Acid sulfate soils: A challenge for environmental sustainability

Markku Yli-Halla
ACID SULFATE SOILS:
A CHALLENGE FOR ENVIRONMENTAL SUSTAINABILITY
Abstract

Acid sulfate (AS) soils contain sulfidic compounds formed in anaerobic conditions. In aerobic conditions, they will oxidize to sulfuric acid, which commonly lowers the pH to 3 – 4. These soils cover approximately 10,000 km² in Finland, mainly on the western coast, and over 170,000 km² globally. Acidity and the metals dissolved from the soil matrix and leached out of the soil are serious threats to aquatic biota. Initially, AS soils were regarded as an exclusively agricultural problem, but since the 1970s nearly all studies of AS soils have been environmentally motivated. Awareness of these soils has also risen in forestry, peat mining, and in engineering projects. Liming and water management are the key methods toward the sustainable use of these soils.
1. Processes in acid sulfate soils

Acid sulfate (AS) soils contain or have contained sulfidic material that can cause severe soil acidification. They are typically formed in the sediments of shallow waters along sea coasts throughout the world. A rough estimate of their global area is over 170,000 km² (Andrisse & Mensvoort, 2006) which is probably a strong underestimation (Fitzpatrick et al., 2010). These soils are particularly common in wet coastal areas of the Tropics, most prominently in Southeast Asia, in West Africa, on almost all coasts of Australia, and in the Caribbean. In the USA, most of these soils are recorded in Maryland and Virginia. In Europe, AS soils were first recognized in the Netherlands but they cover the largest area in the Baltic Basin, particularly in Finland (Purokoski, 1959; Puustinen et al., 1994; Åström & Björklund, 1995; Yli-Halla et al., 1999) but also in Sweden (Öborn, 1989) and Denmark (Madsen et al., 1985).

Prerequisites for the accumulation of sulfidic material are 1) sulfate (SO₄²⁻), abundant in the sea water; 2) fresh organic matter (OM), commonly originating from reeds or mangrove vegetation along the coastline; 3) heterotrophic microbes that can utilize sulfate as their electron acceptor while using OM for energy and carbon; 4) reducing conditions in waterlogged environments; and 5) soluble iron (Fe²⁺), mobilized from the soil material in reduced conditions (Dent, 1986). Sulfate is reduced to hydrogen sulfide (H₂S) which reacts with Fe²⁺ and causes the precipitation and accumulation of iron monosulfide (FeS) in the sediment. These reactions are summarized in the equation below, where CH₂O stands for OM:

\[
\begin{align*}
\text{Fe(OH)}_3 + \text{SO}_4^{2-} + \frac{9}{4} \text{CH}_2\text{O} & \rightarrow \\
\text{FeS} + 2 \text{HCO}_3^- + \frac{1}{4} \text{CO}_2 + \frac{11}{4} \text{H}_2\text{O} & \quad (1)
\end{align*}
\]

Over time, monosulfide is at least partially converted to pyrite (FeS₂). In Finland, the accumulation of sulfidic material took place particularly during the Litorina period (approximately 7,500 – 4,000 years ago), when the temperature and SO₄²⁻ concentration in the sea water were higher than today. Sulfidic material is still forming on the reedy coasts of Finland.

Sulfidic material is stable in waterlogged conditions, and the pH of a waterlogged sulfidic sediment or soil horizon varies from neutral to slightly alkaline. When exposed to atmospheric oxygen, sulfidic material is oxidized in several steps to sulfuric acid and iron hydroxide as demonstrated in the following equations (Dent, 1986):

\[
\begin{align*}
\text{FeS}_2 + \frac{15}{4} \text{O}_2 + \frac{7}{2} \text{H}_2\text{O} & \rightarrow \\
\text{Fe(OH)}_3 + 2 \text{SO}_4^{2-} + 4\text{H}^+ & \quad (2)
\end{align*}
\]

\[
\begin{align*}
2\text{FeS} + \frac{9}{2} \text{O}_2 + (n+2) \text{H}_2\text{O} & \rightarrow \\
\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O} + 2 \text{SO}_4^{2-} + 4\text{H}^+ & \quad (3)
\end{align*}
\]

These reactions result in a sharp decrease in pH because the bicarbonate has leached away (see Eq. 1). Soil pH of 3.5 or below firmly indicates that sulfidic material is actively oxidizing and producing sulfuric acid. Along the Finnish coasts, there are no calcareous sediments to neutralize this acidity.

When released to the soil solution, SO₄²⁻ mostly remains in the pore water and leaches out of the soil during rain and snow melt periods. Leakage from AS soils is commonly recognized as an unusually
Over an undefined number of decades, the stock of the sulfidic material is gradually exhausted and the abundant loading of the substances decreases.

Over an undefined number of decades, the stock of the sulfidic material is gradually exhausted and the abundant loading of the substances decreases.

High electrical conductivity of the discharge water. Decreased soil pH results in the dissolution of metals from the soil matrix. The dissolution of aluminum (Al), occurring abundantly in all soils in sparingly soluble forms, is particularly important. When the soil pH decreases to 4 or below, Al³⁺ will release to the soil solution. The trivalent cation Al³⁺ has a high affinity to the negatively charged sites of soil particles, where it displaces other cations (e.g., Ca²⁺ and Mg²⁺). At the initial stage of the oxidation, SO₄²⁻ in the leachate is mostly accompanied with Ca²⁺ and Mg²⁺, displaced from the cation exchange sites by Al³⁺. When the oxidation continues, the concentrations of Ca²⁺ and Mg²⁺ decrease and the concentration of Al³⁺ increases because the respective horizons become increasingly saturated with Al³⁺ and depleted in exchangeable Ca²⁺ and Mg²⁺ (Hartikainen & Yli-Halla, 1986). Over an undefined number of decades, the stock of the sulfidic material is gradually exhausted and the abundant loading of the substances decreases. However, soil pH is not elevated to the original level but commonly remains around 4, no matter how much the soil is leached.

Often, AS soils are divided into three categories according to each stage of the oxidation process (Fanning & Fanning, 1989). Soils containing sulfidic material that has not yet begun to oxidize are called potential AS soils. Sulfidic material is currently oxidizing in active AS soils. Finally, post-active AS soils no longer contain sulfidic material, and much of their soluble oxidation products have already leached away.

The redox reactions of AS soils have consequences for the solubility and mobility of several elements in the soil. In anoxic conditions, microbial activity, boosted by fresh OM, is the driving force to decrease redox potential and consequent changes in the oxidation states of elements, particularly S and Fe. This is followed by the precipitation of new solid phases (FeS, FeS₂) in the soil/sediment matrix. Upon the introduction of atmospheric oxygen, the redox potential rises again and the oxidation of both Fe and S is launched, changing their solubility. In response to the decreased pH, several metals dissolve into the pore water, increasing the cation exchange reactions. When this system receives excess water, acidic pore water and the many solutes therein leach into the watercourses. Repeated drying and wetting cycles
(i.e., recurrent oxidation and leaching) gradually deplete the sulfidic material, leaving behind an acidic soil nearly saturated with Al\(^{3+}\), while SO\(_{4}^{2-}\) is transported back to the sea. Much of the Fe remains in the soil and is precipitated on the surfaces of soil aggregates.

2. Morphological features of acid sulfate soils

Remarkable morphological changes take place after the sulfidic soil material is exposed to atmospheric oxygen, resulting in spectacular color changes (Fig. 1a). Horizons containing sulfidic material are originally structureless, with no aggregates. These massive horizons are soft, with a very low bearing capacity, but almost impermeable to water. In Finland, where the sulfidic material often contains a substantial amount of FeS, these horizons are easily recognized from their (bluish-) black color (Fig. 1b). In southern Finland, sulfidic material may be dominated by FeS\(_2\), resulting in grey horizons, more difficult to recognize.

After natural or artificial drainage, the soil loses water, gains consistency, and shrinks irreversibly in a process called ripening. Cracks are consequently formed because the drier material no longer fills the space it filled originally. At the earliest stage of the ripening, there are only a few cracks in the soil containing large prismatic aggregates between the cracks. However, the number of the cracks increases and the aggregates become smaller over time. As this occurs, the soil becomes increasingly permeable to water.

![Fig. 1](image-url)
ACID SULFATE SOILS:
A CHALLENGE FOR ENVIRONMENTAL SUSTAINABILITY

The cracking allows air to enter the soil, resulting in the oxidation of the sulfidic material. Divalent Fe is also oxidized after it diffuses from reduced zones to the oxidized environment on the surfaces of the aggregates. There, it precipitates as reddish-brown oxides, which can form a uniform coating onto the aggregate surfaces (Fig. 1a). Therefore, the oxidized horizons of AS soils typically have a strong aggregate structure stabilized by rusty coatings.

Pale yellow spots are also typical of the oxidized horizons of AS soils (Fig. 1c). This color originates from jarosite, KFe₃(SO₄)₂(OH)₆, a mineral that is an intermediate product of the oxidation. This color is diagnostic for AS soils. Jarosite is only stable in soils with a pH<4. In less acidic soil horizons, it is gradually decomposed. Therefore, the presence of jarosite is a good indicator of the most acidic horizon of the soil profile. Schwertmannite, Fe₈O₈(SO₄)₂(OH)₆, is another intermediate, semi-stable product of sulfide oxidation. Both jarosite and schwertmannite are found in the AS soils of Finland. The decomposition of these minerals results in the continued release of acidity according to the following equations (Dent, 1986):

\[
\text{KFe}_3\text{(SO}_4\text{)}_2\text{(OH)}_6 \rightarrow 3\text{FeOOH} + \text{K}^+ + 3\text{H}^+ + 2\text{SO}_4^{2-} \quad (4)
\]

\[
\text{Fe}_8\text{O}_8\text{(OH)}_6\text{(SO}_4\text{)} + 2\text{H}_2\text{O} \rightarrow 8\text{FeOOH} + \text{SO}_4^{2-} + 2\text{H}^+ \quad (5)
\]

A typical feature of AS soils specifically and wet soils more generally is the formation of pipestems around former root channels (Fig. 2), which function in a similar manner as the desiccation cracks. These pipestems serve as routes for atmospheric oxygen, such that the surface of the former root channel is aerobic. Soluble Fe²⁺ oxidizes and precipitates when it diffuses from the water-logged

Fig. 2. Pipestems developed around the former root channels in the subsoil (a). These pipestems consist of soil material cemented by iron hydroxides (b). Root cortex cells and precipitated iron hydroxide can be seen in thin section images (c). Photos by Markku Yli-Halla (a, b) and Larry Wilding and Richard Drees, Texas A&M University (c).
interior of an aggregate to the oxidized environment near the root channel. The resulting precipitate cements the soil particles together, allowing for a strong pipe to be formed. Jarosite and schwertmannite are also commonly observed in these pipestems (Fig. 3).

3. Occurrence of acid sulfate soils

In Finland, AS soils mostly occur below the highest shore-line of the ancient Litorina Sea, which is approximately 30-50 m above the current sea level (a.c.s.l.) in southern Finland and 90-100 m a.c.s.l. in northern Finland. Sulfidic material has gradually emerged from the sea due to isostatic rebound, which has been more pronounced in the north. Not all land between the uppermost shore of the Litorina Sea and the current coast-line consists of AS soils; rather they make up a portion of the fine-grained (silt and finer) soils in this region. Although the most extensive areas of AS soils are located along the Gulf of Bothnia, they have also been found along the southern coast (Purokoski, 1959; Puustinen et al., 1994).

Strongly acidic soils similar to the coastal AS soils can be found in locations far from the sea (e.g., Kivinen, 1944; Räisänen & Nikkarinen, 2000). In these inland soils, acidity has been found to originate from black schists containing pyrite (FeS2). The reactions that occur in AS soils are indeed similar to those that occur in the environments where sulfidic minerals are mined, commonly associated with the acid mine drainage problems.

Fig. 4 demonstrates that the depth of
ACID SULFATE SOILS: A CHALLENGE FOR ENVIRONMENTAL SUSTAINABILITY

The sulfidic material has an impact on the environmental loading caused by drained AS soils. In three agricultural soils, the sulfidic material was found at depths of 65 cm, 150 cm and 190 cm with average discharge water pH levels of 3.5, 3.8 and 4.3 in Liminka, Mustasaari, and Ilmajoki, respectively.

Research on AS soils in Finland began with a focus on agricultural land because crop growth suffered drastically from severe acidity in certain coastal fields (Kivinen, 1944; Purokoski 1959) where sulfidic material was apparent near the soil surface. These fields became productive farmland after liming and effective drainage. These measures elevated the topsoil pH and allowed the soluble products of sulfide oxidation to leach into watercourses.

The occurrence of sulfidic material is not limited to fine-grained soils, which are mostly reclaimed for agricultural use. Sulfidic material is often found below peat layers because it is preserved in a reduced state in peatland environments. In peat extraction areas of Finland, sulfide concentrations of up to almost 5% have been documented in the mineral subsoil (Nystrand et al., 2021). If such a mire is drained for peat excavation, there is a substantial risk of acidification. These sulfidic materials can originate from both the sediments of the Litorina Sea and parent materials containing black schists. Additionally, AS soils can be found under forest vegetation, both in mineral soil forests and on peatlands (Nieminen et al. 2016). Wetland forestry typically involves ditching, which exposes sulfidic material to oxidation and causes acidification in the recipient waters. Only a few forest AS soils have been documented in scientific papers (Lindroos et al., 2007; Saarinen et al., 2013), but other examples can be found in reports (Weppling et al., 1999;
ACID SULFATE SOILS: A CHALLENGE FOR ENVIRONMENTAL SUSTAINABILITY

Auri, 2012). Furthermore, AS soils can occur in sandy environments (Mattbäck et al., 2022) where even low concentration of sulfide can reduce the pH below 4 due to a negligible buffer capacity. However, the loading potential of these soils is low, compared to finer-grained AS soils.

Extensive mapping of AS soils was recently carried out in Finland (GTK, 2020) and an estimate of about 10,000 km$^2$ for AS soils across all land uses will soon be presented (Edén et al., 2022). This estimate includes soils where sulfidic material can be found within three meters of the soil surface. Earlier, it was estimated that the agricultural soils containing sulfidic material or a pH<4.0 within 150 cm of the soil surface cover approximately 1300 km$^2$ in Finland (Yli-Halla et al., 1999). Indeed, the estimates presented for the apparent area of AS soils are highly dependent on 1) the soil depth under investigation, 2) land uses accounted for, 3) the criteria for AS soil materials, and 4) the pH requirements.

For agricultural land use, sulfidic materials occurring at the depths deeper than two meters may be irrelevant because these layers are almost always waterlogged and thus produce negligible acid loading. International soil classification systems, such as the U.S. Soil Taxonomy (Soil Survey Staff, 2014) uses sulfidic material as a criterion for classification only when it occurs within 150 cm of soil surface because it is not considered to be harmful at greater depths. In the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014), the respective depth is 200 cm. However, for engineering purposes – where the soil is often disturbed and allowed to oxidize at greater depths – the presence of the sulfidic material deep in the soil bears an environmental risk.

4. Environmental consequences

Sulfidic material oxidizes in the summer when the groundwater level decreases. During the summer months, there is typically no discharge, meaning that the soluble products of oxidation do not leach out. The peaks of the acidity and solutes occur in the autumn, after rainwater has saturated the soil and subsurface pipes have started to convey excess water into the watercourses. Discharge decreases in the winter and then increases again in the spring, giving rise to the hazards of acidity. Sulfate does not cause low pH, but given that it originates from the same reaction as the acidity, high SO$_4^{2-}$ concentrations usually correlate with low pH in AS soil areas.

In rivers that receive much of their water from AS soil areas there is a risk that the river pH will decrease to levels that are harmful to aquatic biota. Aluminum dissolved by the acidity is considered the most harmful component because it precipitates in the gills of fish, causing suffocation. Fish kills are indeed the ultimate manifestation of acidic discharge and they have been reported mostly on the western coast of Finland, particularly in autumns after dry summers. They allow an intensive oxidation of the sulfidic material and subsequent leaching of acidity. In less severe cases where adult fish survive, the fish reproduction is still hampered,
reducing the fish stock and changing the species distribution (Hudd & Leskelä, 1998; Sutela & Vehanen, 2017).

When the subsurface pipe drainage of the agricultural land extended to AS soil areas on the western coast of Finland, the episodes of strong acidification began to occur more frequently. This occurred because the sulfidic subsoil is more intensively oxidized in a pipe-drained soil, as compared with the earlier drainage, which relied on the shallow open ditches. Major fish kills occurred in Finland in the early 1970s, and the most recent major occurrences were in the winter period 2006–2007 (Sutela et al., 2012). Land use activities resulting in the deterioration of the ecosystem have been increasing since 1600s (Hildén & Rapport, 1993), and the first recorded fish kill in Finland took place in 1843 (Åström et al., 2005). Thus, fish kills have occurred already before agricultural fields were intensively drained. Occasional fish kills have also been reported in inland watercourses induced by peat mining in black schist areas (Wichmann & Ovaskainen, 2012). Sulfidic material dredged and stockpiled on land can also cause local acidification (Johnson et al., 2022).

The dissolution of metals other than Al has also been noted to have a harmful environmental impact. While AS soils are not richer in heavy metals than other soils, the acidity promotes the solubility of the heavy metals (Sohlenius & Öborn, 2004). The pore water of AS soil has been shown to have high concentrations of heavy metals (e.g., zinc) (Lindroos et al., 2007; Yli-Halla et al., 2017). In Finland, metal leakage from AS soils is greater than that of the country’s entire industry (Sundström et al., 2002). However, crops grown in AS soils are not enriched with these metals (Fältmarsch et al., 2010) because their roots do not enter the horizons where the metals are dissolved.

5. Nitrogen content of the acid sulfate soils

More than thirty years ago (Rekolainen, 1989), the monitoring of the river water quality revealed that certain rivers in AS soil areas in western Finland exhibited unusually high concentrations of nitrogen (N). Indeed, AS soils have been found to contain large stocks of mineral N compared to other soils (Paasonen-Kivekäs & Yli-Halla, 2005; Šimek et al., 2011; Yli-Halla et al., 2022). More specifically, this N is mostly located in the subsoil in the form of NH$_4^+$-N (Fig. 5). Over a seven-year period, the monitoring of mineral AS soil in western Finland revealed that an average of 55 kg N ha$^{-1}$ was leached annually through the subsurface drainage system (Yli-Halla et al., 2020), whereas the national average leached from agricultural land is approximately 15 kg N ha$^{-1}$. In this particular field, the N contained in the harvested crop plus the N contained in the discharge made up 148% of the N fertilization. Furthermore, this field produced large emissions of N to the atmosphere, indicating a substantial pool of mobile N in the soil. However, the origin, behavior, and availability to plants of this large N stock is not entirely clear.
6. Mitigation activities

The methods to solve the agricultural problems posed by AS soils include drainage and liming, and these recommendations were developed in the early decades of research on these soils. Since the 1970s, nearly all research on AS soils in Finland has concentrated on their environmental effects. National competence across different disciplines has gradually been built up to understand AS soil processes in the Finnish environment and establish relevant analytical and field methods to identify these soils. In particular, AS soil mapping is the basis for all mitigation activities. Large-scale maps of AS soils have been produced in small areas since the 1970s (e.g., Erviö, 1975; Palko et al., 1985; Weppling et al., 1999), and the national small-scale (1:250,000) map (GTK, 2020) provides guidance regarding where more accurate surveys are needed.

Mitigation activities have been carried out in all sectors of land use, most extensively on agricultural land, and the recommendations have been compiled by the Ministry of Agriculture and Forestry and the Ministry of Environment (2012). Liming of the surface soil (Palko & Weppling, 1994; Åström et al., 2007) has been shown to have little impact on the acidity of the subsoil and drainage water. Lime filter drainage has shown a marked initial effect (Bärlund et al., 2005), albeit with a relatively short duration. Recently, liming of the subsoil by using ultrafine-grained (2.5-µm) limestone through the drainage system has been tested (Stén et al., 2019). Liming of river or ditch water has also been reviewed (Heikkinen & Alasaarela, 1988), and recommended for peat extraction areas (Hadzic et al., 2014).

Preventing further oxidation of sulfidic material by maintaining a high groundwater level is likely the most sustainable way of managing AS soils. In agricultural land, this can be facilitated by controlling drainage and pumping additional water into the drainage system (subirrigation) to prevent lowering of the groundwater level during the dry summer.

Fig. 5. Mineral nitrogen content of an AS soil (a) and an adjacent soil without AS characteristics (b) in Lapua, Finland. Observe the different scales in a) and b). Data from Paasonen-Kivekäs and Yli-Halla (2005).
months (Österholm et al., 2015). These methods of water management are shown to shorten the period during which the sulfidic subsoil is subjected to oxidation, with a slight decreasing impact on the discharge acidity (Virtanen et al., 2016). Stopping drainage of the most severe AS soils, which would practically end the agricultural land use, may seem effective from an acidification perspective. In principle, elevation of the water table into oxidized horizons should reverse the system and reintroduce reducing conditions, consuming acidity. This method appears to work in warm climates (e.g., Karimian et al., 2018), but the low temperatures in Finland makes this approach questionable. In cool soils, Fe$^{3+}$ (abundant in the oxidized zone) is reduced to soluble Fe$^{2+}$. However, due to low temperatures and consequentially low microbial activity, the redox potential is not sufficiently lowered to allow the conversion of SO$_4^{2-}$–S to S$^2_-$–S. Therefore, instead of FeS precipitation, SO$_4^{2-}$–S and Fe$^{2+}$ are leached out of the soil. Upon further oxidation of Fe$^{2+}$ in the watercourse, acidity is regenerated, thus actually transported from the soil to the watercourses (Virtanen et al., 2014). Thus, continued cultivation, controlled drainage, and subirrigation are currently the best methods of managing agricultural AS soils.

Recently, AS soils have emerged as an issue in forest management and engineering projects involving drainage and soil disturbance. Creating awareness in these areas is essential because the AS soils have long been solely regarded as a problem of agricultural land use. A guidebook for forestry in AS soils (Nieminen et al., 2016) encourages the identification of AS soils and recommends a shallow ditching that does not extend to the sulfidic subsoil. Furthermore, guidelines for engineering projects in AS soils have recently been launched (Autiola et al., 2022) involving instructions for sampling and methods of treating sulfidic soil material.

All land use involving the disturbance and oxidation of sulfidic soil material is conducive to the loading of acidity and dissolved metals into watercourses. There is no cheap or easy solution for the proper management of AS soils. While the principal processes and consequent effects of sulfidic soil materials on soil, water, and construction materials are largely understood, much work remains in increasing awareness and developing practical solutions for the sustainable use of AS soils.
References


