Science of the Total Environment 499 (2014) 336–348

Contents lists available at ScienceDirect

Science of the Total Environment

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

A multi-scale comparison of dissolved Al, Fe and S in a boreal acid sulphate soil

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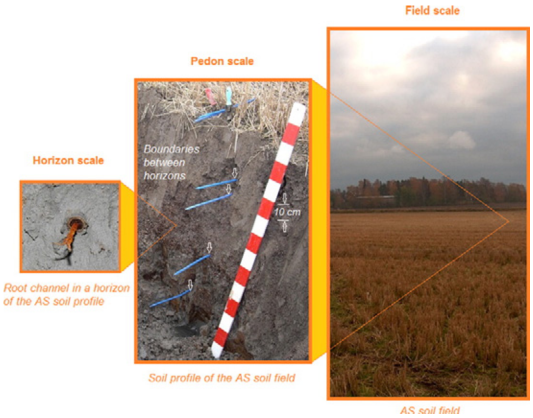
HIGHLIGHTS

- Monolithic lysimeters realistically simulated water management in acid sulphate soil
- The similarity between dissolved elements in lysimeters and the field was verified
- Element concentrations in discharge water followed changes in pore water
- Dissolved element variation was highest at the horizon and lowest at the field scale
- Lowering of the water table caused ripening and changes in soil hydraulic properties

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 June 2014
Received in revised form 16 August 2014
Accepted 23 August 2014
Available online 7 September 2014

Editor: F.M. Tack

ABSTRACT

Acid sulphate (AS) soils are most prevalent in the tropics, but the acidic discharge from cultivated AS soils also threatens water bodies under boreal conditions. Feasible options to reduce the acid load are needed. In this study, the groundwater of an AS field was monitored for 3.5 years, and the efficiency of waterlogging in mitigating the environmental risks caused by acidic discharge was investigated in a 2.5-year experiment with 10 monolithic lysimeters taken from the same field. In order to unravel the transferability of the results from lysimeters to the field scale, the Al, Fe and S concentrations in discharge water from the lysimeters were compared with those in the groundwater of the AS field (pedon and field scale), and in pore water (pedon and horizon scale). In the

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Abbreviations: AS soil, acid sulphate soil; AASS, actual acid sulphate soil; PASS, potential acid sulphate soil; AVS, acid-volatile sulphur; RCG, reed canary grass (*Phalaris arundinacea)*; HWB, high water table treatment in bare soil (without RCG); HWC, high water table treatment with RCG crop; LWC, low water table treatment with RCG crop; $\mathrm{DOC_{pw}}$, dissolved organic carbon in pore water, mg $\mathrm{dm^{-3}}$; PFP, preferential flow paths; WRC, water retention curve; C_{pw}, element concentration in pore water ($\mathrm{Al_{pw}}$, $\mathrm{Fe_{pw}}$, $\mathrm{S_{pw}}$), mg $\mathrm{dm^{-3}}$; C_{dw}, element concentration in discharge water ($\mathrm{Al_{dw}}$, $\mathrm{Fe_{dw}}$, $\mathrm{S_{dw}}$), mg $\mathrm{dm^{-3}}$; C_{gw}, measured element concentration in groundwater ($\mathrm{Al_{gw}}$, $\mathrm{Fe_{gw}}$, $\mathrm{S_{gw}}$), mg $\mathrm{dm^{-3}}$; C_{dwe}, estimated element concentration in discharge water, mg $\mathrm{dm^{-3}}$; C_{h}, element concentration of pore water in *Ap*, *Bg2*, *Bgjc*, *BCg* and *Cg* horizons, respectively, mg $\mathrm{dm^{-3}}$; $h =$ *Ap*, *Bg2*, *Bgjc*, *BCg* and *Cg horizon*; d_{h}, thickness of a horizon, m; K_{s}, saturated hydraulic conductivity, m $\mathrm{day^{-1}}$; ε, water content, $\mathrm{m^3\ m^{-3}}$; ε_{s}, saturated water content, $\mathrm{m^3\ m^{-3}}$; ε_{d}, drainable porosity of horizon, $\mathrm{m^3\ m^{-3}}$; ε_{r}, residual water content, $\mathrm{m^3\ m^{-3}}$; Ψ_{m}, matric suction, cm; α, shape parameter of the WRC model, α_1 and α_2 in the bimodal model, $\mathrm{cm^{-1}}$; n, shape parameter of the WRC model, n_1 and n_2 in the bimodal model; m, $1 - 1/n$ a shape parameter of the WRC model, in the bimodal model m_{i}, $1 - 1/n_{\mathrm{i}}$, i, 1,2; w_{i}, the weighing fraction of WRC sub-curves, i, 1, 2, $\sum w_{\mathrm{i}} = 1$; θ, potential similarity; θ_{i}, the studied similarity level, i, 1,2,3.

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http://dx.doi.org/10.1016/j.scitotenv.2014.08.088

Keywords:
Acid sulphate soil
Similarity
Scales
Aaluminium
Iron
Sulphur

waterlogged bare lysimeters (HWB), the Al, Fe and S concentrations in discharge waters were broadly similar to those measured in the groundwater and followed the changes in the pore water. In the waterlogged cropped (reed canary grass, *Phalaris arundinacea*) lysimeters (HWC), in contrast, the discharge waters were markedly higher in Fe and lower in Al than the groundwater in the field. This outcome was attributable to the reduction of Fe^{3+} to the more soluble Fe^{2+} and the reduction-induced increase in pH, which enhanced the formation of Al^{3+} hydroxy species. Lowering of the water table (LWC) caused soil ripening, which resulted in increased saturated hydraulic conductivity and porosity and enhanced the oxidation of sulphidic materials and acid formation. The responses of Al, Fe and S in drainage waters from HWC and LWC lysimeters resembled previous findings in AS soils. Based on this and the similarity between dissolved element concentrations in the discharge water of HWB lysimeters and groundwater in the field, we conclude that our monolithic lysimeters yielded realistic results concerning the efficiency of various methods in mitigating environmental risks related to cultivated AS soils.

1. Introduction

Acid sulphate (AS) soils occur worldwide, but are mainly located in coastal and floodplain areas. Their drainage, dredging and excavation, giving rise to runoff waters containing high dissolved metal concentrations, cause off-site environmental hazards, including a deterioration in the ecological status of aquatic ecosystems (see e.g. Dent and Pons, 1995; Roos and Åström, 2006). The metals are dissolved from the soil matrix by sulphuric acid, which is formed upon the oxidation of sulphidic materials in the subsoil of AS soils. This oxidation and the acid loading into rivers are dependent on the efficiency of drainage, which enhances soil ripening, i.e. the physical, chemical and biological changes that transform water-saturated sediments to a dryland soil (Dent, 1986). Once initiated, the negative impacts may last for decades (e.g. White et al., 1997; Österholm and Åström, 2004). In Europe, the largest AS soil areas in agricultural use are located on the coast of the Baltic Sea (Andriesse and van Mensvoort, 2006). The formation of acidity is expected to continue in association with the post-glacial isostatic land uplift occurring in the area, regardless of the predicted global sea level rise (Johansson et al., 2004). Furthermore, global climate change is expected to result in longer periods of drought, which will lower the groundwater table (Okkonen and Kløve, 2010). This facilitates the penetration of oxygen deeper into the subsoil and promotes the oxidation of sulphidic materials at increasing depths in the soil profile.

In the tropics, the rehabilitation of severely acidified AS fields by tidal water inundation is reported to improve the quality of discharge water (Johnston et al., 2009a). This is attributable to (1) the dilution of acidity in drains by tidal exchange, 2) the neutralization of acidity by the strongly buffered ocean water and 3) reduction reactions that consume protons and form sulphide minerals in soils. However, on the coast of the Baltic Sea, only rain and snowmelt water or low salinity brackish water having low alkalinity are available for re-establishing high groundwater levels. Therefore, the promotion of reducing conditions may only have a restricted impact on the environmental hazards caused by AS soils. In our previous study (Virtanen et al., 2014), we found that an elevated groundwater level in a lysimeter resulted in the reduction of Fe from the soil matrix, giving rise to a high dissolved Fe concentration in pore water. If the dissolved ferrous iron is not immobilized in the soil profile by sulphidisation, it can be leached and oxidized in the recipient watercourse, with a consequent depletion of oxygen and acidification (e.g. Cook et al., 2000).

Lysimeters have long been used in soil water balance studies (Goss and Ehlers, 2009). They are efficient tools to study water flow and the fate of dissolved substances in soil, because they allow the simulation of water management options in controlled conditions (Bergström, 1990). When comparing the results obtained in lysimeters and in the field, Ritsema et al. (1992) found that, due to intense drainage, potential acid sulphate soil (PASS) horizons were transformed into actual acid sulphate soil (AASS) horizons with characteristics similar to those in the field in terms of the oxidation of sulphides. According to Minh et al. (1998), the accumulation of aluminium in topsoil was in the same range in AS soil lysimeters as in the field. In non-AS soils, Rupp et al. (2010) identified similar responses of the soil redox potential to changes in the water level in a lysimeter and at the field scale. However, in non-AS soils, discrepancies between solute transport parameters in lysimeters and the field were reported by Gasser et al. (2002) with packed lysimeters. Based on numerical simulations, Abdou and Flury (2004) found that lysimeters underestimated the leaching losses of elements if preferential flow paths (PFP) were dominant in the soil, and they recommended caution in interpreting the results. These conflicting findings indicate that the similarity of elements leaching from soil and the similarity of the responses of soil chemistry to water management practices in lysimeters compared to field conditions are not self-evident. Therefore, the relevance of any scale-dependent dissimilarities and associated uncertainties caused by the small scale should be critically considered when extrapolating the results obtained in lysimeters to larger scales (Shirmohammadi et al., 2005) in order to avoid negligible or undesired consequences in the mitigation of hazards caused by AS soils.

In the course of soil ripening, drainage and transpiration by plants result in the formation of a permanent network of cracks in AS soils because of their strong shrinkage tendency (e.g. Dent, 1986; Johnston et al., 2009b). Therefore, in ripe AS soil, the saturated hydraulic conductivity is markedly higher in AASS than in PASS horizons, where it is very low (Joukainen and Yli-Halla, 2003; White et al., 2003). As drainage mostly removes water from the macropores, the dissolved elements in these largely dictate the quality of discharge water in the field. Despite this, the largest amounts of water in AS soil occur in smaller pores (Dent, 1986), where the element concentrations might differ from those in macropores (Rhoades and Oster, 1986). Small pores have a large surface area in relation to the volume of water, and the water is in intimate contact with the soil matrix. Consequently, the processes in soil may have a more direct influence on the composition of the pore water in micropores than in macropores. Depending on the method applied for the extraction of pore water, the water sample may originate from pores of different sizes (Fares et al., 2009). To understand the effects of waterlogging of AS soils, it is essential to know how this affects the water in macropores, in particular, and to what extent its composition is reflected in the pore water samples.

To date, the effects of waterlogging of boreal AS soils have only been studied in a lysimeter experiment, in which the construction allowed the sulphidic materials to be kept in a reduced state at the bottom of the monolithic lysimeters (Virtanen et al., 2013a). Therefore, the practical aim of this study was to assess whether the results obtained at the lysimeter scale can be generalized to the field scale and used as relevant background information for the modelling and planning of mitigation options in AS soils. Our hypothesis was that the waters discharging from AS soils with similar water regimes are chemically similar, irrespective of the scale. The similarity of water quality between monolithic AS soil lysimeters (pedon) and the groundwater of the AS soil field where the monoliths were taken was examined by an approach widely used in other branches of science (Schuirmann, 1987), although not so