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A nationwide acid sulfate soil study — A rapid and cost-efficient approach for characterizing large-scale features

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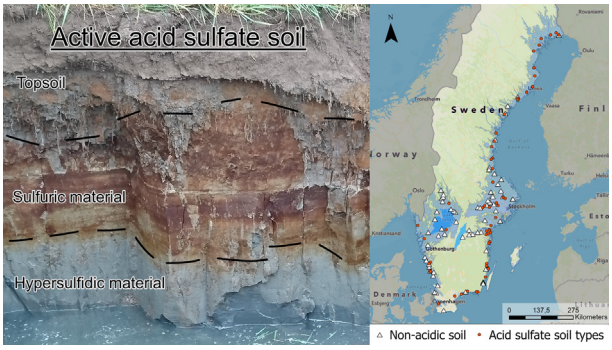
HIGHLIGHTS

- Low-density sampling strategy resolved large-scale acid sulfate soil features.
- Several acid sulfate soil classes were included to provide precise characterization.
- Very acidic soils occurred in areas previously unrecognized for acid sulfate soils.
- Sulfur concentrations correlated with both minimum field pH and incubation pH.

GRAPHICAL ABSTRACT



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ABSTRACT

Acid sulfate soils are sulfide-rich soils that pose a notable environmental risk as their strong acidity and low pH mobilizes metals from soil minerals leading to both acidification and metal contamination of the surrounding environment. In this study a rapid and cost-efficient approach was developed to resolve the main distribution patterns and geochemical features of acid sulfate soils throughout coastal plains stretching for some 2000 km in eastern, southern, and western Sweden. Of the investigated 126 field sites, 47 % had acid sulfate soils including 33 % active, 12 % potential, and 2 % pseudo acid sulfate soils. There were large regional variations in the extent of acid sulfate soils, with overall much higher proportions of these soils along the eastern coastal plains facing the Baltic Sea than the western coastal plains facing the Kattegatt/Skagerrak (Atlantic Ocean). The sulfur concentrations of the soil's parent material, consisting of reduced near-pH neutral sediments, were correlated inversely both with the minimum pH of the soils *in situ* (rS = −0.65) and the pH after incubation (oxidation) of the reduced sediments (rS = −0.77). This indicated the importance of sulfide levels in terms of both present and potential future acidification. Hence, the higher proportion of acid sulfate soils in the east was largely the result of higher sulfur concentrations in this part of the country. The study showed that the approach was successful in identifying large-scale spatial patterns and geochemical characteristics of importance for environmental assessments related to these environmentally unfriendly soils.

1. Introduction

Acid sulfate soils have been described as the nastiest soils on earth. They can occur on coastal plains worldwide and are developed on geological materials that contain iron-sulfide minerals, are low in carbonate phases,

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and typically have a fine-grained (clay-silt) texture (Dent and Pons, 1995). The formation of this soil starts when the sulfide minerals are oxidized to sulfuric acid and secondary Fe(III) phases, *via* mechanisms largely driven by microorganisms, causing the pH of the soil to strongly drop (Högfors-Rönnholm et al., 2022; Karimian et al., 2018; Wu et al., 2013). These processes are typically activated when the ground-water table drops in sulfide-rich waterlogged sediments. This can occur naturally as for example after extended droughts (Fitzpatrick et al., 2017) but is generally caused by artificial drainage primarily for agricultural cultivation but also for forestry and infrastructure development (Fanning et al., 2017; Joukainen and Yli-Halla, 2003). Furthermore, under the oxidizing acidic soil conditions, metals with toxic properties such as Al, Cd, Cu, Mn, Ni, Be, and the rare earth elements existing in soil minerals are released and dissolved in the acidic pore water (Åström et al., 2018, Åström et al., 2010; Virtanen et al., 2014). When the soils are flushed during rains or snow melting, the pore waters are hydrologically activated and discharged, leading to acidification and metal contamination of the surrounding environment (Burton et al., 2006; Hulisz et al., 2022; Nystrand and Österholm, 2013; Unland et al., 2012). This has wide negative effects on surrounding ecosystems (Ljung et al., 2009; Toivonen and Österholm, 2011) and may ultimately affect human health (Fältmarsch et al., 2008; Ha et al., 2019; Ljung et al., 2009).

A major challenge with acid sulfate soils in terms of assessment and control of their environmental effects is that there is only a general idea of where they might exist. There are several reasons for this lack of knowledge including that acid sulfate soils: (i) were not identified on a wide international level until the 1970's (Brinkman and Pons, 1973); (ii) are not distinguished in soil and geochemistry maps on national, regional, and continental scales; (iii) are highly reactive such that they can form in the order of years if land-use changes (*e.g.* the ground-water table drops) and can lose their acidity in the order of decades to centuries and thus, can be very short-lived as compared to other soils in general; and (iv) have mosaic and complex occurrence patterns controlled by levels of sulfide minerals as well as past and current land-use activities. Furthermore, criteria that clearly distinguish acid sulfate soils are still being refined. As a consequence, mapping acid sulfate soils is time-consuming and challenging and thus is being carried out extensively only in a few countries. Hence, there is a general lack of spatial knowledge of these soils both regionally and globally, including in Sweden that is the focus of this study.

Here we present a rapid and cost-efficient approach to unravel the main distribution patterns and geochemical features of acid sulfate soils throughout an entire nation (Sweden) with an area of 528,447 km^2. It is well known that acid sulfate soils occur on the coastal plains in northeast Sweden, but for large parts of the country their extent and character are poorly known or unknown. The approach consisted of four steps: (i) identification of regions where the overwhelming portion of the acid sulfate soils in the country were expected to occur, thus strongly minimizing the area needing to be studied; (ii) identification of quaternary deposits (based on existing nationwide maps) that may carry metal sulfides and thus, can be potentially turned into acid sulfate soils; (iii) low-density sampling focusing on the identified quaternary deposits and key regions; and (iv) carrying out chemical analyses of the soils including field pH, incubation pH, and sulfur concentrations. The approach was an efficient initial step to highlight, characterize, and map acid sulfate soils on a large regional (nationwide) scale and thus, form the basis for more detailed acid sulfate soil assessments and mapping on local scales.

2. Methods

2.1. Study area

The area located under the maximum Holocene (current geological epoch that begun approximately 11,650 years before present) marine limit was the focus of this study (Fig. 1A), as the overwhelming majority of the acid sulfate soils in Sweden were expected to occur within this area. While under the sea level, this area was a substrate for deposition of aquatic fine-grained sediments that were loaded with sulfide minerals if conditions favored sulfate reduction and subsequent formation and accumulation of metal sulfides (Emeis et al., 2002; Karimian et al., 2018). Such sediments have been forming since the brackish Littorina Sea stage (*ca.* 7000 BP – present) of the Baltic Sea development (Emeis et al., 2002; Öborn, 1989; Wastegård et al., 1995). During these periods the relatively high salinity (brackish-water conditions), biological productivity, and inflow of organic matter created ideal conditions for sulfide formation. Sulfide-carrying sediments have also formed prior to this period (*e.g.* Yoldia Sea stage at *ca.* 10300–9500 BP, or Ancylus stage at *ca.* 9500–7000 BP), but to a much smaller extent, as any favorable conditions would have been relatively rare or short-lived in these periods (Emeis et al., 2002; Sohlenius et al., 2001; Wastegård et al., 1995). The postglacial isostatic rebound of northern Europe throughout the Holocene has raised these sediments above sea level and thus, they occur widely in valleys and depressions in the terrestrial landscape under the maximum Holocene marine limit. Prior to the 19th century, these sediments were largely overlain by wetlands and a thin peat layer and were thus waterlogged. However, since then they have been increasingly drained mainly for agricultural cultivation. As a consequence, the groundwater table in the sediments has dropped extensively, exposing the inherent metal sulfides to atmospheric oxygen, eventually leading to severe soil acidification. This has resulted in the development of approximately 1–2 m thick acid sulfate soils, as shown by several geochemical studies (Lindgren et al., 2022; Öborn, 1989; Sohlenius et al., 2009; Sohlenius and Öborn, 2004), and recent mapping efforts by the Geological Survey of Sweden in the northern parts of the country (Geological survey of Sweden, 2022a). There are also other materials than marine and estuarine sediments that can contain sulfides and thus, develop into acid sulfate soils. These include Holocene lake sediments that may have been oxidized as a result of artificial lake drainage, and black schist materials that typically are rich in sulfide minerals (Lavergren et al., 2009). Therefore, both of these materials can add to the extent and coverage of acid sulfate soils in the country. Soils developed on black shales were not considered in this study.

2.2. Sampling

The basis for the fieldwork was Geological Survey of Sweden quaternary-deposit maps (Geological Survey of Sweden, 2022b) that exist for the entire area under the maximum Holocene marine limit. These maps identify several types of quaternary deposits that potentially contain sulfide minerals, the driver for the formation of acid sulfate soils. Accordingly, the focus was primarily on mudclays (gyttjalera) and secondly on postglacial clays. Silt, mud (gyttja), or sand were targeted where clay-soils were rare or did not occur on the quaternary-deposit maps. Hence, except at a few sites where the sampled material was sandy ($n = 11$), the collected materials were fine-grained consisting of clay and silt. Whenever possible, samples were taken from agricultural fields partly due to landowners having extensively converted areas with fine-grained sediments into agricultural lands *via* artificial drainage (Sohlenius and Öborn, 2004; Yli-Halla et al., 1999) and due to their easy accessibility. A total of 126 sites were sampled (Fig. 1A, Table S1) while making an effort to maintain a regular spread of sampling sites. All sites were < 120 m above sea level and 75 % < 40 m above sea level. The relatively low sampling frequency in the north where a wide area has been below the Holocene marine limit (Fig. 1A) was due to the well-known occurrence of acid sulfate soils in these regions (Geological survey of Sweden, 2022a).

At each site, a soil profile was obtained to a depth of 2 m using a 1 m long sampling auger with a 1 m extension rod. Basic field notes and observations of the soil were gathered (assessment of grain size, quaternary-deposit type plus overall homogeneity, and other notable observations) and the pH was measured at every 10 cm. For further chemical characterization, a sample was taken from the deepest part (reduced zone) of the soil profiles (120 sites) where pH was high due to reducing conditions. Furthermore, two samples were taken from different depths of

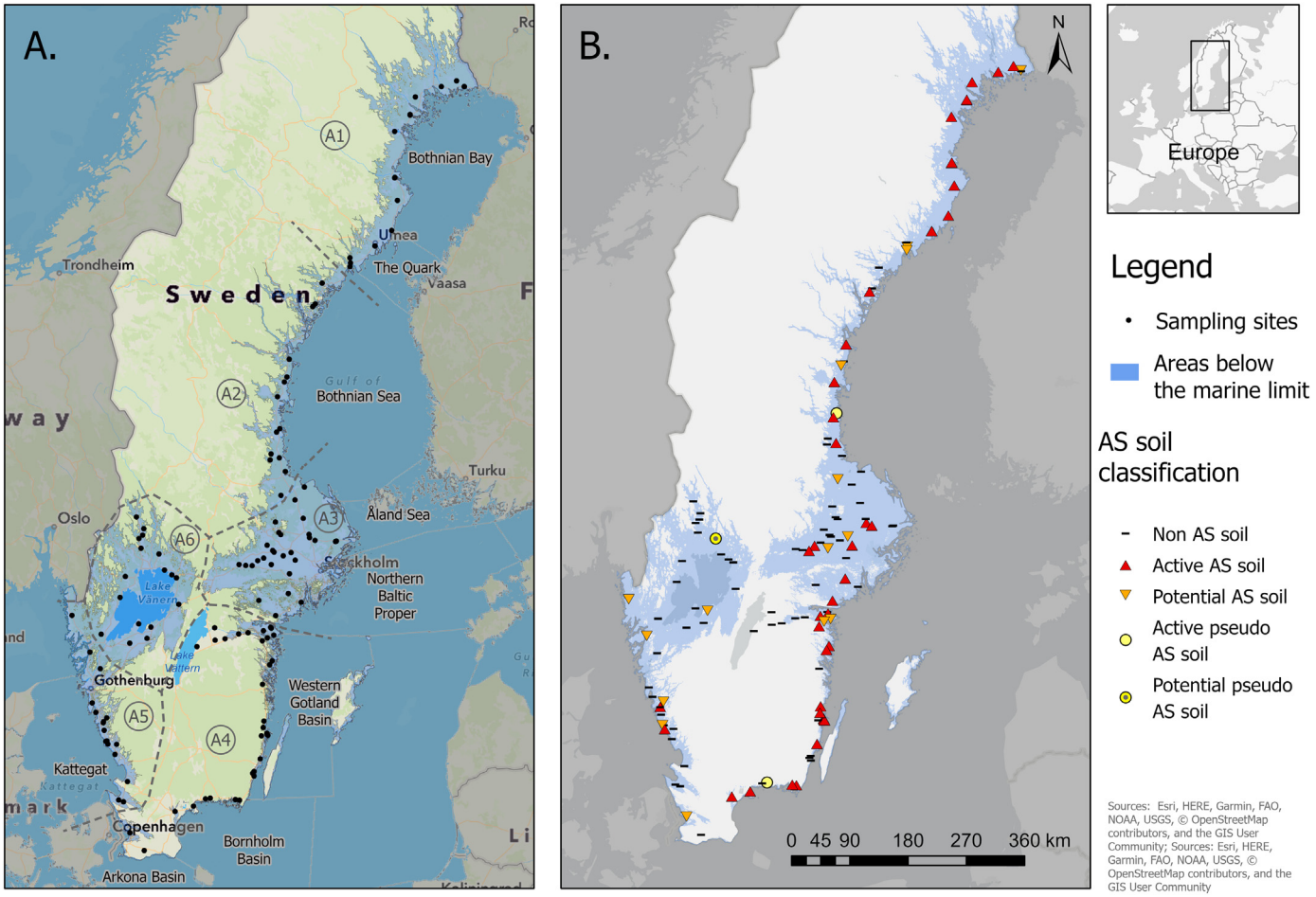

Fig. 1. Sampling sites in Sweden with areas A1 – A6 marked and the area below the Holocene marine limit indicated (A) plus the occurrence of acid sulfate (AS) soils in the country (B).

the reduced zone at two of the sites (0.9 m and 1.8 m, respectively at both sites) as the soil homogeneity was in question. The samples were collected and stored in generic plastic zip lock bags.

2.3. Chemical analyses

The soil samples obtained from the reduced zone (n = 122) were incubated at room temperature in a laboratory in order to determine the pH decrease upon oxidation. Accordingly, the soil materials in the open sampling bags (thus exposed to atmospheric oxygen) were regularly moistened with de-ionized water and homogenized to ensure full oxidation of the entire sample. The pH was measured after 19 weeks, at which point the pH of the samples was determined to have stabilized, according to procedures described in previous work (Boman et al., 2018; Creeper et al., 2012).

A portion (0.25 g) of each soil sample (dried and pulverized) was subject to a four-acid-digestion (HF, HNO_3, $HClO_4$, and HCl) and the obtained solution was analyzed for total sulfur and calcium concentrations with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The analytical precision was estimated based on ten samples selected at random, prepared in duplicate, and analyzed independently and anonymously (Gill, 1997). The precision was <1 % for sulfur and < 5 % for calcium.

2.4. Classification of acid sulfate soils

The soils were defined based on a recent scheme for classification of boreal acid sulfate soils with defined pH levels and drops that result from metal-sulfide oxidation (Boman et al., 2018). An “active acid sulfate soil” has an *in situ* pH minimum <4.0 (sulfuric material) or 4.0–4.5 (pseudosulfuric material) if in the underlying reduced material pH drops by at least 0.5 pH units to <4.0 on incubation (hypersulfidic material). A “potential acid sulfate soil” has an *in situ* pH minimum >4.5 with underlying hypersulfidic material. Such a soil may easily turn into an active acid sulfate soil if the groundwater table drops further into the hypersulfidic material. An “active pseudo acid sulfate soil” has an *in situ* pH 4.0–4.5 without underlying hypersulfidic material. A “potential pseudo acid sulfate soil” has an *in situ* pH minimum >4.5 and underlying reduced material for which the pH drops by at least 1.0 units to 4.0–4.5 on incubation (pseudohypersulfidic material). Finally, if none of these criteria are fulfilled, the soil is classified as a “non-acid sulfate soil”, that is, a minimum pH > 4.5 both *in situ* and after incubation of the underlying reduced material. A summary of the scheme is given in Table 1.

2.5. Subdivision of Sweden

Sweden was subdivided into six areas (A1 – A6) to aid the presentation, interpretation, and discussion of the results (Fig. 1A). The division was based on the sea basin that the coastlines face and was thus arbitrary, in particular inland. A1 covers the northernmost coastal area along the Bothnian Bay and the Quark. A2 covers the mid-eastern coastal areas bordering the Bothnian Sea. A3 stretches inland and borders in the east the Åland Sea and Northern Baltic Proper. A4 covers the south and southeastern coastal areas facing the Western Gotland Basin, Bornholm Basin, and Arkona Basin. A5 covers the west-coast area facing the saline water of Kattegat, whereas A6 covers a western inland area around Lake Vänern corresponding to the

Table 1
Acid sulfate soil classification according to the most recent classification proposed for boreal acid sulfate soils (Boman et al., 2018). *In situ* pH is the lowest pH in the soil profile measured immediately in the field. Incubation pH is the pH of the underlying reduced zone after being incubated (exposed to oxygen) in the laboratory.

Classification	*In situ* pH		Incubation pH
Non-acid-sulfate soil	> 4.5	and	> 4.5
Active acid sulfate soil	< 4.0	–	–
	4.0–4.5	and	< 4.0 (≥ 0.5 unit pH drop)
Potential acid sulfate soil	> 4.5	and	< 4.0 (≥ 0.5 unit pH drop)
Active pseudo acid sulfate soil	4.0–4.5	and	≥ 4.0
Potential pseudo acid sulfate soil	> 4.5	and	4.0–4.5 (≥ 1.0 unit pH drop)

area opposite (west of) A3. The division between A3 and A6 was based on the marine limit maximum, separating the east and west sides of the country. The division between A4 and A5 was put at the narrowest point of the Öresund bay, separating the Atlantic Ocean and the Baltic Sea. The surveyed sites (n = 126) were distributed among A1 – A6 as follows: 17, 14, 28, 33, 17, and 17, respectively.

3. Results

3.1. Acid sulfate soil occurrence

Out of the 126 sites (Fig. 1A), 59 (47 %) were classified as acid sulfate soil types, while 67 (53 %) were non-acid sulfate soils. Of the 47 % acid sulfate soils, 33 % were active, 12 % were potential, and 1.6 % plus 0.8 % were active pseudo and potential pseudo, respectively (Table 2). The active acid sulfate soils were identified based on both an *in situ* pH < 4.0 (n = 22) and an *in situ* pH 4.0–4.5 with underlying hypersulfidic material identified *via* incubation (n = 19). Only two soil samples with a field pH of 4.0–4.5 did not have underlying hypersulfidic material, which showed that the vast majority of soils with field pH in this range (90 %) have parental materials that can become severely acidified when oxidized.

There were large regional variations in the occurrence of acid sulfate soils (Fig. 1B). In A1, the active type was dominating (71 %), whereas in A3, A5, and A6 non-acid sulfate soils were dominating (65–88 %; Table 2). In A2 and A4 there was an approximately equal share of active and non-acid sulfate soils. Potential acid sulfate soils occurred in all areas representing 6–24 % of the soils (Table 2). The pseudo acid sulfate soils, which were rare, were identified at one site in each of A2, A4, and A6 (Fig. 1B, Table 2).

3.2. Sulfur and pH

There were large regional variations both in the minimum *in situ* pH (Fig. 2A) and in the pH after incubation of the reduced material (Fig. S1). The pH was overall very low in A1 both *in situ* (minimum range 3.5–5.7; minimum median 3.9) and after incubation (range 2.0–5.3, median 2.5). Whereas the three areas with the largest share of non-acid sulfate soils (A3, A5 and A6) had considerably higher pH, with the median *in situ* minimum ranging from 5.1 to 6.2 and the median after incubation from 6.3 to 6.6 (Table 3). The lowest pH value both *in situ* and after incubation was found in A4 (2.7 and 1.9, respectively). The corresponding figures for the other areas were 3.5–4.7 and 2.0–3.7, respectively (Table 3).

Large regional variations existed in the sulfur concentrations of the reduced material (Fig. 2B). The median sulfur concentration was very high in A1 (0.89 %) and A4 (1.01 %), with the latter area having the six highest values (> 2.0 %) with the maximum as high as 6.03 % (Table 3, Table S1). In contrast, the median sulfur concentration was low in A3 (0.07 %), A5 (0.07 %) and A6 (below detection). The maximum sulfur concentration was low in A6 (0.18 %) but high in all other areas (> 1.40 %) (Table 3). Of all analyzed samples (n = 122), 21 had sulfur concentrations below detection of which half (n = 11) were in A6 and zero in A1.

The Spearman correlation coefficient between sulfur concentrations in the reduced material and lowest field pH was −0.65 (p < 0.01). In detail, at sulfur concentrations <0.05 % (n = 48), the lowest pH values were > 4.0 and with the majority of samples within 5.0–7.0 (Fig. 3A). At 0.05–0.22 % sulfur (n = 30), the pH values were spread between 2.9 and 7.1. At ≥0.30 % sulfur (n = 44) the pH values were between 3.0 and 5.0, except for seven sites that had higher values up to 7.5 (Fig. 3A). At a given sulfur concentration > 0.10 %, the pH values in the west (A5 – A6) were overall considerably higher than in the east/south (A1 – A4; Fig. 3A).

The Spearman correlation coefficient between the sulfur concentrations and incubation pH of the reduced material was −0.77 (p < 0.01). At sulfur concentrations <0.05 %, all pH values were > 4.2 and with the majority within 6.0–8.0 (Fig. 3B). At 0.05–0.22 % sulfur, the spread of pH values was broad, ranging from 2.3 to 8.0. At ≥0.30 % sulfur all pH values were < 3.6, except for three outliers (sulfur concentrations of 1.3, 1.4, and 0.8 %) that had pH values of 5.8, 6.1, and 6.4, respectively (Fig. 3B).

The requirement in the utilized soil-classification system that the acidification shall be caused by sulfide oxidation was confirmed by elevated sulfur concentrations in the reduced material of all active and potential acid sulfate soils (≥ 0.05 %; Fig. 4). With a few exceptions, low sulfur concentrations were measured in the non-acid sulfate soils and overall intermediate sulfur concentrations in the few pseudo acid sulfate soils (Fig. 4).

Table 2
Percentage of various types of acid sulfate (AS) soils within the six areas of Sweden (A1 – A6).

Area	Non-AS soil % (n)	Active % (n)	Potential % (n)	Active pseudo % (n)	Potential pseudo % (n)
A1	12 (2)	71 (12)	18 (3)	0 (0)	0 (0)
A2	43 (6)	36 (5)	14 (2)	7 (1)	0 (0)
A3	69 (19)	25 (7)	7 (2)	0 (0)	0 (0)
A4	42 (14)	45 (15)	9 (3)	3 (1)	0 (0)
A5	65 (11)	12 (2)	24 (4)	0 (0)	0 (0)
A6	88 (15)	0 (0)	6 (1)	0 (0)	6 (1)
A1 - A6	53 (67)	33 (41)	12 (15)	1.6 (2)	0.8 (1)

n = number of sites.

4. Discussion

4.1. Sulfur content and its effect on pH

Previous sulfur-speciation studies of the hypersulfidic material of boreal acid sulfate soils have shown that the total reduced sulfur (TRS) is composed of a mixture of pyrite and metastable iron sulfides and that sulfur species other than TRS are minor (Backlund et al., 2005; Boman et al., 2008; Nystrand et al., 2021). As a consequence, there is a strong correlation between concentrations of total sulfur and TRS in these soils/sediments (Mattbäck et al., 2022). This feature was also evident in the total sulfur *versus* incubation pH of the samples from the reduced zone: at sulfur concentrations <0.05 % the pH was typically between 6.0 and 8.0, at ≥0.30 % typically <3.6, and in-between (0.05–0.30 %) there was a high degree of variability in pH (Fig. 3B). However, whereas sulfur concentrations <0.02 % resulted in pH > 5.0, at sulfur concentrations ≥0.02 % there were two contrasting trends in the S-pH plot (Fig. 3B).

The first trend showed increasing sulfur concentrations that resulted in strongly decreasing pH values down to <2.0 at the highest sulfur concentrations and the second trend for which the pH stayed much higher at corresponding sulfur concentrations and only dropped to just below 6.0 in a single sample despite sulfur concentrations reaching >1.0 % (Fig. 3B). The trend with high pH values may be caused by the presence of carbonates that would neutralize part or most of the acid. The occurrence of this mineral group was not determined, but the total calcium concentrations gave an indication. For the low-pH trend all samples (61/61) had calcium concentrations <2.0 %, whereas for the high-pH trend approximately half of the samples (10/19) had substantially higher calcium concentrations of

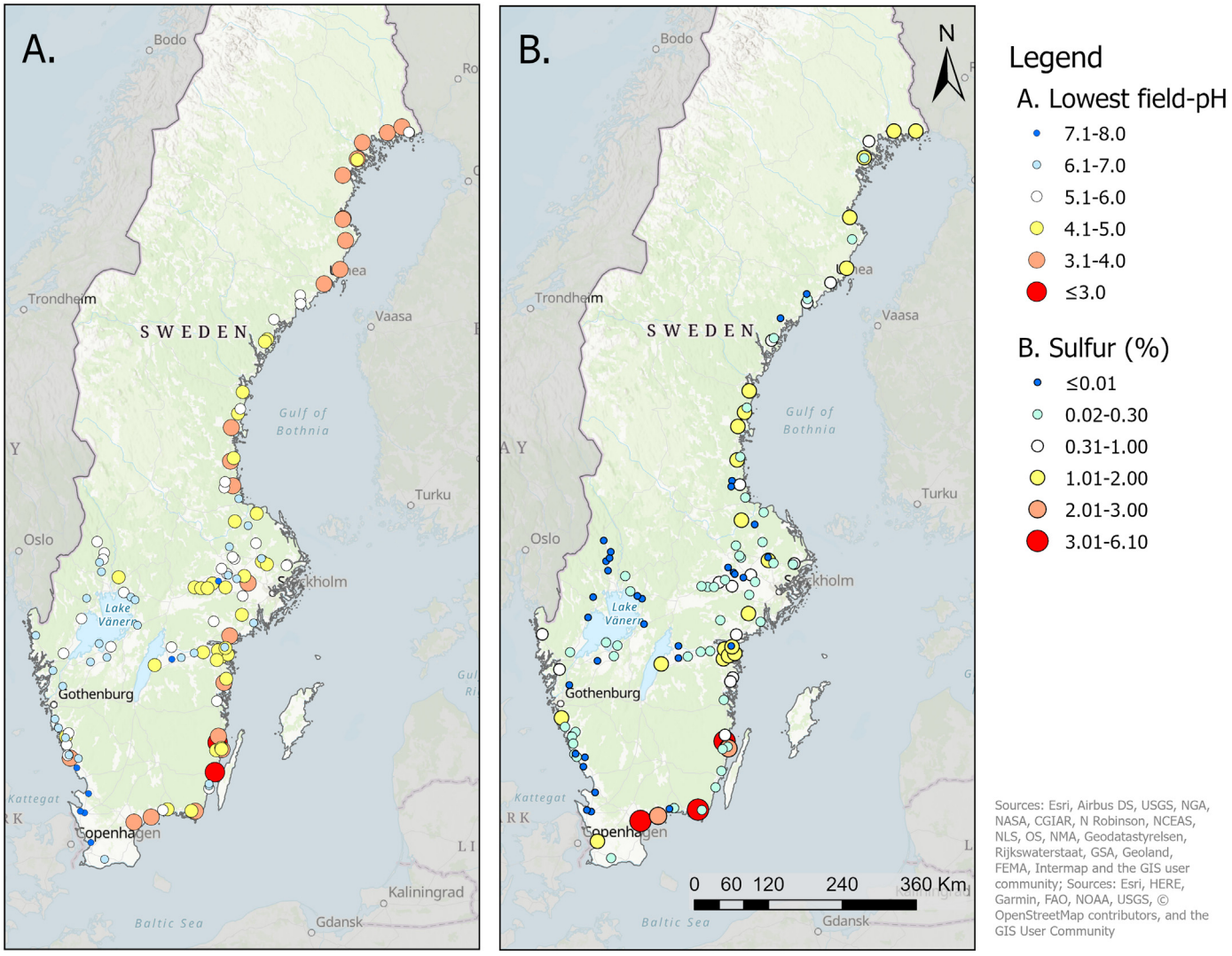

Fig. 2. Lowest *in situ* soil-profile pH (A) and the total sulfur concentrations in the reduced zone (B) at each site.

2.5–14 % (Figs. S2, S3). This pointed to the occurrence of calcite in approximately half of the high-pH trend sediments, causing protons produced by iron-sulfide oxidation to be largely buffered by carbonates. An additional cause for the high-pH trend may be the rare occurrence of unusually high concentrations of other sulfur species than TRS, such as organic sulfur or sulfate minerals, which would not produce protons on aeration and thus keep pH high also at relatively high sulfur levels (Clark et al., 1996; Sullivan et al., 1999). In future similar studies, carbonate and organic matter could be added to the analytical protocol.

There was also an inverse correlation between the sulfur concentrations in the reduced zone and the minimum pH in the overlying aerated soil zone (Spearman correlation: −0.65). This showed that the sulfur abundance had a substantial effect on how far the pH decreased when the reduced material oxidizes and acidifies. There was however large scatter in the plot (Fig. 3A) that was not unexpected because in addition to the sulfur abundance, the pH can be affected by: (i) occurrence and concentration of carbonate minerals (Dalhem et al., 2019) and (ii) the age and ripening of the soil, that is, whether the soil was in an early phase with active oxidation and thus still declining in pH, in a quasi-steady-state, or in a late phase where a substantial amount of the acidity has already been consumed and/or leached (Sukitprapanon et al., 2016).

Table 3
The lowest pH measured *in situ* in the soil profiles, the pH after incubation (oxidation of material from the reduced zone in laboratory for 19 weeks), and total sulfur concentrations of material from the reduced zone across the different areas of Sweden (A1 – A6).

Area	Lowest pH *in situ*	Incubation pH	S %	S %
	Median (min - max)	Median (min - max)	Median (min - max)	5th - 95th percentiles
A1	3.9 (3.5–5.7)	2.5 (2.0–5.3)	0.89 (0.01–1.84)	0.03–1.77
A2	4.7 (3.6–6.0)	3.9 (2.1–7.6)	0.32 (Bd–1.71)	Bd–1.53
A3	5.1 (3.6–7.1)	6.6 (2.4–8.2)	0.07 (Bd–1.46)	Bd–1.14
A4	4.6 (2.7–7.4)	3.5 (1.9–7.9)	1.01 (Bd–6.03)	0.01–4.65
A5	6.2 (3.6–7.4)	6.3 (2.3–8.0)	0.07 (Bd–1.42)	Bd–0.96
A6	6.1 (4.7–6.8)	6.5 (3.7–7.3)	Bd (Bd–0.18)	Bd–Bd
A1 - A6	5.2 (2.7–7.4)	5.3 (1.9–8.2)	0.09 (Bd–6.03)	Bd–2.79

Bd = Below detection.

4.2. Nationwide spatial features

The area A1 had by far the highest proportion of active acid sulfate soils (71 %) and lowest proportion of non-acid sulfate soils (12 %), and also the lowest median pH both in terms of minimum in the field (3.9) and after incubation of the reduced material (2.5) (Tables 2 & 3). These features agreed well with the high concentrations of sulfur (dominated by TRS) in the soils of this area (median of the reduced zone: 0.89 %). These results

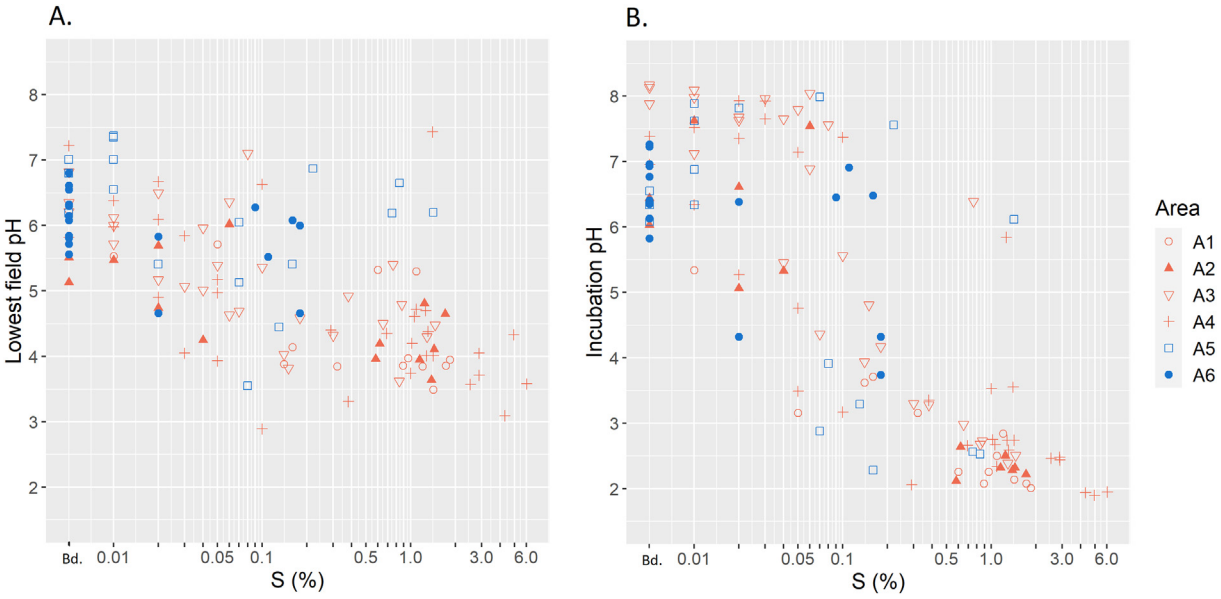

Fig. 3. Total sulfur concentrations in the reduced zone plotted against the lowest pH values measured in the field (A) and the pH after incubation of the material from the reduced zone (B).

were also in line with the well-known occurrence of sulfidic fine-grained sediments and acid sulfate soils in this area, as reported by the Geological Survey of Sweden (2022a) and several previous soil geochemical studies (Christel et al., 2019; Öborn, 1989; Öhlander et al., 2014; Sohlenius et al., 2009). The rate of the isostatic land uplift in this area (8–12 mm/year) is higher than in the south (A3 – A6: 0–8 mm/year), which means that the sediments relatively close to the coast, which were sampled in this study (Fig. 1A), were deposited at greater depths than corresponding sediments in the south (Steffen and Wu, 2011). As sulfate reduction may be more favorable at great depths, the high S concentrations and associated low pH and high proportion of active acid sulfate soils in A1 can at least partly be related to this geophysical feature.

In contrast, area A2 that bordered the Bothnian Sea (Fig. 1A) had much lower S concentrations (median: 0.32 %) reflected in a lower proportion of active acid sulfate soils (36 %) and higher median pH both *in situ* (4.7) and after incubation (3.9) (Tables 2 & 3). Furthermore, the landscape of A2 was topographically more varying, which was in contrast to the flatter, wider landscape in A1. Part of A2 covered the regional area known as "Höga kusten" (the High Coast), which is a hilly coastal region with frequent bedrock outcrops that will have experienced more notable erosion during the land uplift. These features may tentatively suggest that the differences between A1 and A2 was due to differences in the depositional environment with the soil parent material (sediments) in A2 being deposited in smaller basins at relatively shallower depths.

The A3 area included the third largest lake in the country (Mälaren) and is generally considered as an area that may have quite widespread acid sulfate soil occurrences supported by previous geochemical studies carried out in this region (Lax, 2005; Sohlenius and Öborn, 2004). However, this

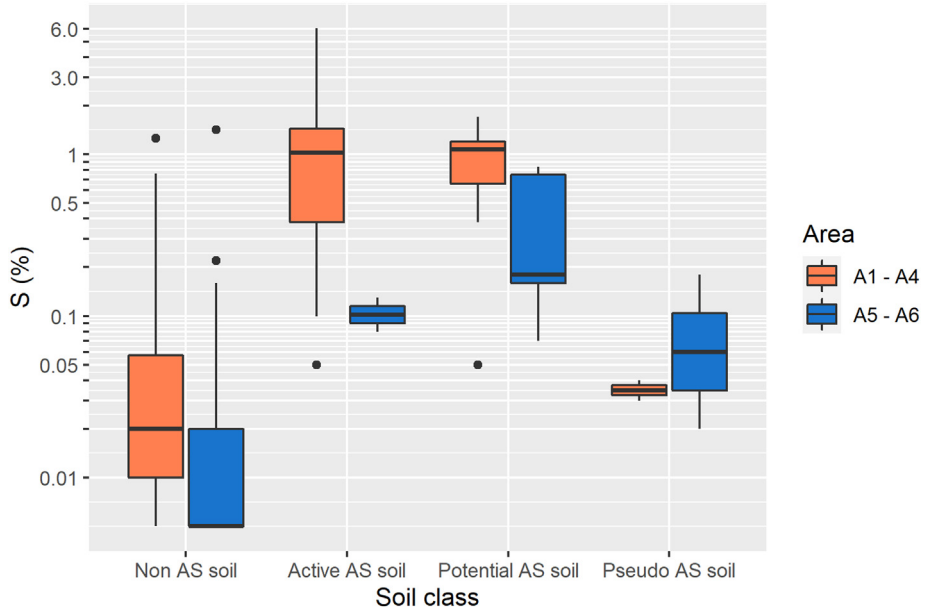

Fig. 4. Sulfur concentrations in the reduced zone across the acid sulfate (AS) soil classes for the east/south coast (A1 – A4) and the west (A5 – A6) coast of Sweden.

area had a high proportion of non-acid sulfate soils (69 %). Furthermore, the map in Fig. 2A showed that in this area the minimum pH was rarely <4.0 (only at two sites) and the sulfur concentrations of the reduced material were mostly <0.3 % (in 71 % of the sites). Hence, the soils sampled in this area were frequently quite low in sulfur and not developed into acid sulfate soils. However, 25 % of the surveyed sites were still covered by active acid sulfate soils, which means that environmental problems typically related to these soils, such as acidification and metal contamination of surface waters (Österholm and Åström, 2008; Toivonen et al., 2019; Unland et al., 2012), will occur in this area at least on a local level.

The A4 area has been largely unrecognized in terms of acid sulfate soils and their impact on the environment. However, a recent study by Shahabi-Ghahfarokhi et al. (2022) found that extensive iron-rich precipitates that have caused degradation of plant and animal life in the Water Kingdom Biosphere Reserve in south Sweden were the result of leaching of nearby acid sulfate soils with high sulfur concentrations (2.3–5.5 % in the reduced zone) and low pH (reaching below 3.0). The results presented here showed that the Biosphere Reserve site was not an exception, as in the A4 area active acid sulfate soils were identified at 45 % of the sites, the lowest pH in the entire country was measured (2.7 *in situ* and 1.9 after incubation), and the sulfur concentrations were very high (median: 1.01 %, 95th percentile: 4.65 %, and maximum: 6.03 %) (Table 3). Based on these data and findings, it seems very likely that the environmental effects of acid sulfate soils in the A4 area are considerably larger than presently recognized, although the total area covered with these soils is likely to be relatively small considering the generally narrow coastal belt that has been below sea level in this area (Fig. 1A). Previous studies confirm that even small areas of acid sulfate soils can have a considerable effect on the environment such as Roos and Åström (2005), Hulisz et al. (2022), and Lindgren et al. (2022).

The area A5 had low sulfur concentrations, similar to those in A3 (Table 3), which was reflected in a high share of non-acid sulfate soils (65 %), a low share of active acid sulfate soils (12 %), and overall high pH both in field (minimum median 6.2) and after incubation (median 6.3). As this area was in the west and thus has been covered with the saline (sulfate-rich) Atlantic Sea water, the low sulfur abundance was not due to lack of sulfur in the system during sediment formation. The fine-grained (clay-silt) quaternary deposits mainly targeted in the study were less common in A5, leading to five out of 17 sampled sites having sandy material (in the other areas 1–2 sandy sites were sampled in each). Of the sandy sites, two were classified as potential acid sulfate soils, which means that only three out of the 11 non-acid sulfate soils were sandy. Hence, the grain size was not a main driving factor for the relatively low share of acid sulfate soils in this area. Overall, the risk of large and widespread soil acidification was therefore small on the coastal plains on the west coast. However, it is possible that beneath the postglacial sand that is widespread in this part of the country, there are sulfide-bearing fine-grained sediments that were not reached with the 2 m profiles of this study. These sediments may be exposed and acidified where the groundwater table is continuously or intermittently low. Furthermore, while sandy quaternary deposits can become severely acidic, the total potential acidification and metal release are much lower and of shorter duration in coarse-grained compared to fine-grained acid sulfate soils (Mattbäck et al., 2022). Hence, the two sandy potential acid sulfate soils may have already lost their acidity in the oxidized part of the profile.

The area A6 had even lower sulfur concentrations than A5, with also the 95th percentile below detection limit (Table 3). As this area, like A5, has been covered with the saline (sulfate-rich) Atlantic Sea water, the low sulfur concentrations was likely not due to lack of sulfur in the system during sediment formation. Hence, it seems like the conditions for reduction of sulfate to sulfide have been overall subdued in this area. This may be partially related to the depositional environment, as the sites in A6 generally lay higher above the sea level than the sites the other areas (A1 – A5). Hence, the parent material would have been deposited at relatively shallower depths, which may have made sulfate reduction less favorable. The low sulfur content was reflected by high pH both in field (minimum median 6.1; minimum 4.7) and after incubation (median 6.5 and minimum 3.7), resulting in no single detected active acid sulfate soil in the area. Thus, the soils around the Lake Vänern are not of general concern in terms of acidification.

For areas A5 and A6 taken together, the minimum *in situ* pH values were at a given sulfur concentration > 0.10 % ($n = 10$) overall considerably higher (4.5–6.9) than in the east and south (A1 – A4) (Fig. 3A). This resulted; for example, in a lower share of active acid sulfate soils in A5 (12%) than in A3 (25%) although the two areas had similar concentrations of sulfur (Table 3) plus calcium (Fig. S3) and showed overall similar behavior in the incubation tests (Fig. 3B). Taken together, this indicated that sulfur-rich (> 0.10 %) soils in the west (A5 & A6) had in general lost a considerable amount of acidity and are thus becoming relic acid sulfate soils of less environmental concern. This may have occurred as a result of drainage during a long period that would eventually exhaust the soils in acidity. However, in the incubation test, the ten A5 – A6 soils with >0.10 % sulfur produced considerably lower pH values with six of them having a value <4.5 and plotting on the low-pH trend (Fig. 3B). This showed that if the groundwater table drops in such soils, for example as a result of extended drought or intensified artificial drainage, active acid sulfate soils are likely to form.

5. Conclusions

A rapid and cost-efficient approach was successfully applied in resolving the main distribution patterns and geochemical features of acid sulfate soils over a large area (below Holocene marine limit in Sweden). It was shown that there were large variations in the probability of acid sulfate soil occurrence in different parts of the country. The probability was very high in northeast (area A1), which was well known, but high also in the southeast (area A4). In contrast, the probability of acid sulfate soil occurrence was very low around the lake Vänern (area A6) as well as relatively low on the west coast (area A5) and in Mälardalen (area A3). This pattern was to a large extent explained by sulfur concentrations, as there were strong inverse correlations between sulfur concentrations of the reduced zone (parent material) and the pH both *in situ* (minimum in oxidized zone) and after incubation (oxidation) of the reduced material. These regional differences revealed the extent to which acid sulfate soil related environmental problems are likely to occur in various parts of the country, and showed where more detailed acid sulfate soil assessments and mapping are needed. Determination of carbonate and organic-matter concentrations could be favorably included in future studies, as these two parameters would facilitate the interpretation of some of the patterns.

CRediT authorship contribution statement

Alexandra Nyman: Conceptualization, Formal analysis, Methodology, Investigation, Resources, Writing – original draft, Writing – review & editing, Visualization. **Anders Johnson:** Conceptualization, Investigation, Methodology, Resources, Writing – review & editing. **Changxun Yu:** Investigation, Project administration, Resources, Writing – review & editing. **Gustav Sohlenius:** Conceptualization, Resources, Writing – review & editing. **Marina Becher:** Conceptualization, Resources, Writing – review & editing. **Mark Dopson:** Conceptualization, Project administration, Supervision, Writing – review & editing. **Mats Åström:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.161845.

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