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## Journal of Hydrology

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



# Hydrological processes behind annual and decadal-scale variations in the water quality of runoff in Finnish catchments with acid sulfate soils

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#### ARTICLE INFO

Article history:
Received 17 July 2012
Received in revised form 7 January 2013
Accepted 16 February 2013
Available online 5 March 2013
This manuscript was handled by Andras
Bardossy, Laurent Charlet, Editor-in-Chief,
with the assistance of Ewen James Silvester,
Associate Editor

Keywords:
Acid sulfate soils
Acidity
River
Water quality
Land use
Climate change

#### SUMMARY

In this study we assess long- and short term temporal variations in the impact of acid sulfate (a.s.) soils on river water quality. We demonstrate how such variations depend on changes in hydrological conditions driven by land use, meteorological variations and potential changes in climate with important implications on mitigation strategies, water ecology and utilization of water resources. Quality of river water discharging into the Larsmo-Öja Lake in Midwestern Finland was studied by using long term water data collected during 1963-2009. Acid sulfate soils are extremely acidic soils (pH < 4) that are known to discharge very large amounts of acidity and metals into recipient water courses, and this was also evident in the study area where extreme acidic events have occurred frequently. Looking at the whole study period, there was an abrupt and consistent decline in pH in the late 1960s and early 1970s in the main river (Esse River) that coincided with extensive drainage works that dropped the ground water level, enabling oxidation of sulfidic soils and transport of acidity to the rivers. Since then, there is a trend of decreasing acidic events and rising pH values, probably due to a continuous depletion of the acidic pool in the existing a.s. soils. In the short run, water quality varied greatly due to varying hydrological conditions between seasons and years. Generally, the impact from a.s. soils was highest during high runoff in autumn and spring, and therefore, neutralization of acidity in discharge water by liming would at such occasions be very demanding. The relationship between the runoff and water quality was, however, somewhat different during different seasons. As expected, dry summers (low ground water levels) were found to increase the impact from a.s. soils in the subsequent autumn, but only if runoff was high. Towards the end of the study period winters tended to become warmer with higher runoff and spring floods tended to occur earlier. Thus, events with bad water quality during the winter months have become more common and acidic spring surges occur earlier. Seen from the data in this study, it is obvious that potential changes in the future climate will have significant consequences on the impact from a.s. soils on water courses.

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#### 1. Introduction

The estimated cover of acid sulfate (a.s.) soils worldwide is 17–24 million hectares, concentrated mainly in coastal areas (Andriesse and van Meensvoort, 2006). In Europe, these soils can be found to a large extent on the coastal plains of Western Finland, and consist of fine-grained sediments originating from the Littorina- and Postlittorina Sea (7500–0 BP) (Puustinen et al., 1994; Yli-Halla et al., 1999). In normal conditions in boreal environments, peat lands and coniferous forests are a source of organic acids to rivers and lakes, which, in turn, control pH in many water courses (Kortelainen and Mannio, 1990; Kortelainen et al., 1989; Kortelai

nen and Saukkonen, 1995; Laudon et al., 1999; Mattsson et al., 2005, 2007). However, many water courses in Western Finland that drain a.s. soils show an opposite relationship between organic acids and pH or acidity due to the acidic and metal rich discharge from a.s. soils that overshadow any other source of acidity (Edén et al., 1999; Mattsson et al., 2007; Österholm and Åström, 2004; Palko and Weppling, 1994). In these water courses, sulfate (released when sulfides are oxidized) correlate negatively with pH and positively with acidity, while organic acids seems to rather decrease acidity by binding to metals (Driscoll, 1985; Edén et al., 1999; Rask and Tuunainen, 1990; Toivonen and Österholm, 2011; Witters et al., 1990).

The a.s. soils are mainly developed after anthropogenic drainage operations that lower the ground water level, and thus enable oxidation of the sulfidic sediments (Österholm and Åström, 2004). With good drainage, typically subsurface pipes at 1.0–1.4 m, the ground water can be quickly lowered to 0.5 m or more during

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spring, which is required for the heavy machinery and tillage. However, if the discharge is not regulated, the ground water will easily drop to the depth of the ground water pipe early in the summer (Österholm et al., 2012). During summer and early autumn the evapotranspiration mostly exceeds precipitation. This will cause a further drop of the ground water in the well-structured soils, commonly to 1.5-2.5 m, exposing even the deep lying sulfides to oxygen (Åström et al., 2007; Österholm et al., 2012). As a result, the sulfides oxidize to sulfuric acid which causes an extreme drop in pH (<4.0) which, in turn, causes potentially toxic metals (e.g. Al, Cd, Co, Cu, Mn, Ni and Zn) to dissolve from soil minerals. These sediments mainly have a low buffering capacity due to minerals with a low ion-exchange capacity and a low carbonate content. The topsoil on farmland fields are limed more or less regularly, but the lime has very little or no effect on the quality of the discharge water (Åström et al., 2007). During snow melt and heavy rains, percolating water transports acidity, dissolved metals and sulfate to nearby streams (Åström and Björklund, 1995, 1997; Österholm and Aström, 2008; Palko and Yli-Halla, 1988, 1990) causing fish kills and a decline in fish stocks (Åström et al., 2005; Hildén and Rapport, 1993; Hudd et al., 1986; Hudd and Leskelä, 1998).

In this paper we study the four rivers discharging into Larsmo-Öja Lake in Midwestern Finland (Fig. 1). The lake is an artificial freshwater basin that was embanked from the sea to serve as a water resource for the industries in the area. The water level is regulated, and the lake is also an important reproduction area for fish and a popular recreational area for fishing and recreational houses. However, there are a.s. soils in the catchment releasing high amounts of acidity and metals to the rivers (Palko and Alasaarela, 1988; Palko and Yli-Halla, 1993; Roos and Åström, 2005a;

Toivonen and Österholm, 2011). Similar to a.s. soil-affected water courses elsewhere, the rivers and the lake have suffered from massive fish kills on several occasions, degrading the ecological, recreational and property values. The main study site, Esse River, is also the source of drinking water for the town of Jakobstad with 20,000 inhabitants. While impurities in river water can be sufficiently removed by modern technology in water plants, unpredicted events with bad water makes maintenance more difficult and expensive. Similarly, as such events also affect the recipient lake, they pose a challenge to the industry in the area that uses the lake as a fresh water reservoir.

The objective of this work is to assess short- and long-term trends in the impact from a.s. soils (mainly indicated by pH and electric conductivity) on water courses in the Larsmo-Öja Lake area where extensive long-term water data (1963–2009) was available. We examine how such trends are caused by anthropogenic and natural changes in hydrological conditions (indicated by runoff). We demonstrate that changes in hydrological conditions, including potential climate change, have a great impact on temporal water quality variations in areas with a.s. soils, with important implications on the utilization of water reservoirs, mitigation strategies and the survival of different species in affected waters.

#### 2. Methods

#### 2.1. Data

Discharge from a.s. soils is characterized by low pH and high concentrations of ions (sulfate and dissolved metals, e.g. Al). There is no tidal sea water intrusion into the streams affecting pH or

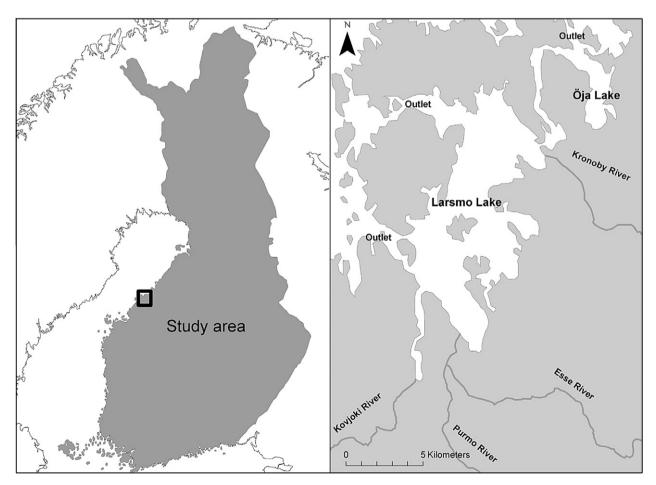


Fig. 1. The Larsmo-Öja Lake system in Midwestern Finland. Embankments not visible in this scale.

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