

# Mapping, impacts, characterization and extent of acid sulfate soils in Finland



PETER EDÉN<sup>1</sup>, ANTON BOMAN<sup>\*2</sup>, STEFAN MATTBÄCK<sup>2,4</sup>,  
JAAKKO AURI<sup>3</sup>, MARKKU YLI-HALLA<sup>5</sup> AND PETER ÖSTERHOLM<sup>4</sup>

<sup>1</sup> *Rantakatu 7 B 40, FI-65100 Vaasa, Finland*

<sup>2</sup> *Geological Survey of Finland (GTK), Teknologiakatu 7, P.O. Box 97, FI-67101 Kokkola, Finland*

<sup>3</sup> *Geological Survey of Finland (GTK), Vuorimiehentie 5, P.O. Box 96, FI-02151 Espoo, Finland*

<sup>4</sup> *Geology and Mineralogy, Åbo Akademi University, Akatemiankatu 1, FI-20500 Turku, Finland*

<sup>5</sup> *Department of Agricultural Sciences, University of Helsinki, Viikinkaari 9, P.O. Box 56, FI-00014, Helsinki, Finland*

## Abstract

Acid sulfate soils (ASS) cause big problems worldwide due to their potential to form sulfuric acid during oxidation of sulfidic materials, resulting in very acid soil (pH <4.0). Impacts include acidification of soil and water, leaching of metals, decreased nutrient supply, deterioration of water fauna and flora, and corrosion of infrastructure. These soils also exhibit poor geotechnical properties. Finland has the largest occurrences of ASS in Europe, mainly along the coast of the Baltic Sea. The EU Water Framework Directive brought about wide co-operation to reduce the harmful impacts of ASS in Finland. One urgent step was to localize and characterize the occurrences of ASS. The more than 10 year-long programme, led by the Geological Survey of Finland (GTK), started in 2009 and field work was completed in 2021. During the programme observations, measurements, sampling and analyses were made at 23 000 sites in an area of 5 010 000 ha. Traditionally ASS in Finland have been considered to comprise fine-grained sulfidic sediments and/or their oxidized layers, occurring on agricultural land along the coast below the highest shoreline of the Littorina Sea transgression. This study recognized and classified significant occurrences of other types of potentially harmful ASS materials: (1) coarse-grained ASS (sand), (2) organic ASS (peat) and (3) unsorted ASS (till material). The methods, definition and classification of Finnish ASS have been revised. We calculated the extent of ASS along the coast to be about 1 000 000 ha corresponding to 21% of the area covered in the past by the Littorina Sea, and three to six times more than earlier estimates. In addition, some occurrences of ASS were recognized inland, mainly related to black shales and sulfidic ores. The mapping data can be accessed via the GTK map service ([www.gtk.fi](http://www.gtk.fi)) providing information about the distribution and properties of ASS.

Keywords: Acid sulfate soils, ASS extent, environmental impact, sulfide oxidation, ASS mapping methods, Littorina Sea, Finland

\*Corresponding author (e-mail: [anton.boman@gtk.fi](mailto:anton.boman@gtk.fi))

Editorial handling: Antti Ojala (email: [antti.e.ojala@utu.fi](mailto:antti.e.ojala@utu.fi))

# 1. Introduction

## 1.1. General overview of acid sulfate soils

Acid sulfate soils (ASS) are a big environmental problem worldwide, due to their potential to form sulfuric acid owing to the oxidation of sulfidic materials, leading to very acid soils (pH <4.0) and release of metals in harmful concentrations (e.g., Ljung et al. 2009 and references therein). Acidic and metal-rich effluents cause deterioration of streams, estuaries and groundwater, and corrosion of infrastructure. ASS have poor geotechnical properties, which may lead to expensive additional measures in construction and infrastructure building. Therefore, ASS have been described as “*the nastiest soils in the world*” (Dent & Pons 1995).

Acid sulfate soils are commonly found in low-lying land bordering coasts, covering about 20 million ha worldwide, e.g., in western Africa, Australia, Southeast Asia, Central and South America, according to the commonly cited compilation of Andriessse & van Mensvoort (2006). However, Fitzpatrick et al. (2008, 2010) have communicated more occurrences in Australia, or approximately 6 million ha ASS along coastal zones and 16 million ha in inland environments. Many scientists are today using the figure 50 million ha to describe the worldwide extent of ASS (Michael et al. 2017).

In Europe, the largest and most studied ASS occurrences are found in Finland, Sweden and Denmark. In Finland the extent has earlier been estimated to 158 000 ha (Yli-Halla et al. 2012), in Sweden 50 000–140 000 ha (Öborn 1994) and in Denmark 140 000 ha (Madsen et al. 1985), all applying different criteria. Considerable occurrences are described from northern Germany (Gröger 2013) and the Netherlands (Westerveld & van Holst 1973). In Russia ASS have been described from the eastern parts of the Gulf of Finland (Kivinen 1944), from the White Sea region (Putkinen pers. comm. 2012), Karelia (Krasilnikov & Volodin 1996), and the St Petersburg area (Krasilnikov pers. comm. 2018). Acid sulfate soils

occur in East Anglia in England in former tidal fens and marshes, now agricultural land (Dent et al. 1976). Some ASS sites have recently been described from the coast of Poland (Hulisz 2016; Hulisz et al. 2017, 2020), and from Spain (Catalán et al. 2019). Small occurrences were identified in the present project near Alta, northern Norway, and probably exist in the Baltic states, too.

Generally, ASS materials in Finland are classified as follows (Boman et al. 2023 this volume); non-oxidized or sulfidic materials have a near-neutral pH and are commonly referred to as hypersulfidic materials, due to their potential to produce an acidic soil horizon (pH <4.0; pH <3.0 in organic soil materials) if disturbed or otherwise exposed to oxygen. Partly or fully oxidized ASS materials with very low pH are referred to as sulfuric materials. Acid sulfate soil materials refer to soil, sediment, peat and other materials, which are, (1) in situ non-oxidized and contain significant amounts of oxidisable sulfides (hypersulfidic material), (2) partially oxidized with variable ratios of existing acidity to unoxidized sulfides (sulfuric or hypersulfidic material), and (3) completely oxidized with no remaining sulfides, but measurable existing acidity left (sulfuric material) (e.g., Dear et al. 2023). In practical work, technical reports, and discussions with stakeholders; the terms active or actual ASS (active/actual ASS materials) and potential ASS (potential ASS materials) are commonly used instead of the terms “sulfuric” and “hypersulfidic”.

## 1.2. Need for mapping acid sulfate soils in Finland and aim of the study

Until the 1950s, ASS were in Finland mainly considered a problem for agriculture (Kivinen 1944; Purokoski 1959). Starting in the 1950s, intensive subsurface drainage of agricultural land with pipes installed to depths of 1.0–1.2 m, and draining of boggy forests and peatlands, led to a significantly increased release of acidity and metals to surface waters (e.g., Åström & Björklund 1995; Österholm & Åström 2002, 2004; Roos & Åström 2005).

This caused deterioration of waters and fish kills (Hudd & Leskelä 1998), and in the 1960s, ASS was recognized as a serious environmental problem.

Due to the irregular occurrences of ASS and because expertise and responsibilities were divided between several authorities, no nationwide coordinated steps were taken to reduce the harmful consequences of these soils until the beginning of this century. The EU Water Framework Directive (2000/60/EC), a legislative instrument adopted to restore ground and surface waters in Europe to a “Good Status”, brought about co-operation between authorities and organisations. After large fish kills in 2006–2007, GTK and collaborating organisations established a working group to find tools to reduce the harmful effects of ASS in Finland.

Simultaneously, the Ministry of Agriculture and Forestry and the Ministry of the Environment drew up a National Strategy for Acid Sulfate Soils (Ministry of Agriculture and Forestry 2011). Acid sulfate soils were also included in the Programmes for Implementation of River Basin Management Plans 2010–2015 and 2016–2021 (Ministry of the Environment 2011, 2016). The documents pointed out the importance of immediate localisation and classification of ASS.

With the aim to localize, develop methods for sampling, mapping and classification, and to determine criteria for characterization of ASS in Finland using uniform and internationally compatible methods and criteria, the mapping programme started in 2009. The expected information was seen essential when choosing and directing measures to mitigate the harmful effects of ASS.

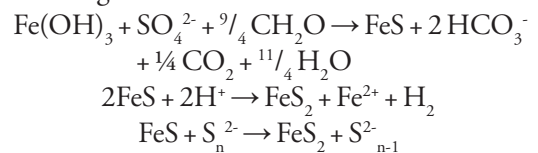
In this article we present the background and need for the national ASS mapping programme, description of the methods used, and the main results. GTK was responsible for the coordination and implementation. Åbo Akademi University and the University of Helsinki were main partners, and the co-operation with Regional Environment Centres and agricultural and forestry organisations was an essential component. During the long-term programme many research and development projects, including mapping with GTK as partner, were car-

ried out by different organisations and authorities. Results from these regional and/or subject-specific projects have significantly contributed to the implementation of the overall programme.

## 2. Processes in acid sulfate soils and their impacts

### 2.1. Redox reactions and formation of acid sulfate soil materials

Hypersulfidic materials are formed under water-logged, anaerobic and reducing conditions in soil materials rich in organic matter. They range from fine-grained sediments to sand and peat and contain metastable iron sulfides (e.g., mackinawite (FeS), greigite (Fe<sub>3</sub>S<sub>4</sub>)) and/or pyrite (FeS<sub>2</sub>). The formula FeS is here used for all types of metastable iron sulfides. The net process can be described as follows: Sulfur (sea water) + iron (stream water or bottom sediment) + bacteria + energy (organic debris) → iron sulfides. A complex series of reactions can be presented by the following equations (Dent 1986; Butler et al. 2004, with references), where CH<sub>2</sub>O stands for organic matter:



As long as the sulfidic sediments remain water-logged and in their reduced state, they are chemically stable and cause no harm. Through human activities, such as agriculture and forest drainage, excavation, peat mining, dredging, land reclamation and construction, sulfidic material is exposed to oxygen and oxidizes, leading to the formation of sulfuric acid. If the amount of acidity exceeds the neutralizing capacity of the soil, pH decreases to values below 4, which is conducive to dissolution and leaching of metals from the soil. After this process, associated with physical consolidation and structure formation called “soil ripening” (initial stage of soil development), the hypersulfidic soil has turned into sulfuric soil (Pons & Zonneveld 1965) (Fig. 1).



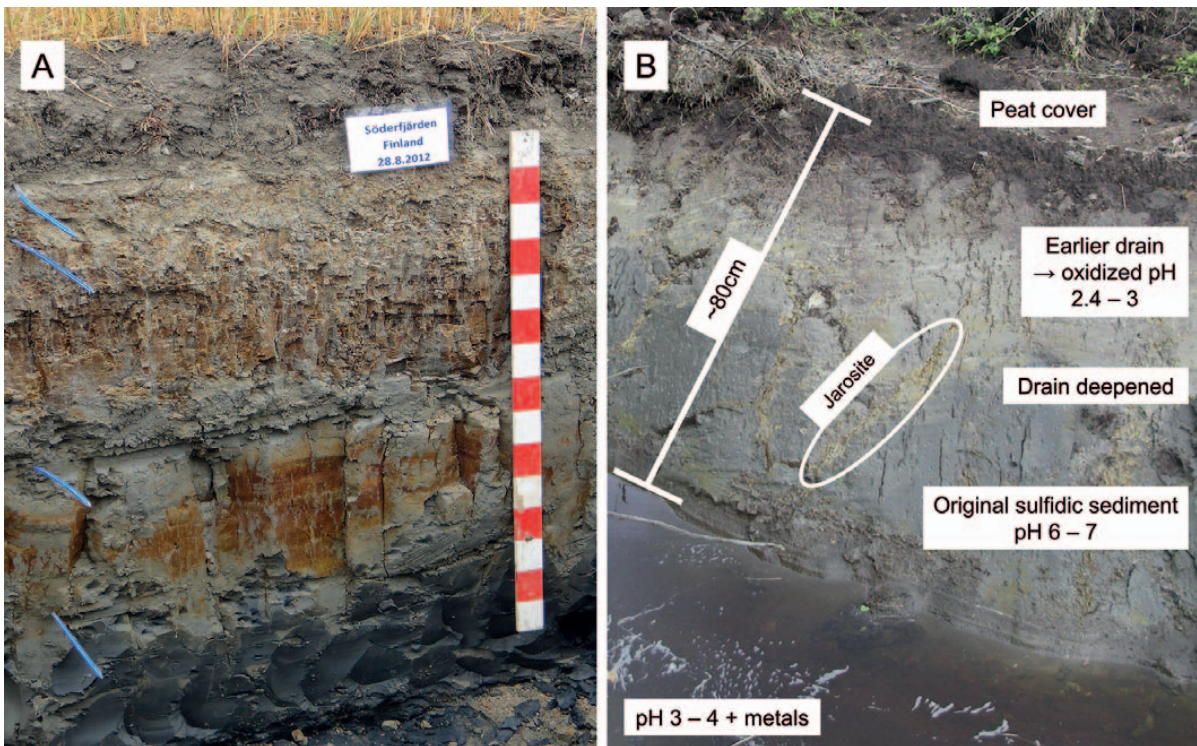
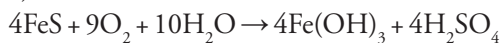


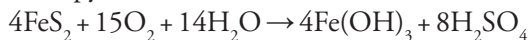
Figure 1. A. Acid sulfate soil profile in Söderfjärden, Vaasa, western Finland. The measuring board is 150 cm. The uppermost 30 cm consist of the plough layer, 30-100 cm is a sulfuric horizon developed after draining in the 1920s (hand dug), and 100-150 cm another oxidized layer developed after subsurface drainage in the 1960s. Below 150 cm is black and reduced hypersulfidic material. B. Grey sulfuric horizon with pale yellow jarosite below a thin peat layer. The original drain has been deepened and the exposed dark (slightly oxidized) hypersulfidic material will oxidize into a sulfuric horizon. Photos: GTK / Peter Edén.

The complex overall oxidation processes and production of sulfuric acid can be described as follows: lowering of water table → oxygen + bacteria (*Thiobacillus*) → microbiological processes → exposed sulfides oxidize and react with water to sulfuric acid. The reaction steps, including hydrolysis of iron, can be simplified into two equations (van Breemen 1973; Nordstrom 1982; Ahern et al. 2004):

1) for metastable iron sulfides:



2) for pyrite:



In Finland, these processes were first recognized by Aarnio (1924) and described by Kivinen (1944). During the oxidation process, the reduced and dark sediments change colour to grey with reddish or orange brown iron hydroxides (Fig. 1), and pH

decreases from >6 to <4. In many places, pale-yellow jarosite,  $\text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2$  (Fig. 1B), forms when pH decreases below 3.7 (Palko 1994), and orange-reddish brown schwertmannite,  $\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4) \cdot n\text{H}_2\text{O}$  (Yu et al. 2023), is also common.

## 2.2. Problems related to acid sulfate soils in Finland

### 2.2.1. Environmental impacts

The low-lying, sulfidic sediments are in a natural state waterlogged, and when uplifted from the sea, commonly covered with a layer of peat. These soils, occurring naturally along the coast, cause no harm if undisturbed. The formation of sulfuric soils due to natural drainage caused by land uplift is of minor importance, instead modern land-use has





Figure 2. Contaminated acid (pH about 4) and metal-rich water from acid sulfate soils (ASS) meeting the main stream of a river. Brown Fe-Mn- and white Al-precipitates blur the water in the mixing zone. Photo: Peter Österholm.

triggered and accelerated the process (Österholm & Åström 2004). Strongly increased draining of forests and peatlands, and particularly deep subsurface draining of agricultural land from the 1960s onward, together with excavation, dredging and intense construction activities, have exposed thick layers of sulfidic sediments for oxidation in a short time. The consequent mobilization of acid and dissolved metals has created big environmental problems like poor or bad ecological status and less than good chemical status of many stream waters and estuaries (Fig. 2), especially in the central part of the west coast (e.g., Åström & Björklund 1995; Österholm & Åström 2002, 2004; Roos & Åström 2005; Westberg 2016). The load of acidity and metals can be ten times higher from subsurface drains than from open drains, which are shallow and less conducive to oxidation of sulfidic layers (e.g., Palko & Yli-Halla 1993; Edén et al. 1999).

Potential impacts include acidification of soil and groundwater, de-oxygenation of surface water, poor water quality, deterioration of aquatic fauna

and flora, and corrosion of constructing materials like concrete and metals. Fish kills are the most visible impacts (e.g., Hildén et al. 1982; Fältmarsch et al. 2008; Sutela et al. 2012). Furthermore, ASS can have significant negative impacts on nutrient uptake by plants, agricultural productivity, biodiversity, fisheries and recreation (e.g., Åström 1998a; Ahern et al. 2004; Gröger 2013).

Intensified subsurface and forest draining was clearly attributed to repeated fish kills during the period 1969–1977 (Hudd & Leskelä 1998). Thereafter, severe fish kills have been reported in 1986, 1996 and during the winter 2006–2007, after a dry summer promoting oxidation of sulfidic materials.

In the acidic waters many metals (including Al, Cd, Co, Cu, Mn, and Ni) are in a dissolved phase and toxic to biota. Particularly, dissolved Al has acute effects on fish and other aquatic organisms (Nystrand & Österholm 2013). Frequent failure in the production of fish offspring, rather than the visible fish kills, has been suggested as the primary

factor leading to declining fish stocks (Hudd et al. 1994; Hudd & Kjellman 2002; Toivonen et al. 2020). Some affected streams in western Finland are in practice avoid of fish (Sutela et al. 2012).

Typically, the metal concentrations in the parent sulfidic sediments are not, or just slightly, higher than in non-ASS soils. However, streams in ASS landscapes have 10–50 times higher acidity, electrical conductivity, sulfate, Al, Cd, Co, Cu, Ni, and Zn concentrations and considerably lower pH (4–5) than the regional background (pH 5–6) and average Finnish and Fennoscandian rivers (Edén & Björklund 1993; Åström & Björklund 1995; Lahermo et al. 1996; Åström 2001). Indeed, ASS release 10–100 times more metals (Al, Cd, Co, Mn, Ni, and Zn) into watercourses than the entire Finnish industry (Sundström et al. 2002).

Streams in ASS landscapes are continually transporting loads of acidity and metals, which are ultimately precipitated in and outside the recipient estuaries, when the water is gradually diluted and neutralized with brackish seawater. According to speciation modelling, Al, Cu, La and U, together with organic matter, precipitate closest to the river mouth, while Co, Mn, Ni, and Zn occur further out in the estuary (Nordmyr et al. 2008; Nystrand & Österholm 2013). Iron is largely precipitated as ochre (iron hydroxide) already in the subsurface drainage system and the draining ditches and only a small part reaches the rivers and the sea. Metal-rich sediments are thus piling up in the sea, and will cause new problems as land uplift makes them targets for dredging and different forms of land use. There is a risk for both chemical and physical mobilisation of metals. Virtasalo et al. (2020) studied the distribution of metals in sediments in the Kvarken Archipelago outside the recipient system of the Laihianjoki and Sulvanjoki rivers south of Vaasa, impacted by ASS. The contents of Cd, Co, Cu, La, Mn, Ni, and Zn increased during the 1960s and 1970s concomitantly with the intensive drainage of the ASS landscape. The metal enrichment in sea-floor sediments is currently detectable 25 km seaward from the river mouths. The authors conclude that the metal contents are very likely to cause detrimental effects

on marine biota more than 12 km out from the river mouths.

Furthermore, ASS contain large quantities of organic matter and nitrogen and can, therefore, be sources of greenhouse gases like CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and SO<sub>2</sub>, and nitrate leaching during oxidation (Westberg 2016; Yli-Halla et al. 2020).

### 2.2.2. Impacts on infrastructure and in construction

Not until the 2010s had much attention in Finland been paid to the problems caused by ASS on infrastructure and in construction. The acidity corrodes concrete and steel, which increases the costs for materials and repairs. In addition, the poor geotechnical properties of ASS may cause big problems when building roads, railways, bridges and houses or blocks of houses. Typical problems are poor stability, compression and disturbance of the sediments during excavation and construction. Problems occur particularly in the Helsinki metropolitan area, the Turku area, and other regions along the coast where urban development is fast.

Three examples highlight the types of additional work (increasing costs): (1) The building of a bypass highway with 2+2 lanes in Vaasa, western Finland. The road crosses sulfidic sediments for a distance of 2 km. The 4–16 m thick sediments forced to carry out measures such as: column (diameter of 70 cm) stabilisation 246 000 length-m, mass stabilisation 115 000 m<sup>3</sup>, and pre-loading embankment 8 200 m<sup>2</sup> (Autiola et al. 2012), (2) The building of the big Tripla Mall and enlargement of the Pasila railway station in Helsinki, with deposits of sulfidic sediments about 5 m thick and totalling 80 000 m<sup>3</sup> (SITO 2015), and (3) A parking garage beneath the market square in Turku in 9 m thick sulfidic sediments (Visuri et al. 2021; Peter Österholm). In cases 2 and 3, the sulfidic sediments had to be excavated and safely taken care of. To combat such problems, guidelines for engineering projects in ASS have recently been launched, involving instructions for sampling, recognition, analyses and methods for treating sulfidic soil materials (Autiola et al. 2022).



### 3. Study area

The latest glaciation ended in Finland 11 500–10 000 years ago, and the sulfidic sediments started to form ca. 8 000 years ago during the brackish Littorina Sea stage of the Baltic Sea. The fine-grained (<63  $\mu\text{m}$ ) ASS materials have typically deposited in shallow coastal waters, bays, estuaries

and flood plains (Fig. 3), where the input of organic matter is high and the conditions for sulfide formation are favourable. The climate was 2–3 °C warmer, more humid, and the salinity higher compared to the present Baltic Sea. These conditions were favourable for production of organic material and sulfides (Koivisto 2004; Salonen et al. 2011; Widerlund & Andersson 2011).

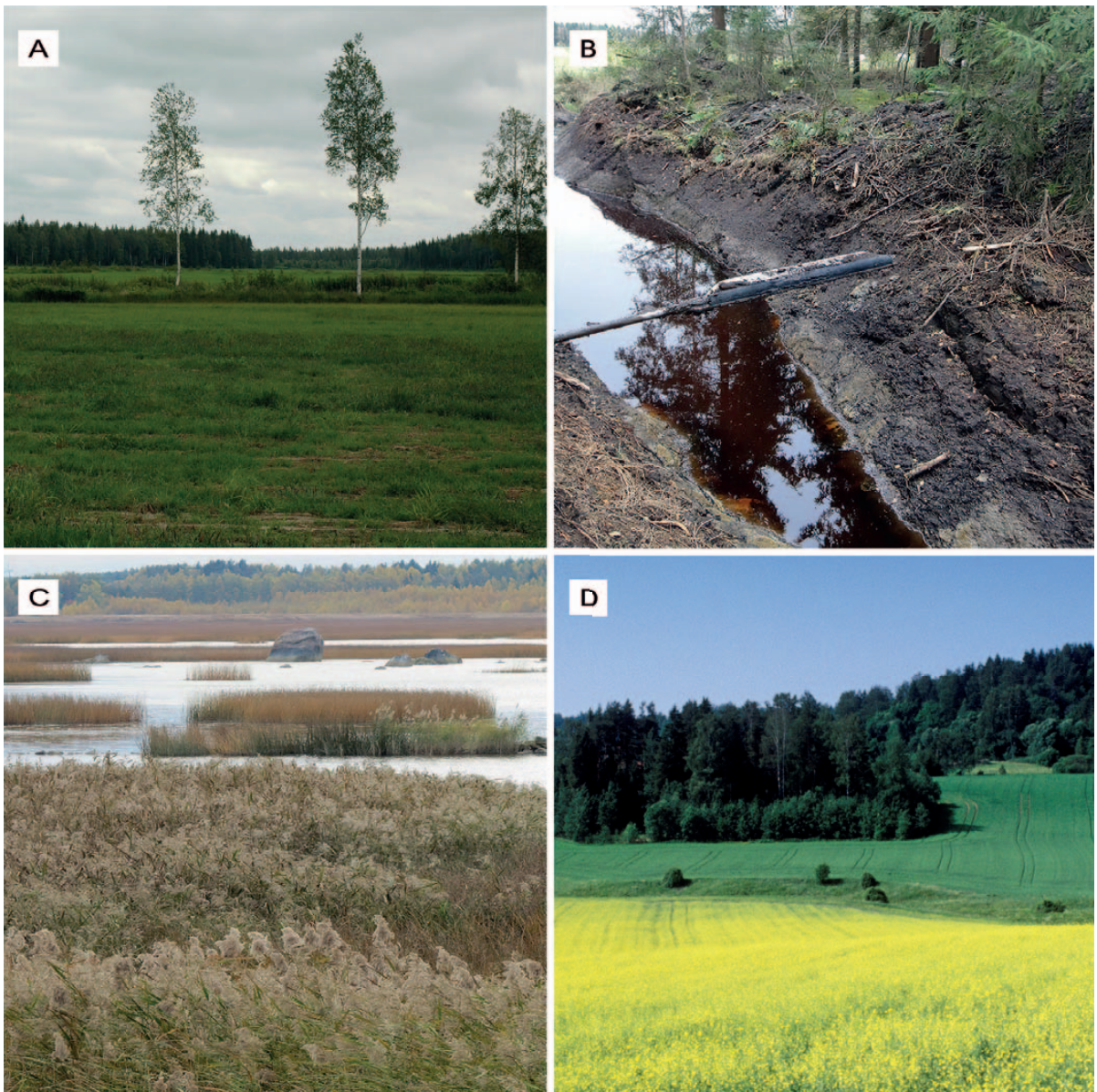


Figure 3. Typical acid sulfate soil landscapes. A. Flat river-valley landscape in Siikajoki, western Finland. B. Peat covering sulfidic material in a swampy forest, cleared for agriculture in the background, Kokkola, western Finland. C. Sulfidic sediments forming today in a shallow bay with common reed (*phragmites australis*) and common club-rush (*Schoenoplectus lacustris*) in Vaasa, western Finland. D. Rolling landscape with a small brook, southern Finland. Photos: GTK / Olli Breilin, Jaakko Auri, Peter Edén and Jari Väättäinen.

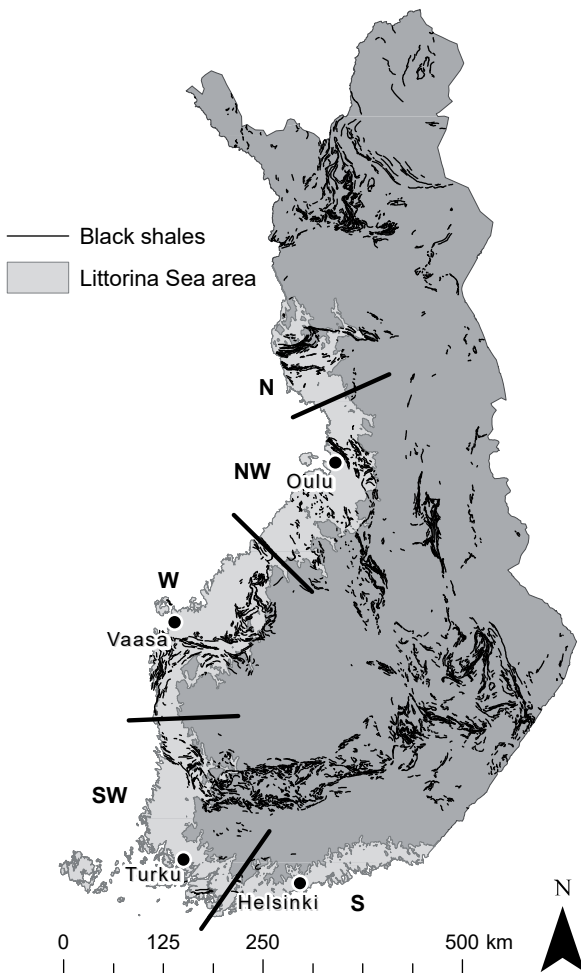


Figure 4. Maximum extent of the Littorina Sea about 8 000 years ago (Ojala et al. 2013) and geographical regions referred to in the text: S=southern, SW=southwestern, W=western, NW=northwestern, N=northern. The distribution of black shales in the Finnish bedrock (Bedrock of Finland - DigiKP) is also shown.

As a result, gyttja-containing sediments and gyttja (2–20% and >20% partly decomposed organic material, respectively) are common and the sulfide content is quite high (0.5–1.0%) (e.g., Åström & Björklund 1997).

During the last 50 years, ASS in Finland have almost entirely been considered to comprise fine-grained sulfidic sediments occurring on agricultural land along the coast (Fig. 3) below the maximum transgression and the corresponding highest shoreline of the ancient Littorina Sea. This type, the

traditional ASS, is the dominant type in Finland causing most harm. Therefore, our study was initially concentrating on fine-grained sediments in this ca. 5 010 000 ha large area, hereafter called the Littorina area (see Figure 4). These flat areas, at low elevation and free from stones, have been easily cleared and drained for agricultural purposes.

Sulfidic sediments are still forming along the flat, rising shores, in river estuaries, shallow sea bays and flood plains. The post-glacial isostatic rebound varies today from 2–6 mm year<sup>-1</sup> in the southern-southwestern regions to 7–9 mm year<sup>-1</sup> in the western-northwestern-northern regions (Fig. 4), and the total uplift after the Littorina transgression is 30–60 m and 70–100 m, respectively (Ojala et al. 2013; NLS 2021).

## 4. Methods and implementation of the mapping project

### 4.1. Planning and preparation

The mapping was designed to include the following steps: (1) preliminary study of existing data and planning of the sampling and mapping phase, (2) extensive field surveys, (3) analytical work and pH-incubation, (4) processing survey data and classifying sampling sites, and (5) compilation of an ASS occurrence map and reporting.

In the first phase, we compiled a predictive ASS occurrence map for the coastal regions at scale 1:1 000 000. The map was produced using artificial neural networks (ANN), where new point observations were combined with input covariates consisting of existing data from GTK and the National Land Survey of Finland (NLS):

- Quaternary geology maps, scale 1:20 000 and 1:200 000
- Peat-survey data (peat thickness and bottom sediment)
- Low-altitude airborne geophysics
  - Imaginary component of electrical conductivity (3 kHz)



- Real component of electrical conductivity (3 kHz)
- Apparent characteristic resistivity of electrical conductivity (3 kHz)
  - Terrain database of NLS
  - Laser-scanning data of NLS

Quaternary geology maps were used to delineate areas with sorted sediments and peat from glacial till, eskers and bedrock outcrops. In this way it was possible to delineate the areas potential for ASS and decrease the target area for field surveys roughly by 50%. Observation sites were planned at a density of 1–2 sites/km<sup>2</sup> depending on morphology and geology (see Fig. 5).

Fine-grained soils, especially ASS, and peat have a high electrical conductivity and appear clearly on the electromagnetic maps. The national peatland maps in Finland include interpreted information about the texture, and for some sites the presence of sulfides, in the base sediments under the peat. This information was used in the mapping process. Acid sulfate soils typically occupy topographic lows

and low-relief areas, and a LIDAR-based digital elevation model (DEM) was used to target the field surveys.

## 4.2. Sampling

The field survey was performed using a percussion drill and a 1-m long gouge auger (Fig. 6), which can be extended down to the required sampling depth (3 m as a rule). Replicate control samples were taken from about 5% of all observation sites. The field observations are of two types: (1) Reconnaissance observations and (2) Research observations. The reconnaissance observations were used for quick assessment in order to get an overview of the spatial occurrence of ASS in a localized area. We made on-site visual observations about the lithostratigraphy (texture, structure, colour, unit relations and contacts), groundwater level/oxidation depth and possible sulfides. Field pH was measured in a few points along the core and samples were chosen (in plastic bags and later chip trays) from all

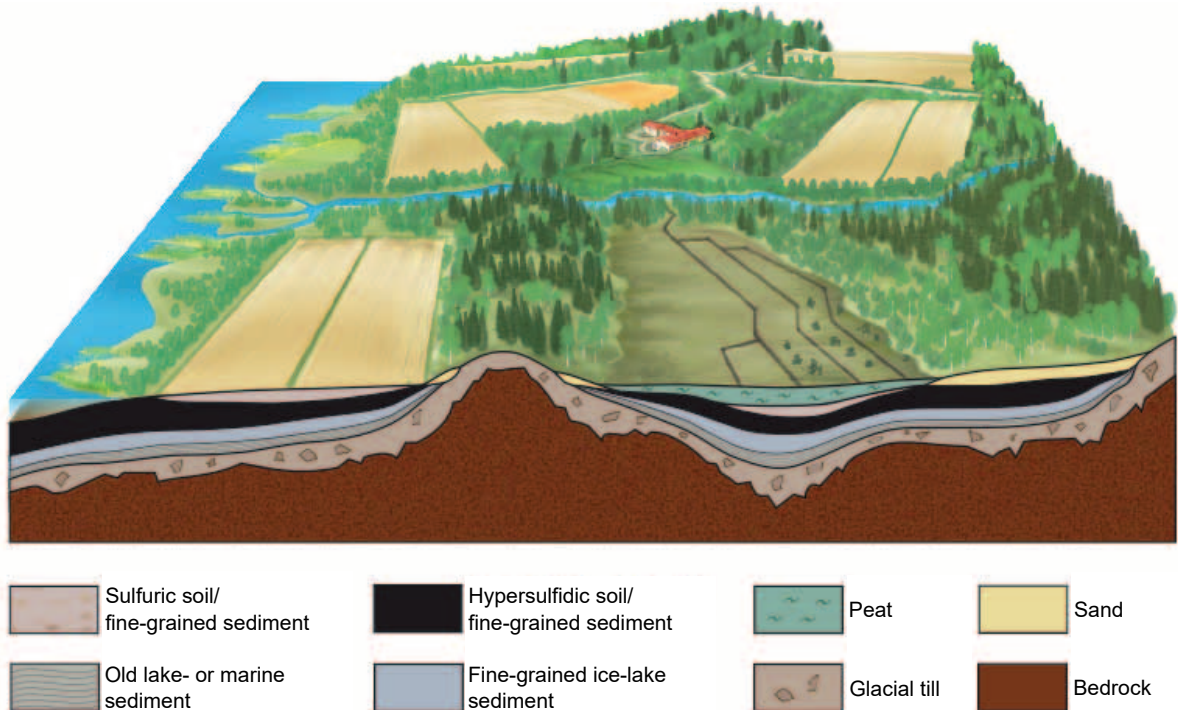


Figure 5. Conceptual model (not to scale) of typical acid sulfate soil landscapes and profiles. Drawing by Harri Kutvonen, GTK.



Figure 6. Percussion drill and samplers (A) in operation (B). Photos: GTK / Krister Dalhem.

lithological units for further laboratory analysis and incubation. This information was used to target the research observations, which provide more detailed information on the properties of that occurrence.

The research observations are representative of ASS in a specific area and distributed as evenly as possible along the coast. At these sites we used a sampler with a diameter of 3 cm and measured pH and took samples at 20 cm intervals down to 2–3 m. The same observations were made and samples stored as described above. The profile and the surroundings were photographed. About 7% of the sites are research observations.

### 4.3. Analyses

Selected samples (n=7500) were analysed at Labtium Oy (FINAS accredited laboratory). Mineral soil samples and some organic soil samples were air dried (105 °C), crushed and digested in *Aqua Regia*, after which they were analysed with ICP-OES for 31 elements: Ag, Al, As, B, Ba, Be,

Ca, Cd, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Sr, Th, Ti, V, Y, and Zn. Some samples were also analysed for grain size (sedigraph or sieved) and for organic matter (loss on ignition, LOI). In the beginning of the mapping programme, organic soil materials (peat) were analysed for total S using dry combustion and IR detection, and later using microwave-assisted *Aqua Regia* digestion and analyses with ICP-OES for the mentioned 31 elements.

### 4.4. Soil incubation

Incubation of soil is considered the best approach to determine whether it contains sulfidic materials as it lets the soil “speak for itself” (Dent 1986). During the aerobic incubation, acid-generating oxidation reactions will occur. If the amount of acidity produced during the oxidation exceeds the acid-neutralizing capacity, the soil will acidify, indicated by a substantial drop of pH. This type of incubation is used for identification of hypersulfidic materials

in the U.S. Soil Taxonomy (Soil Survey Staff 2022) and in the WRB (IUSS Working Group WRB 2015).

Soil subsamples were incubated, at GTK, in plastic bags and small sample containers, later chip trays were deemed to be the most suitable (Fig. 7). Subsamples were prepared in 2–10 mm thick layers allowing them to incubate at room temperature under moist conditions close to field capacity (regular addition of deionized water), following the procedures described by Creeper et al. (2012). The pH was measured using Hamilton Flatrode and Filltrode electrodes, in the field during sampling, after about 9 weeks in the laboratory, and if necessary, incubation continued up to 19 weeks. Based on the incubation-pH, the samples were classified as ASS or non-ASS material.

#### 4.5. Compiling map products

The field survey (overview mapping) was completed in 2021. More than 23 000 sites were studied, about 7 500 chemical analyses were made and around 40 000 samples incubated and measured for pH.

The conventional ASS occurrence map (1:250 000) was produced using the field observations and laboratory analyses (classified points; primary material), together with the existing data from GTK and NLS listed in Section 4.1. as input covariates. The map shows the probability of occurrence of ASS (high, moderate, low and very low probability) in the Littorina area. The map compilation was carried out manually in ArcMap environment. The aim was to delineate probability areas: the *high probability class* had a probability of >75%, indicating that >75% of the sampling points were classified as ASS, whereas the corresponding figures for the *moderate, low, and very low probability classes* were 50%, 10%, and 0%, respectively. The minimum area of digitized polygons was approximately 6 hectares.

The ASS occurrence map is published and available in the “Acid sulfate soils” map service (Geological Survey of Finland 2023). It



Figure 7. Sample container (chip-tray) used for incubation of collected samples. The pH is measured by inserting the pH-electrode directly into the moistened sample. Photo: GTK/ Hannu Hirvasniemi.

provides information about the distribution and properties of ASS in Finland (Fig. 8). In addition to the probability map, the map data include the reconnaissance and research site locations, indicating whether the point is classified as ASS or non-ASS. The point symbols also indicate the measured depth of the unoxidized sulfidic material from soil surface and where lithologies or horizons change. At the research observation sites, more detailed information, such as background information for the site, photos and a profile diagram showing lithostratigraphy, depth curves for  $\text{pH}_{\text{field}}$ ,  $\text{pH}_{\text{inc}}$ , and S-contents, are available.

## 5. Results and discussion

At the start of the project in 2009, we assumed that ASS in Finland comprise mainly fine-grained sediments (<0.063 mm; clay, silt, gyttja) containing >0.2% sulfur and occurring along the coast, i.e., traditional ASS. However, during the process we recognized that there are considerable occurrences of other types of ASS, i.e., coarse-grained, organic and unsorted ASS (Section 5.3.). The methods,



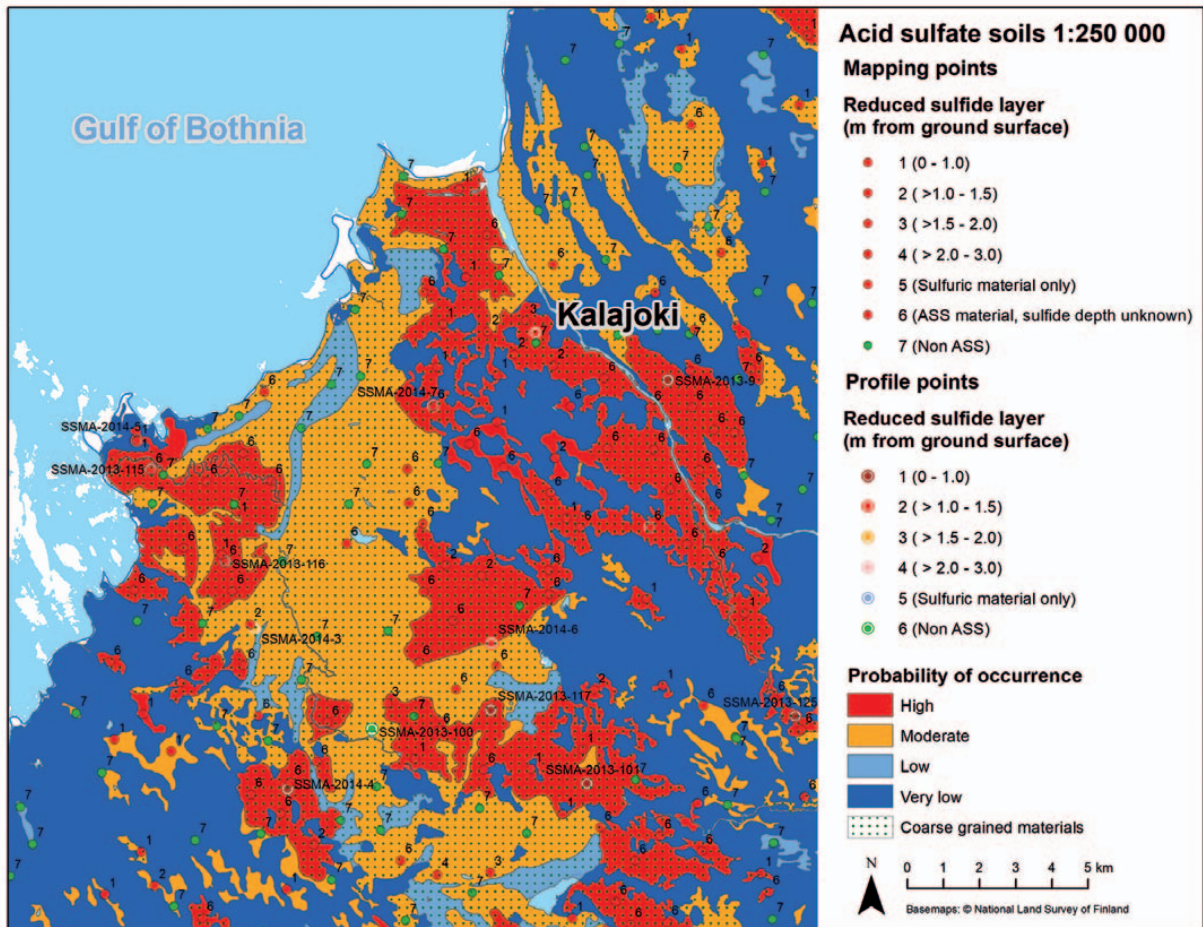


Figure 8. Screen capture from GTK's acid sulfate soil (ASS) map service (1:250 000), the Kalajoki district in western Finland (Geological Survey of Finland 2022).

definition and classification of ASS materials all evolved during the process as we gathered new information and experience.

### 5.1. Classification of acid sulfate soils in Finland

Globally, ASS and their diagnostic materials are not yet classified in an entirely harmonized way. However, the common denominator for an ASS is soil pH, which in some horizons is, has been, or can be, lowered to values below 4 due to sulfide oxidation. Most classification systems for ASS materials follow the Soil Taxonomy (Soil Survey Staff 2014, 2022), WRB (IUSS Working

Group WRB 2015, 2022) and the Australian soil classification (Isbell & NCST 2021). There are, however, some limitations in these systems, particularly the depth to which the ASS materials are a classification criterion. They may not recognize ASS in areas with intensive and deep drainage (often >2 m) of isostatically uplifted marine sediments, like in Finland. Therefore, slightly different diagnostic criteria and classification were developed in Finland (and Sweden) based on the extensive soil data collected during the mapping programme and in other projects and workshops. The new classification is described here and in more detail in Boman et al. (2023 this volume).

The primary purpose of soil mapping and classification is to serve as a basis for land use activities, and the soil name should indicate the essential soil properties. Land-use practices determine the depth from which ASS materials have harmful effects. According to earlier international classification systems the ASS characteristics have to occur within 125 cm (FAO 1988) or 150 cm (U.S. Soil Taxonomy, Soil Survey Staff 2014). In the latest classification from the IUSS Working Group WRB (2022) there are no such criteria. In Finland, almost all agricultural land requires artificial drainage, and sulfidic layers even below 2 m are oxidized and have adverse effects on drainage water (Joukainen & Yli-Halla 2003). Sulfidic horizons deeper in the soil are particularly important in construction and infrastructure building. In the present project, the occurrence of ASS materials down to 2–3 m depth was always classified as ASS, whatever the depth within the drilled profile. Our new definitions and diagnostic criteria for ASS and ASS materials largely follow those established by the International Acid Sulfate Soil Working Group (Sullivan et al. 2010), with some modifications and inclusion of the new ASS materials (Boman et al. 2023 this volume). In short, the most important modifications are:

(1) Slightly different meaning of hypersulfidic and hyposulfidic materials compared to current classification systems (Sullivan et al. 2010; Isbell & NCST 2021; IUSS Working Group WRB 2022) due to the addition of a lower pH value for organic soil materials (peat).

(2) Re-introduction of the term “para”, originally introduced by Pons (1965) to describe ASS materials that do not completely fulfil the diagnostic criteria of ASS materials (pH <4.0) in current classification systems. They may nonetheless have a strong negative impact on the environment due to sulfide oxidation and may have a much higher acidifying potential than coarse-grained soils classified as ASS (Visuri et al. 2021; Mattbäck et al. 2022a). Para-acid sulfate soil materials are not shown on the map and are not included in the extent of ASS.

## 5.2. General observations

The largest and most problematic occurrences of ASS occur in the western, northwestern and northern regions, covering 24–29% of those areas, where the land uplift has been strongest and the highest shoreline of the Littorina Sea at present is 70–100 m.a.s.l. However, the variation is large and for example, the Pyhäjoki catchment area (133 600 ha) has 6% ASS, whereas ASS occupy about 45% of the small Vörå catchment (22 300 ha). In the southern and southwestern regions, ASS cover 10–18% of the land below the highest Littorina shoreline (30–60 m.a.s.l.) (Auri et al. 2022).

Coarse-grained ASS (sand) are more common in the northern-northwestern-western regions compared to the southwestern-southern parts of the country. A likely reason is that larger rivers capable of transporting coarser sediment are more common in the first mentioned area, in which there are also more glaciofluvial deposits, that have been a source for extensive sandy littoral deposits and a possible environment for sulfide formation. Forestry is the most common type of land-use in regions dominated by coarse-grained and organic ASS, whereas fine-grained ASS and agriculture are the most common ASS landscapes in southwestern and southern Finland. The soil material in non-ASS landscapes is usually glacial till but in southwestern and southern Finland non-ASS landscapes more often consist of bedrock outcrops (Mattbäck et al. 2022b).

In southern Finland, sulfidic sediments generally have a greyish green colour, indicative of a higher  $\text{FeS}_2$ :FeS ratio, whereas in the western-northwestern-northern regions, massively black sulfidic sediments, indicating a lower  $\text{FeS}_2$ :FeS ratio, are more common (cf. Boman et al. 2008, 2010). The proportion of pyrite (cf. Boman et al. 2008) is bigger in southern Finland because of higher salinity, temperature and organic activity (cf. Sohlenius & Öborn 2004).

### 5.3. Newly defined acid sulfate soil materials

According to previous studies (Åström & Björklund 1997; Österholm & Åström 2002) and our results, fine-grained ASS materials with a strong buffering capacity generally need to have an S content higher than ~0.2% to drop pH below 4.0 when oxidized or incubated. In the early stage of the programme, we in several regions discovered large occurrences of coarse-grained soil material (sand, 0.063–2 mm), which was acidified (pH <4.0) when oxidized, even if the S content was only ~0.01–0.1% (Mattbäck et al. 2017, 2022a). We also found abundant peat with elevated S contents up to 5% (max 11%), and glacial till with low S contents (<0.1%), which acidify to pH <3.0 and pH <4.0, respectively, during incubation. These three materials behave as ASS.

Such materials have sporadically been described earlier as sources of acidic effluents (e.g., Kivinen 1944; Purokoski 1959; Yli-Halla et al. 1999; Räisänen & Nikkarinen 2000; Hadzic et al. 2014; Visuri et al. 2021). We call them coarse-grained ASS, organic ASS, and unsorted ASS and they are described below. The new types also occur inland, outside the Littorina area, especially in areas where black shales (see Fig. 4) and sulfidic ore zones have been exposed for glacial erosion.

#### 5.3.1. Coarse-grained acid sulfate soil materials

It soon became evident that coarse-grained materials (sand) in several places displayed a substantial pH-drop <4.0 during soil incubation, thus fulfilling the criteria for ASS, even where the S content was only ~0.01–0.1%. Though their acidity is low compared to fine-grained ASS materials, they may have an environmental impact of regional importance. Coarse-grained ASS occur in old river deltas, estuaries, littoral deposits and washed beach deposits. The last mentioned were formed when glaciofluvial sediments were exposed to strong littoral erosion during the post-glacial rebound.

There are several sand-pit lakes in the western-northwestern regions with pH about 3.5 (Mattbäck et al. 2017). Acidic water has escaped from sand-pit lakes and caused large fish kills in receiving waters at least in Kokkola and Liminka (Österbottningen 2007; Oikarinen pers. comm. 2012). In the Siikajoki river in the northwestern region, fish kills have occurred frequently over the years (Sutela et al. 2012) and our study revealed that large areas of coarse-grained ASS are the probable source.

In many cases, coarse-grained ASS are difficult to recognize in the field. While traditional hypersulfidic soils comprise dark gray or black sulfidic parent materials, such colours are rare in coarse-grained ASS, most likely due to the lack of monosulfides. Typically, a sulfuric horizon with pH <4.0 is absent and minimum field pH is normally 4.5–6. The S content is commonly very low (<0.1%) (Mattbäck et al. 2017), but pH drops rapidly from around 6 to well below 4.0, even below 3.0, during incubation. This is a consequence of a very poor buffering capacity due to low specific surface area, quartz-feldspathic mineralogy, low content of organic matter and lack of cation exchange sites on the weathered soil minerals (Ahern et al. 2004; Dear et al. 2023; Mattbäck et al. 2017).

Fine-grained ASS materials usually release one or two orders of magnitude more potentially harmful elements than coarse-grained ASS materials (Mattbäck et al. 2022a). However, the mobilisation of such elements from coarse-grained ASS is still considerably higher than from coarse-grained non-ASS. Although the S concentrations and acidities in the sulfidic coarse-grained parent materials are significantly lower (10–100 times) compared to fine-grained ASS materials, the pH-values seem to be similar after a 19-week incubation (Fig. 9) (Visuri et al. 2021; Mattbäck et al. 2022a).

Leaching of acidity and metals from fine-grained ASS can go on for decades, or even one hundred years (Österholm & Åström 2004). Coarse-grained ASS may cause considerable environmental problems, but not as long-lasting as traditional ASS (cf. Mattbäck et al. 2022a). During sand mining, coarse-grained ASS materials are



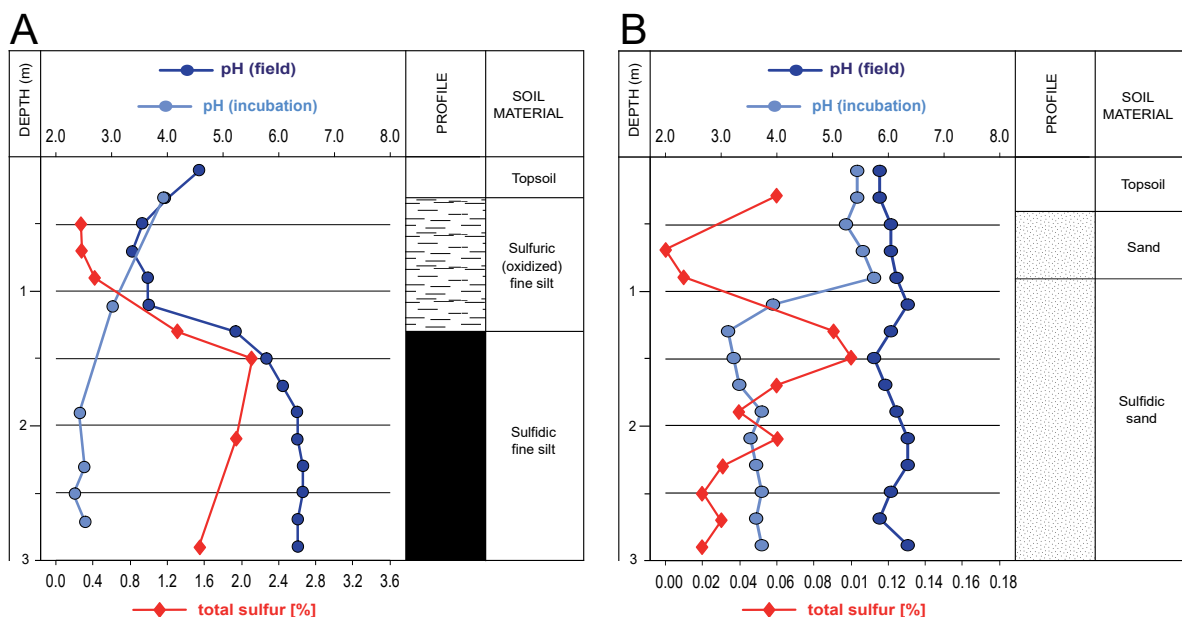


Figure 9. A. "Traditional" fine-grained acid sulfate soil profile (JMAU-2010-13) from Pyhäjoki, western Finland. B. Coarse-grained acid sulfate soil profile (SSMA-2014-6) from Kalajoki, western Finland.

stockpiled and/or the groundwater table is lowered, and any acid that has been generated is likely to be quickly mobilized.

Acid sand-pit lakes have been described earlier (e.g., Piispanen & Nykyri 1997), and acid sand materials have in a few cases been described as sources for acidic effluents (Purokoski, 1959; Yli-Halla et al., 1999). However, this survey is the first time in Finland where significant and mappable areas of coarse-grained materials have been recognized, studied and defined as ASS (Mattbäck et al. 2017, 2022a).

### 5.3.2. Organic acid sulfate soil materials

Peat covers about 10 million ha in Finland. Peat has high S contents (by weight) compared to inorganic soils, with a mean of 0.24% S and maximum content above 20% for 32 517 samples from 4 254 peatlands (7784 sampling points) all over the country (Herranen 2009). In the present study, the highest S concentration (11%; in Veteli) was found in peat.

Organic acids naturally occurring in peat may decrease pH below 4.0 (Shotyk 1988), but values of 2–3 indicate the presence of sulfuric acid, usually due to oxidation of iron sulfides (Thomas 2006). During incubation, the pH in peat may drop to values well below 3 (Fig. 10) (Hadzic et al. 2014). Therefore, a lower pH limit (pH <3.0) is used to classify peat as organic ASS materials. Peat classified as ASS materials has been documented, among others, in Denmark (Madsen et al. 1985), northern Germany (Gröger 2013) and Australia (e.g., Dear et al. 2023). Scattered occurrences in Finland have been reported earlier (Yli-Halla et al. 1999; Hadzic et al. 2014; Visuri et al. 2021), but the present study is the first to define, classify and localize vast areas of peat as organic ASS. Organic ASS can, like fine-grained ASS, be a source of environmentally harmful acid effluents rich in harmful elements, when exposed to air (more than half of the peatlands have been drained). The problems are accentuated in peat-mining areas (Mäkilä et al. 2012; Hadzic et al. 2014; Visuri et al. 2021).

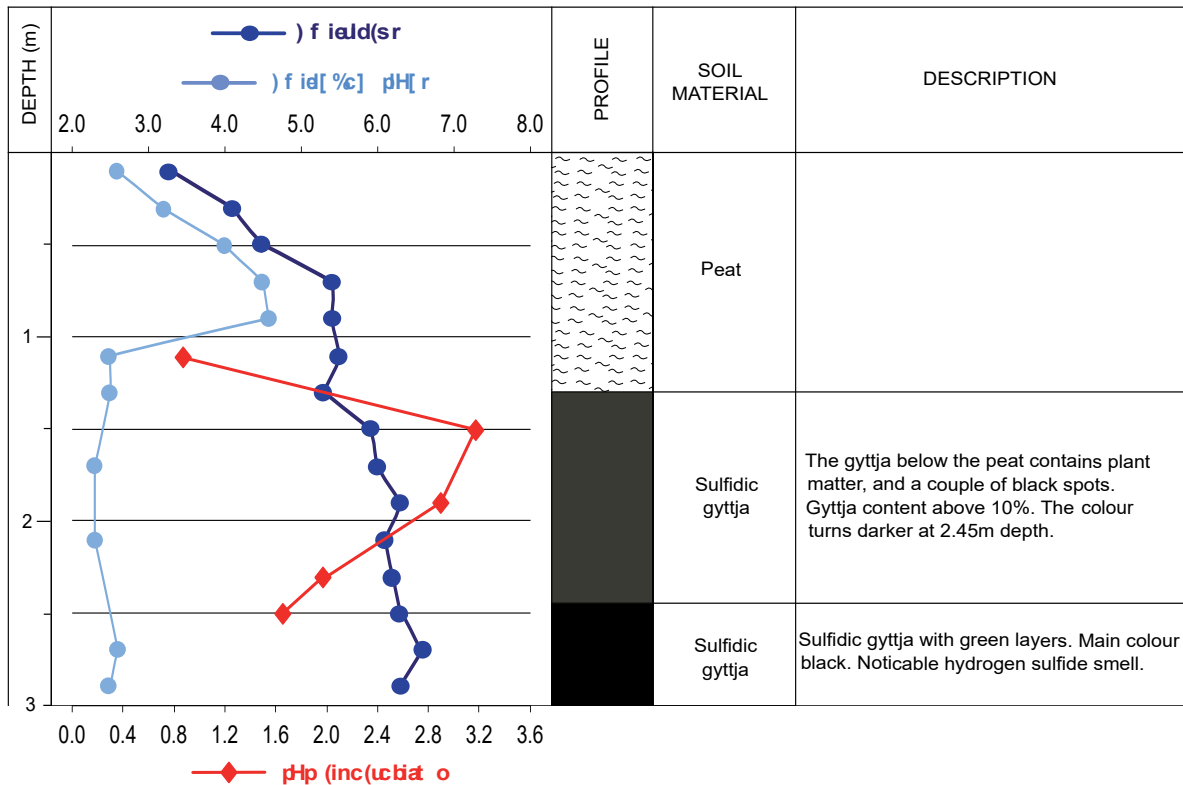


Figure 10. Profile from Hömossdiket, Kronoby, western Finland. Peat on sulfidic gyttja (Auri et al. 2012).

Organic ASS materials occur in peatlands and estuaries within the Littorina area, and inland they occur in association with black shales (see Fig. 4). Exceptionally high contents of Co, Ni, and Zn in peat often indicate the presence of black shale zones nearby (Virtanen & Lerssi 2006; Herranen 2009; Herranen & Toivonen 2018). Dissolved S and metals (Co, Cu, Fe, Mn, Ni, U, and Zn) are mobilized and can be incorporated in the peat by capillary rise, or move short or long distances with groundwater and precipitate in the reducing environment in peat (cf. Mäkilä et al. 2012; Hadzic et al. 2014).

### 5.3.3. Unsorted acid sulfate soil materials

During the latest glaciation, the inland ice tore away fragments of sulfide-rich black shales and mineralizations, which were mixed in unsorted till (Fig. 11), and usually transported less than

one km (Salminen & Hartikainen 1985), and in many places covered with sand, eskers or peat. Occurrences of such till, with pH values <4.0 in their oxidized parts and after incubation, thus fulfilling the criteria for ASS, is consequently defined as unsorted ASS.

Unsorted ASS may exhibit low pH-values and their S content (0.02–0.2%, max 1%) is usually similar to that of coarse-grained ASS (Autiola et al. 2022). Because glacial till contains varying proportions of coarse- and fine-grained particles, their buffering capacity varies greatly. Unsorted ASS materials are not very common, but locally pose environmental risks similar to other ASS materials. Thus, they should be considered in planning and land-use in regions with bedrock exposing black shales and sulfidic ores.



Figure 11. Oxidized unsorted acid sulfate soil material with pH 3.5, containing boulders and fragments of black shale, in this case transported only a short distance. Photo: GTK / Stefan Mattbäck.

## 5.4. Extent of acid sulfate soils in Finland

### 5.4.1 Earlier estimations

The first inventory of ASS along the coastal plains of Finland, based on field observations, pH and S determinations for 1259 samples from “suspect” farmland, was made by Purokoski (1959). He concluded that ASS cover about 38 000 ha in the coastal regions. Erviö (1975) showed that this estimate is too low, because in the drainage basin of river Kyrönjoki alone in western Finland, he mapped 35 000–40 000 ha ASS. Some local mapping projects were accomplished in the 1980s (e.g., Palko et al. 1985, 1987). The first

comprehensive estimate of the distribution of ASS was published by Puustinen et al. (1994). It was based on a wide-spaced inventory of drainage status, cultivation practices and phosphorus load from agricultural fields, including 1 065 sites over the whole country. Each sample, down to 2 m depth, represented 2 100 ha. Within the Littorina area, 160 sites were registered with field pH <5.0 and with a typical redox gradient, representing approximately 336 000 ha of ASS according to those criteria.

Yli-Halla et al. (1999) used international criteria based on the FAO-Unesco Soil Map of the World (FAO 1988) and U.S. Soil Taxonomy (Soil Survey Staff 1996) to re-classify the data of Puustinen et al., ending up at no more than 130 000 ha. Later, Yli-Halla et al. (2012) made even more thorough



calculations and concluded that there are at least 158 000 ha of cultivated fields with minimum pH <4.0 and sulfidic materials within 2 m below soil surface, classifying as ASS according to the contemporary classification systems. The methods and classification criteria applied in these surveys are not comparable with each other nor with the criteria we use today (Sullivan et al. 2010; IUSS Working Group WRB 2015, 2022; Boman et al. 2023 this volume).

Some calculations of the extent of ASS have recently been made with varying techniques and in different areas along the coast. Beucher et al. (2015) used maps surveyed by conventional mapping (10 catchments, including 3 271 research and reconnaissance points from GTK's data) combined with spatial modelling techniques (14 catchments including 765 research and reconnaissance points from GTK's data) as a test to estimate the extent of ASS on GTK's half-baked map. They counted that 12% or 260 000 ha of the total investigated area (2 130 000 ha) were high-probability ASS areas.

GTK and the Geological Survey of Sweden (SGU) have jointly mapped ASS occurrences in the northern part of the Littorina area (Becher et al. 2018). They used a method developed in Denmark (Madsen & Jensen 1988) to determine the extent of ASS. They counted how many of the observation sites were ASS/non-ASS within each of the four ASS classes. For example, if 90% of the sites within a specific area of high probability is recognized as ASS, it means that 90% of that area is ASS. They counted an area of 310 600 ha in five catchments in the northwestern region on the Finnish side. The probabilities were 93.4%, 54.9%, 6.5%, and 2.7% for the high, medium, low and very low probability classes, respectively. Their results showed that 25% of that particular area is ASS.

As of recently, digital soil mapping (DSM) techniques have been utilized for regional ASS mapping in Finland (Beucher et al. 2014, 2015; Estévez et al. 2022). Future ASS maps and updates at GTK will be produced using DSM.

#### 5.4.2. Calculation of the extent of acid sulfate soils in Finland

The final ASS map of Finland (1:250 000), compiled in this project, contains information on the distribution and properties of ASS in ca. 23 000 observation sites in the Littorina area. Fine-grained and organic ASS are marked as ASS, while coarse-grained ASS are indicated on the map with a dot pattern (Fig. 8). Unsorted ASS and inland ASS are not shown on the map and are not included in the calculated extent.

The extent of ASS was calculated based on the approach previously used in Denmark (Madsen & Jensen 1988; see preceding Section) using the following formula:

$$\begin{aligned} \text{Area of ASS} = & [\text{area of the high probability class}] \times [\text{the probability \% of the high probability class}] \\ & + [\text{area of the moderate probability class}] \times [\text{the probability \% of the moderate probability class}] \\ & + [\text{area of the low probability class}] \times [\text{the probability \% of the low probability class}] \\ & + [\text{area of the very low probability class}] \times [\text{the probability \% of the very low probability class}] \end{aligned}$$

Table 1. The probability of encountering acid sulfate soils in four probability classes in the Littorina area in Finland.

	Probability class			
	High	Moderate	Low	Very low
Probability	93 %	56 %	5 %	3 %
Extent, ha	486 390	365 091	58 410	92 649
Total extent, ha				1 002 539

The calculations show that in Finland we have slightly more than 1 000 000 ha of ASS along the coast (Table 1). The Åland Islands, the Kimito Island and the Replot Islands, together covering an area of 240 000 ha, have not been studied, which means that 21% of the mapped area is ASS. One million ha is 3–6 times more than earlier estimates, although we use a lower threshold pH than Puustinen et al. (1994) but the same as Yli-Halla et al. (2012). The main reasons are: (1) Our mapping programme utilized considerably more observation sites, about 23 000 versus 160, and covered the

whole Littorina area, (2) The depth criteria for ASS classification was removed and corings were generally drilled to 2–3 m, (3) New classification criteria have been adopted and new types of ASS were introduced, and (4) Puustinen et al. (1994) and Yli-Halla et al. (1999, 2012) investigated only agricultural fields, while this study covers all land uses, and large occurrences of ASS are also found in swampy forests and peatlands. In a detailed study in Hömossdiket, western Finland, GTK mapped a small drainage basin of 4 800 ha, where about 50% of the peatlands and swampy forests on peat, and 15% of the whole basin, were underlain by sulfidic (mineral or organic) sediments (Auri et al. 2012). In the northwestern and northern parts of the coast 40–80% of the ASS occurrences are situated in varying types of forests and peatlands, the highest percentages appearing in the northernmost part (Edén et al. 2014; Hannukkala et al. 2015).

Comparing the final map with data from Corine Land Cover (Finnish Environment Institute 2022), reveal that ca. 41% of the ASS in Finland are agricultural land, ca. 55% are forests, drained peaty forests, drained forested peatland and open peatland (open bog and marsh). A small proportion occurs in urban environments (Auri et al. 2022).

### 5.5. Evaluation of applied methods

This study is the first comprehensive project for mapping ASS in Finland, using the latest and internationally compatible methods and criteria. The project lasted six years longer than planned. The main reason was that, for half a century, ASS in Finland had been considered to comprise fine-grained sulfidic sediments occurring on agricultural land along the coast of the Littorina area, and this soil type was therefore prioritized over other soil types in the first years of the mapping. Recognizing that there are significant occurrences of other ASS types, caused a major change of the original plan by extending the focus to these types and also forced to re-visit some of the surveyed areas.

The compilation of a predictive ASS map using artificial networks (ANN) (Section 4.1.) was

useful for pointing out potential ASS, especially in areas with predominantly clay, silt and peat deposits. However, coarse-grained and unsorted materials were not given equal importance in the modelling algorithm and therefore the predictive ASS map was not very accurate in areas underlain by e.g., river delta deposits and beach/littoral sediments. Looking back, the recognition of coarse-grained and unsorted ASS would perhaps have been quicker if the sampling scheme would have been prepared randomly using a grid system and if more samples, covering all soil materials, would have been collected and analysed (incubation-pH) immediately from the start. This would, however, most likely have delayed the mapping even more as the access to field sites would have become more cumbersome (e.g., lack of a road network) and because a denser soil sampling consequently would have required more time. However, due to the desired duration of the mapping project, funding was not available for such an approach. Compiling a predictive map using machine learning techniques would still be a wise choice if an all-inclusive test sampling of soil types is included.

The upside with the long mapping process was the improvements made regarding experience, knowledge, classification, methods, equipment and logistics in all phases of the process. Improved knowledge about how to localize and identify ASS are important in risk assessment and land use. The ASS map service and the large amount of data and soil samples can be useful in many ways in the future, for instance in AI applications. Another important outcome is the large network of research organisations, universities, authorities, stakeholders and target groups, that has evolved during the project. The co-operation is ongoing and new projects starting, both in Finland and internationally.

## 6. Conclusions

Acid sulfate soils constitute a major environmental problem worldwide, and Finland has the largest known ASS occurrences in Europe. In Finland, ASS

have traditionally been considered to comprise fine-grained sulfidic sediments occurring on agricultural land along the coast below the highest shoreline of the ancient Littorina Sea. The main results of this comprehensive mapping programme are:

- The mapping methods, definition and classification for the study of ASS in Finland have changed and improved significantly.
- Three new types of ASS materials have been defined, classified and incorporated in the ASS family: (1) Coarse-grained ASS (e.g., sand), (2) Organic ASS (e.g., peat), and (3) Minor occurrences of unsorted ASS (till). These three types occur not only along the coast, but also inland. Like the traditional fine-grained ASS, these types also cause environmental threats; organic ASS may cause severe problems during peat draining and extraction, while coarse-grained and unsorted ASS cause problems at least on a local scale. The possibility for ASS and environmental problems should be considered also inland, especially in areas with black shales and ore zones.
- There are about 1 000 000 ha of ASS along the coast of Finland. This is ca. 21% of the land in the Littorina area, and six times more than earlier estimates. The most important reasons for the big increase in area of ASS are: modified classification criteria, inclusion of new types of ASS, deeper observations (2–3 m), significantly more research sites (23 000), and the inclusion of all forms of land use, particularly peatlands and low-lying swampy forests in addition to agricultural land.
- The traditional, fine-grained ASS are the dominating type causing most harm. On the west coast the biggest problems are encountered in agriculture and as deterioration of surface water. In the Helsinki Metropolitan area, in southern Finland and around cities along the coast, ASS are a serious problem in infrastructure building and in all land use.

- The mapping data at scale 1:250 000 is available on GTK's map service. It is intended to be used for mitigation and prevention of problems caused by ASS in regional planning on a general scale, land-use planning, water management, agriculture and forestry.

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