Geoderma xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

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

Seija Virtanen[a,*], Markku Puustinen[b], Markku Yli-Halla[c]

[a] *Drainage Foundation sr, Simonkatu 12 B 25, 00100 Helsinki, Finland*
[b] *Finnish Environment Institute (SYKE), Mechelininkatu 34a, 00251 Helsinki, Finland*
[c] *Environmental Soil Sciences, PO Box 56, 00014, University of Helsinki, Finland*

ARTICLE INFO

Keywords:
Acid sulfate soils
Drainage
Soil texture
Hydraulic conductivity
Redox potential
Nitrate

ABSTRACT

Acid sulfate soil leachates deteriorate the aquatic ecosystems of their recipient waters around the world. In Finland, AS soils are located mainly on the coast of the Baltic Sea, where rivers and estuaries suffer from acid leachates and waters do not meet with the criteria of good water quality set by the EU. Field drainage of cultivated AS soils is attributable to leaching of acidity, but regardless of various mitigation measures, the acidity of discharge water in these areas has not decreased significantly. In order to better understand the pathways involved in the formation of acidity, the redox status of 56 Finnish AS soil fields was examined using redox potential and pH data measured down to 2 m. The findings indicated that the oxidation of soils has occurred at depths below the drainage pipes, with the median being at a depth of 1.6 m. In fields cultivated for a long time, soil texture had a stronger effect on the depth of the redox interface than the drainage method; open ditch drainage and subsurface drainage; oxidation being faster in sandy and silty soils than in clayey soils. The isostatic land uplift also seems to affect the depth of the redox interface in the long run. Most of the studied fields had been cultivated for at least 30 years prior to the study. However, the pH values of the soils were still very low, probably due to actual and retained acidity. The prevention of oxidation of sulfidic materials in subsoils is important, but measures for neutralizing the acidity are needed. Without them it seems that the leaching of acidity will continue and may decrease only slowly. However, severe droughts during summers and the reclamation of unripe AS soils for any purpose will increase the leaching of acidity.

1. Introduction

Acid sulfate (AS) soils cover over 17 million ha of the land area of the globe, mostly in coastal areas in the tropics (Andriesse and van Mensvoort, 2006). In Europe the largest AS soil areas in agricultural use are located in boreal latitudes in Finland (Fig. 1a). These boreal AS soils were mainly formed at the bottom of the ancient Littorina Sea ca. 8000–3000 years ago (Andrén et al., 2011). Since the Littorina Sea stage, isostatic land uplift has resulted in the expansion of land area on the coast of the Baltic Sea by 50,100 km^2 in Finland (Edén et al., 2012), and each year 700 ha of land is gained from the sea (Kakkuri, 2012). The land uplift rate is greatest on the coast of the Gulf of Bothnia (9 mm year^{-1}) and slowest on the coast of the Gulf of Finland (4 mm year^{-1}) (Fig. 1a). The land below the highest shoreline of the Littorina Sea has been estimated to consist of at least 600 to 1300 km^2 of cultivated AS soils (Yli-Halla et al., 1999) and up to 3300 km^2 (Puustinen et al., 1994) or even more (Beucher et al., 2015), depending on the criteria of classifying a soil as an AS soil.

In Finland, almost all fields are poorly drained in their natural state and need artificial drainage before they can be properly cultivated. Therefore, in order to increase the productivity of fields and achieve self-sufficiency in agricultural production, field drainage has been promoted by, e.g., subsidies ever since Finland gained its independence in 1917 (Aarrevaara, 2014). Subsurface drainage of fields boomed from the 1960s to the end of the 1980s and over 1 million ha, or 46% of the total field area of Finland, was subsurface-drained during this time period, the current figure being 67% (TIKE, 2013). In the past, regardless of better drainage, the yields from AS soil fields were still poor due to sulfurization, until excess agricultural liming was found to neutralize the acidity, thus making them fertile. Today AS soils are highly valued for their excellent crop yields (Uusi-Kämppä et al., 2012). However, sulfuric acid, which is formed in the oxidation of iron sulfides in subsoils, continues to cause acidification deeper in the soil and dissolves metals therein also. The leaching of acidity and metals hampers water quality and deteriorates the aquatic ecosystems in their recipient watercourses (e.g., Hudd and Leskelä, 1998; Toivonen and Österholm,

---

[*] Corresponding author.
E-mail address: seija.virtanen@tukisaatio.fi (S. Virtanen).

http://dx.doi.org/10.1016/j.geoderma.2017.05.020
Received 15 September 2016; Received in revised form 28 March 2017; Accepted 3 May 2017
0016-7061/

Please cite this article as: Virtanen, S., Geoderma (2017), http://dx.doi.org/10.1016/j.geoderma.2017.05.020

2011) as well as in the estuaries of the northern Baltic Sea (e.g., Nordmyr et al., 2008; Nystrand et al., 2016). The environmental impacts of the generation of sulfuric acid in boreal cultivated AS soils resemble those of other AS soil areas throughout the world, e.g., in Australia (Mosley et al., 2014a) and Vietnam (Phong et al., 2013). Therefore, the examination of different oxidation pathways of sulfidic materials in boreal AS soils may contribute to better understanding in the development of efficient water protection measures in other AS soils affected areas too.

Fish kills were noticed in AS soil areas of Finland as early as in 1834 (early fish kills were compiled by Manninen, 1972). In the 19th century the cause of the land uplift and its environmental consequences were unknown and the rise of arable land from the sea was welcome (Topelius 1893 in Kakkuri, 2012). The role of field drainage being attributable to the oxidation of sulfides was first noticed in the 1930s but widely recognized in the 1980s. Conventional agricultural liming was found to be inefficient for the neutralization of drain waters in these AS soil fields (Palko, 1994). That initiated the development of various mitigation measures to prevent oxidation of sulfides, e.g., by restricting oxygen penetration into subsoils by controlled drainage or sub-irrigation (Österholm et al., 2015; Palko, 1994), by increasing the pH of subsoils in order to restrict oxidation of sulfides by ferric iron (Fe^{3+}) (Engblom et al., 2014), and the waterlogging of acidic soil layers by fresh water (Virtanen et al., 2014a). Unfortunately, these methods have not yet been proven to substantially decrease the leaching of acidity, and consequently the goals of the EU Water Framework Directive regarding good quality of surface waters in AS soil areas by 2015 (EU, 2015) were not reached. A new timeframe to reach the goals was set to extend to 2027.

The aim of this study was to examine oxidation of sulfidic materials in subsoils from a soil redox potential standpoint. Two different approaches not previously used in boreal AS soils were applied to extensive field data from cultivated AS soils. Our hypothesis was that the oxidation of sulfidic materials is caused mainly by the artificial drainage of fields in the AS area in Finland. In this study the redox interface was defined as the depth where soil redox status turns into the sulfate (SO_4^{2-}) reduction range. To test the hypothesis, we studied the relationship between the depth of the redox interface and 1) drainage methods, 2) the age of drainage system, 3) soil texture, and 4) the isostatic land uplift in the area.

2. Materials and methods

The data used in this study originates from an in-depth survey of field drainage in Finnish fields made in 1988–1992 (Puustinen et al., 1994) where 1065 fields were investigated. In that study, the area of AS soils in Finland was estimated using a classification criteria different from Soil Taxonomy (Soil Survey Staff, 1996) with, e.g., pH criteria for AS soils: $pH < 5$ in Puustinen et al. (1994) and $pH < 4$ in Soil Taxonomy (Soil Survey Staff, 1996). The data was revisited by Yli-Halla et al. (1999) to assess the AS soil areas in Finland according to the Soil Taxonomy (Soil Survey Staff, 1996), FAO – Unesco system (1988) and the ILRI classification (Dent, 1986), and to assess the depth of sulfidic materials on the basis of soil pH in Finnish cultivated AS soil fields (Yli-Halla et al., 2012). For this study, the 56 fields in the data of Puustinen et al. (1994) which, according to Yli-Halla et al. (1999) met the criteria of *Typic Sulfaquepts* or *Sulfic Cryaquepts* according Soil Taxonomy (Soil Survey Staff, 1996), were selected. The data from Puustinen et al. (1994) was randomly sampled from different areas in Finland so that the weight of each area corresponded with the proportion of cultivation of that particular area to the total cultivated area across the country (for more detail, see Puustinen et al., 1994; Yli-Halla et al., 1999; Yli-Halla et al., 2012). The location of the studied fields, the dominant soil texture class in different parts of Finland, and the highest seashore of the Littorina Sea are presented in Fig. 1b. The texture classes in Fig. 1a and those of the selected fields are broadly similar to the international texture classifications (see Fig. 3a). The land uplift rate of each field was determined according to their location.

The cultivation practices, drainage history and the conditions of each field were recorded in detail in the original survey. The mean depth of the subsurface drainage pipes in the fields was ca. 1 m ($n = 427$ fields, Puustinen et al., 1994), and therefore a depth of 1 m was defined as the drainage depth in this study. The average depth of main drains or outlets was 1.6 m (with the standard deviation of 0.6 m; $n = 55$), and the median 1.6 m (range from 0.6 to 3.5 m). In subsurface drainage pipes iron oxide clogging was observed in four fields but only in three of them was the wetness of the fields caused by this. In each field, two soil profiles had been augered (gouge auger, ø 22 mm) in order to measure soil pH (WTW pH 91, Ingold 406 M6, ± 0.1) and redox potential (Eh, mV, WTW pH 91, Pt 400P6, with temperature correction, ± 0.3 mV) in situ at a depth of every 10 cm from the soil surface down to 2 m. Soil texture had also been determined by finger assessment every 10 cm down to a depth of 2 m from the augered soil samples, and the determination had been controlled by analyzing the soil samples at a depth of 30–40 cm, initially by using test sieving and then the sedimentation method (sedigraph) for the finest soil fractions. The saturated hydraulic conductivity (K_s) of soil had been measured in two replications at a depth of 30–40 cm using the infiltration method (Puustinen et al., 1994).

In the study of Puustinen et al. (1994), soil Eh was used to assess the chemical drainage depth, i.e., the depth where redox potential is 0 mV. However, in their approach soil pH was not taken into account, even thought it was measured. In this study the pH values were also included in the examination. Firstly, the Eh-pH diagrams were depicted according to Garrels and Christ (1965) at the drainage depth (1 m) and at the deepest measurement depth (2 m) for clayey, and silty and sandy AS soil profiles separately, in order to evaluate differences between soil textural types. Secondly, the redox interface was determined from the Eh-pH diagrams of each individual soil profile from the soil surface to a depth of 2 m (Supplementary material S1). In the Eh-pH diagrams, boundary lines for the stability of water, iron ($Fe^{2+} \leftrightarrow Fe^{3+} + e^-$; $\log K = -13.5$), pyrite ($1/14\ FeS_2 + 1/7 H_2O \leftrightarrow 1/7\ SO_4^{2-} + 1/14\ Fe^{2+} + 11/7\ H^+ + e^-$; $\log K = 6$) and ferrihydrite ($Fe(OH)_3 + 3H^+ \leftrightarrow Fe^{3+} + 2H_2O$; $\log K = 3.7$) (Appelo and Postma, 2005) at the representative activities of Fe^{2+} (0.4 mmol), Fe^{3+} (10 μmol) and SO_4^{2-} (10 mmol) ions are presented. Thirdly, the redox interfaces were estimated in each soil profile using a rough general pH conversion method, where the depth of the redox interface was defined as the depth where the redox potential at pH 7 was lower than −100 mV, which is considered to be the threshold for the SO_4^{2-} reduction zone (Reddy et al., 2000). The conversion of Eh at pH in situ ($pH_{in\ situ}$) to pH at 7 was made according to Eq. (1), where $f_{pH} = 59$ mV (Rowell, 1981).

$$Eh7 = Eh - f_{\mathrm{pH}} \times (7 - pH_{in\ situ}) \tag{1}$$

The conversion method contains uncertainties because the conversion coefficient (f_{pH}) based on the Nernst equation varies within different redox couples (Pourbaix, 1966; Rowell, 1981). In addition, redox potential may be a mixed potential in soils due to numerous redox couples, which may have an impact on the coefficient. In experiments f_{pH} has been found to vary from −6 mV to −256 mV (Fiedler et al., 2007). In addition, various threshold values of SO_4^{2-} reduction have been presented, with values varying from 0 to −200 mV, e.g., (Fiedler et al., 2007). In our soil profiles the Pearson correlation coefficient between the depth of the redox interface calculated using the conversion method (Eq. (1)) and the inspection of the Eh-pH diagrams was 0.951 ($p < 0.001$, $n = 83$; Fig. 2 and Supplementary material S1). Therefore, in this study the depths of the redox interfaces were calculated by the conversion method. The sensitivity of the results was examined by way of calculating the depth of the redox interface at the thresholds values of 0 and −200 mV as well. In this study the pH