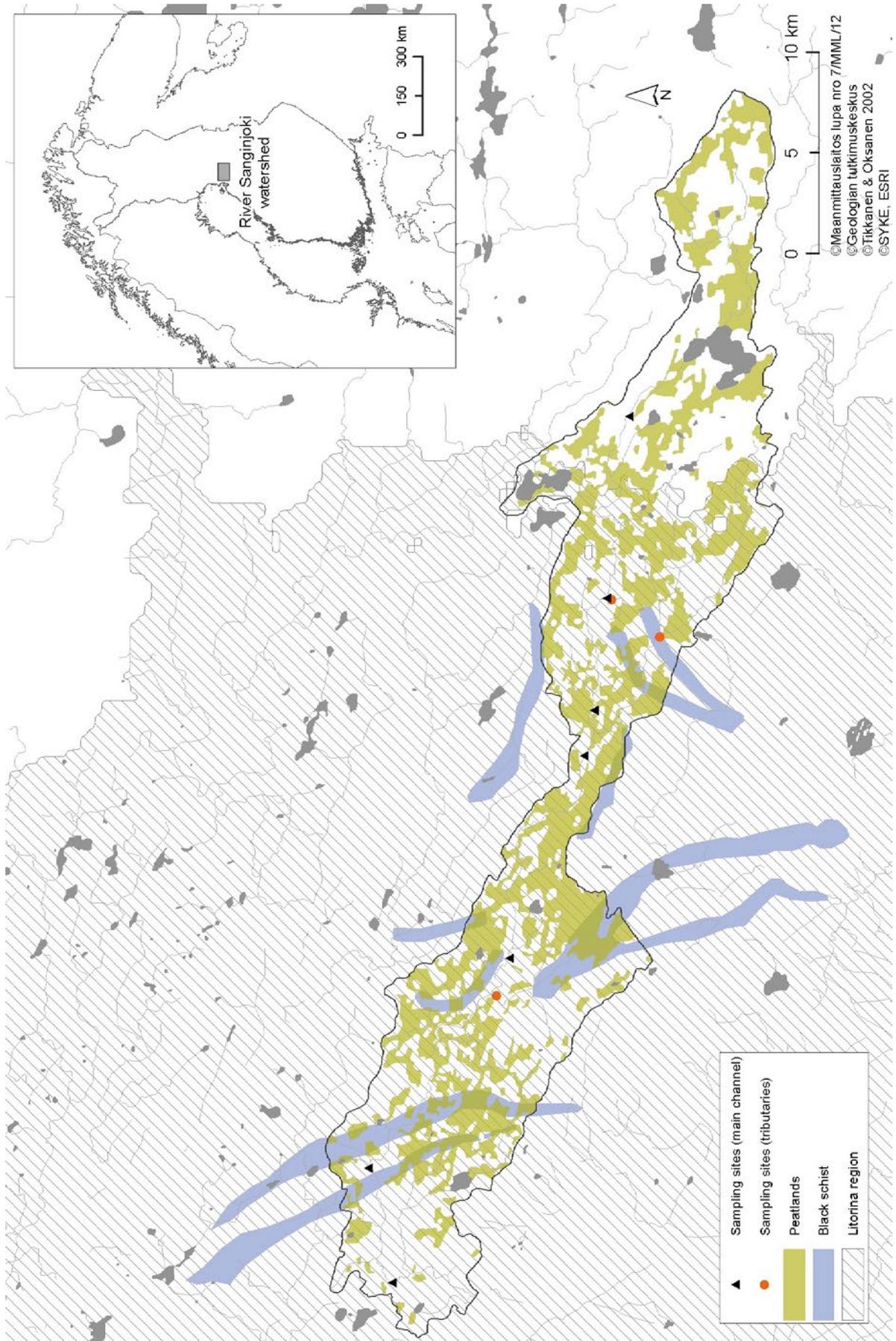
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The River Sanginjoki watershed in northern Finland is one of the most notable recreational sites in the Oulu region. It is one of the tributaries of the River Oulujoki and has a total catchment area of 400 km², of which the proportion of lakes is 2.7% (Mykrä et al. 2012). The average annual discharge (MQ) of the river is 4.6 m³/s (Ekholm, 1993). The catchment is mainly covered by forests and peatlands, which are intensively drained for land use (e.g. forestry purposes). Furthermore, around 79% of peatland forests and 38% of forests on mineral lands are ditched (Mykrä et al. 2012). Besides the high coverage of peatlands, sulfide-bearing soils that have emerged from the former Baltic Sea due to post-glacial isostatic land uplift and black schist regions can also be found within the catchment area (see Fig. 1).

Due to the nature of the catchment geology and land use (e.g. forestry, agriculture, etc.), the River Sanginjoki has experienced intensive but temporary periods of increased acidity, especially during autumn runoff (Laajala et al. 2006). Pulses of low pH detected during autumn flood peaks are harmful to stream biota and have been found to decimate, for example, fish and crayfish populations. The pH value has frequently dropped under 5.5 in the lower parts of the river main channel and even lower (< 5) in the tributaries. Due to the multifaceted geology (Fig. 1) of the catchment, assessment of the origin of the acidity in the main channel of River Sanginjoki is challenging. However, the high coverage of peatlands and sulfide-bearing sediments/till in the watershed give indications that the acidity is most probably induced by: 1) the oxidation of sulfide-bearing sediments, 2) leaching of dissolved organic matter (e.g. humic and fulvic acids) from peatland dominated regions or 3) a combination of both aforementioned factors.

The origin of the acidity was investigated via a water sampling program that covered ten sampling sites in the watershed (Fig. 1). The sampling frequency was 12 sets of samples in 2010 (May–October) and 2 sets in 2011 (April–May). The total number of samples taken was 139. Sampling sites were selected on the basis of low pH values detected by continuous pH measurements in the watershed and gathered GIS data. Alkalinity (Gran method), pH, conductivity, total organic carbon (TOC), dissolved organic carbon (DOC), chloride (Cl⁻), sulfate

Fig. 1. Location of the study site in the River Sanginjoki watershed. Red circles denote the sampling locations (3) in the tributaries and black triangles denote the sampling sites (7) in the main channel. The map also shows the postglacial isostatic land uplift area (lined area) and black schist regions (green) and black schist regions (blue) in the drainage basin.



(SO₄²⁻), metals (Na, K, Ca, Mg, Ba, Al, Ti, Mn, Zn, Fe), total elemental sulfur (S), nitrate (NO₃⁻), and ammonium (NH₄⁺) were analyzed in the Finnish Accreditation Service (FINAS) accredited Environment Measurement and Testing Laboratories.

Organic anion (A⁻) concentrations were calculated using a model of Kortelainen (1993), which describes the dissociation of organic acids as a function of pH. Non-marine sulfate (*SO₄²⁻) and the sum of non-marine base cations (*BC = Ca²⁺ + K⁺ + Na⁺ + Mg²⁺) were estimated using a model that applies a sea salt correction, which is based on the ratios of sulfate and aforementioned cations to chloride in seawater (Mattsson et al. 2007). Non-marine base cation normalized organic anion ([A⁻]/[*BC]) and non-marine sulfate ([A⁻]/[*SO₄²⁻]) concentrations were then used in the assessment of the origin of the acidity in the catchment of River Sanginjoki.

The organic anion concentration exceeded the non-marine sulfate concentration in all main channel sampling sites in the river and in 18 out of 20 samples in the tributaries. Furthermore, the low pH values were associated with high DOC concentrations in the drainage basin, whereas no correlation between sulfate and pH was found in the main channel or in the tributaries. The longer-range (1991–2010) chemical oxygen demand (COD_{Mn}) concentrations (n = 249) were also associated with lower pH values (r = -0.54, p < 0.001), whereas no correlation between sulfate and pH (n = 122) was found in the long-range (1998–2001) data collected from the HERTTA database.

The sulfate concentration varied from 1.2 to 5 mg dm⁻³ in the main channel and from 2.1 to 18 mg dm⁻³ in the tributaries. Detected electrical conductivities varied from 21 to 52 µS cm⁻¹ in the main channel and from 24 to 65 µS cm⁻¹ in the tributaries. Furthermore, the dissolved organic carbon concentrations varied from 14 to 44 mg dm⁻³ in the main channel and from 18 to 54 mg dm⁻³ in the tributaries. The highest DOC concentrations were detected in autumn 2010. The average (n = 12) organic anion and sulfate concentrations in the river were also observed to increase cumulatively downstream in the main channel. In conclusion, both the dominance of the organic anion and also the hydro-geochemical characteristics of the river drainage basin indicate that the temporary low pH values in the River Sanginjoki are mainly caused by leaching of organic acids from the peatland dominated areas.

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MANAGEMENT OF SULFIDE-INDUCED ACIDITY IN PEAT HARVESTING (SUHE): METHODS FOR PREDICTING AND MANAGING ACIDIC LOADS TO WATERS FROM PEAT EXTRACTION AREAS

by

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Different methods are being tested for the prediction and/or more rapid detection and treatment of acid sulfate soil drainage in peat extraction. The acidity of the runoff waters can either be induced by the oxidation of sulfur-rich soils containing sulfidic minerals (mainly iron sulfides) or by leaching of organic acids (mainly fulvic and humic acids) (Andriess and van Meensvoort 2006 & Kortelainen 1993).

There are two common types of sulfide-rich regions in Finland, Sweden and Estonia: (1) sulfide-bearing marine sediments that have emerged from the former Baltic Sea due to postglacial isostatic land uplift, and (2) coastal and inland black schist areas including the bedrock and/or the corresponding overlying till within their immediate glacial dispersal area. Undisturbed sediments/tills are normally harmless, but when excavated or drained, the oxidation of sulfides in contact with air and water produces extremely acid soils with increased acidity and metal loading in recipient streams. In addition to changes in catchment hydrology, climate change may increase the environmental impacts induced by land use.

This study is focusing on peat lands underlain by sulfide-bearing sediments/till and the purpose is to develop new methods for the prediction and rapid detection of acidic discharge from areas used for peat extraction. In addition, continuous and transient passive treatment methods will be developed for acidic runoff management. Although the methods developed in this study are being optimized for peatland conditions, it is expected that the results could also be exploited within other types of land use.

One of the main aims of this study is also to determine potential regional differences in the acidification capacity of peatlands in sulfide-rich regions. In particular, we aim to evaluate the different impacts of the abundances of ferrous sulfides and disulfides in coastal sediments and sulfides in black schist materials. The results will be utilized in developing more accurate tools for sulfide area



Fig. 1. A typical drainage network in a peat extraction site.

risk assessment, assuming that clear and classifiable differences will be discovered. Moreover, the suitability of different adaptation methods (e.g. growing of sphagnum, rewetting, etc.) to be used on peatlands after peat extraction has ended will also be evaluated.

The study is being conducted within a project entitled ‘Impact Management of Sulphide-Soil-Induced Acidity in Peat Harvesting (SuHE). Partial funding is being provided by the European Regional Development Fund (ERDF) via the Centres for Economic Development, Transport and the Environment in North Ostrobothnia and Lapland. Other funding entities include the Council of Oulu Region, Vapo Oy, Turveruukki Oy, Nordkalk Oy Ab, SYKE, the University of Oulu, Metla and Åbo Akademi. More information on the project can be found from the internet site: www.environment.fi/syke/suhe.

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CONSEQUENCES OF REDUCED WATER FLOWS TO THE LOWER MURRAY REGION

by

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The Coorong, Lower Lakes and Murray Mouth region is a complex ecosystem that encompasses riverine, lentic, wetland, terrestrial, littoral, freshwater, estuarine, marine and hypersaline habitats. It exists at the terminus of Australia's largest river system, the Murray-Darling, and was designated as a Ramsar site in 1985. It is an Icon Site under The Living Murray Initiative, and will be listed as a Key Ecological Asset under the forthcoming Murray-Darling Basin Plan.

Between 2006 and 2010, River Murray flows were at historically low levels due to over-allocation and drought across the Murray-Darling Basin. As a result, inflows into the Lower Lakes were not able to replenish evaporative losses and average lake levels dropped to unprecedented lows. In April 2009, average water levels were at their lowest in Lake Alexandrina, one metre below sea level (Fig. 1). Evapoconcentration led to salinity levels in both Lakes increasing beyond values normally associated with freshwater environments. At the height of drought conditions in 2009, salinity in the Goolwa Channel region of Lake Alexandrina exceeded 25,000 EC.

Low lake levels resulted in the exposure of previously submerged sulfidic sediments known as acid sulfate soils (ASS). By March 2009, over 20,000 hectares of ASS had been exposed in Lakes Alexandrina and Albert, posing substantial risks to the region's ecology and local communities. Acidic water of pH < 3 pooled in some ASS hotspot areas, greatly impacting on environmental conditions.

Significant management actions were instigated to mitigate the exposed ASS and to reduce further ASS exposure. A three-tiered approach was developed, which included prevention measures to keep soils submerged, bioremediation to facilitate sulfate reduction and neutralisation to treat acid water.

The development of these management techniques required collaboration with many partners across Australia. The South Australian Department for Environment and Natural Resources and the South Australian Environmental Protection Agency coordinated research efforts and trialled recommendations on the ground. The process, from scientific understanding to on-ground actions, occurred rapidly. Modifications of the management response occurred weekly subject to monitoring results, and a truly adaptive management approach was undertaken.

The acid sulfate soil crisis within the region divided the community. However, through active communication and involvement in defining the issues, community groups formed a critical loop in understanding the complexity of ASS in the region. One initiative involved an extensive community soil-monitoring program developed with CSIRO that involved 85 people, undertook 51 surveys and col-

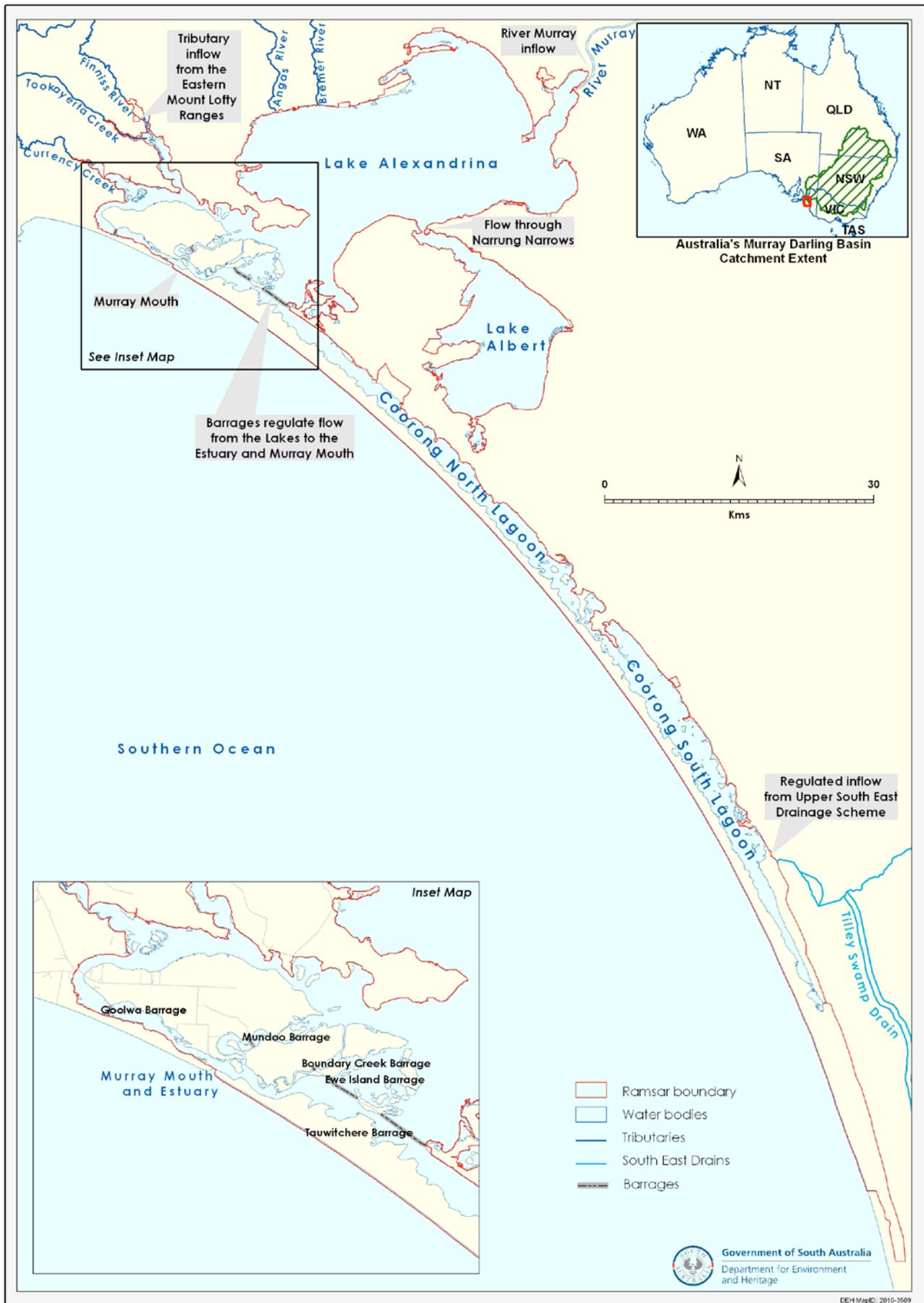


Fig. 1. The Coorong, Lower Lakes and Murray Mouth region

lected 486 soil samples.

The use of vegetation to combat acidification by stabilising exposed lake beds and facilitating sulfate reduction through carbon addition has provided other benefits aside from the management of ASS. The bioremediation project has now developed into a 5-year restoration program utilising community nurseries and employing community members to undertake restoration actions.

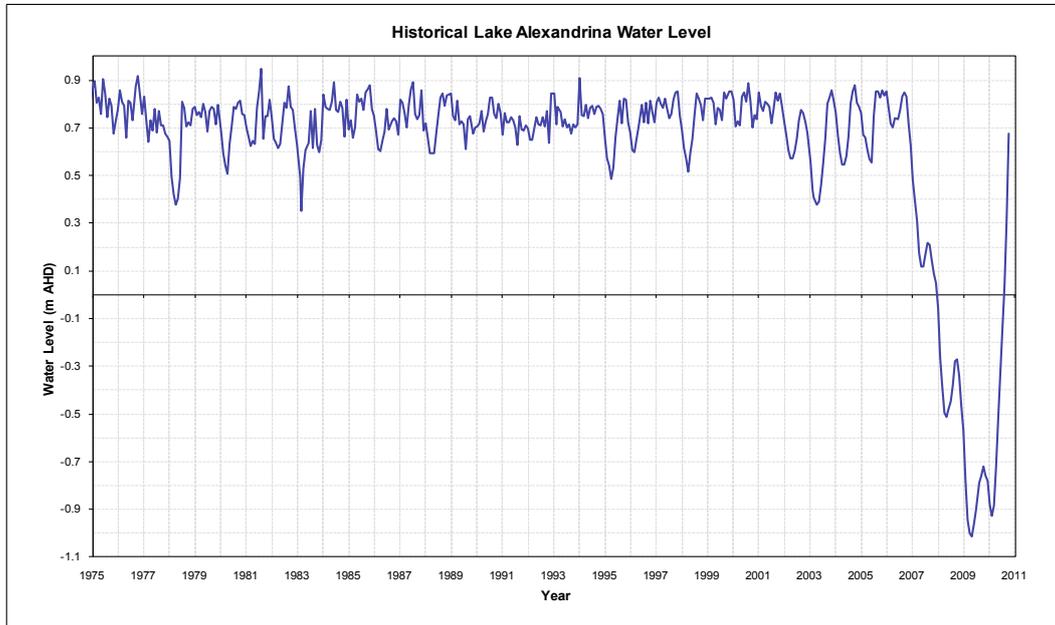


Fig. 1. Lake Alexandrina water levels (1975–2011).

MOBILIZATION OF ACIDITY AND METALS DURING REFILLING OF A DRIED WETLAND: A COMPARISON OF LABORATORY AND FIELD DATA

by

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The mobilization of acidity, metals and metalloids from oxidised acid sulfate soils is dependent on both chemical (mineral dissolution, exchange, sorption) and physical (advection, diffusion, dispersion) processes, i.e. it is a reaction-transport problem. Predicting the impacts of contaminant mobilization on water quality or ecosystem recovery following drying phases using models is difficult because the impacts are highly scenario dependent. Scaling issues also make it difficult to extrapolate laboratory-based data to the wetland scale, particularly due to the inherent spatial and temporal heterogeneity of natural wetland systems. During a recent long-term drought in south-eastern Australia, many wetlands (containing sulfidic soil materials) dried completely. Over this period, different views were held by stakeholders on what the impacts might be following refilling of these wetlands, primarily due to a lack of data and relevant case studies.

A rapid metal mobilization study was undertaken on acid sulfate soil materials from a dried wetland (Nelwart Lagoon) adjacent to the River Murray in South Australia, which was previously disconnected from the river to maximize water savings (Shand et al. 2009). The study site is an ox-bow lake that was disconnected from the River in late 2007. The marginal sandy soils and dominant clay soils acidified as the wetland dried due to the presence of hypersulfidic materials (Shand et al. 2010). Refilling of the wetland in 2009 (Fig. 1) offered the oppor-



Fig. 1. Nelwart Lagoon prior to refilling and post refilling.

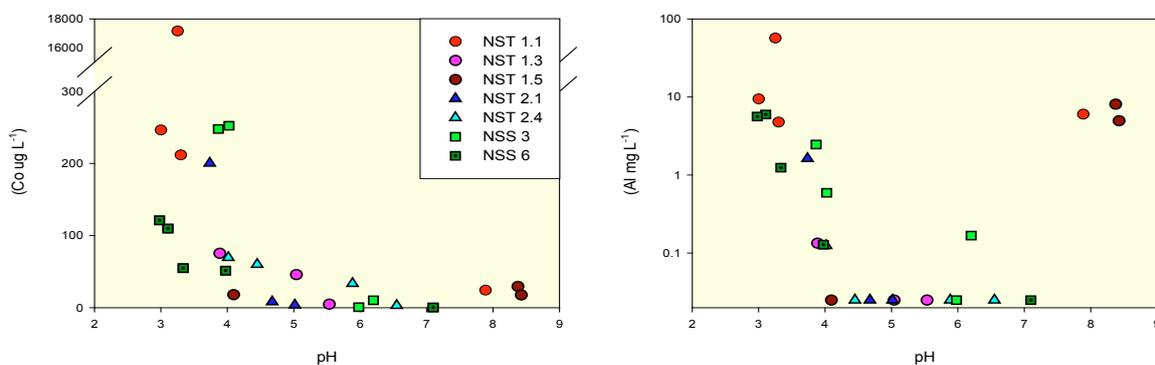


Fig. 2. Relationship of selected metal concentrations with solution pH.

tunity to monitor impacts on surface water as well as soil layers, and to assess the timescales over which recovery is likely to take place by natural remediation.

Analytical data on the soils prior to refilling showed that the chemistry of the soils was spatially heterogeneous (e.g. net acidity varied from -153 to 1318 mol H⁺/tonne, with a median of 98 mol H⁺/tonne). Surface mineral efflorescences attested to the fractionation of acidity towards the surface. Rapid (24 hr) metal release experiments with de-ionized water indicated hazards from acidification and metal and metalloid release. The range in pH and solute concentrations highlighted the extreme spatial heterogeneity across the wetland and with depth. The main control on the release of metals and metalloids was the pH of the soil solution (Fig. 2), although colloidal transport may be important at higher pH levels.

For a number of metals (e.g. Ni, Co), the highest concentrations were released from the shallowest soil layers. This correlated with many major elements such as Cl and SO₄, as well as high TAA and retained acidity.

During refilling of the wetland, acidification of the source River Murray water was very rapid (minutes), as alkalinity was consumed during soil–water interactions. There was also an initial rapid release of many metals (Figure 3). Although the pH of the surface water in the wetland increased to circumneutral over the following days as the wetland filled, alkalinity showed a significant decline. The pH of the surface waters then decreased to pH < 4 as buffering by alkalinity was lost. Most metals and metalloids were lost from solution after the initial pH increase, but increased again as pH fell (Fig. 3), although not to the same concentration as during the initial flush. The surface waters in the wetland remained acidic for another 6 months. Further increases in metals occurred over this timeframe, but were mainly related to evaporation, with most solutes behaving conservatively in solution. Following a top-up of the wetland in December 2010 (Fig. 3), the surface soil materials became sulfidic as internal alkalinity generation progressed via reduction reactions. Metal concentrations then returned to low levels.

The rapid metal mobilization tests were effective at identifying which metals and metalloids would be released to solution during refilling of the wetland. Furthermore, with the dilution factors used in the extractions (15 g field moist soil: 150 ml deionized water), the concentrations were of the same order of magnitude as found in the waters. However, the dynamics of metal mobilization in the surface waters cannot be explained by such metal release studies due to the number of potential scenarios with regard to the watering regime and soil–surface water–groundwater interactions. Laboratory dynamic tests are likely to prove much more useful in determining within-soil dynamics. Nevertheless, the impacts on surface waters are largely controlled by hydrological processes, and any laboratory results should be extrapolated with caution. Extensive cracking and ped formation during initial drying (Fig. 1), as well as observed stratification in water quality, remain as challenges to detailed modelling.

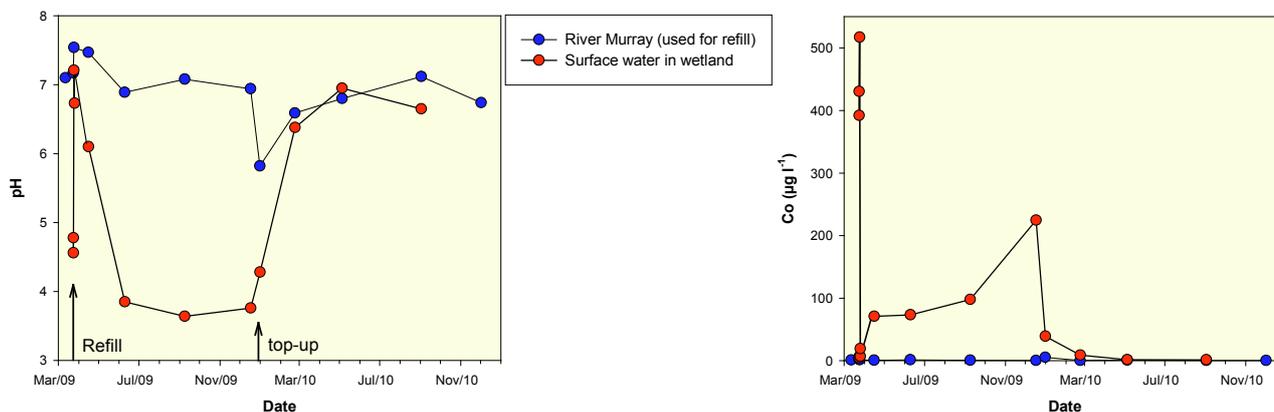


Fig. 3. Monitored pH and dissolved cobalt data for a wetland and River Murray during and post refill.

The rapid tests provided a good indicator of the hazard from acidity and trace metals and form useful underpinning data for risk assessment. The real-time monitoring of the wetland provided a number of conclusions relevant to wetland management where the soils contain sulfidic or sulfuric materials. In particular, the impacts from refilling dried wetlands containing acid sulfate soils can be severe. The data also show that the process of natural remediation can take a significant time if insufficient alkalinity is present within the system or generated by natural reactions, thus providing important underpinning science for the management of wetlands impacted by acid sulfate soils.

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MICROBIAL COMMUNITY IN BOREAL ACID SULFATE SOIL: VERTICAL DISTRIBUTION, ACTIVITY ASSESSMENT AND POTENTIAL FOR GREENHOUSE GAS EMISSIONS

by

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Acid sulfate (AS) soils generate both on-site and off-site environmental problems. In addition to well-known ones (Fe and H₂S toxicity to plants in flooded soils, Al toxicity to plants in drained soils, plant nutrient deficiencies resulting from imbalances in the availability of soil nutrients, sulfuric acid formation and consequent chronic toxicity in streams and reservoirs causing massive fish kills), we propose another potentially serious off-site effect of AS soils: we hypothesize that they might also be a significant source of greenhouse gases.

It has been found that subsoil horizons of Finnish AS soils contain significant amounts of organic carbon (e.g. Yli-Halla 1997) and mineral nitrogen (Paasonen-Kivekäs and Yli-Halla 2005). The occurrence of large amounts of organic matter and nitrogen in subsoil could facilitate large emissions of carbon gases, namely CO₂ and CH₄, and nitrogen gases, especially N₂O, if the soil conditions support the required microbial transformations.

The rate of decomposition of soil organic matter largely depends on the activity of the soil microbial community. Although the physicochemical properties of AS soils have been extensively investigated, there is a lack of data on the microbial communities in the boreal AS soils common along the coastline of the Baltic Sea. In a recently published study (Šimek et al. 2011), basic microbiological properties of the AS soil located near Helsinki were determined, and compared with the properties in a non-AS soil from the same region. The main goal was to obtain basic information on the microbial community in a typical boreal AS soil. The present paper summarizes our previous findings.

The soils were sampled from the research farm of the University of Helsinki, located on the Gulf of Finland, which is part of the Baltic Sea (for a site description, see Mokma et al. 2000). The AS soil is in agricultural use and was classified as a Sulfic Cryaquept. The non-AS soil was located approximately 1000 m from the AS soil and was classified as Typic Cryaquept.

The carbon and nitrogen content and microbial activity, prerequisites for greenhouse gas production, were determined in the AS and non-AS soils to depths of 165–180 cm. The two pedons differed substantially in the C_{org} content

in the C horizons, the content being much lower in the non-AS ($0.30 \pm 0.01\%$) than in the AS soil ($3.20 \pm 0.02\%$). The depth distribution of total nitrogen in the soil profiles roughly followed the pattern of C_{org} . Consequently, large carbon and nitrogen stocks ($110 \text{ Mg } C_{\text{org}} \text{ ha}^{-1}$ and $15 \text{ Mg } N_{\text{tot}} \text{ ha}^{-1}$) were confirmed in the C horizons of the AS soil but not in the non-AS soil ($30 \text{ Mg } C_{\text{org}} \text{ ha}^{-1}$ and $5 \text{ Mg } N_{\text{tot}} \text{ ha}^{-1}$). Moreover, in the BC and C horizons, high ammonium concentrations were found, reaching $84.0 \pm 0.6 \text{ mg kg}^{-1}$ in the Cg2 horizon of the AS soil.

Basal respiration (BR), determined as CO_2 production during laboratory incubation of soil samples in aerobic conditions, differed substantially among the different horizons of both soils (Fig. 1A). Surprisingly, BR in the AS soil was higher in the deepest horizon (Cg2) than in the Ap horizon, although the difference was not statistically significant. BR followed roughly the same pattern in soil profiles as the concentration of C_{org} .

In both the AS soil and the non-AS soil, the changes in substrate-induced respiration (SIR) with depth were similar to those for BR. In the non-AS soil, SIR decreased from its highest value in the Ap horizon down through the Bg1 and Bg2 horizons, and then slightly increased in the deeper horizons (Fig. 1B). In the AS soil, SIR decreased from its highest value in the Ap horizon down through the next three horizons (Bg1, Bg2, and Bgjc), but then substantially increased in the three deepest horizons, BCgc, Cg1, and Cg2. Like BR, SIR in the AS soil was surprisingly high (about $33 \mu\text{g } \text{CO}_2\text{-C g}^{-1}\text{h}^{-1}$) in the Cg2 horizon of the AS soil.

The abundance of culturable bacteria (expressed as the CFU counts) in the AS soil was high in the surface horizon (Ap), decreased in the B horizons, and again increased to the highest values in the C horizons. The average values (CFU $\times 10^6 \text{ g}^{-1}$ dry soil) for Ap, Bgjc, and C horizons were 27.89 ± 1.01 , 0.32 ± 0.06 , and 53.06 ± 7.44 , respectively. The pattern of CFU counts in the non-AS was similar to that in the AS soil, but abundances were generally lower in the non-AS soil than in the AS soil. In the AS soil, the ratio of culturable to total cells (C/T) was highest in the deeper horizons, lowest in the B horizons, and intermediate in the surface horizon. In the non-AS soil, the C/T ratios had two maxima, one in the Bg1 horizon and the other in the 1Cg horizon.

We suspect that the microbial community found in the subsoil of the AS soil originated with the genesis of AS soil and has been supported by the large stocks of accumulated carbon and mineral nitrogen in the C horizons. If these permanently water-saturated subsoils are cultivated and exposed to oxygen and their microbial activity consequently increases, large carbon and nitrogen stocks are likely to be mobilised, resulting in increased emission of greenhouse gases.

CONCLUSIONS

Boreal AS soils may contain more organic carbon and total and mineral nitrogen than corresponding non-AS soils. The surprisingly high microbial abundance of culturable cells and microbial activity in the C horizons of the AS soil is probably caused by microbial communities formed during the genesis of these soils and that still exist but remain largely inactive (unless the soil is drained and aerated). The abundant carbon and mineral nitrogen stocks in the deep layers of AS soils serve as a substrate and provide nutrients for enhanced aerobic microbial growth when oxygen diffuses into the layers. The mineralization of temporarily buried organic matter in the subsoil of AS soils can be conducive to large emissions of CH_4 , CO_2 and N_2O . Additional studies on boreal AS soils are needed to assess their potential contribution to increases in greenhouse gas fluxes.

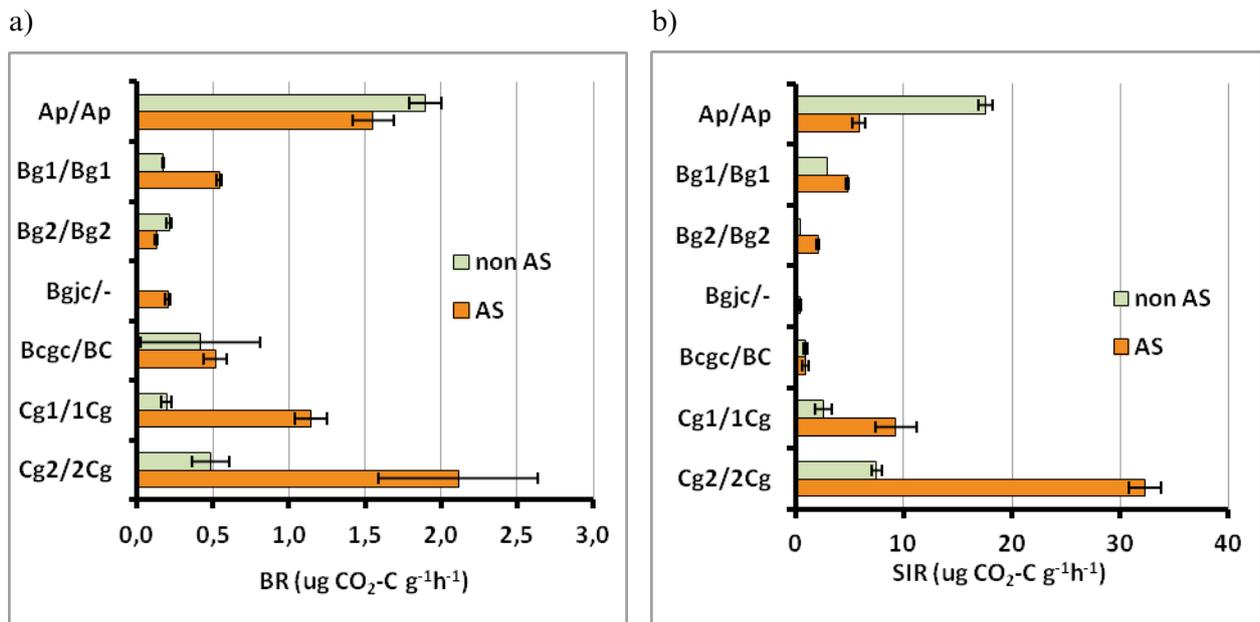


Fig. 1. Basal respiration (BR) (A) and substrate induced respiration (SIR) (B) in different horizons in the AS and the non-AS soil. Values are means and standard deviations of five replicates.

ACKNOWLEDGEMENT

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NITROUS OXIDE EMISSIONS FROM ACID SULFATE SOIL AT HIGH AND LOW GROUNDWATER LEVEL IN A LYSIMETER EXPERIMENT

by

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In Finland, the discharge waters of more than 200 000 ha of cultivated acid sulfate (AS) soils have reduced the quality of recipient waters along the Baltic coast because of sulfuric acid production by the oxidation of sulfides in these soils (Roos & Åström 2006). In subsurface-drained AS soils, the sulfidic sediments formed during the Litorina stage of the Baltic Sea are typically located deeper than 1 m in the subsoil C horizons, which also contain large amounts of carbon and nitrogen and are potentially high in microbial activity (Simek et al. 2011). Controlled drainage and a high groundwater level are possible means of mitigating the oxidation and acid formation in AS soils. However, a high groundwater level can concurrently increase denitrification and the emission of nitrous oxide (N₂O) from soil to the atmosphere (MacDonald et al. 2010). For this reason, N₂O emissions from acid sulfate soils with high and low groundwater levels were monitored in a lysimeter experiment. The monitoring of N₂O emissions from acid sulfate soils was carried out in 2010 as part of the CATERMASS LIFE+ project (<http://www.ymparisto.fi/syke/catermass>) in a lysimeter experiment set up to study the impacts of the groundwater level on the growth of reed canary grass and changes in the soil chemistry and acidity of discharge waters (Virtanen et al. 2010). Eight lysimeters were cropped with reed canary grass, and two lysimeters were left bare. The lysimeters were 200-litre PVC tubes (diameter 50 cm) containing an 80-cm-thick undisturbed subsoil monolith with oxidized (B horizons) and reduced (C horizon) layers of AS soil overlain by a 20-cm layer of non-acid topsoil. The AS soil taken from the Patoniitty field (60°13' N, 25°0' E) at the Viikki Experimental Farm of the University of Helsinki was classified as Sulfic Cryaquept (Mokma et al. 2000, Yli-Halla et al. 2008), and topsoil from the field of Taka-Hakala had a humic fine sandy texture. The experiment was carried out in a glasshouse compartment with a glass roof and wire-netted walls at the Viikki campus of the University of Helsinki. The lysimeters were equipped with groundwater control and instrumented for measurements of the redox potential, water content, temperature and pore water composition at various soil depths. The experimental treatments were drainage down to the top of the originally reduced C horizon in a cropped lysimeter (LWC), and waterlogging up to the bottom of the topsoil in a cropped lysimeter (HWC) and in a bare lysimeter (HWB).

The groundwater levels were adjusted to the aimed depths at the beginning of the growing season. One week later, all lysimeters were fertilized with solutions

containing recommended amounts of nutrients for reed canary grass (N 90, P 5 and K 40 kg/ha). The lysimeters were watered from above at 2–3-day intervals with artificial rainwater according to the local long-term average rainfall. Gas emissions were measured biweekly with closed chambers from early May to mid-October, and daily during two 3-day periods with simulated heavy rain. The emission chambers were steel cylinders (diameter 16 cm, total height 25 cm inserted 10 cm into the soil) closed with neoprene membrane lids during measurement. At 1, 20, 40 and 60 min after closing the chambers, gas samples (7 ml) were taken into 3-ml Exetainer[®] vials capped with butyl rubber septums. The gas composition was analysed by GC. The concentrations of dissolved nitrogen and carbon in pore water at 10 cm depth were determined at each emission measurement (Shimadzu TOC-VCPH/CPN).

In all experimental treatments, the amounts of dissolved nitrogen and N₂O emission were largest in early May immediately after N fertilization. In the cropped soil, they decreased rapidly over time and remained low during the rest of the monitoring period (Fig. 1). In contrast, the bare soil was much richer in dissolved N compared with the cropped soil immediately after fertilization. For this reason, the amounts of dissolved N and N₂O emission in the bare soil decreased more slowly over time than in the cropped soil. With a high groundwater table, the water content at 15 cm depth was always about 40%, which corresponded to a maximum of 10–15% air space and degrees of saturation exceeding 70%. Such conditions generally indicate at least temporarily deficient aeration in soil. Accordingly, the largest N₂O emissions were observed immediately after fertilization. In this experiment, however, oxygen deficiency did not impede the growth of reed canary grass, even with a high groundwater level. Instead, high groundwater increased the growth of reed canary grass, probably by enhancing the plant water supply and reducing acidity (Epie et al. 2012).

With a low groundwater table, the water content in the topsoil during the growing season was usually only about 15% (corresponding to 40% air) and the

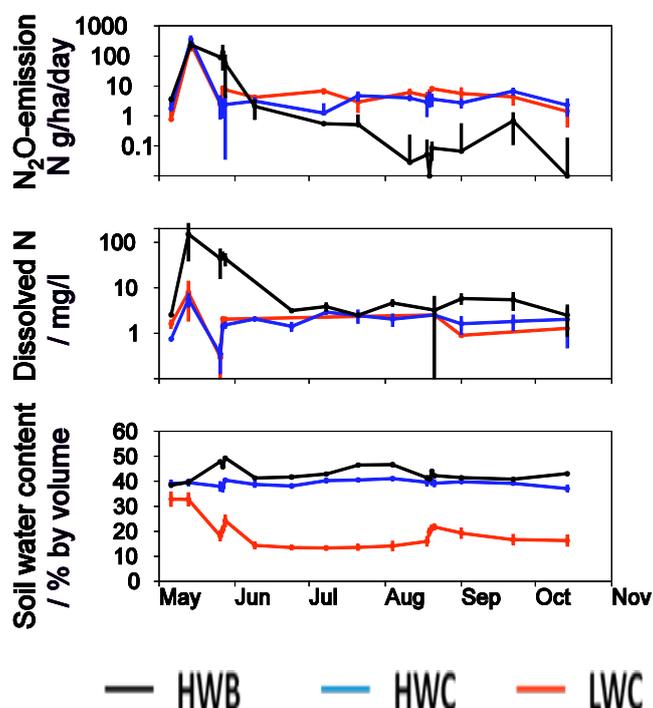


Fig 1. The emission of N₂O from soil, the concentration of dissolved N in pore water (10 cm depth), and the water content (15 cm depth) at different experimental treatments (mean ± standard error, n = 2-4).

degree of water saturation was below 30%. In such soil, plants do not generally suffer from oxygen deficiency and the amount of denitrification is small. However, at the time of the largest N₂O emissions, immediately after fertilization, the water contents in the low groundwater level treatments were still above 30% (degree of saturation about 60%), allowing significant denitrification. The large N₂O emissions early in the monitoring period were no doubt caused by the denitrification of fertilizer nitrogen. In cropped lysimeters, the N₂O emissions were roughly similar, irrespective of the groundwater level. The total N₂O emissions during the 161-day monitoring period corresponded to about 4.0 ± 0.7 kg (N) / ha in all treatments

According to the results, nitrogen fertilization causes large N₂O emissions from AS soils immediately after fertilization in a similar manner to other soil types. Plant nutrient uptake efficiently reduces the dissolved N in pore water and the N₂O emissions from soil to the atmosphere. Although the cumulative N₂O emissions were rather high, a high groundwater level did not increase the total N₂O losses during the monitoring period. The results of this experiment do not support the view that a high groundwater level would significantly increase N₂O emissions from AS soils to the atmosphere.

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SULFIDIC SEDIMENTS AND ACID SULFATE SOILS IN SWEDEN

by

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In Sweden, sulfidic sediments and acid sulfate (AS) soils occur in areas that have been covered by marine or brackish water after the retreat of the latest inland ice. These deposits are present in low-lying areas in eastern Sweden, but most frequently occur along the coast of northern Sweden. The latter area has been subjected to larger isostatic uplift than southern Sweden, and sulfidic sediments deposited on former deep bottoms have consequently been uplifted.

During the last ten years, several studies on AS soils and sulfidic sediments have been carried out at the Geological Survey of Sweden (SGU). One main objective has been to evaluate whether data collected by SGU can be used to identify these deposits. This evaluation includes biogeochemical data, maps of unconsolidated deposits and airborne geophysical data (Sohlenius et al. 2004). Another objective has been to evaluate different methods to identify sulfidic sediments. These include ground geophysical measurements of electric resistivity (Sohlenius et al. 2007), and geochemical characterisation of both AS soils and sulfidic sediments (Sohlenius & Öborn 2004, Lax & Sohlenius 2006). Last year, SGU initiated a survey in northern Sweden, which includes the characterisation of sulfidic sediments and AS soils with the same methodology as used by the Geological Survey of Finland (GTK). The first results from this survey are presented on a poster at this conference (Aroka et al. 2012). Furthermore, SGU has started to store observations of sulfidic deposits made by external actors in a database.

It is often, but not always, possible to identify sulfidic sediments and AS soils in the field. In northern Sweden, sulfidic sediments are often coloured black by iron monosulfides. The sulfidic sediments further south are often dominated by pyrite (Sohlenius and Öborn 2004) and are consequently not black in colour. The AS soils are often characterised by long vertical cracks that are coated with iron hydroxides and sometimes with the addition of the yellow mineral jarosite. It has been shown that many elements are mobilised and leached out from the AS soils, which causes high concentrations of these elements in watercourses (Lax 2005). The total contents of trace elements are, however, not higher in the sulfidic sediments than in other fine-grained deposits in Sweden. The intense leaching of certain elements is due to strong weathering caused by the acid conditions in the AS soils. The mobilised elements may partly emanate from the oxidised sulfide minerals, but weathering of silicate minerals is probably the most important source (Sohlenius and Öborn 2004).

SGU's maps of unconsolidated deposits can be used to identify areas where sulfidic sediments may occur. In southern Sweden, these deposits often occur in areas mapped as clay gyttja. In areas situated close to the coast of northern

Sweden a large proportion of the clay or silt occurs in sulfidic sediments. Observations of sulfidic sediments are most frequent in areas that have recently been uplifted above the sea level. SGUs shoreline displacement data and the maps of unconsolidated sediments have been combined by the use of ArcGIS, and the resulting GIS product can be used to identify areas where sulfidic sediments and AS soils are likely to occur. The resulting map is supported by observations from both SGUs surveys and external actors, e.g. the Swedish Transport Administration.

SGUs biogeochemical data show the content of several elements in plants sampled in small watercourses. The content of certain elements (e.g. nickel and yttrium) in these plants are often relatively high in areas with AS soils. This is due to the extensive leaching of these elements from the AS soils. Certain other elements (e.g. lead) are, however, not extensively leached from the AS soils and consequently not enriched in the plants. By using the Ni:Pb and Y:Pb ratios, calculated from the biogeochemical data, combined with the map of unconsolidated deposits, it is possible to identify some of the areas where AS soils have developed (Lax 2005).

Areas with sulfidic sediments often coincide with areas with a low electrical resistivity, which is shown by results from SGUs airborne geophysical measurements. However, these data only give a rough view of where sulfidic sediments may occur. To obtain more detailed information, several ground geophysical methods, measuring the electrical resistivity, have been tested. These studies include sites in both northern and southern Sweden, where the occurrence of sulfidic sediments has been documented by stratigraphic studies. The results



Fig. 1. An excavation in an acid sulfate soil situated close to the coast in northern Sweden. The uppermost metre of the profile is characterised by the occurrence of iron hydroxides and a pH of around 3.5. The acid conditions were probably established when the area was cultivated and the groundwater table lowered. The deepest-lying sediments in the lower part of the excavation are sulphidic sediments, which are coloured black by iron monosulfides and have sulphur contents between 0.5 and 1%. These sediments have started to oxidise during the short period since the excavation was made, explaining the greyish colour of the originally black, lowermost sediments.

show that the sulfidic sediments have a lower resistivity than surrounding deposits, which is probably due to a relatively high salt concentration in the pore water of these deposits. Ground geophysical data can consequently be used to interpret both the thickness and areal extension of sulfidic sediments. These interpretations must, however, be confirmed with results from direct observation (drillings or excavations).

SGUs data can be used to interpret where sulfidic sediments occur and where AS soils have developed. These interpretations must, however, be confirmed with field studies. Furthermore, modern SGU data do not cover all parts of Sweden where sulfidic sediments may occur. In the forthcoming years, more data will be collected, improving the possibility of delineating areas where these problematic deposits occur. Furthermore, in northern Sweden, the SGU database of unconsolidated deposits is currently being updated and observations of sulfidic sediments are being included. As a consequence of these activities, a database with data from the most problematic areas will be available in the future.

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COLUMN LEACHING EXPERIMENTS ON ACID SULFATE SOILS FROM THE RISÖFLADAN EXPERIMENTAL FIELD (VASA, FINLAND)

by

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The authors are participating in a three-year project, PRECIKEM. The aim of the project is to find and demonstrate chemical methods for mitigating the oxidation of sulfides and the simultaneous formation of sulfuric acid on farmlands. Subsurface irrigation with oxidation-inhibiting chemicals mixed into irrigation water is an important part of the project. This paper presents laboratory-scale column leaching tests with water, a dye tracer solution and calcium carbonate suspensions to simulate the large-scale irrigation experiments. Calcium carbonate injected as a suspension directly into the environmentally critical subsoil is not considered merely as a neutralizing agent but also as an oxidation-inhibiting chemical de-activating the acidophilic bacteria that mediate pyrite oxidation.

Acid generation by acid sulfate soils depends not only on the form and concentration of iron sulfides present in the soil but also on the permeability and structure of the soil. Especially important is the presence of water-conducting channels and wide pores in the soil. Depending on the soil structure, part of the sulfides may be inaccessible to oxidation.

The structure and properties of soil from the acid

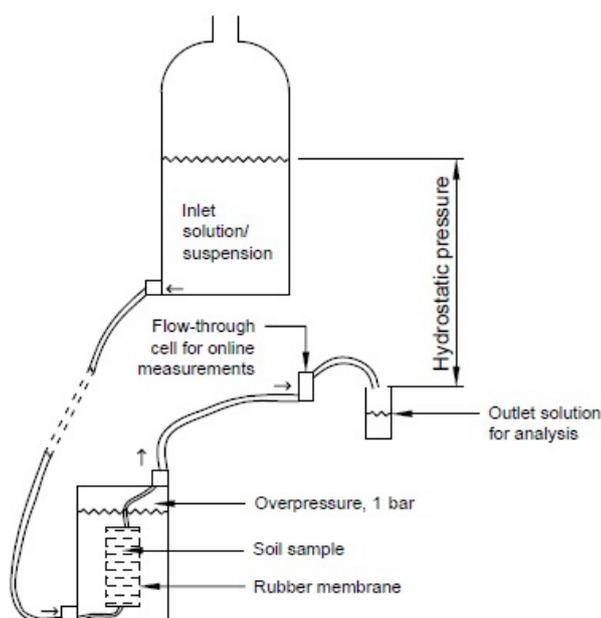


Fig. 1. Experimental set-up for the column leaching tests.

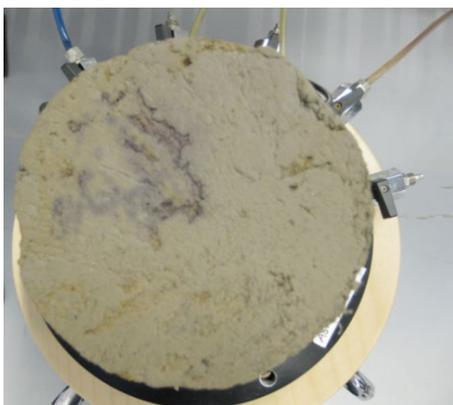


Fig. 2 (on the left). Cross-section of a soil sample after three days of flow of Alizarin solution. The dark-violet colour marks the regions around the channels in the soil where the dye was adsorbed.



Fig. 3 (on the right). Cross-section of a soil sample after the flow of 6.4 dm³ of calcium carbonate suspension through the column during eight days.

sulfate soil region at Risöfladan in Vasa was investigated by passing water and solutions/suspensions of selected reagents through soil samples in a column apparatus. Samples of soil were collected from the Risöfladan experimental field in Vasa by drilling plastic tubes into the ground. The obtained cores of 14.2 cm in diameter were then cut into 10–15-cm-long samples of the shape of a cylinder. The samples were placed in the column apparatus and the flow of water or the solution or suspension was initiated by employing a hydrostatic pressure difference of up to 3 m (Fig. 1).

Experiments with the aqueous solutions of Alizarin Red S dye showed that the flow of water through the soil is not uniform, as illustrated in Figure 2. Wide pores or even channels exist in the structure of the soil, and water or a solution preferably flows through them. Experiments with the suspensions of calcium carbonate showed that it is possible to introduce calcium carbonate to the soil without the destruction of the soil structure, as shown in Figure 3.

The flow rate, pH, conductivity and the concentration of sulfate, nitrate and chloride in the effluent were measured to characterize the soil samples and the emission of sulfuric acid from the soil. There is considerable variation in the permeability of the soil depending on the depth, but also between various samples taken from the same depth. Figures 4 and 5 show the results from a leaching test started with water but changed to a calcium carbonate suspension (5 g dm⁻³) after 9.8 dm³ water was passed through. In the beginning, the flow rate, indicated by the green line in Figure 4, goes down very rapidly. To ensure a reasonable flow, the driving hydrostatic pressure difference was increased from 60 to 160 cm after passing 1.8 dm³ of water through. The increase in the driving hydrostatic pressure difference probably opened new channels, resulting in a disproportionate increase in the flow rate. A minor increase in the driving hydrostatic pressure difference, and consequently in the flow-rate, took place when changing water to a calcium carbonate suspension, but in general the flow rate decreased slowly during the 5-day experiment.

The sulfate originally present or produced in the oxidation process was washed out from the soil, as illustrated by the decreasing concentration in the effluent. However, after introducing the calcium carbonate suspension, a sudden increase in the sulfate concentration of the effluent was observed. The minor fluctuation in the sulfate ion concentration and conductivity (Fig. 5) can be explained by the changes in the flow rate. As shown in Figure 5, pH is fairly constant at ca. 4, but suddenly increases to ca. 6 after introducing the calcium carbonate suspension.

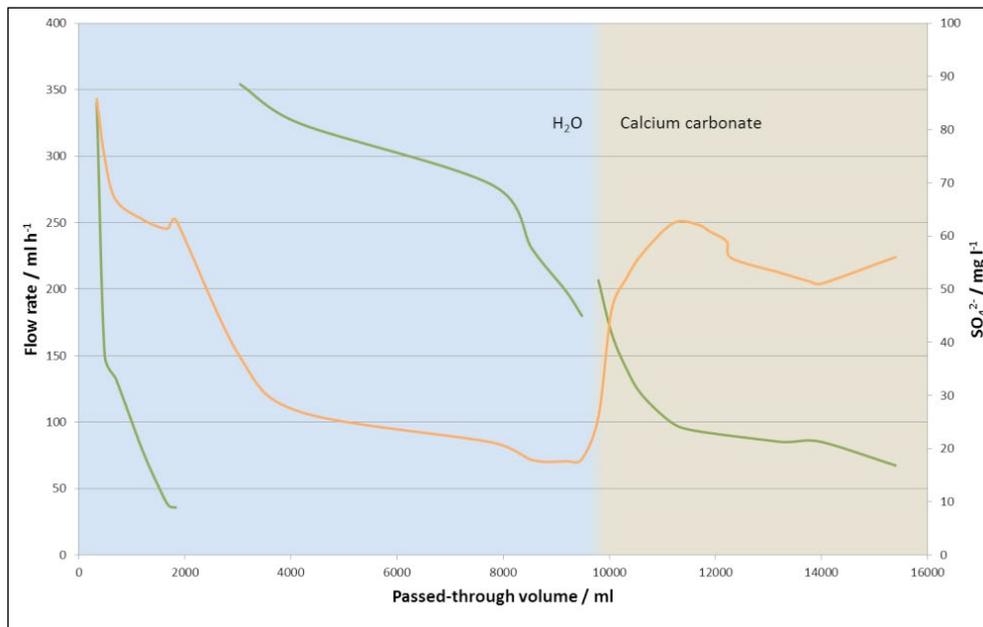


Fig. 4. The green line and left y-axis indicate the flow rate in a column leaching experiment. The driving hydrostatic pressure difference was increased twice, at the passed-through volumes of 1.8 dm³ and 9.8 dm³, resulting in discontinuities in the flow rate. The orange line and right y-axis indicate the sulfate ion concentration in the effluent of the experiment. The 10-cm soil sample, taken from the depth of 60...70 cm, was leached with 9.8 dm³ of pure water for two days. After this, 5.6 dm³ of calcium carbonate suspension (5 g dm⁻³) was used in the leaching for three days.

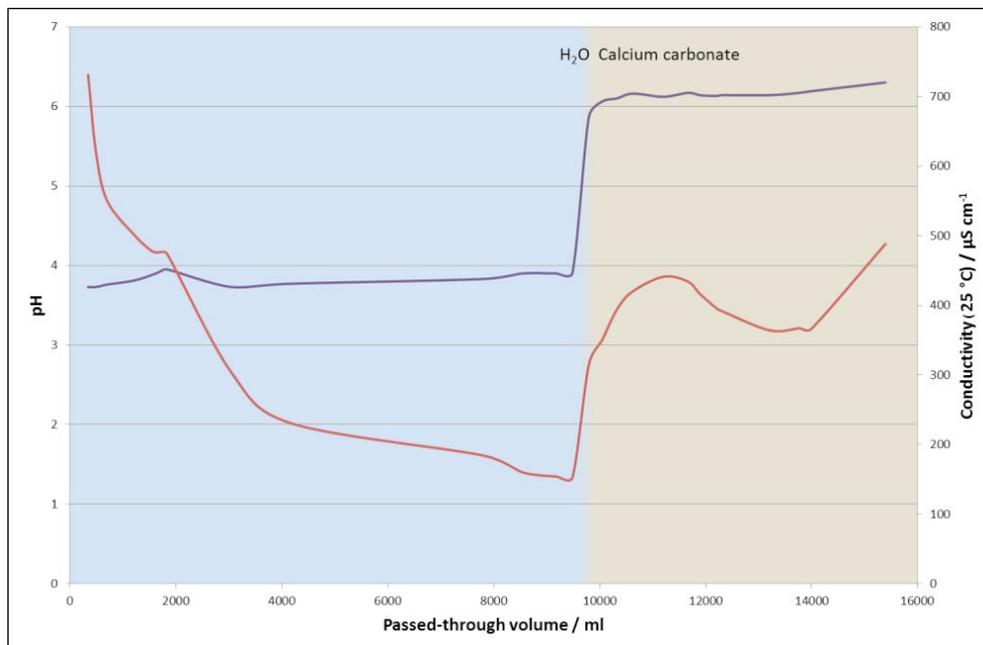


Fig. 5. The pH (blue curve and left y-axis) and conductivity (red curve and right y-axis) of the effluent of the column leaching experiment discussed in Figure 4.

ACKNOWLEDGEMENTS

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ARSENIC AND ZINC BIOAVAILABILITY IN ACID SULFATE ENVIRONMENTS

by

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We carried out detailed arsenic speciation and trace metal analysis in ground waters, surface waters and drain waters from our field sites using high-performance liquid chromatography–inductively coupled plasma mass spectrometry (LC-ICP-MS) and ICP-MS analysis. Arsenic and zinc concentrations fluctuated in drain waters after rainfall events to concentrations that exceeded species protection levels and Australian water quality guidelines. Inorganic arsenic species, arsenate and arsenite accounted for all of the mobile arsenic species, with concentrations of up to 22 µg As l⁻¹ predominantly as arsenate, and zinc concentrations of up to 80 µg l⁻¹. Following these findings, we are trialling the use of diffusive gradients in thin film devices and biological modelling tools in order to predict the potential bioavailability of these contaminants in drain waters to aquatic organisms.

ACID SULFATE SOILS AND THEIR MANAGEMENT: A GLOBAL PERSPECTIVE

by

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The soil materials we call *acid sulfate soils* have been recognised for many centuries as having important properties and behaviour in common. Previously, this group of soil materials has been identified by names including *argilla vitriolacea* (Linnaeus, 1735), and colloquially as *katteklei* (i.e. *cat clay*) soils, with the term *cat* implying “malign and mysterious qualities” (Dent & Pons, 1995). Such historic *ad hoc* classification implies that there has long been utility in grouping these soil materials together.

At the 1st International Symposium on Acid Sulphate Soils held in Wageningen in 1973, Professor Leen Pons defined acid sulfate soils “as all materials and soils in which as a result of processes of soil formation, sulfuric acids either will be produced, are being produced, or have been produced in amounts that have a lasting effect on main soil characteristics”. The essential concept common to these definitions of acid sulfate soil was the effect of (or potential for) sulfuric acid production as a result of the oxidation of iron sulfide minerals in causing severe acidification (e.g. soil pH < 4). This concept is still central to current definitions of acid sulfate soil in the main soil taxonomies (e.g. USDA Soil Taxonomy, World Reference Base, The Australian Soil Classification).

The initial concept of what constitutes *acid sulfate soil* was underpinned by a considerable body of outstanding science conducted by many researchers around the globe both before 1973 and after. This research largely focused on understanding the formation, nature and distribution of these soil materials, the examination of acidification-related issues arising from their mismanagement, and on the management of acid sulfate soils to prevent and ameliorate acidification. However, since the last global perspective taken on acid sulfate soils (i.e. Dent and Pons, 1995), our knowledge of the processes and environmental consequences associated with soil materials whose properties and behaviour are dominated by their iron and sulfur redox biogeochemistry has continued to expand considerably, including (n.b. further details and references to the research outlined below can be found in the recent review by Sullivan et al. (2011)):

- elucidating further the role of both sulfide and secondary minerals in the behaviour and properties of these soil materials. This includes developing a better understanding of:
 - the mineralogy, formation and distribution of monosulfide minerals such as greigite (Fe₃S₄) and mackinawite (tetragonal FeS) and the role of these monosulfides in controlling the behaviour of soil materials when in sufficient concentrations;
 - the pedological conditions that confer stability, or conversely instability, to jarosite (KFe₃(SO₄)₂(OH)₆), a common secondary mineral of many sulfuric acid sulfate soils, and;

- the widespread distribution of schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)$) and its likely importance in controlling the behaviour of sulfuric acid sulfate soil materials (n.b. schwertmannite was only officially named in the early 1990s);
- understanding the conditions that are conducive to the production and emanation of a wide variety of often noxious gases (e.g. H_2S and SO_2) from acid sulfate soils;
- understanding the conditions that lead to chronic scalding (i.e. de-vegetation) of acid sulfate soil landscapes and the management approaches that can be used to successfully treat such areas;
- determining the importance of acid sulfate soil biogeochemistry on the mobilization of a wide range of metals, metalloids, nutrients and rare earth elements into the waterways of landscapes containing these soil materials;
- developing analytical techniques for acid sulfate soil materials that are low cost and accurate (and hence suited for routine laboratory analysis), especially for the reduced inorganic sulfide fractions and the partitioning of metal fractions into behaviourally important fractions;
- recognition of the substantial groundwater issues (i.e. severe acidification, and metal and metalloid mobilisation) that can occur in acid sulfate soil materials at appreciable distances (up to several km) from where extended and intensive groundwater abstraction has taken place;
- developing approaches that can be used for the detailed systematic mapping of likely acid sulfate soil distribution across landscapes using GIS techniques and advanced DEM.

In parallel with this expansion in our understanding of these soil materials, the term *acid sulfate soil* has, over the last decade or so, been used to accommodate a broader suite of sulfide-mineral containing and/or affected soil materials than was encapsulated in the initial concept of *acid sulfate soil*. Whether these new acid sulfate soil materials experience severe acidification is not always related to the level of concern directed towards them. What does connect these new acid sulfate soil materials with the initial concept of *acid sulfate soil* is that their properties and behaviour are dominated by their iron and sulfur redox biogeochemistry.

Such taxonomic ‘expansion’ is exemplified by recent advances in acid sulfate soil taxonomy that have broadened the range of soil materials considered to be embodied by the term ‘acid sulfate soil’ (e.g. Sullivan et al. 2010). For example, this taxonomic revision has created two new definitions of acid sulfate soil materials, “monosulfidic” and “hyposulfidic” for sulfide-containing soil materials. Soil materials in both of these classes both 1) may not or do not acidify severely upon oxidation, yet exhibit behaviours that may be dominated by their iron and sulfur redox biogeochemistry (usually involving iron sulfide minerals), and 2) can impact severely on the environment and hence are of concern to both scientists and land managers. Such taxonomic expansion for acid sulfate soils has proved useful for the recognition and management of environmental issues created by appreciable transformations involving the redox biogeochemistry of sulfur (and usually also iron) in soils and sediments (e.g. MDBA 2010; EPHC&NRMMC 2011). Such impacts need not be directly related to or caused by severe acidification processes and include:

- 1) deoxygenation of water bodies,
- 2) mobilization of metals, metalloids, nutrients and rare earth elements,
- 3) the production of noxious gases,
- 4) impacts on food security,
- 5) scalding of landscapes, and,
- 6) impacts on human health.

Our appreciation of the landscape settings in which acid sulfate soil materials occur has also broadened appreciably since the past global perspective of acid sulfate soils, often in parallel with our increased understanding of their iron and sulfur redox biogeochemistry. For example, sub-aqueous soil materials (often also acid sulfate soil materials) are now recognized as a class of soil materials in some soil taxonomies (e.g. Demas et al. 1996). There has also been recognition for soil taxonomic inclusion into *acid sulfate soil* of materials with acid sulfate soil properties and behaviour, but located deeper from the soil surface than the current 2 metres depth limit for soil materials that operates in some soil taxonomies (Yli-Halla, pers. comm.). Whereas Dent and Pons (1995) addressed only tidally-formed coastal acid sulfate soils in their global perspective, recent research has also shown a widespread occurrence of acid sulfate soil materials in:

- inland settings as a result of dryland and irrigation salinization,
- the subaqueous soils of inland wetlands, lakes and waterways etc.
- exposures of 'acid sulfate soil' regolith materials in e.g. roadside cuttings and other excavations, and
- estuarine and marine materials deposited on land as the result of dredging activities.

The regulation of certain land uses based on the presence of acid sulfate soil materials has advanced rapidly in some regions over the past decade or so. For example, in Western Australia, acid sulfate soil management is covered by the state's Contaminated Sites Act in recognition of the capacity of these soil materials to contaminate their own and surrounding environments if not managed appropriately. In the last decade across Australia, the disturbance of acid sulfate soils by developments such as roads, housing estates and marinas has now usually required prior approval from regulatory authorities. Such approval is generally only given when appropriately detailed and satisfactory Acid Sulfate Soil Management Plans (ASSMPs) have been submitted to the appropriate regulatory authorities. To meet with regulatory approval, these ASSMPs must demonstrate that no unacceptable environmental harm will result from those developments disturbing acid sulfate soil materials. These ASSMPs usually provide assurance that suitable monitoring and reporting activities will take place during the pre-development, development, and post-development phases, and that appropriate contingency planning has been undertaken should any of the agreed trigger values in the ASSMP be exceeded.

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SUBSURFACE IRRIGATION AND CONTROLLED DRAINAGE IN REDUCING THE ACID DISCHARGE TO SIIKAJOKI RIVER IN NORTHERN OSTROBOTHNIA, FINLAND

by

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The catchment area of Siikajoki River is included in the risk zone of acid sulfate (AS) soils in Finland. The river is one of the coastal rivers entering the Gulf of Bothnia, Baltic Sea, about 60 km south of Oulu. The catchment area of the Siikajoki River is principally used for agriculture and forestry. Agricultural land and a substantial part of the forest are artificially drained, subjecting the sulfidic materials in the subsoil to oxidation and resulting in the production of acidic drainage waters. As in many other coastal rivers in Finland, water quality in this river is strongly dependent on summer weather conditions and is occasionally poor. In autumn 2006 there was a dramatic decrease in fish stocks because after a very warm and dry summer, autumn rains leached large amounts of acidity from the surrounding fields and forests into the river. Following this season, AS soils have received attention in the area. It is expected that the greenhouse effect will strengthen extreme weather conditions (warm summers, wet winters), resulting in increased acid flows from AS soils.

In autumn 2009, the Siikajoki office of MTT Agrifood Research Finland (N 64° 41,2', E 25° 5,3') established a field trial located on the riverside in order to investigate drainage methods to reduce the acidic load to the river. The experimental field represents typical AS soil in the area, about 48 m above sea level, and according to Soil Taxonomy it can be classified as either a Sulfic Cryaquept with a histic epipedon, or a Typic Sulfohemist. The plough layer is organic (organic matter content approximately 18%) and the texture of the subsoil is generally dominated by either fine silt or clay. Sulfidic materials usually start at 1–2 m depth from the soil surface. The methods that were studied were: 1) subsurface irrigation to maintain the groundwater level continuously at 80–90 cm from the soil surface, 2) controlled drainage, where the outflow of drainage water was restricted but no additional water was pumped into the drainage system, and 3) conventional drainage with subsurface pipes. All the drainage plots were 2 ha in area. New drainage pipes were installed to the depth of 1.2–1.3 m. This is slightly deeper than the typical depth 1.0 m in the area. The measurements (water quality, water height and water flow) were usually recorded from drainage wells from the beginning of the spring flow in April to the end of the autumn flow in December. The weather conditions during the experimental period - with warm and dry summers and very snowy winters - were conducive to the oxida-

tion of sulfidic materials, which generated appreciable strongly acidic discharge.

Subsurface irrigation was planned to prevent the water table decrease in summer. The desired water level of 80–90 cm below soil surface was assumed to keep the sulfidic materials in a water-logged state and thus prevent their oxidation. The irrigation water (pH over 6) was pumped almost continuously from the river into the well of the drainage system. Irrigation was started in May and was stopped in mid-September (2010) and in late August (2011). The amounts of irrigated water were 5500 m³, i.e. 275 mm (2010) and 1900 m³, i.e. 95 mm (2011). The irrigation power costs in the 2 ha test area were only about €47 in 2011, and in theory, the costs in 2011 could have been about €136, but because of the demanding irrigation arrangements to maintain a sufficiently high water level in the trial area, they were about €1100.

Water tables in the conventional and controlled drainage areas fluctuated considerably during the growing seasons. A few weeks after the spring flood, the water level in the well of the conventional drainage area decreased below the trench depth. In the well of the controlled drainage area, the water level in 2010 decreased below the trench depth at the end of July and returned to this level after only a couple of weeks. The river beside the test area is more than 3 m lower than the trench depth of the test area. Thus, during a dry period the water levels in the experimental field can be relatively low.

The plots for controlled drainage and subsurface irrigation were next to each other, parallel to the river, at the lowest end of the field. They were topographically equivalent, with the sulfide layer starting about 1.4–1.5 m below the soil surface. The pH of drainage water from the controlled drainage area was continuously below pH 3.5. In the area subjected to subsurface irrigation for the whole summer, the pH of the water increased to values above 4.0 by the end of the season. The very low pH of 2.9–3.3 in both plots at the beginning of the monitoring period could have been partly caused by the oxidation and subsequent production of acidity that took place during the installation of the drainage pipes.

The discharge from the conventional drainage plot was expected to be the most acidic, because the soil profile was obviously the most effectively drained. However, the pH of the drainage water from this plot typically ranged between 3.8–4.5, being higher than in the two other plots. This outcome may be explained by two reasons. Firstly, the trench depth (1.1–1.3 m) was slightly shallower in this plot than in the others. However, a more important factor affecting the water quality was the topographic position, reflected in the characteristics of the soil profile. This plot was at the top of the test field (the field was nevertheless quite flat), and oxidation may have already been completed in the upper soil layers. Consequently, the acidic oxidation products may have been leached away earlier. Augering of the soil revealed that in a part of this plot the sulfide layer was not found within 3 m of the soil surface. However, in lower parts of the same plot it started within 1.5 m from soil surface.

Subsurface irrigation and controlled drainage methods did not have a clear effect on the obtained yield levels in first two trial years. Yields appeared to be more dependent on the surface conditions (nutrient availability and soil structure) of the ground. In 2010, the best barley yields were obtained from the subsurface irrigation area (4050 kg/ha) and the worst from the area with normal drainage (3800 kg/ha), if slag was not added to the area. If slag was added, there were no differences in yields between drainage methods. In 2011, the highest barley whole crop silage yield (9400 kg/ha) was obtained from the normal drainage area and the lowest (8700 kg/ha) from the irrigated area, but the differences in these yield results were not statistically significant. The local landowners are interested in the environmental impacts of AS soils and on the methods that are recommended to alleviate the problem. They are usually prepared to control the water level, and some of them are willing to plan irrigation arrangements, but they need financial support to cover the costs.

SENSITIVITY OF THE ENDANGERED FRESHWATER PEARL MUSSEL, *MARGARITIFERA* *MARGARITIFERA*, TO PH, IRON AND ALUMINIUM IN AN ACID SULFATE SOIL RIVER

by

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River Ähtävänjoki is one of the acid sulfate rivers on the west coast of Finland. The river has a small, population of the endangered freshwater pearl mussel *Margaritifera margaritifera*, but the reproductive success of the mussel in River Ähtävänjoki is very low. The low pH values and high iron (Fe) and aluminium (Al) concentrations periodically observed in the river water may have adverse effects on the mussel population. The freshwater pearl mussel has a glochidium larva, which is parasitic on fish. Glochidia are released in autumn into the water to infect salmon or trout, the fish host of the mussel. After the 9-month parasitic stage, the fully developed glochidia drop on the river bottom to start their benthic life, which may last up to 150 years. Especially the early life stages—glochidium larvae and juveniles—of the pearl mussel may be sensitive to low pH and metal exposure. However, to our knowledge, no tolerance tests have been performed.

Therefore, we applied laboratory experiments in which we exposed glochidia larvae, fish-attached glochidia and juveniles of the pearl mussel to low pH and increased Fe and Al by using realistic pH (6.0–4.5), Fe (0.5–2.0 mg L⁻¹) and Al (0.25–1.0 mg L⁻¹) levels observed in the present study site, River Ähtävänjoki.

The survival of glochidia released by the mussels decreased with decreasing pH, increasing Fe and increasing Al, as well as with increasing Fe + Al concentration in a 72-h exposure. All glochidia died within 24 h in pH 4.5 and Fe 2.0 mg L⁻¹. It is notable that in good conditions the glochidia lived up to 18 days in the laboratory. When infected trout, *Salmo trutta*, were exposed to increased Fe and Al from four days before to 76 days after infection, the numbers of encysted glochidia did not differ from unexposed control fish. In juvenile mussels, a slight decrease in survival was observed in lowered pH and increased Al and a combination of Al + Fe in a 168-h experiment.

The results suggest that episodes of low pH and high metal concentration may harm glochidia and potentially contribute to the local decline of *M. margaritifera*. As the freshwater pearl mussel also occurs at low densities in some other acid sulfate soil rivers of the west coast of Finland, the present results indicate that the acid sulfate problem may have consequences, among others, for the conservation of this endangered species in this region.

DEVELOPING A METHOD TO REDUCE ACIDITY AND CONCENTRATIONS OF SOLUBLE METALS IN SURFACE WATERS ORIGINATING FROM ORGANIC ACID OR SULFATE RICH DRAINAGE AREAS

by

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Acid sulfate soils and low-pH peatlands are very common in the river basins around the Gulf of Bothnia. Intensive drainage, among other factors, has increased organic acid and acid sulfate leaching from these areas. Low pH values and high metal concentrations appear during increased runoff periods, particularly after dry seasons when soil sulfides and certain metals have been oxidized (e.g. Fe) or mobilized because of low pH (e.g. Al). Flooding alone can also increase the leaching of organic acids from pristine or drained peatland areas to surface waters, causing lowered pH values. Low pH pulses caused by oxidation or increased runoff in drained areas are harmful to biota in affected streams and can even lead to visible fish kills.

To decrease the water acidity and effect of toxic metals, a low granular-lime ditch weir equipped with a pipe for lower discharges was planned. The construction of the so-called lime filter weir is based on the water neutralizing effect of limestone, mainly in pH-critical discharges, to avoid an unnecessary increase in pH and consumption of lime reactivity (and mass) other than at critical times. The higher the discharge, the larger an area of lime participates in neutralizing reactions (Fig. 1). In higher flows, the ditch water runs slowly over the limestone area with small part of the water flowing also inside the crushed lime. The dimensioning of the cross-section, the length of the weir (several metres with 0.1–0.2% gradient) or sizing and gradient of the low-flow pipe depends on the basin hydrology. These are necessary factors, for instance, in preventing weakened draining utilities upstream, in preventing excessively high velocities to enable enough time for reactions or in avoiding lime erosion. The individual pH-critical discharge of the watershed should be determined with measured data on pH values and runoff. To ensure the stability of lime and to avoid erosion in overflow situations at the end of weir, the last section is anchored, e.g. with coarse gravel or stones. To diminish the accumulation of trash, suspended solids or hydrolyzed metals, the structure can be equipped with a sediment storage pit upstream from the weir and an obstruction barrier for the pipe.

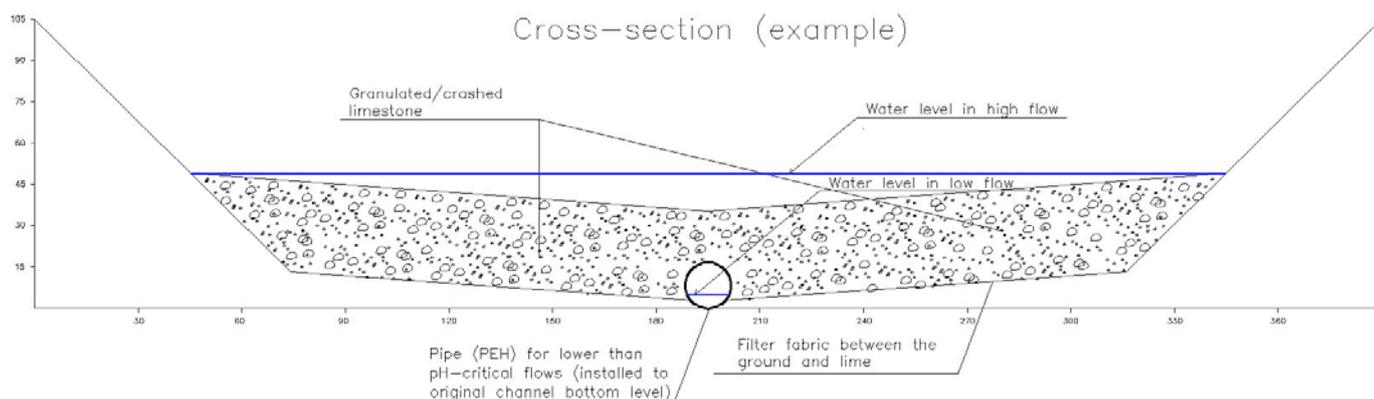


Fig. 1. The main principles of the lime filter weir (cross-section).

Three weirs were built in low-pH forest ditches ($F = 2.5$, 10 and 2.5 hectares) of the River Sanginjoki basin in March 2010 and two in ditches flowing through agricultural and forest draining areas ($F = 10^{(1)}$ and $100^{(2)}$ hectares) of River Pyhäjoki⁽¹⁾ and Lake Ruonanjärvi⁽²⁾ basins in March 2012. The surface waters in these basins flowing into the Bothnian Bay suffered from very low pH (3.6–4.8) especially in higher flows, and fish kills had already appeared in the main channels and tributaries downstream. The control for the effect of each weir comprised water samples 3–5 m upstream and downstream from the weirs and from downstream channels before and after the limed ditches, including water height measurements. Analyses included alkalinity, pH, acidity, total organic carbon (TOC), sulfate (SO_4^{2-}), phosphorus (P), phosphate (PO_4^{3-}) and the metals Al and Fe. In spring 2012, concentrations of the metals Mn, Zn, Ti and Sr were also analyzed. To approximately assess the proportions of total and inorganic aluminium, the samples were filtered (0.2 μm). Samples have been analyzed in the Finnish Accreditation Service (FINAS) accredited Environment Measurement and Testing Laboratories.

The origin of acidity seems to differ between the studied ditches in Sanginjoki, Pyhäjoki and Ruonanjärvi basins. Although the ditch masses in Sanginjoki contained black schists and sulfate-rich clays, the amounts of sulfate and organic carbon show that the organic acidity more likely than the oxidation of sulfides depresses the pH (TOC 21–74 mg l^{-1} , SO_4^{2-} 0.3–4.2 mg l^{-1}). The Al concentration was also lower (77–690 $\mu\text{g l}^{-1}$) in Sanginjoki than in typical acid sulfate suffering watersheds. In the Pyhäjoki and Ruonanjärvi basins, sulfate (150–260 mg l^{-1}), TOC (8.7–27 mg l^{-1}) and metal concentrations (Al 1800–6500, Mn 800–810, Sr 200–480 $\mu\text{g l}^{-1}$) were instead related to an acid sulfate origin, although TOC may partially explain the presence of humic compounds and therefore also potential organic acids.

According to 15 reference and limed samples (2010–2012) in each Sanginjoki ditch studied, filter weirs have increased the pH from 4.2–5 to levels of 4.9–7.1. As planned, the effect seems to arise when the discharge increases over the mean flow (MQ) and the pH of surface waters decreases, except immediately after the implementation, when the pH also rose by an unnecessarily large amount in lower, noncritical flows. In the ditch with a 10 ha basin, the increase has been 0.54 pH units, and ditches with 2.5 ha basins 1.14 and 0.73 units on average (range 0.1–2.2). The alkalinity has increased by 0.13, 0.46 and 0.29 mmol l^{-1} , while the acidity has decreased by 0.12, 0.19 and 0.18 mmol l^{-1} on average. The rise in pH or the weirs themselves appeared to have no effect on the concentrations of Fe, Al, SO_4^{2-} , TOC, P or PO_4^{3-} , although some accumulation of Fe compounds in lime surfaces was visible. No differences between the amounts of inorganic Al (0.2 μm filtration) in limed or non-limed samples have appeared, which may be

due to the considerable amounts of humic compounds and complexation of aluminium with humus also occurring at pH levels of < 5.5. After two years the buffering and pH-raising effect of weirs in the Sanginjoki basin has remained, although the failure in sizing of the low-water pipe has caused greater erosion and lime consumption in one of the ditches. While monitoring is still ongoing, studies to test the method in more acid sulphate-influenced basins with larger catchments and ditches in the Pyhäjoki and Ruonanlahti areas are to be carried out in 2012–2014.

The need for neutralizing surface waters should be considered as a result of improper anthropological actions. To address this need, cost-effective methods for the mitigation of biologically harmful pH problems are being sought, for instance with help of funding from the European Regional Development Fund (ERDF) and several municipalities, companies and local fishery collectives of North Ostrobothnia, Finland. The main co-operation projects associated with these pilot studies have been “City and Water – Ecological enhancement and improvement of the recreational value of River Sanginjoki” carried out by University of Oulu, Center for Economic Development, Transport and the Environment North Ostrobothnia and Finnish Environment Institute SYKE, and “Prevention of acid waterload in the Siikajoki–Pyhäjoki area” carried out by Agrifood Research Finland, the Geological Survey of Finland, the Center for Economic Development, Transport and the Environment North Ostrobothnia, the Finnish Game and Fisheries Research Institute and the University of Oulu.

INTENSIFIED LAND USE ON ACID SULFATE SOILS AS A TRIGGER FOR FISH KILLS IN AN EMBANKED FRESHWATER RESERVOIR IN MID-WESTERN FINLAND

by

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Lake Larsmo-Öja used to be a part of the brackish Bothnian Bay, but embankments were built across narrow straits in the 1960s due to the industrial need for fresh water. The artificial lake has since then suffered from repeated acidic events and fish kills. Because water courses in Finland are exposed to several sources of acidity, e.g. acidic rain, naturally occurring humic acids and discharge from acid sulfate (AS) soils, there has been considerable debate about the cause of the fish kills. The building of the embankments is also often blamed for the problems, as the well-buffered brackish seawater is prevented from entering the lake to dilute and neutralize the acidic water. The aim of this study was to identify the cause of the acidity-related problems that the lake is exposed to.

Data on water quality from routine sampling during 1961–2009 in Lake Larsmo-Öja were obtained from the Environmental Information System at the Centre for Economic Development, Transport and the Environment in Finland (HERTTA database), and data on water quality in the River Esse from 1964–2009 were provided by the Jakobstad water plant. Additional sampling was conducted during different hydrological conditions in 2007 in the numerous low-order streams and the four rivers discharging into the lake. Analyses on water samples included pH, electric conductivity (EC), sulfate, acidity and total organic carbon (TOC). Metals characteristic for watercourses affected by discharge from AS soils (Al, Co, Cd, Cu, Mn, Zn and Ni) (Österholm & Åström 2004, Roos & Åström 2005) were also analyzed. Spearman rank correlation ($p = 0.05$) was used for statistical analyses.

Compared to medians in low-order streams in Finland (Lahermo & Väänänen 1996), concentrations of Cd, Cu, Mn, Zn, sulfate, Al, Ni and Co in low-order streams discharging into Lake Larsmo-Öja were 2–141 times higher, while pH was more than one unit lower. Concentrations of the same elements were also high in all of the four rivers discharging into the lake. Median concentrations in the most metal-rich river (Kovjoki River) were 1.7–23 times higher and the pH was almost one and a half units lower than in another river in the region with only a minor influence from AS soils (River Lappfjärd, Roos & Åström 2005). Sulfate (released by sulfide oxidation) in the low-order streams and rivers correlated positively with acidity, as well as with concentrations of the metals mentioned above ($r_s = 0.55$ – 0.98), and negatively with pH ($r_s = -0.88$ for low-order streams and $r_s = -0.85$ for rivers). In contrast, a positive correlation between

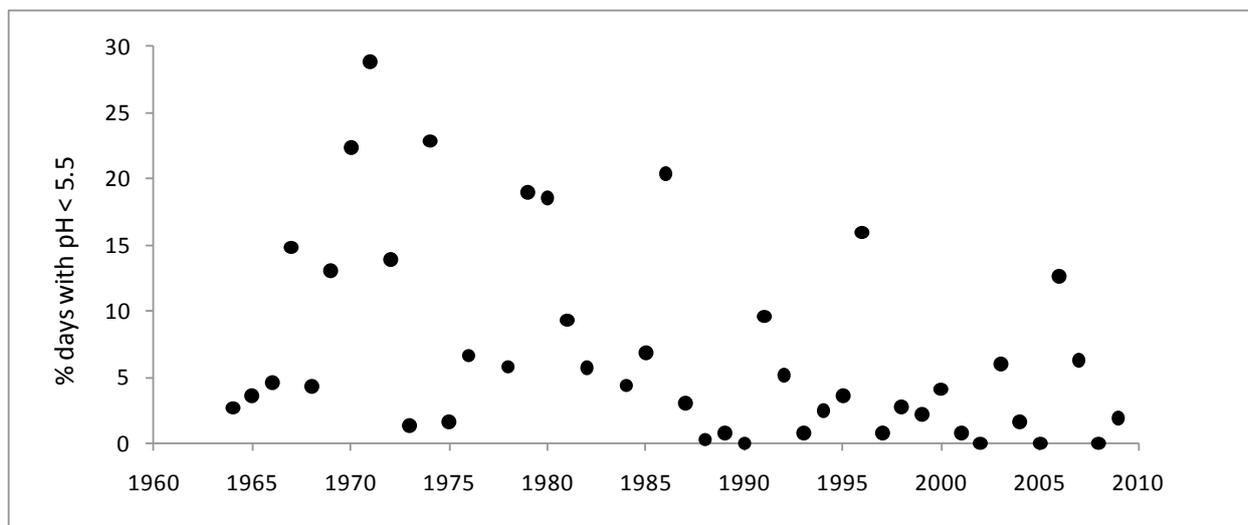


Fig. 1. Percentage of days per year with pH < 5.5 in the River Esse, 1964–2009.

TOC and pH ($r_s = 0.77$) and a negative correlation between TOC and acidity, as well as the metals ($r_s = -0.45$ to -0.82), was found in low-order streams. These geochemical patterns clearly demonstrate that the low pH, high acidity and concentration of elements are a result of sulfur oxidation in AS soils. On the other hand, humic acids (represented by TOC) seem to improve water quality in watercourses affected by AS soils by buffering the strong sulfuric acid, and by binding to metals, making them less bioavailable (Driscoll 1985).

A significant drop in pH in the River Esse (Fig. 1) and the recipient Lake Larsmo-Öja took place in the late 1960s, and several years after they were characterized by pH below 5.5, and even as low as 5.0. The first recorded massive fish kills took place in 1969 and 1970 (Bonde & Lax 2003). Corresponding acidification also took place in many other rivers in mid-western Finland, and was a result of intensive drainage projects in sulfidic clays, i.e. a result of human land use (Åström et al. 2005, Hilden & Rapport 1993). As a consequence, water quality in Lake Larsmo-Öja deteriorated not only due to the embankments in 1962, but probably more importantly as a result of the increased acidic load from the discharge water, starting in the late 1960s.

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SPECIATION OF TRACE METALS IN THE SOIL SOLUTION OF AN ACID SULFATE FOREST SOIL BY THE DGT METHOD

by

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Diffusive gradient in thin films (DGT) is a speciation method (Davison & Zhang 1994) that consists of a three-layer system where metal cations and labile complexes that pass a 0.45 µm filter are diffused through a well-defined polyacrylamide gel and accumulated in resin. Different kinds of resin gels are available, for example Chelex for metals, Fe oxide for phosphate and AgI for sulfide measurements.

Percolation water samples from zero-tension lysimeters were taken at 20 and 40 cm depths in May 2011 from a spruce stand site on acid sulfate soil (endogleyic Regosol) on the western coast of Finland (Uusikaarlepyy) and from a reference forest site (haplic Arenosol) in central Finland (Juupajoki). The DGT samplers were deployed in the soil water in the laboratory for 24 hours and metals accumulated into the Chelex resin were eluted with 0.1 M HNO₃ and analysed with ICP AES. Trace metals accumulated in DGT were compared with the total dissolved concentrations of metals also analyzed by ICP AES.

Total concentrations of Al in the acid sulfate soil water were high, being 163 and 109 mg l⁻¹ at 20 and 40 cm depths, respectively. The DGT available fraction was 15 and 13 mg l⁻¹ at 20 and 40 cm, respectively. In the Juupajoki samples the total Al concentrations were lower: 0.8 mg l⁻¹ at 20 cm and 0.5 mg l⁻¹ at 40 cm depths. The amounts of aluminium accumulated in the DGT from the Juupajoki samples were 0.4 mg l⁻¹ in the 20 cm and 0.3 mg l⁻¹ in the 40 cm sample. Thus, the proportion of DGT-available Al was about 10% of the high total dissolved Al concentrations in the acid sulfate soil, while it was roughly half of the total dissolved amount at the reference site.

Results of the DGT-available fraction and the total dissolved concentrations of Al, Cu, Fe, Ni and Zn for the two sites studied are presented in Table 1. Information on metal speciation is important in predicting toxicity and mobility.

Table 1. The DGT-available and total dissolved concentrations of Al, Cu, Fe, Ni and Zn (mg l⁻¹) in soil percolation water from the acid sulfate soil site Uusikaarlepyy and from the reference site Juupajoki.

Site	Depth/ cm	DGT Al	TOTAL Al	DGT Cu	TOTAL Cu	DGT Fe	TOTAL Fe	DGT Ni	TOTAL Ni	DGT Zn	TOTAL Zn
Uusi- kaarlepyy	15	15	163	0.066	0.102	0.60	1.72	0.277	0.969	0.280	4.694
	40	13	109	0.054	0.092	0.49	1.51	0.229	0.688	0.226	3.144
Juupajoki	20	0.4	0.8	0.002	0.005	0.07	0.05		<.0100	0.008	0.017
	40	0.3	0.5	0.003	0.007	0.01	0.00	0.002	<.0100	0.010	0.005

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GREENHOUSE GAS EMISSIONS AND NUTRIENT LOSSES TO WATER FROM AN ACID SULFATE SOIL WITH DIFFERENT DRAINAGE SYSTEMS

by

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Finland has Europe's largest areas of acid sulfate (AS) soils (1000–2000 km² in agricultural use). They originate from anoxic basins of the former Baltic Sea, where sulfate reducing bacteria converted sulfate to sulfides. Due to land uplift (3–9 mm year⁻¹), these sulfide-bearing sediments have emerged above the current sea level. By reclamation, burning of the peat cover and heavy liming, AS soils are among the most productive farmlands in Finland. When exposed to oxygen, due to uplift or drainage, sulfides are oxidized to sulfuric acid, which makes the soil extremely acid (pH 2.5–4) and increases the solubility of metals, including Al, Cd, Co, Ni and Zn. AS soils may also be a significant source of greenhouse gases and nutrient leaching. The aim of this study was to find out whether it is possible to reduce the harmful environmental effects of cultivated AS soils by raising the groundwater table. The effects of different drainage systems on greenhouse gas emissions and on nutrient losses from AS soils to water were studied on a demonstration field in Ostrobothnia, West Finland.

The field (18.4 ha) with three different drainage systems and management practices was established on silt loam soil at Söderfjärden. The treatments were: 1) conventional drainage with subsurface pipes installed to the depth of ca. 1.1 m, 2) a controlled subsurface drainage system, and 3) a controlled subsurface drainage system with additional pumping of water to drainage pipes during dry periods to elevate the groundwater level. Spring barley and spring wheat were grown on the field in 2010 and 2011, respectively. Greenhouse gases (N₂O, CO₂) were measured for one year in 2010–2011. At the same time as the groundwater level was recorded (Österholm et al. 2012), drainage water samples were collected for analyses of total N, NO₃⁻-N, NH₄⁺-N, total P, PO₄³⁻-P, SO₄²⁻, Al, Cd, Ni, Co, pH, acidity and electrical conductivity (EC) from the control wells of the drainage systems at the lower end of the plots. Additionally, the groundwater

level, drainage water flow, EC and pH in the outflow of drainage water as well as soil temperature and moisture, precipitation, and air temperature and humidity were continuously recorded. Soil profiles (0–25 and 25–40 cm) were sampled for analyses of nitrogen (NO_3^- -N, NH_4^+ -N), pH and EC in spring and autumn. Macronutrients (Ca, K, Mg, P and S; extracted by 0.5 M ammonium acetate + 0.5 M acetic acid, AAAC pH 4.65), micronutrients (Cu, Fe, Mn, Zn; AAAC-EDTA extraction) as well as Co and Ni (AAAC-EDTA extraction) were analysed from the plough layer in spring 2010. The grain yield (presented at 15% moisture content) was estimated by harvesting an area of 13–21 m² in triplicate from each drainage system. The quality of the yield was estimated by determining the test weight (kg hl⁻¹) and 1000-seed weight. Concentrations of N in grains and straw was analysed with the Kjeldahl method and those of Ca, K, Mg, P, Cu, Fe, Mn, Zn, Cr, As, Cd, Pb, Co, Mo, Ni and S were analysed with ICP-AES or ICP-MS after wet digestion using concentrated nitric acid. Preliminary results are presented in this paper.

The addition of water (250 m³ ha⁻¹) to the controlled drainage system kept the groundwater level over the most critical soil layers, whereas the level dropped under the surface of critical soil layers in controlled drainage and in ordinary drainage systems in summer 2011 (Österholm et al. 2012). The average flux of nitrous oxide was 79 g N ha⁻¹ day⁻¹, which is high compared to mineral soils in general and high even if compared to organic soils. Extremely high nitrous oxide emissions from AS soils have also been found in Australia (Denmead et al. 2010) and Denmark (Petersen et al. 2012). A correlation was found between the flux rate and the groundwater level so that the lowest flux rates were recorded with a high groundwater level ($r = -0.34^{***}$). A correlation was also found with soil moisture ($r = -0.34^{***}$) and soil temperature ($r = 0.58^{***}$) at 30 cm. Fluxes of carbon dioxide measured as total ecosystem respiration were not especially high and they were also correlated with groundwater level ($r = -0.47^{***}$) and soil temperature ($r = 0.92^{***}$). However, since there were just nine measurement occasions during the year, and no significant differences in the greenhouse gas emissions between the three drainage treatments, the effect of water table management remains unclear.

High NO_3^- -N concentrations (9.9–31 mg l⁻¹) in water samples were measured from all drainage systems with variation over time, but there have been no differences between the drainage systems so far. Contrary to NO_3^- -N, concentrations of NH_4^+ -N (< 0.50 mg l⁻¹) and total P (< 0.065 mg l⁻¹) were small. The drainage outflow varied from 220 to 280 mm in 2011 and the annual NO_3^- -N load was estimated to be as high as 50 kg ha⁻¹. The drainage water was very acid (pH 3.8–4.4) and had a very high EC (91 to 300 mS m⁻¹) and concentrations of sulfate (300–1600 mg l⁻¹), Al (> 10 mg l⁻¹), Cd (> 2 µg l⁻¹), Ni (> 400 µg l⁻¹) and Co (> 150 µg l⁻¹) in all treatments. There were significant and coherent variations for these variables between seasons and years. In general, the pH was lowest and concentrations of sulfate and metals highest in autumn, but the potential effects of different treatments were not yet distinguishable. Trends in the groundwater level, pH, EC and water flow as well as soil moisture and temperature in each treatment can be observed from raw data available on the Internet (<http://www.ehp-data.com>).

Soil pH varied from 6.6 to 7.1 and from 5.4 to 6.5 in the plough layer (0–25 cm) and in the subsoil (25–40 cm), respectively, due to previous liming. In soil, the amounts of NO_3^- -N (24–35 kg ha⁻¹) and NH_4^+ -N (10–16 kg ha⁻¹) were higher than is common in Finnish mineral soils without dung applications. The concentrations of macronutrients and micronutrients were, however, typical of Finnish soils. The yields of spring barley and spring wheat (4000 to 5400 kg ha⁻¹ and 5500 to 5900 kg ha⁻¹, respectively) were above the Finnish average. Due to large variation, no differences in yields were detected between the different drainage systems. There were also no differences in the test weights (56–57 and 85 kg for



Fig. 1. Measuring of greenhouse gases on the Söderfjärden field in spring 2011. (Photo © Rainer Rosendahl, ProAgria Rural Advisory Centre of Ostrobothnia).

barley and wheat, respectively) or in 1000-seed weights (32–34 and 37 g for barley and wheat, respectively) between the treatments. Total N yields of barley and wheat were 80–110 kg ha⁻¹ and 140–150 kg ha⁻¹, respectively (mostly resulting in negative N balances with application of N fertilizer of 90 kg ha⁻¹ yr⁻¹). During the first two years, the metal concentrations of cereals were within the adequate range and there were no significant differences in concentrations of nutrients or harmful metals in the harvested crops.

The results showed that at the beginning of the experimental period (two growing seasons), nitrate losses to water were high but raising of the ground-water level had no detectable effects on the losses or on nutrient and metal concentrations of spring cereals, or on soil pH. However, the results suggested that greenhouse gas emissions might be lowered by the controlled drainage system with additional pumping of water, but the result has to be verified with further measurements. This study has been conducted within the framework of the EU-Life+ programme in a project entitled Climate Change Adaptation Tools for Environmental Risk Mitigation of Acid Sulfate Soils (CATERMASS).

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SULFUR REDUCTION AND OXIDATION PROCESSES, FROM WETLAND SCALE TO MICRO SCALE, IN AN INLAND ACID SULFATE SOIL OF THE LOWER MURRAY-DARLING RIVER FLOODPLAINS, AUSTRALIA

by

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Inland acid sulfate soil systems have recently been found to be ubiquitous throughout the wetlands of the Murray-Darling River floodplains, Australia, associated with high water levels and salinity. Coastal acid sulfate soil systems have been shown to cause significant landscape, water and infrastructure degradation. However, little is known about the driving processes of sulfide accumulation and subsequent oxidation within recent inland sulfidic wetlands, an essential component of acid sulfate soil management. Several recent studies have focused on inland sulfide formation or oxidation, but none have conceptualized in detail the driving processes of sulfur from formation to oxidation. This study has identified and integrated the processes that control the storage and dynamics of sulfur, under reducing and oxidizing conditions, from the wetland to micro scales, in the Loveday Basin inland acid sulfate soil system of the lower Murray-Darling River floodplains in South Australia.

The 330 ha Loveday Basin was originally a natural floodplain wetland periodically connected to the Murray River. Since 1972 the wetland has been used as an evaporation basin to dispose of saline irrigation waters, and any connection to the Murray River is now controlled by weirs. The wetland is a closed system for salts, concentrated during evaporation, and has largely maintained a water cover for decades. The wetland is currently hypersaline and identified as containing sulfidic sediments. Recent partial draining exposed some of these sulfidic sediments to the atmosphere. This has produced adjacent reduced and oxidized sediment profiles that allow for direct comparison in this study.

At the wetland scale, pyrite was found to be largely restricted (~90 w/w% of sulfides in the basin) to a distinct 40-cm-thick wetland clay unit, rich in clays (>94 w/w% clay) principally as smectite (~24 w/w% smectite). The deposition of wetland clays at a rate of 1 cm/yr demonstrates that the 40-cm-thick unit, and associated sulfides, has largely formed since the managed disconnection of the wetlands from the river channel in 1972. This shows that in addition to increased salinity, the managed water flows and permanent inundation of the wetland has

also increased the deposition of wetland clays and promoted the preservation and accumulation of sulfides as pyrite.

Recent partial draining of the sulfidic sediments has exposed them to the atmosphere, resulting in sediment wetting and drying as well as extensive sulfide oxidation on the wetland scale. Physically, the exposed surface of the basin has formed prominent desiccation features, during the drying of shrinking clays, producing sediment cracks through the sulfidic sediments. Chemically, the exposed sediments have developed highly variable concentrations of sulfide (<0.002 to 1.31 w/w% S), sulfate (0.04 to 5.67 w/w% S), carbonate (<0.005 to 1.69 w/w% C) and acidity (pH 3.2 to 8.6) compared with un-oxidised sulfidic sediments that have not undergone wetting and drying regimes. In addition to sulfide oxidation during drying, the periodic rewetting of sediments has resulted in localized sulfate reduction, further adding to the complexity of sulfur and carbon distribution. This shows that, on the wetland scale, the draining of sulfidic sediments results in a wetting and drying regime that produces high variability and complex distributions of sulfur and carbon.

At the scale of sediment profiles (~50 cm depth), stable isotopes of organic carbon ($\delta^{13}\text{C}$), inorganic carbon ($\delta^{13}\text{C}$) and sulfur ($\delta^{34}\text{S}$) have been used to elucidate the process of sulfide formation within un-oxidised sulfidic sediments. The $\delta^{13}\text{C}$ values of organic carbon indicate that *in situ* microbial mats ($\delta^{13}\text{C}$ -19.97‰ to -20.56‰) are currently the dominant source of sedimentary organic material for sulfate reduction, as opposed to *in situ* or allochthonous vegetation ($\delta^{13}\text{C}$ -28.62‰ to -31.50‰). Inorganic $\delta^{13}\text{C}$ values of sedimentary carbonate indicate that organic carbon mineralization during sulfate reduction ($\delta^{13}\text{C}$ fractionation of ~+10‰), within the microbial mat, is currently the dominant source of carbonate ($\delta^{13}\text{C}$ -6.80‰ to -9.00‰). Sulfide mineral $\delta^{34}\text{S}$ trends down the sediment profile ($\delta^{34}\text{S}$ +2.92‰ to -19.67‰) show strong increasing fractionation from surface water sulfate ($\delta^{34}\text{S}$ +15.83‰), indicating sequential sulfate reduction within the benthic microbial mat over time. These results demonstrate that the microbial mats are the primary source of organic carbon, carbonate and sulfides within the Loveday Basin and are driving the formation of the sulfidic sediment (Wallace et al. 2009).

The draining of sulfidic sediments (which resulted in the complex distributions of sulfides, sulfate, carbonate and acidity on the wetland scale) is found to produce predictable zoning of sulfides, sulfate, carbonate and acidity within individual desiccation features, on the sediment profile scale. The zoning is produced within desiccation features by capillary action, driven by surface evaporation. Sulfides are oxidised at the exterior of desiccation features and preserved within the wet interiors. Upward vertical capillary advection redistributes solutes and sulfide oxidation products, which are concentrated as salt efflorescence at the exterior of desiccation features. The capillary advection, in combination with sulfide oxidation and periodic horizontal through-flow, also leaches carbonate, separating carbonate from sulfides. This results in a positive net acid generation potential and acidic hot spots. These findings show processes that produce acidity on the sediment profile scale in spite of the closed system having an excess buffering capacity from carbonate on the wetland scale (Wallace et al. 2006).

On the micro scale, pyrite framboids largely (>50 vol.%) exist in pore spaces, free of organic material. This suggests that the majority of sulfide, produced from sulfate reduction within the microbial mats, diffuses into organic-poor sediments, subsequently forming pyrite at a distance from the site of sulfate reduction. The wide variety of pyrite micromorphologies and cross-cutting features indicate that pyrite framboids are formed in multiple generations and under a range of chemical conditions. This is consistent with periodic changes in water levels and salinity during wetland management. The pyrite micromorphology demonstrates that sulfide production from the microbial mats is episodic, depending on the chemical conditions resulting from water management, and can

be sufficiently high to allow sulfide migration to form pyrite at a distance from organic material.

During sulfidic sediment exposure, at the micro scale, pyrite framboids oxidize through the formation and expansion of bacterially catalyzed (identified by DAPI staining and 16s PCR DGGE) acidic microenvironments (inferred from jarosite, pH <3, and iron oxide, pH >4, micromorphologies), which expand from between pyrite crystals into the soil matrix. The formation of acidic microenvironments allows acidic sulfide oxidation in bulk pH neutral sediment profiles. The diffusion of oxidants to the pyrite surface, rather than pyrite surface area, appears to limit the degree of sulfide oxidation in both acidic and pH neutral sediments. These results show that acidic microenvironments allow for rapid acidic sulfide oxidation within bulk pH neutral sediments (Wallace et al. 2008).

The integration of the above findings of sulfur oxidation and reduction, from the wetland to the micro scale, allows for a conceptual understanding of sulfur storage and dynamics in inland acid sulfate soils of the lower Murray-Darling River floodplains. The results of this study show that the Loveday Basin has undergone three distinct phases over time. Pre-1972, prior to the regulation of basin waters, the sediments underwent regular wetting and drying cycles with no significant accumulation of sulfides. From 1970 to 2000, water regulation and partial disconnection from the river channel resulted in the accumulation of sulfide-rich wetland clays. Post-2000, partial draining of sulfidic sediments has produced extensive sulfide oxidation and complex, but predictable, physical and chemical heterogeneity. These three phases are principally controlled by the prevailing water regime. The integration of results in this detailed study shows how the complexity of chemical processes at the micro scale controls landscape evolution at the wetland scale.

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IMPACTS OF ACID SULFATE SOILS ON RIVER BIOTA IN FINNISH RIVERS

by

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Agricultural land use utilizing modern subsurface drainage techniques in the area of acid sulfate soils (ASS) in Western Finland has intensified the acidification of river waters. The acid and metal loads from these soils have caused a widespread deterioration in the ecological status and fish stocks of rivers in the region. Exact information on ASS impacts has covered only a few larger rivers. In order to clarify the ecological impacts of AS soils, diatom, macroinvertebrate and fish assemblages were sampled. In addition, water quality, including metal concentrations, was monitored. Joint sampling in 2010 and 2011 was accomplished in 22 rivers and at about 100 study sites selected to cover a wide range in the impact strength of ASS soils. Responses of the biota to differences in water quality and other environmental parameters were analyzed and the ecological status of rivers was assessed. This study is part of a multidisciplinary EU Life project, CATERMASS (Climate Change Adaptation Tools for Environmental Risk Mitigation of Acid Sulfate Soils). The project is still ongoing and the sampling is continuing in 2012. Here, we present preliminary results from the first two sampling years.

Riverine fish communities at rapids were sampled by electrofishing. Fish assemblages indicated a strong response to pH. Intolerant fish species, e.g. bullhead (*Cottus gobio*), brown trout (*Salmo trutta*), grayling (*Thymallus thymallus*) and burbot (*Lota lota*), were usually not caught at sites with an average pH < 6 (Fig. 1). Perch (*Perca fluviatilis*) and pike (*Esox lucius*) indicated high tolerance to low pH. However, the most acidified river (average pH 4.55) appeared to be totally fishless. Besides low pH and accompanied releases of aluminium and other toxic metals, studied fish assemblages were also impacted by nutrient (P,N) and solids loading from agriculture. Fish assemblages indicated a low ecological status, especially in rivers with a low pH induced by acid sulphate soils.

Epilithic diatoms were brushed from five cobbles collected from rapids. The ACID index was used to assess the state of acidity in streams. The ACID index score varied in the studied streams from 1.6 to 5.9, indicating a range from very acid to near neutral conditions. Diatom communities had the strongest response to the pH value of the previous spring. This results from the increase in acido-

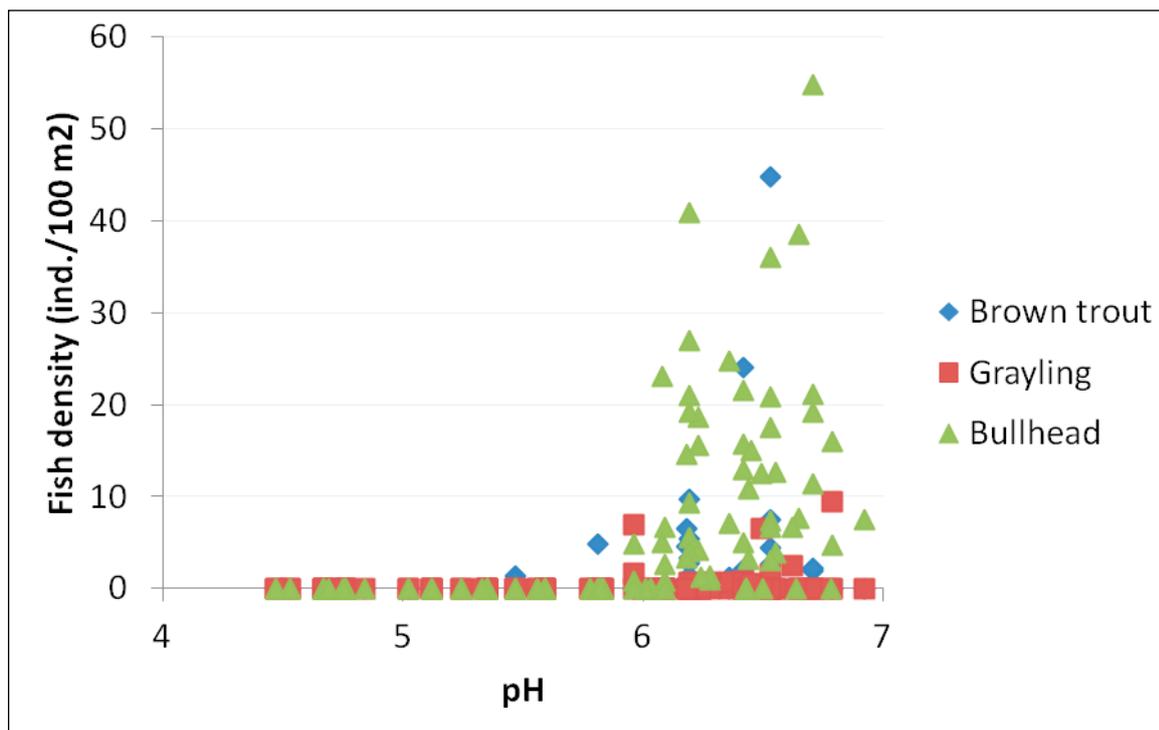


Fig. 1. Fish density of three intolerant fish species in 22 ASS rivers sampled by electrofishing.

philic and especially acidobiontic species in the streams with a low pH value in spring. Typical diatom species in these low pH streams were *Pinnularia subcapitata*, *Frustulia erifuga*, *Eunotia bilunaris*, *Tabellaria flocculosa*, and *Eunotia exigua*.

Macroinvertebrates were sampled by standardized kick net method with six replicates from each riffle site. Metrics measuring the ecological status of macroinvertebrates indicated variable responses to AS-soil runoff. The sites with the most acid conditions had a low diversity and a poor/bad ecological status, while the macroinvertebrate communities in AS-soil rivers with no recent acidity periods appeared to resemble those rivers with no acidity effects.

The concentrations of several metals were clearly elevated in the most acid rivers and exceeded environmental quality standards set, e.g. for cadmium. In addition, special problems related to the deterioration of the ecological status included extreme peaks of aluminium concentrations during the high discharge and low pH conditions in ASS rivers.

ACID SULFATE SOILS AS A DILEMMA FOR REACHING A GOOD ECOLOGICAL STATUS IN SURFACE WATERS

by

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In Ostrobothnia, Western Finland, recent classification of the ecological and chemical status of surface waters according to the Water Framework Directive (WFD) resulted in failures to reach environmental quality objectives, i.e. a good status, in most surface water bodies. In Finland, the chemical status is less than good in surface waters mainly due to the loading of cadmium from acid sulfate (AS) soils.

Harmful priority substances listed in WFD Annex X exceed the concentration levels stated in the Directive on Environmental Quality Standards (Directive 2008/105/EC), Annex II. The main reason for the deterioration of both the chemical and ecological status of water bodies is intensive drainage of AS soils and the resulting seasonally low pH and high concentrations of cadmium, nickel and aluminum. The intensive drainage and modification of land for agricultural and forestry purposes have exposed acid sulfate layers to oxidation, leading to a low pH and enhanced leaching of metals. Negative ecological effects are highlighted especially in the downstream parts of the rivers, but recent surveys in the upper reaches have demonstrated elevated concentrations throughout the river continuum in many basins.

In this study we discuss in detail the ecological and chemical classification of rivers and how the environmental objectives are supposed to be reached by the end of 2015, as stated in the Program of Measures and River Basin Management Plans. These waters have a prolonged time for achieving a good chemical and ecological status, with a deadline of 2027. We have demonstrated that a wide variety of measures are needed to both communicate the complex issue and to achieve the targets of a good ecological and chemical status in Ostrobothnian surface waters by not later than 2027.

In the Program of Measures (POM) and the River Basin Management Plans (RBMP), the poor chemical status with several measures in close cooperation with landowners, their interest groups and advisory organizations, water pollution control organizations and other actors in the river basin area are assessed. Management planning in river basins with the close cooperation of interest groups has enhanced the identification of problems in this particular area, and all parties are working hard to concentrate their efforts effectively. Management plan actions include more detailed mapping of AS soils, adjustment of drain-

age conditions, using controlled subsurface pipe drainage (CPD) and enhanced guidance for individual farms. Nonetheless, these actions are highly expensive and the time span to observe an impact on the ecological and chemical status in surface waters is probably much longer than the final goal for a good ecological status stated in the WFD.

A detailed monitoring program conducted within the Life+ project Catermass (Climate Change Adaption Tools for Environmental Risk Mitigation of Acid Sulfate Soils) revealed that even smaller river basins, previously less studied, are suffering from heavy metal loads and will therefore be assessed as having a bad or poor ecological and chemical status. In the ongoing RBMP, even some new smaller river basins (>100 km²) and smaller lakes (>1 km²) will be classified, and their ecological and chemical status will most likely also be bad or poor. Moreover, these will most likely need to be managed with the same kinds of specific actions designed for areas with AS soils as the larger river basins.

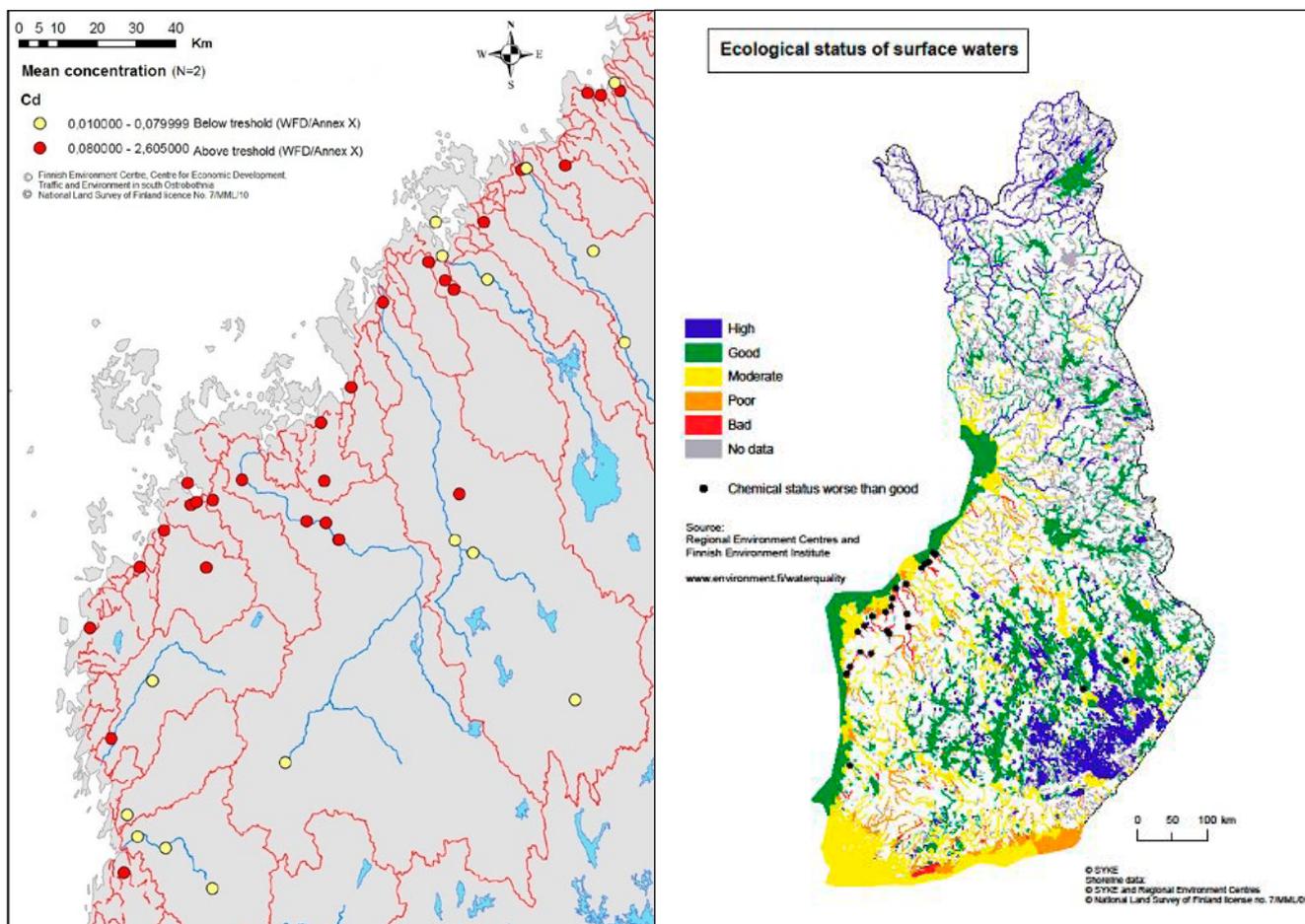


Fig. 1. Detailed sampling shows how heavy metal loads from acid sulfate soils in the Ostrobothnian area in Western Finland are exceeding thresholds stated for harmful priority substances in the Water Framework Directive (WFD), Annex X, and concentration levels stated in the Directive on Environmental Quality Standards (Directive 2008/105/EC), Annex II. This is causing a bad or poor ecological status and worse than good chemical status of surface waters.

PEAT PRODUCTION ON SULFIDE SOIL: CASE LINNUNSUO IN EASTERN FINLAND

by

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The Linnunsuo peat production area is located about 15 km east of the city of Joensuu in Eastern Finland (Fig. 1) and has been in use since 1987. The block in question has an area of 120 ha.

The bedrock of the Linnunsuo bog area belongs to the Paleoproterozoic Tohmajärvi Formation, in which greywacke represents the host rock. This area is also situated in the Hammaslahti metallogenic zone enriched by copper and zinc. The nearest black shale zone is 5 km to the SW from the Linnunsuo bog.

In terms of Quaternary geology, the area is located on the NE side of a connected esker continued from Salpausselkä II. There, the main Quaternary deposit consists of bottom till. Gravel and sand formations formed by the last ice regression can also be seen. In the area of Kontiolahti, the directions of ice flow have been aged at two different times, the younger one orientated from W to E and the older one from NW to SE. Based on the soil samples taken from the bottom of the Linnunsuo bog, the subsoil is medium fine sand. This sediment layer has probably been formed on the bottom of an ancient lake created at the stage of the last ice regression.

The sediment was sampled on three occasions (late November 2010, May 2011, and July 2011) from different locations. The total sulfur content varied from 0.03 m% to 0.36 m% of dry matter. The soil was severely acidified at only



Fig 1. Location of the Linnunsuo peat production area

two locations, having pH and electrical conductivity values of 3.8 and 19 mS m⁻¹ and 3.7 and 29.6 mS m⁻¹, respectively.

The production area was nearing its end as the peat layer grew thinner. The first indications of sulfidic till could be seen in water quality monitoring data from the early 2000s, as the pH temporarily decreased to 3.1 but then returned to the normal, slightly acidic level of around pH 6. Severe impacts of the sulfidic till underlying the peat were, however, noticed in the summer of 2010, when after an atypically warm and dry period, heavy rainfall resulted in acidification of the receiving watershed and fish kills. In November 2010 the pH in the run-off water from the site had a pH of 2.9 and electrical conductivity of 150 mS m⁻¹. The same phenomenon occurred again in the summer of 2011, after which the part of production area was closed and the drainage ditches were blocked.

ALUMINIUM AND IRON CONCENTRATIONS IN PORE WATER OF AN ACID SULFATE SOIL: THE SOIL RESPONSE TO WATERLOGGING

by

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Discharge waters from cultivated acid sulfate (AS) soils are hazardous to ecosystems of the recipient waters because of their acidity and elevated concentrations of toxic metals. Increased proton activity in pore water promotes the weathering and dissolution of aluminium (Al) compounds as a consequence of soil acidification. Oxidation of ferrous iron (Fe) sulfides produces ferric iron that in oxic soil usually precipitates to iron (hydr)oxides in a process producing more protons in pore water and further enhancing soil acidification.

One option for improving the quality of pore water is to restrain the diffusion of oxygen into sulfidic soil horizons, thereby preventing the formation of sulfuric acid by permanent water saturation. In permanently saturated soil, reduction reactions are commenced and pH is increased as protons are consumed. Because the response of pore waters to waterlogging has not previously been studied in boreal AS soils, we arranged a lysimeter experiment in which we monitored the impact of prolonged waterlogging on iron and aluminium concentrations in pore water of boreal AS horizons. We hypothesized that waterlogging results in anoxia and starts reduction reactions. These, in turn, elevate soil the pH, which favours the precipitation of aluminium hydroxide. Furthermore, iron concentration in pore water was assumed to increase as result of the reductive dissolution of ferric oxides by soil microbes.

The lysimeter experiment consisted of ten similar monoliths of an AS soil (*Sulfic Cryaquepts*) (Mokma et al. 2000). The monoliths included oxidized sulfuric B horizons and a reduced sulfidic C horizon. Eight lysimeters were cropped and two were bare. The cropped monoliths were subjected to two water table treatments (four replicates): in the low water table treatment (LWC) the soil was allowed to drain normally down to the top of the originally reduced horizon, whereas in the high water table treatment (HWC), the whole AS soil monolith was waterlogged up to the bottom of the topsoil (0–20 cm). The bare lysimeters had only the high water table treatment (HWB). In the experiment, the climate conditions resembled those in the field. The soil surface in the lysimeters was exposed to open air, but the deeper soil layers were insulated against frost and direct sunshine. Watering was carried out with artificial rainwater corresponding to the long-term local rainfall data. Data on soil redox status, moisture, temperature and electrical conductivity were logged, and pore water samples were extracted at 1–2-week intervals (Rhizon, MOM) in the Ap, Bg2, Bgjc, BC and C horizons throughout the year. The elemental composition of pore water was

analyzed by ICP-OES (Thermo Scientific, ICAP 6000) and pH was measured by an ISFET pH meter. The experiment lasted from autumn 2008 until the end of 2010 (28 months).

The redox status of different soil horizons varied depending on the soil water saturation during the experiment. The Bg2 and Bgjc horizons were mostly oxid throughout the experiment in LWC, and the originally reduced BC and C horizons turned partly oxid at the end of the experiment. Conversely, in HWC the Bg2 and Bgjc horizons turned anoxic and both BC and C horizons remained in their originally reduced state throughout the experiment. In the cropped soil the reduction was faster in comparison to the uncropped lysimeters. In LWC the pH of pore water remained at its original level or decreased, but in HWC and HWB it increased, even if only slightly in HWB.

At the beginning of the experiment, the Al and Fe concentrations in the pore water were similar in the same horizons of lysimeters, but already in the second year significant differences in concentrations were observed between treatments ($p < 0.001$) in the Bg2, Bgjc and BC horizons. The highest Al concentrations were measured in the Bgjc and BC horizons of LWC, where the mean Al concentration (\pm standard error of mean) was $97 \pm 11 \text{ mg dm}^{-3}$ and $103 \pm 7 \text{ mg dm}^{-3}$, respectively. In the same horizons, Al concentrations were $1.6 \pm 0.2 \text{ mg dm}^{-3}$ and $3.4 \pm 0.2 \text{ mg dm}^{-3}$ in HWC, respectively. In the C horizon, Al concentrations were low in all treatments throughout the experiment.

The changes in dissolved Fe concentrations were the opposite to those of Al. The Fe concentrations of pore water were significantly lower in LWC than in

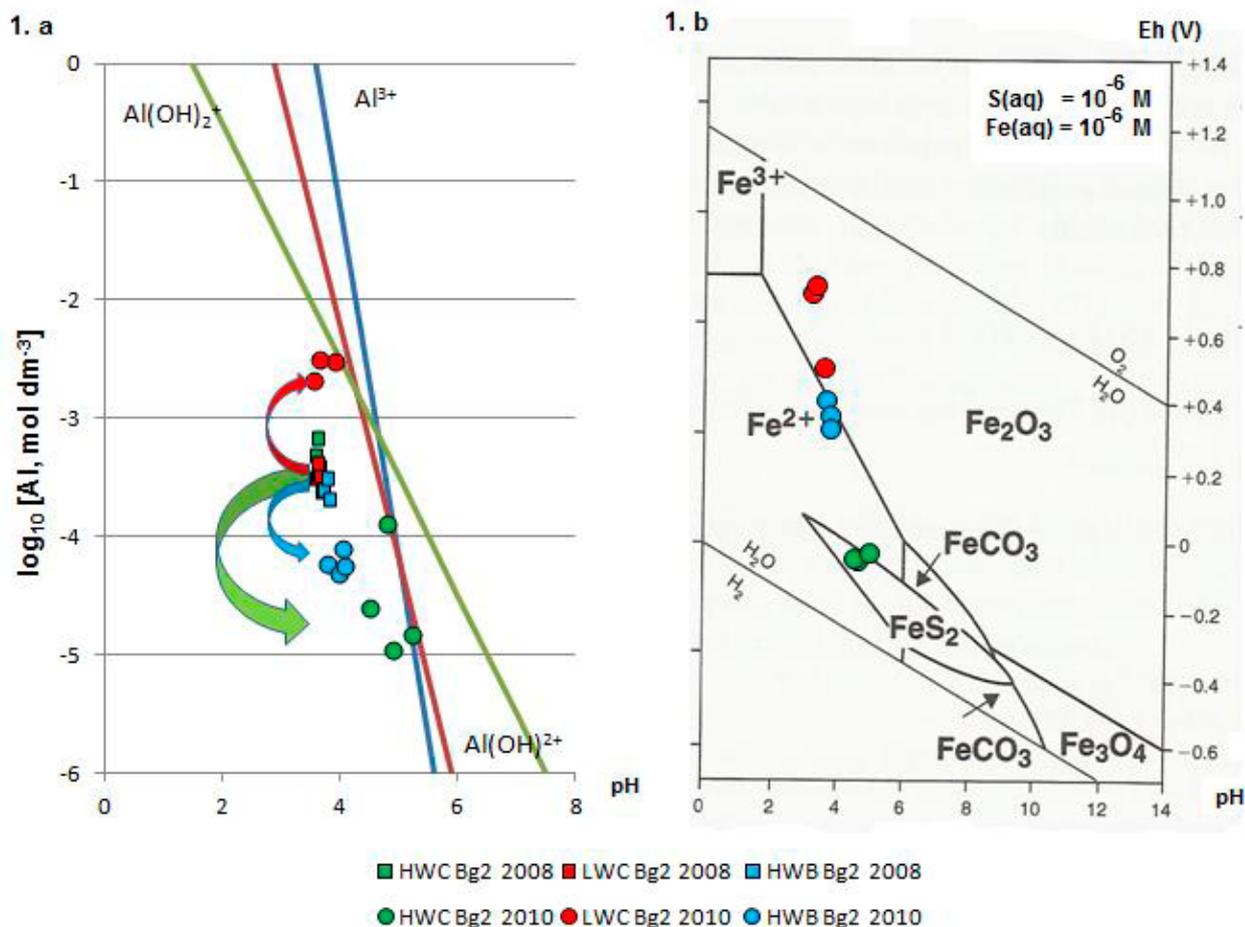


Fig.1. Aluminium concentrations and pH in the lysimeters drawn on the solubility diagram of aqueous Al-hydroxy complexes (1a) and pH and redox potentials (1b) drawn on the Eh-pH diagram of the dominant aqueous species and stable solid phases of iron (1b) at the end of experiment (2010) in the Bg2 horizon of the lysimeters. Values are means of 2 to 4 replicates.

HWC in Bg2 and Bgcj horizons in 2009 and 2010. The highest concentrations were measured in the Bg2 and Bgcj horizons of HWC, on average $285 \pm 19 \text{ mg dm}^{-3}$ and $246 \pm 12 \text{ mg dm}^{-3}$, respectively. When BC and C horizons were oxidized in LWC, the Fe concentrations markedly increased and at the end of the experiment they were higher than in the corresponding horizons of HWC.

Reduction induced by prolonged waterlogging resulted in a gradual rise in pH in the sulfuric horizons of AS soil in the lysimeter. This response was retarded in the uncropped lysimeters, which provides evidence of the importance of microbiological catalysis in redox processes. The rise in soil pH supposedly significantly decreased the Al concentration in the pore water of HWC. Accordingly, the high Al concentrations in LWC can be explained by the low pH (Figure 1a). The high Fe concentration in HWC was mainly attributable to reduction reactions (Figure 1b). They were supposedly microbially catalyzed, because equally high Fe concentrations were not observed in the bare lysimeters. High Fe concentrations in pore water of AS soils have been reported in warmer conditions in paddy rice fields (Ponnamperuma 1985). These high concentrations were not expected in the present study in boreal conditions, where high iron concentrations have not been observed in the discharge waters from AS soils (Österholm 2004). One reason for this substantial difference is probably the rapid oxidation of ferrous iron in water outlets. The increased Fe concentrations in pore water of the BC and C horizons of LWC in summer 2010 could be explained by the dissolution of iron sulfides due to oxidation, which was also confirmed by lowered pH in these horizons.

Our results support the hypothesis that the prolonged waterlogging of the B horizon could mitigate the hazardous environmental impacts of AS soils by decreasing the Al concentration in the pore water. The increased pH of pore water in these horizons is not necessarily related to that of discharge water, because the high ferrous iron concentration in pore water may induce acidity when oxidized in drains and streams. However, the main advantage of waterlogging is that the permanent soil water saturation of the C horizon preserves the sulfides in a chemically reduced state and thus prevents massive acid loads arising from potential acid sulfate soil horizons.

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MICROBIAL POPULATIONS IN ACID SULFATE SOILS: POTENTIAL ROLE IN METAL AND ACID RELEASE

by

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Soils containing metastable iron sulfides (FeS_n ; $n = 1.0\text{--}1.3$) and pyrite (FeS_2) are found in the region around Vaasa, Finland. If the iron sulfides present in these “potential” acid sulfate soils (PASS), which contain sulfidic material, are exposed to air, oxidation reactions can mobilize acidity and metals, and they are subsequently termed “actual” acid sulfate soils (AASS) with sulfuric horizons. If uncontrolled, these reactions can have a major effect on the iron and sulfur cycles and cause significant environmental damage. The environmental pressure to identify occurrences of PASS is increasing due the requirement to drain land for residential housing, agriculture, or industry. Metastable iron sulfides in PASS may abiotically rapidly oxidize to form Fe^{3+} -containing minerals and elemental sulfur, as well as other inorganic sulfur compounds (Ward et al. 2004), while the subsequent oxidation of sulfur and FeS_2 may be catalyzed by indigenous microorganisms (Schippers & Sand 1999). The role of acidophilic microorganisms (pH optimum ≤ 5) in the formation of acidic, metal-laden solutions by catalyzing sulfide mineral dissolution is well documented (Dopson & Johnson 2012). Despite this, knowledge of the microbial populations in PASS and AASS and their potential role in metal and acid release is limited.

PASS and AASS were sampled from the Risöfladan experimental field, Vaasa, which contains around 0.5% sulfur as approximately 50% FeS_n ($n = 1.0\text{--}1.3$; metastable iron sulfides) and 50% FeS_2 . Soil samples from a vertical depth profile at 30, 75, 127 and >180 cm beneath the surface were aseptically sampled (Fig. 1) and frozen until analysis for the presence of microorganisms.

The presence of microorganisms was investigated by genomic DNA extraction, amplification of the 16S rRNA gene and cloning into a plasmid vector (Dopson & Lindström 2004), and individual taxonomic units were identified by restriction fragment length polymorphism. Examples of unique species were then DNA sequenced. In addition, indigenous acidophilic microorganisms were enriched in the laboratory in stirred tank reactors containing 5% (wt/vol) PASS or AASS in sterile water at natural pH values as well as after adjustment to pH 3 (Dopson and Lindström 2004).

Biological leaching in stirred tank reactors demonstrated metal and acid release. The unoxidized fraction had an initial pH of 7.9 that decreased to 3.0 after



Fig. 1. Vertical profile of acid sulfate soil showing (from top to bottom) top soil, oxidized material, the oxidized/unoxidized boundary, and dark grey metal sulfides. Photograph courtesy of Rainer Rosendahl.

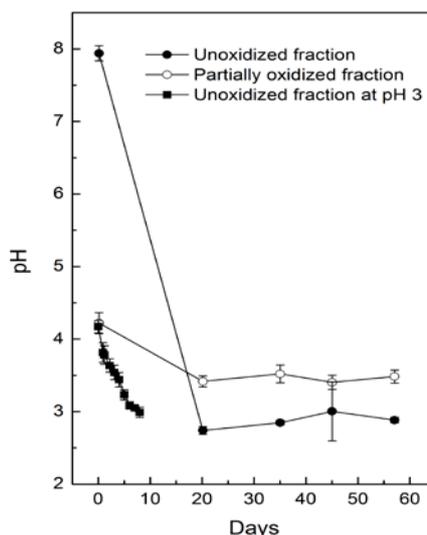


Fig. 2. pH decrease in stirred tank bioreactors of the unoxidized, partially oxidized, and unoxidized (at pH 3) fractions. The unoxidized fraction with an initial acidic pH was inoculated with an enrichment culture of microorganisms previously grown on PASS at low pH.

45 days of leaching, while the total iron increased from 22.4 to 30.7 mM. The partially oxidized fraction had an initial pH of 4.2 that decreased to 3.5 (Fig. 2), while the total iron also increased. Evidence for biological activity was observed via a decrease in the Fe^{2+} concentration, suggesting microbial oxidation of Fe^{2+} to Fe^{3+} . Finally, stirred tank reactors inoculated with an enrichment culture of indigenous microorganisms at pH 3 had a more rapid increase in total iron and decrease in pH (Fig. 2), as well as a decrease in the Fe^{2+} concentration from 2.2 to 1.2 mM after 8 days. This suggested that the partially oxidized ASS contains indigenous microorganisms capable of catalyzing metal and acid release at an acidic pH.

The microorganisms sampled from the PASS and AASS in the Risöfladan experimental field and in the stirred tank reactors will be identified by molecular phylogenetic methods and compared to the environmental conditions within the soil. In addition, the microorganisms will be evaluated for their ability to catalyze metal and acid release from PASS.

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VARYING DEPTH OF SULFIDIC MATERIALS: A CHALLENGE TO SUSTAINABLE MANAGEMENT

by

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The vulnerability of *sulfidic materials* to oxidation and acidification is dependent on their depth from the soil surface. Land use strongly affects the degree to which they are subjected to aerobic conditions, because the required drainage intensity is dependent on the human activities that are carried out in the area. Some acid sulfate soils under forest vegetation are likely have *sulfidic materials* close to soil surface (< 1 m). They most commonly have an aquic moisture regime and a histic horizon protecting the *sulfidic materials*, but ditching may expose them to oxidation. Peat mining is an important industry in Finland. Particularly in the coastal areas, many peatlands have sulfidic subsoils vulnerable to oxidation after extraction of the peat layer. Because the isostatic rebound after the Ice Age continues at the annual rate of about 0.5–0.8 mm on the western coast of Finland, *sulfidic materials* are currently emerging from the sea. These new meadows with *sulfidic materials* at a shallow depth (<0.5 m) are commonly reclaimed for agriculture of varying intensity. However, acid sulfate soils are most intensively used for conventional arable agriculture, where effective drainage is needed. Recognizing the depth of the *sulfidic materials* is a prerequisite for utilizing acid sulfate soils in an environmentally sustainable way in any land use. However, the depth of *sulfidic materials* in Finland has been published only for a very limited number of soils. In this paper we present estimated depths of *sulfidic materials* on the basis of a national survey of agricultural soils. In addition, *sulfidic materials* in peat mining areas and meadows newly emerged from the sea are briefly discussed.

A nationwide survey of agricultural fields for investigating the drainage status was carried out in 1989–1992. Altogether, 1065 fields were augered to the depth of 2.0 m. The selection of the fields has been described in detail in Puustinen et al. (1994) and in Yli-Halla et al. (1999). Each sampled field represented about 2100 ha of agricultural land. There is no bias towards acid sulfate soils, which probably occur in the material in the same frequency as they exist among the fields of Finland. Soil texture was estimated and pH and redox potential were measured *in situ* at intervals of 10 cm. Even though many soil characteristics important for classification, e.g. the sulfur concentration and decrease in pH upon aerobic incubation, were not measured, acid sulfate soils could rather reliably be identified from the data collected. For this paper the data were revisited in order to determine the probable depth of *sulfidic materials*. It was concluded that a soil contained *sulfidic materials* within 2 m of soil surface if, in some part of the profile, the minimum pH in the mineral soil was below 4.5 and there was

a sharp decrease in the redox potential, indicating water saturation immediately below the minimum pH. A low pH was assumed to be caused by the oxidation of *sulfidic materials* that still occur in the reduced horizons. We are aware of the weaknesses in this approach. For example, in soils with poor drainage, *sulfidic materials* may not have been oxidized at all, and owing to pH > 4.5 throughout the profile, these soils escape the present selection. However, we think that this is a minor deficiency from a practical point of view. All agricultural soils in Finland are artificially drained and *sulfidic materials* of ecological significance have therefore been most likely at least partially oxidized, resulting in low pH values in some part of the soil profile. The soil profiles where the low pH could be solely attributed to peat and soils outside the basin of the former Littorina Sea were not included in the study.

In our investigation there were 230 soil profiles with a minimum pH < 4.50 (Table 1) in the subsoil below 30 cm. We concluded that 77 of them (162,000 ha) may meet the current criteria of Thionic Gleysols/Cambisols/ of the WRB system, requiring that the diagnostic properties are met within 100 cm of the soil surface. Including Bathythionic classes (diagnostic properties between 1.0–2.0 m of soil surface), the number of soil profiles increased to 126 (264,000 ha). According to U.S. *Soil Taxonomy*, diagnostic properties occurring within 150 cm of the soil surface, 96 soil profiles (202,000 ha) would obtain names indicating (acid) sulfate features, mostly falling into *Sulfic Cryaquepts*.

Out of the 88 soils with a minimum pH ≤ 4.0, in 42 cases the lowest pH in the soil profile occurred between 51–100 cm, in 26 cases between 21–50 cm and in 19 cases between 101–150 cm. *Sulfidic materials* likely occurred in 75 of these soils (158 000 ha) within 200 cm of the soil surface, most commonly (40 soils) at 101–150 cm and at 151–200 cm (24 soils), with a few cases at the shallow depth of 70–100 cm, and in none closer than 70 cm of the soil surface. In the large group of soils with a minimum pH of 4.01–4.49, the occurrence of *sulfidic materials* was likely in 44 (92,000 ha) out of the 154 soils, more commonly in soils with minimum pH of 4.01–4.29. The depth of *sulfidic materials* was again most commonly within 101–150 cm of the soil surface. Most soils with a minimum pH between 4.01–4.49 were oxidized throughout the investigated depth and contained only small amounts or no *sulfidic materials*.

In artificial drainage with open ditches, the ditch depth within a field seldom exceeds 70 cm. Therefore, this traditional method of drainage did not usually touch the *sulfidic materials* that in most cases occurred well below the ditch bottom. Instead, subsurface drainage pipes are installed to the depth of 100–120 cm, and in substantial areas they did hit the *sulfidic materials*. In subsurface pipe drainage, the water table is effectively lowered in spring to allow early agricultural operations in the field. Evapotranspiration in summer causes a further decrease of the water table, commonly to depths of 1.5–2.5 m (Joukainen & Yli-Halla 2003, Yli-Halla et al. 2009), contributing to gradual oxidation of *sulfidic materials* within these depths. Indeed, the problems with the acid load to watercourses have increased with the increasing prevalence of drainage with subsurface pipes. *Sulfidic materials* as deep as 2.5 m from the soil surface can have a strongly adverse effect on drainage water quality (Joukainen & Yli-Halla 2003).

Table 1. Depth of *sulfidic materials* in soil classes of different minimum pH values

Depth, cm	pH <3.5	pH 3.50–4.00	pH 4.01–4.50	Total
20–50	0	0	0	0
51–100	1	8	9	18
101–150	10	30	25	65
151–200	8	16	13	37
No sulfide within 200 cm	4	9	107	120
Total	23	63	154	230

Peat mining is practiced on about 65,000 ha in Finland. Part of these areas are located in the coastal acid sulfate soil areas, and some are underlain by black shales containing pyrite and other sulfide minerals. High sulfur contents have been measured in the bottom layer of these mires (Herranen 2010). In the native state of a mire, the *sulfidic materials* are protected, but the removal of peat exposes them to oxidation. Previously waterlogged layers become the topsoil. In this land use, *sulfidic materials* can easily be closer to soil surface than in the agricultural soils, where *sulfidic materials* were only found at 70 cm or deeper, resulting in intensive oxidation and acidic drainage waters. On the flat coasts of Finland, meadows that have just emerged from the sea can also have *sulfidic materials* within 20 cm of the soil surface (Yli-Halla et al. 2008, Boman et al. 2010), but the drainage waters are readily diluted by the brackish water and may not be a substantial threat to the quality of the coastal sea.

The closer to the soil surface the *sulfidic materials* occur, the more water management measures are needed to keep them submerged. Our data show that about 250,000 ha of agricultural land may contain *sulfidic materials* within the depth that is gradually oxidized by conventional subsurface pipe drainage. Fortunately, the most problematic ones, within 1.0 m of the soil surface, may cover only 38,000 ha of agricultural land. However, the fields where *sulfidic materials* started no deeper than 1.0–.5 m of the soil surface were the most common in the early 1990s after about two decades of intensive drainage. These soils probably still contain a vast acidifying potential, a challenge for agricultural water management. High loads of acidity can also be generated from certain peat mining areas when the sulfidic materials are exposed to oxidation after peat removal. In these areas, measures have to be developed to prevent local damage to the surface waters.

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ENRICHMENT AND SPECIATION OF METALS IN ESTUARINE SEDIMENTS AFFECTED BY ACID SULFATE SOILS IN WESTERN FINLAND

by

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In coastal areas of Western Finland, discharge from artificially-drained acid sulfate soils (ASS, c.a. 3000 km²) is estimated to export hundreds of tons of toxic metals (such as Mn, U, Cd, Al, Cu, Ni, and REEs) and acidity each year into receiving estuaries (Åström & Spiro 2000, Peltola & Åström 2002), imposing ever-increasing challenges on the management of the biologically-sensitive estuarine ecosystems. Recent studies have shown that estuarine sediments from this region tend to be polluted with precisely the metals extensively leached from ASS (Nordmyr et al. 2008a, Nordmyr et al. 2008b). In this study, the speciation status of these metals across a 4.7-metre sediment core, collected from the estuary of the Vörå River (50 km north of Vaasa), was investigated. Additionally, porewaters retrieved at 10 depths (15–200 cm) were analysed for metal concentrations and organic carbon content.

In line with the result of Nordmyr et al. (2008a), the upper part of the sediment core was found to be characterized by elevated concentrations of metals such as U (up to 12.7 ppm), Zn (up to 572 ppm), Co (up to 130 ppm), Cd (up to 2.15 ppm), Ni (up to 100 ppm), Cu (up to 74 ppm), and rare earth elements (up to 1456 ppm). Two upper sections of the core (the highlighted and enlarged “a” and “b” sub-regions in Fig. 1) were periodically loaded with exceptionally high amounts of Mn. The concentration peaks in the “a” and “b” regions were over 100 times higher than in the lowest section (background values).

Considering the high organic matter content (about 20%) and neutral pH conditions in the sediments, Mn is expected to be present largely as Mn carbonates (rhodochrosite or kutnohorite), partly as Mn oxyhydroxides or Mn sulfide, depending on redox biogeochemical processes. High Mn concentrations in porewaters, ranging from 12.3 to 27.3 mg/l, were most probably constrained by the Mn carbonates. In particular, the enormous amount of these authigenic Mn minerals provides potentially efficient scavenging pathways for the other metals enriched in the sediments. Thus, Mn mineralogy across the sediment profile and its influence on the fate of other concurrent contaminants are of great interest, and will be examined by combining Mn X-ray absorption spectroscopy (XAS)

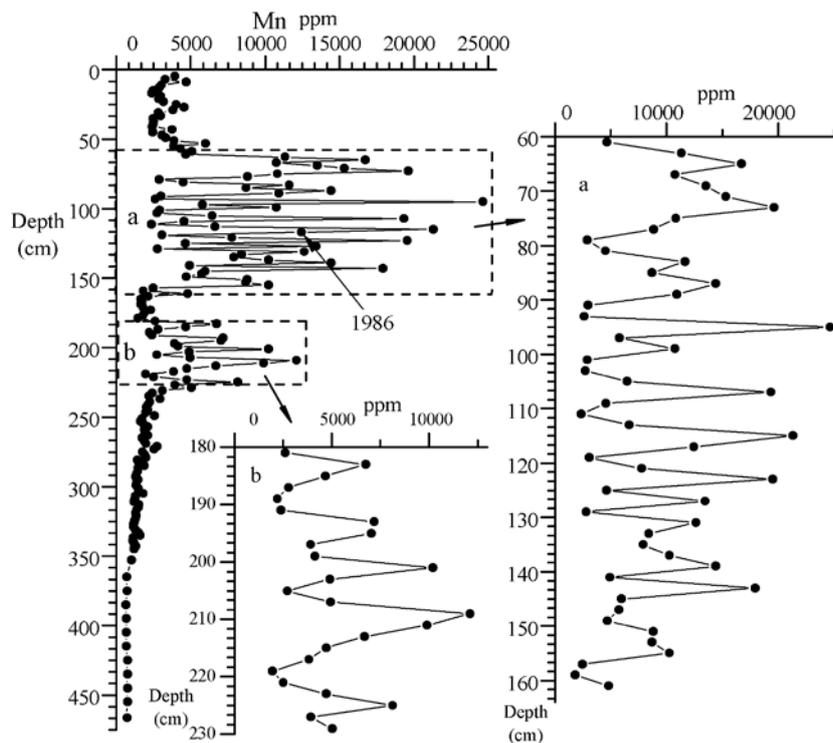


Fig. 1. The vertical distribution of Mn in the sediment core

and a new sequential extraction scheme optimized for Mn. The results of these analyses will be presented.

The ^{137}Cs peak reflecting the 1986 Chernobyl fallout was detected at the depth of 120 cm, giving an unexpectedly high sedimentation rate of c.a. 4.8 cm/year over the last 15 years. Furthermore, the results of ^{14}C dating suggest that sediments at the depths of 303 cm and 320 cm were deposited in approximately 1660 and 1600, respectively. The chronological data collectively imply that the sedimentation rate has increased by one order of magnitude as a result of the initiation of intensive ditching activities in farmland and forest.

The knowledge acquired through this study, together with previous studies on the same area, will allow us to quantify the impact of artificial drainage of ASS on the metal loading and chemical status of estuarine sediments, and to further unravel the mechanisms regulating contaminant transportation and fate in ASS-impacted landscapes.

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LABILE AND EXCHANGEABLE METAL CONCENTRATIONS IN AUSTRALIAN COASTAL ACID SULFATE SOILS: MECHANISMS CONTROLLING METAL MOBILITY

by

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The conversion of coastal lowland sulfidic sediments for agricultural activities has been a common practice and has caused substantial acidification and degradation of adjacent estuarine water quality and ecosystems in Eastern Australia. The aluminium (Al) and other metals released from these soils cause the asphyxiation of fish, and other aquatic organisms, but also limit nutrient availability and contribute to further acidification of the system. The reactive or exchangeable pool of these metals is environmentally significant as it can leach into the soil solution and be released into adjacent water bodies. This study aimed at investigating the mobilisation pathways of metals in ASS with a particular emphasis on Al.

Column and batch experiments were used to study the release of metals from ASS material under different soil redox conditions. Samples were collected in the Tweed Shire area in north-eastern NSW. Columns were then left under reducing (periodical inundation) or oxidising conditions (low rainfall). Porewater and solid samples were regularly collected to investigate the temporal variability of metal mobilisation and partitioning. A 6-step sequential extraction procedure was used for all metals and isotopic exchange was also used as a method of investigation for Al using ²⁶Al and analysis by accelerator mass spectrometry (AMS) (Collins 2009, Garcia-Rodeja. et al. 2004).

In contrast to that normally observed in ASS, the results indicated that the mobility and transport of Al and other metals is enhanced at higher pH values (from pH > 4.5) in soils containing a large concentration of natural organic matter (NOM). Furthermore, the exchangeability of metals showed a correlation with dissolved organic matter (DOM), suggesting the complexation of metals, particularly Al, by NOM. The results also showed that 1M KCl greatly underestimates the exchangeable concentration of Al, for soils rich in NOM. While 0.2M CuCl₂ extracted more metals in OM-rich soils due to the strong competitiveness of Cu for organic ligands (Kleja et al. 2005), it still underestimated the true isotopic exchangeable concentrations in most cases.

Our findings suggest that Al and other metals might be mobilised not only under acidic conditions but also at higher pHs due to OM complexation. The implications of these results for both the characterisation methodology of OM-rich ASS and for their effective remediation will be discussed.

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METAL CONTAMINATION OF ESTUARIES AND THE INNER ARCHIPELAGO IN WESTERN FINLAND

by

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Acid sulfate soils, largely developed as a result of the drainage of agricultural land, are leaching large amounts of acidity and toxic metals to drains, resulting in the deterioration of water quality and occasional mass fish kills in many creeks in western Finland. When the contaminated creek water eventually reaches the creek mouth, the sudden rise in pH causes the dissolved metals to flocculate, resulting in metal-rich suspended materials within the estuary and inner archipelago. When these metal-rich suspended materials ultimately settle, they form metal-contaminated bottom sediments in waters as shallow as a few meters. Consequently, high concentrations of several metals, including manganese (up to 2%) and aluminium (up to 10%), have been identified in this kind of sediment in ecologically sensitive areas and where coastal recreational activities and rural development are expanding. Additionally, it has been found that a high proportion of the metal load of these sediments is weakly bound to the sediment particles, which is of concern considering that in many areas these sediments will eventually be disturbed as a result of the natural isostatic land uplift and increasing dredging activities in the region. The entire scenario, which is an on-going and voluminous acid sulfate soil off-site effect, was only recently recognized and has thus as yet not received attention among the general public and responsible authorities. The issue is likely to grow into a discouraging, costly and environmentally problematic acid sulfate soil off-site effect in the near future.

MINIMIZING SULFIDE OXIDATION ON ACID SULFATE FARMLANDS BY ENHANCED CONTROLLED DRAINAGE AND SUBSURFACE IRRIGATION

by

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Acid sulfate soils (AS soils) that have developed as a result of intensive agricultural drainage of waterlogged sulfide-bearing sediments are common on the coastal plains of Finland. It is now well recognized that these AS soils discharge very high amounts of acidity and metals, with severe consequences for several river and estuarine systems (e.g. Hudd 2000). On the other hand, within agriculture these soils are highly valued for their excellent crop yields, and there is therefore strong socio-economic pressure to keep them in intensive use. Consequently, there is an urgent need to find economically viable solutions for managing acid sulfate soils in an environmentally sustainable way.

Best management practices on AS soils vary and need to be adapted to different environments, but in most cases, the most obvious aim of mitigation strategies is to minimize the oxidation of sulfides. As agricultural machinery and crop roots generally require a groundwater level of at least 0.5 m below the surface, conventional farming practices lead to significant oxidation of sulfides. In Finnish farmlands, where subsurface pipe-drainage is commonly used, the groundwater typically drops down to 1.5–2.5 m in dry summers, i.e. much lower than necessary for farming purposes. Such drought events are critical, as they enable deep oxidation of soils that have the highest sulfide pools, and may also lead to crop failure due to a lack of water. Moreover, future climate change may further increase the risk and intensity of such events with serious consequences for water courses.

In order to avoid soil drought and associated sulfide oxidation, controlled subsurface pipe drainage (CPD) has become increasingly popular in AS soil areas in Finland. Although CPD has been widely adopted, studies on this technique on Finnish AS soils are very limited and thus little is known about its effects on the groundwater level and soil geochemistry. However, previous experience indicates

that the effects on groundwater may be modest due to strong evapotranspiration, by-pass flow to the main drain through soil cracks and macro pores and/or poor management. In this study we examined the effects of CPD on the groundwater level and soil geochemistry in a silty (Pedersöre) and a clayey (Söderfjärden) AS soil field in midwestern Finland. By-pass flow to the main ditch and adjacent fields was prevented by a vertical plastic sheet along field borders (a new technique described separately in this abstract series by Österholm et al.), and on one of the sub-fields subsurface irrigation was trialled.

The Pedersöre field (5.8 ha, c. 100 km north of Vaasa) was drained with shallow open ditches and used for farming within the first half of the 20th century, after which it became forested (mainly birch trees). In 2008–2009 the field was re-converted into farmland with three hydrologically isolated (vertical plastic sheets to 1.8 m depth) sub-fields, each having subsurface drain pipes at 1.1–1.5 m depth, a control well and plastic sheets to prevent by-pass flow into adjacent drains. The soil was first characterized in spring 2009, before drainage after the forest had been removed and the soil surface had been levelled/prepared. The soil was silty and had been oxidized down to c. 2.3 m with a minimum pH around 3.5. At some sites, significant occurrences of old iron(hydr)oxide-covered root channels were found down to c. 2 m. However, large amounts (> 0.1%) of pyrite (operationally defined as the S-fraction extractable with an acidic CrII solution) and total acidity up to 200 mmol kg⁻¹ (end point pH 5.5) was still present in the partly oxidized zone. Thus, further oxidation of this zone should be prevented. As expected, parent sediments had higher sulfide contents, with pyrite typically >0.2%, and small amounts (typically ≤ 0.1%) of monosulfide (operationally defined as the S-fraction extractable with 6 M HCl + 0.1 M ascorbic acid) that gave the parent sediment a blackish colour. As installation of the CPD system required somewhat dry conditions, we were not able to store the winter/spring water during the first year of operation (2009), and as a result the groundwater dropped at most to c. 2 m, i.e. to the maximum depth of previous soil development. However, the actual acidity did not increase due to this, but was markedly similar to conditions before CPD. The second year of operation (2010) was very challenging, as the summer was very hot and dry. Nevertheless, although the groundwater level decreased by 10 cm per week or more during the hottest period in July, the groundwater was still above 1.5 m throughout the summer.

The Söderfjärden site (18.4 ha) near the town of Vaasa had more intensive drainage, but the oxidation depth was more shallow (c. 1.7 m) and the pH somewhat higher (minimum pH c. 4.0) than at Pedersöre. The content of monosulfides was also clearly higher in the parent sediment. The site had a previously installed CPD system (similar to Pedersöre), but some improvements were made in 2010, including the installation of vertical plastic sheets along the main drain and between sub-fields. Due to these installation works, we were not able to store winter/spring water in the first year of operation/monitoring in 2010. As a consequence of this, and due to the very dry and warm weather (evapotranspiration up to 10 cm per week), the groundwater dropped down to c. 2 m in summer, i.e. even below the visible oxidation depth. However, in one of the sub-fields, the groundwater was raised by subsurface irrigation to c. 0.8 m on one occasion in mid-June and remained above 1.5 m throughout the rest of the summer. Subsurface irrigation had also been conducted in previous summers, and although systematic monitoring had not previously been conducted, there was a very obvious change in groundwater behaviour after installation of the plastic sheet; previously the groundwater level dropped rapidly and by-pass flow through the soil cracks and macropores was observed along the main drain. In 2011, the remaining winter/spring water after sowing was stored. Nevertheless, without subsurface irrigation, the groundwater dropped to c. 1.5 m and c. 2.0 m below surface in the lowest and the highest part of the field, respectively. Moreover, as compared to conventional pipe drainage in the adjacent sub-field, the ground-

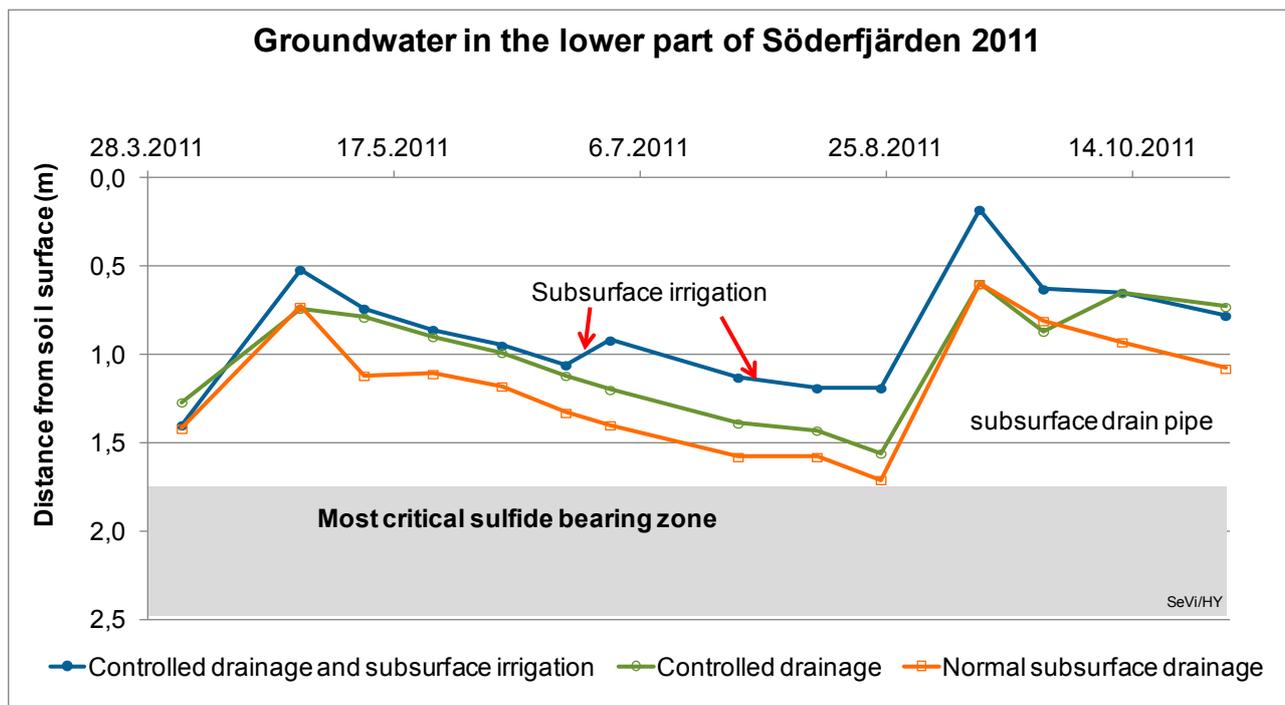


Fig. 1. Groundwater levels for the three sub-fields in the lower part of the Söderfjärden study site in 2011.

water was “only” c. 20 cm higher in the lowest part of the field and no difference was found in the upper part during the most critical time in summer (results for the lower part shown in Fig. 1). However, subsurface irrigation on two occasions (in total 25 mm) in the summer of 2011 had a marked effect on the groundwater level and prevented it from dropping into the most critical sulfidic zone below 1.5 m (Fig 1).

Altogether, it seems that the CPD system alone may have only a rather limited effect on the time and depth of sulfide oxidation, especially in shallow soils, due to strong evapotranspiration in warm summers. Moreover, as groundwater recharge was shown to be very unlikely in summer, it is crucial that the outflow is regulated as early as possible in spring. The experiment with subsurface irrigation combined with by-pass flow prevention was very promising; it prevented oxidation of the most critical soil layers and was a convenient way to keep the soil moisture at an optimal level for crops. However, the effects of long-term use of this technique need to be followed up, in particular the potential build up of salts in the soil.

This study has been conducted within the framework of the EU-Life+ programme in a project entitled Climate Change Adaptation Tools for Environmental Risk Mitigation of Acid Sulfate Soils (CATERMASS).

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BY-PASS FLOW PREVENTION ON FARMLANDS WITH CONTROLLED DRAINAGE

by

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Drainage with horizontal subsurface drainpipes (DP; Fig. 1) is a common technique used in modern farming. In Finland, DP systems are typically installed relatively deep, between 1.0–1.4 m, to maximize drainage efficiency (higher hydraulic gradient), among other effects. Drainage efficiency is particularly important after snowmelt in the spring, enabling sowing as early as possible. However, the remaining groundwater continues to be rapidly removed (in pace with the water level in the main drains) to the depth of the pipes (Fig. 1), making the soil more vulnerable to droughts in the summer. Moreover, when applied on sulfide-bearing sediments, the low groundwater level enables sulfide oxidation and the subsequent development of deep acid sulfate soils (AS soils), which has very severe consequences for recipient water courses. As a consequence, controlled pipe drainage (CPD) has become increasingly popular. In this system, the subsurface drain pipes are led into a “control well” where the height of the outflow to the main drain can be adjusted (Fig. 1). After snowmelt, the outflow is set to its lowest position (or bottom valve opened) in order to maximize the outflow until conditions are good for sowing. After that, the outflow is set to its highest

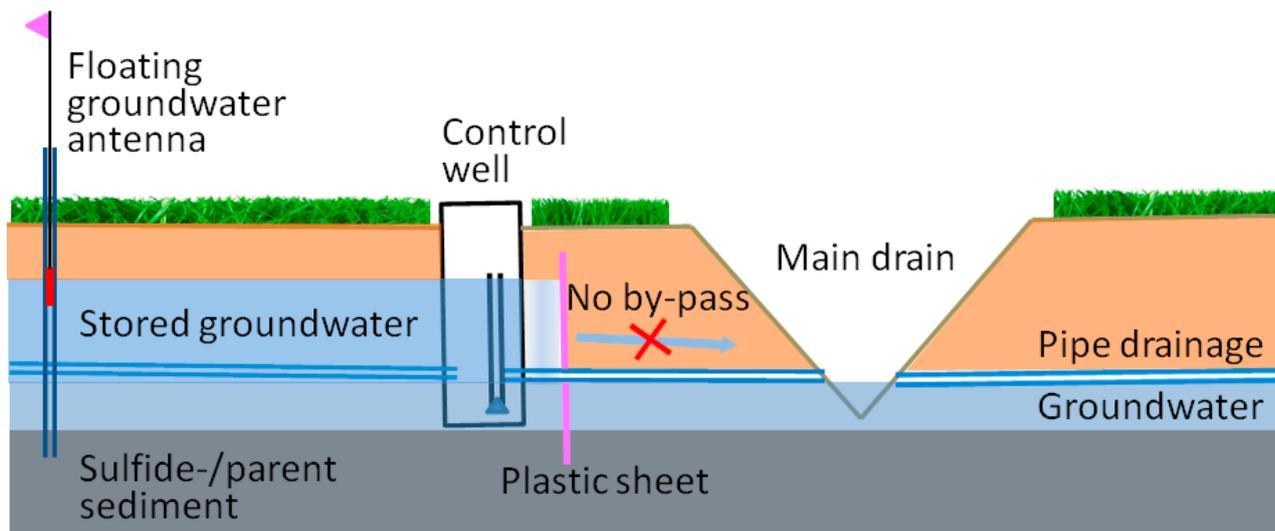


Fig. 1. On the left: controlled pipe drainage used to store excess groundwater and a plastic sheet to prevent by-pass flow. On the right: conventional pipe drainage causing a rapid groundwater drop.

position (c. 60 cm below ground) in order to store the remaining groundwater for potential summer droughts. In case of heavy rain events, it may occasionally be necessary to increase the outflow during the summer. Although CPD should enable a higher groundwater level, experience shows that the groundwater level can still sink very low due to strong evapotranspiration in warm summers. Another important problem observed by the authors is by-pass flow (BPF) to main drains through macropores and soil cracks (Fig. 2). Here, we illustrate practical aspects of CPD and BPF prevention with a vertical plastic sheet, including (1) installation issues and costs, (2) the benefits of BPF when using subsurface irrigation and (3) a tool to aid in the management of the CPD system.

In principle, groundwater and by-pass flow can be controlled/prevented by damming up main drains (reversing the hydraulic gradient towards the field) in the summer. However, as permission is required by law from all land owners using the same drain, this may be difficult. Therefore, in 2009 we tested another approach to BPF prevention by installing a vertical plastic sheet along main drains (Figs 1 and 3) in a structured AS soil in Pedersöre (100 km north of Vasa), midwestern Finland. A narrow 1.8-m-deep trench was dug along the main drain with machinery used for installing subsurface drainage. Armoured plastic sheets (1.5 x 40 m), developed for roof constructions and available in hardware stores, were manually placed in the trench, 30 to 180 cm from soil surface. It was, however, relatively tedious to keep the plastic sheet in place when the trench was filled by an excavator, and several workers were therefore needed. Later, in similar trials on two fields near Vasa in 2010 and 2011, our contractor (Nybacks gräv) improved the technique by attaching both the plastic roll and a large steel plate, to keep the plastic in place, behind the vehicle (Fig. 3). Initially, until filling the trench with an excavator, the plastic sheet was conveniently fixed in the proper position by dropping soil against the steel plate with a shovel. In this way, the plate prevented the inserted soil from pulling down the plastic. In latter study areas, two men were able to install c. 400 m of plastic sheet in one working day, at a cost of c. €4/m (typically <€400 ha⁻¹) with everything included.

A convenient tool for groundwater monitoring and proper management of CPD has been developed by Rainer Rosendahl; an “antenna” with a floater in the lower end is inserted into a conventional groundwater pipe in the middle of each field (Figs 1 and 3). Thus, as the antenna is floating on groundwater, it will rise and sink with corresponding changes in the groundwater level and help the farmer to set an appropriate level of outflow.

In one of the study fields with CPD, subsurface irrigation through the control well (Fig. 2.) has been applied for several years to enhance crop growth. Prior to BPF prevention, the field had to be irrigated about every second week



Fig. 2. Subsurface irrigation through a control well (left) and soil structure with large cracks (right)



Fig. 3. Machinery for installing the plastic sheet (left and middle pictures) and a groundwater pipe with a “floating antenna” to show the groundwater level (right picture).

to maintain a high groundwater level and BPF was observable along the main drain. There was a very significant change after installation of the plastic sheet; irrigation (in total c. 25 mm in a warm summer) was required only about twice each summer to maintain a good water balance and significantly hamper the oxidation of sulfides in deeper soil. While it seems obvious that the combination of CPD, BPF prevention and subsurface irrigation has the potential to be a very good investment for both agricultural and environmental reasons, research is still needed to investigate the long-term effects on soil and water geochemistry, also including potential salinity issues with this technique.

Experiments presented in this study were financed/supported by the EU Life+ programme (CATERMASS), EAFRD programme (PRECIKEM), Finnish Field Drainage Association, Maa- ja vesitekniikan tuki, MTK, Renlunds stiftelse, Oiva Kuusisto säätiö, Aktiastiftelsen in Vasa, ÖSP, KWH-Pipe and Nordkalk. We also want to acknowledge pioneer farmers Mats Nylund, Stefan Östman, Arne Lervik and Tom Backlund for their cooperation. Photographs: courtesy of Rainer Rosendahl.



7th International Acid Sulfate Soil Conference, Vaasa, Finland 26 August- 1 September 2012

This volume contains papers presented during the 7th International Acid Sulfate Soil Conference (7IASSC) in Vaasa, Finland (26.8.–1.9.2012). The conference consisted of three days of scientific sessions with oral and poster presentations, a mid-conference whole-day field tour and a two-day post-conference excursion in the Vaasa region. The 7th IASSC was jointly organized by the Geological Survey of Finland (GTK) and the Working Group of Acid Sulfate Soils of the International Union of Soil Sciences (ASS WG).

Acid sulfate soils (ASS), also referred to as the “nastiest soils in the world”, are soils that contain or have contained metal sulfides that oxidize under aerobic conditions and, subsequently, typically produce very severe acidity and metal pollution. Acid sulfate soils cover extensive areas, particularly in coastal areas of South-East Asia, the Caribbean, Western Africa, Australia and around the Baltic Sea. These soils are heavily exploited for a wide variety of purposes in different parts of the world, often causing serious environmental damage. Much still remains to be done in order to find management solutions for sustainable land use. The presentations in the 7th IASSC, representing authors from five continents, reflect the broad scope of issues that are related to ASS, including biogeochemical soil processes, soil mapping and characterization, environmental effects and management issues in a changing climate.