Oxidation of iron sulfides in subsoils of cultivated boreal acid sulfate fields – an examination based on soil redox potential and pH measurements

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Acid sulfate (AS) soils in Finland are mainly formed on the bottom of the ancient Litorina Sea. Since then isostatic land uplift has resulted in the expansion of land area on the coast of the Baltic Sea by 50100 km² in Finland. Depending on the criteria, at least 600 to 1300 up to 3300 km² of that are cultivated AS soils (1, 2). These soils have gone through several anthropogenic processes such as reclamation of AS soil marshes into arable land by burn clearing, draining and poldering. These measures have initiated the sulfuricization of soils. In addition, natural processes such as evapotranspiration particularly in exceptionally dry summers lower the groundwater table of the fields deeper than drainage alone and also cause sulfuricization, acid discharge pulses and hazards to the aquatic ecosystems of the recipient waters. Major fish kills have been reported as early as in 1834 and most recently in 2006.

Sulfuricization is initiated by the oxidation of sulfidic materials by oxygen. This process is accelerated when microbially catalysed oxidation by ferric iron begins in acidic conditions. Such conditions are not prevailing in the neutral or nearly neutral subsoils which commonly contain the largest pool of sulfides. However, nitrate reduction to N_2 (g) or NH_4^+ coupled with the oxidation of sulfidic materials has been reported in circumneutral aquifers (3), wetlands and brackish sediments (4). Sulfide-induced nitrate reduction was suggested to occur also in subsoils of boreal AS fields based on redox equivalent calculations (5). In this study reactions that might cause sulfuricization were explored by using theoretical redox ranges and a large data set of soil pH and redox potential at different soil profile depths on cultivated Finnish AS fields.

The data of this study originates from a profound field drainage survey (2), from which the fields meeting the criteria of *Typic Sulfaquepts* or *Sulfic Cryaquepts* (1) of Soil Taxonomy were selected. Nearly all fields had been cultivated more than 30 years. If subsurface drained, preceding drainage had been open ditch drainage. Some fields were subsurface drained already before the 1940's. The clayey AS fields (n=9, clay 30-65%) were subsurface drained whereas among the silty AS fields (n=48) part of them was drained by open ditches or some had a sufficient natural drainage to allow cultivation.

During the survey, soil pH and redox potential (E_h) had been measured *in situ* on each field from two soil profiles every 10 centimetres down to the depth of two meters. The measurements were depicted in E_h -pH diagrams with the lines for dissociation of water to H₂ (g) or O₂ (g), a stability line for nitrate reduction to ammonium, as well as lines for reduction of iron and sulfate (6, 7).

In clayey AS fields, reducing conditions were found closer to the soil surface than in silty AS soils. In clayey AS soils at the depth of 100 cm the soil redox status of most profiles was in the range of iron reduction, while it was in the nitrate reduction range in four profiles, in sulfate reduction range in two profiles and in only one profile Fe^{3+} was dominant dissolved iron species (Fig. 1a). In all clay fields at the depth of 200 cm the soil redox status was in the iron or sulfate reduction range (Fig, 1 b). Quite differently, in silty AS fields the redox status at 100 cm was mostly in the nitrate reduction range (Fig. 1c) and at 200 cm the redox status was still in the nitrate reduction range in five profiles and redox status was favouring iron reduction in the majority of the profiles (Fig. 1d).

According to our findings the redox status in subsoils of AS fields is related to soil texture. This is in agreement with findings that clay soils have more redox capacity than coarser soils (8) and therefore also higher poise. In addition, the structure of clayey subsoils is commonly massive and therefore the air entry value is higher than that of coarser silty soils (9). Consequently, oxygen is able to penetrate into silty soils more easily than into clay soils when groundwater table drops. Furthermore, the saturated hydraulic conductivity of clay soils is much lower than that of silty soils, thus the transport of oxidizing solutes, such as nitrate, is faster in silty than clay soils. These physical features may cause the difference in the depth of reducing layer between AS soils with different textures.

These findings suggest that nitrate might assist the oxidation of sulfides and contribute to sulfuricization. On the other hand, the high nitrate concentration of the discharge waters from AS soils (10) does not support the idea of abundant consumption of nitrate by reduction coupled with the oxidation of sulfides in subsoils above the drain pipes. However, in the study referred above shows that there is nitrate available for the oxidation of sulfides below the drainage depths, and that the reduction of nitrate coupled with the oxidation of sulfides can occur even deeper. That would be in accordance with the findings that sulfides oxidation coupled with reduction of nitrate occurs below redox interface (8) and the findings that the subsoils of Finnish AS fields contain high NH_4^+ pools (11).



Figure 1. E_h and pH in clayey and silty AS fields at 100 and 200 cm below soil surface. Dissociation of water to H_2 (g) or O_2 (g), theoretical lines for NO_3^- reduction to NH_4^+ and SO_4^{-2-} reduction to H_2S/HS^- , line for $Fe^{2+/}Fe^{3+}$ as well as empirical line for Hydric Soils (red line). In the diagram the lines indicate equal activities of dissolved species.

It is commonly known that redox potential of soils is spatially and temporally highly variable, and the empirically measured values may be influenced by multiple oxidizing and reducing agents. Therefore, the theoretical values may differ from those in the fields. However, this examination, which is based on large data of AS soils, shows that sulfuricization coupled with reduction of nitrate might exist particularly in silty AS soils. Our findings highlight the need of further studies on this issue also with other methods.

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