Science of the Total Environment 485–486 (2014) 130–142

Contents lists available at ScienceDirect

Science of the Total Environment

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

# Response of pore water Al, Fe and S concentrations to waterlogging in a boreal acid sulphate soil

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## HIGHLIGHTS

- Waterlogging was conducive to reduction reactions in AS soil monoliths.
- Poorly ordered iron oxides and low pH poised reduction reactions in the Fe range.
- Sulphate was not reduced to sulphide in the lysimeters.
- Dissimilatory reduction reactions resulted in high Fe concentrations in pore water.
- Reduction markedly lowered $Al_{pw}$, despite the slight increase in pH.

## ARTICLE INFO

*Article history:*
Received 1 November 2013
Received in revised form 7 March 2014
Accepted 16 March 2014
Available online 3 April 2014

Editor: F.M. Tack

*Keywords:*
Acid sulphate soil
Waterlogging
Redox status
Aluminium
Iron
Sulphur

## ABSTRACT

Environmental hazards caused by acid sulphate (AS) soils are of worldwide concern. Among various mitigation measures, waterlogging has mainly been studied in subtropical and tropical conditions. To assess the environmental relevance of waterlogging as a mitigation option in boreal AS soils, we arranged a 2.5-year experiment with monolithic lysimeters to monitor changes in the soil redox potential, pH and the concentrations of aluminium (Al), iron (Fe) and sulphur (S) in pore water in response to low and high groundwater levels in four AS soil horizons. The monoliths consisted of acidic oxidized B horizons and a reduced C horizon containing sulphidic material. Eight lysimeters were cropped (reed canary grass, *Phalaris arundinacea*) and two were bare without a crop. Waterlogging was conducive to reduction reactions causing a slight rise in pH, a substantial increase in Fe ($Fe_{pw}$) and a decrease in Al ($Al_{pw}$) in the pore water. The increase in $Fe_{pw}$ was decisively higher in the cropped waterlogged lysimeters than in the bare ones, which was attributable to the microbiologically catalysed reductive dissolution of poorly ordered iron oxides and secondary minerals. In contrast to warmer climates, $Fe_{pw}$ concentrations remained high throughout the experiment, indicating that the reduction was poised in the iron range, while sulphate was not reduced to sulphide. Therefore, the precipitation of iron sulphide was negligible in the environment with a low pH and abundant with poorly ordered Fe oxides. Increased Fe in pore water counteracts the positive effects of waterlogging, when water is flushed from fields to watercourses, where re-oxidation of Fe causes acidity and oxygen depletion. However, waterlogging prevented further oxidation of sulphidic materials and decreased $Al_{pw}$ to one-tenth of the initial concentrations, and even to one-hundredth of the levels in the low water table lysimeters.

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*Abbreviations:* AS soil, acid sulphate soil; AASS, actual acid sulphate soil; PASS, potential acid sulphate soil; HWC, cropped high water table treatment; LWC, cropped low water table treatment; HWB, bare high water table treatment; RCG, reed canary grass; $Al_{pw}$, Al concentration in pore water, mg dm$^{-3}$; $Fe_{pw}$, Fe concentration in pore water, mg dm$^{-3}$; $S_{pw}$, S concentration in pore water, mg dm$^{-3}$; $C_{org}$, soil organic carbon, %; $DOC_{pw}$, dissolved organic carbon in pore water, mg dm$^{-3}$; $Fe_o$, iron extracted by acid ammonium oxalate (pH 3) in the dark, mg dm$^{-3}$; CEC, cation exchange capacity, ammonium acetate extraction at pH 7.0, cmol kg$^{-1}$; $E_m$, soil redox potential, mV; $E_h$, soil redox potential relative to the standard hydrogen electrode at 298 K, mV; $E_{ref}$, the redox potential of reference electrode, 199 mV for Ag/AgCl; $T_m$, soil temperature, K; $f_t$, temperature correction factor of reference electrode; $pH_{pw}$, pH of pore water; $f_{pH}$, correction factor for converting $E_h$ to pH 7; $E_{h7}$, soil redox potential relative to the standard hydrogen electrode at 298 K and pH 7, mV; MQC, method quality control and the MQC solutions for cations, anions and reference water samples of different element concentrations, $MQC_c$ $MQC_a$ $MQC_{1,2,3}$, respectively; CBE, charge balance error, %.

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http://dx.doi.org/10.1016/j.scitotenv.2014.03.071
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## 1. Introduction

Acid sulphate (AS) soils have been referred to as the nastiest soils in the world because their reclamation for cultivation causes hazardous onsite and offsite effects (Dent and Pons, 1995; Sullivan, 2012). Onsite effects such as soil acidification result not only in elevated concentrations of dissolved aluminium (Al) and restrict the growth of plants (Moore et al., 1990; Kirk, 2004), but also in extreme cases lead to AS soil scalds (Rosicky et al., 2004). As for the offsite effects of AS soils, their acid discharge waters cause the deterioration of aquatic ecosystems in rivers and estuaries (Cook et al., 2000; Vehanen et al., 2012), and thus exert detrimental effects on businesses based on ecosystem services (Ljung et al., 2009). In addition, AS soils are found to emit quantities of greenhouse gases (Macdonald et al., 2011; Regina, 2012) and are even assumed to negatively affect human health (Fältmarsch, 2010). Therefore, sustainable measures to prevent the offsite effects of AS soils are urgently needed.

AS soils are located worldwide in various climatic regions, and their genesis and physicochemical characteristics therefore vary (Dent and Pons, 1995), but the reaction patterns and environmental impacts are the same: sulphide-bearing material with a low acid buffering capacity (potential acid sulphate soils, PASS) is oxidized when exposed to atmospheric oxygen, and the formation of sulphuric acid (the overall Eqs. (1) and (2)) after Dent (1986) acidifies soil (actual acid sulphate soils, AASS) and initiates the mobilisation of toxic metals into the soil solution (e.g. Dent, 1986; Åström, 1998; Powell and Martens, 2005; Gröger et al., 2011). Once exposed to oxygen, the acid discharge can last for decades (e.g. White et al., 1997; Österholm and Åström, 2004). This phenomenon highlights the importance of controlling the oxidization reactions in PASS horizons.

$$FeS_2 + {}^{15}/_{4}\,O_2 + {}^{7}/_{2}\,H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4\,H^+ \tag{1}$$

$$2FeS + {}^{9}/_{2}\,O_2 + (n+2)H_2O \rightarrow Fe_2O_3 \cdot n(H_2O) + 2SO_4^{2-} + 4\,H^+ \tag{2}$$

The mitigation of the environmental hazards in AS soils by waterlogging or elevating the groundwater can be based on two principles: 1) restricting the oxidation of sulphidic materials by keeping the PASS horizons permanently water saturated to suppress sulphuric acid formation and 2) neutralisation of the acidity of AASS horizons through reduction reactions or the application of alkaline agents such as lime. Reduction reactions consume protons and increase the soil pH. Consequently, the concentration of pH-sensitive elements or the most toxic monomeric species of metals in the soil solution decreases (Essington, 2003, p. 198). It is generally known that oxygen is the terminal electron acceptor in the microbial oxidization of organic matter in aerobic soils. When it is depleted, the successive terminal electron acceptors in the sequence of lowering energy yields are nitrate, manganese, iron and sulphur according to the following equations (Kirk, 2004, p. 109):

$$4\,NO_3^- + 5\,CH_2O + 4H^+ \rightarrow 2N_2 + 5\,CO_2 + 7H_2\,O \tag{3}$$

$$2\,MnO_2 + CH_2O + 4H^+ \rightarrow 2Mn^{2+} + CO_2 + 3H_2\,O \tag{4}$$

$$4\,Fe(OH)_3 + CH_2O + 8H^+ \rightarrow 4Fe^{2+} + CO_2 + 11H_2\,O \tag{5}$$

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O. \tag{6}$$

Even though reduction reactions alleviate soil acidity, the negative effects of reduction may nullify the positive ones. The reduction products, e.g. $Fe^{2+}$, $Mn^{2+}$ and $H_2S$, are at high concentrations toxic to plants (Rorison, 1973; Moore et al., 1990; Jerling, 1999). However, the concentrations of toxic compounds decrease when precipitates are formed, but if they remain in soil solution they will be flushed from fields to watercourses (Cook et al., 2000). In the recipient waters, this means that the re-oxidation of $Fe^{2+}$ to $Fe^{3+}$ and hydrolysis reactions concomitantly produce protons and consume dissolved oxygen. Therefore, the waterlogging of oxidized soil horizons (AASS) does not necessarily mitigate environmental hazards.

Based on laboratory experiments, Ward et al. (2004) concluded that waterlogging produces favourable results only when combined with other mitigation methods. In the coastal acid sulphate soils in Australia, the improvement in the quality of discharge water with tidal re-flooding has been intensively studied in recent years (e.g. Powell and Martens, 2005; Johnston et al., 2012). Dilution with tidal marine water improves the quality of drainage waters (Johnston et al., 2005). Laboratory experiments have indicated that highly saline marine water temporarily lowers the pH and increases the concentrations of toxic elements in the soil solution (Wong et al., 2010). However, the combination of waterlogging with tidal marine water, replacing acidified freshwater with tidal water and the liming of drainage water was found to improve water quality in the long term (Johnston et al., 2009a). The neutralising effect was mainly attributable to reduction (57–74%) and the inherent alkalinity of marine water (25–42%), the contribution of hydrated lime being only 1% (Johnston et al., 2012). Waterlogging is also reported to result in the precipitation of Fe sulphides, concomitant with the decrease in trace element concentrations in the soil solution (Keene et al., 2010). This outcome requires that $H_2S$ is generated by reducing reactions.

The largest AS soil areas of Europe are found around the Baltic Sea. The conditions in this boreal area differ greatly from those of areas with a warmer climate, e.g. in terms of the salinity of the water, temperature, precipitation and crops, so that the promising results obtained in the subtropics or tropics are not necessarily applicable to boreal conditions. For example, the neutralisation capacity of freshwater in non-calcareous areas is lower than that of marine water (see Stumm and Morgan, 1996, p. 149; Saarinen et al., 2010), and reduction reactions proceed more slowly because of the lower temperature (e.g. Rabenhorst and Castensons, 2005). However, the impact of waterlogging of drained AS soil has not been investigated in boreal conditions until now.

Theoretically, regulation of the elemental composition of soil solution by means of water management is a sustainable mitigation strategy in AS soils. Because the pH and soil redox status control the fate of elements, knowledge of their responses to changes in the groundwater level can form the basis for the development of tools to control environmental risks. Until now, the transformation of aluminium ($Al_{pw}$), iron ($Fe_{pw}$) and sulphur ($S_{pw}$) concentrations in pore water under contrasting water management practices at boreal latitudes has not been studied. For this reason, we set up a sophisticated lysimeter experiment to unravel the impact of prolonged waterlogging with freshwater on an AS soil consisting of three AASS and one PASS soil horizon. The experiment was carried out using lysimeters with and without plants in order to unravel the contribution of vegetation on the transformation processes. Our hypothesis was that 1) waterlogging initiates the precipitation of Fe sulphides and causes the Fe and S concentrations to decrease, and 2) the rise in pH due to reduction reactions decreases the solubility of Al and restrains its mobility. This study also provided novel information on the elemental composition of pore waters in boreal AS soils, for which no previous pore water data exist.

## 2. Material and methods

### 2.1. Soil

Soil monoliths for lysimeters were taken in summer 2008 from a poldered, cultivated AS soil field (Patoniitty) of the University of