

Identifying the Impact of Acid Sulfate Soils on a Humic Boreal Lake

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Abstract

Many rivers and watercourses in western Finland have experienced several massive fish kills during the last decades caused by acidity and high metal levels. Naturally occurring humic acids make watercourses in this area acidic, but additional acidity is created by the artificial drainage of sulfide-bearing sediments. This has caused confusion and debate about the causes to the fish kills. This study identifies the sources of the acid and metal load on a humic boreal lake. Acid sulfate soils (a.s. soils) with a pH minimum of 3.2, high concentrations of sulfur and corresponding high titratable acidity were found in the drainage area of the lake. In stream waters, the concentrations of acidity and metals were high, and correlated well with sulfate (sulfide oxidation is the only potential source). A negative correlation between acidity and organic carbon (indicator of humic acids) was found. This confirms that the main reasons for acidity and related fish kills in the area are caused by a.s. soils, not humic acids from forest and/or peat areas.

Key Words

Geochemical exploration.

Introduction

Large areas on the Finnish coast are covered with fine-grained sulfide-bearing sediments. When these sediments are drained, sulfuric acid is created by oxidation of the sulfides. Soil minerals dissolve in this acidic environment (pH<4) releasing large quantities of metals. The acidic water flushes the potentially toxic metals to streams (Åström and Björklund 1995, 1996) causing ecological damage (Hudd *et al.* 1984).

In large parts of western Finland sulfide rich sediments developed in a shallow brackish sea hundreds to thousands of years ago. Due to a flat topography and a fast rate of land uplift (up to 8 mm per year), large areas of sea sediment has been lifted above sea water level. Today the sulfide rich sediments (0.2 to 2 % sulfur) occur in areas up to 90 m above current sea level (Erviö 1975). Even though these soils are located high above sea level, they have a high groundwater level in their natural state. This is due to the flat topography and a peat layer that protects it from drying. Some of these sediments also lie under shallow lakes. In general, the sulfide minerals in these soils remain inert if left in their natural state (Boman *et al.* 2008, Österholm and Åström 2004).

These fine-grained soils are, if drained and limed, easy to cultivate and very nutrient rich, and are therefore largely in agricultural use. The draining of these soils has occurred mainly during the last 50 years when the use of effective subsurface pipe drainage became common. Since then, many watercourses have become severely acidified. Because of the artificial draining, the oxidation depth in the a.s. soils extends down to 2.0 m. However, because of granitic bedrock and soil rich in humic acids, watercourses in northern Europe are naturally acidic (Laudon *et al.* 2000). It may therefore be difficult to distinguish acidity occurring naturally from acidity derived from reclamation of a.s. soils. To do this, water samples were taken during four occasions in 2007 from all the main ditches, small streams and the four rivers discharging into Larsmo and Öja Lake, an artificial freshwater reservoir. The analysis included pH, electric conductivity, acidity, total organic carbon, sulfate and metals. Soil samples from ten farmland sites in the catchment were also analysed for pH, acidity, metals and sulfur.

Acidity in soil

Soil profiles were taken from farmlands located 0-25 m above sea level. Seven of the profiles can be regarded as acidic (pH < 4) a.s. soils, with a pH-minimum of 3.2. Three profiles can be regarded as semi-acidic a.s. soils, because despite a higher pH (minimum pH 4.1-4.5), they still have high concentrations of sulfur. The median oxidation depth is 1.9 m. The titratable peroxide acidity (Modified method after Ahern *et al.* (2004), Acid Sulfate Soils Laboratory Methods Guidelines version 2.1) in the oxidised and reduced zones in the profiles from the drainage area correlates well with sulfur content (Fig 1), which indicates that the

severe acidity is caused by sulfide oxidation.

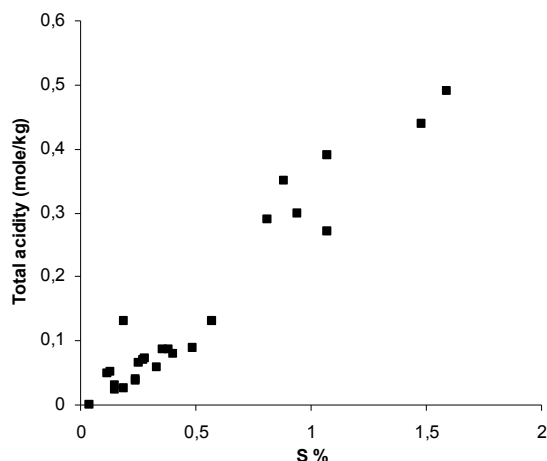


Figure 1. Sulfur versus total acidity in soil.

Acidity and metals in water

The median pH of low-order streams and rivers that discharge into Larsmo and Öja Lake is 4.7 and 5.0 respectively. These low pH values could in principle be caused by organic acids. However, there was a negative correlation ($p = -0.73$) between total organic carbon (TOC) and acidity in the water samples (Fig 2). In contrast, pH had a negative correlation with sulphate, whereas acidity and a number of metals known to be associated with a.s. soils had a positive correlation with sulfate (Figure 3). According to numerous studies (Åström & Björklund 1997, Åström 1998, Nordmyr *et al.* 2008 and Österholm *et al.* 2005), Fe does not leach from a.s. soils in any great extent. However, in the current study area (Larsmo and Öja Lake), Fe is likely to be enriched by a.s. soils in some of the more severely affected watercourses (Figure 3).

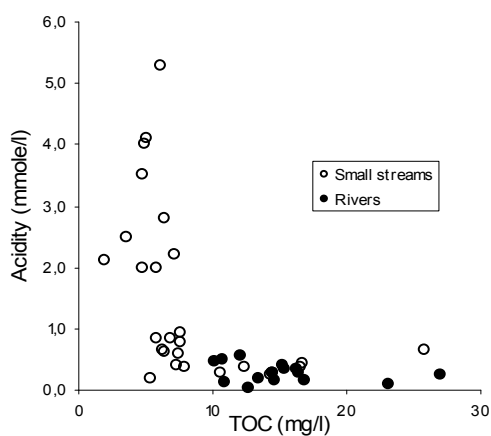


Figure 2. Total organic carbon versus acidity of water.

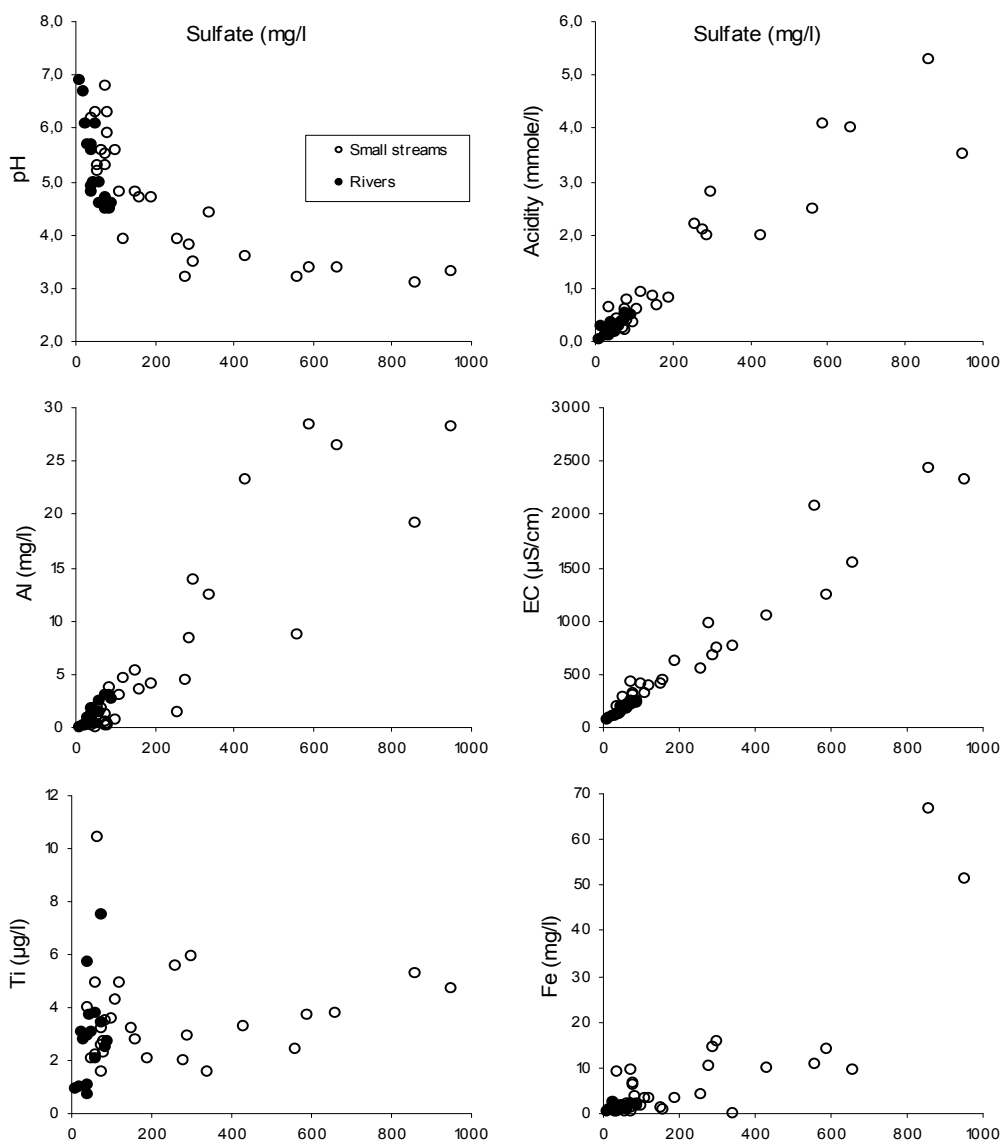


Figure 3. Sulfate versus pH, acidity, Al, EC, Ti and Fe of water in small streams and rivers.

Conclusions

It is common that humic acids cause a low pH-level in boreal watercourses, potentially harmful for biota. In the study area, however, sulfur in the soil correlated positively with soil acidity, and sulfate in recipient water correlated negatively with pH and positively with acidity and potentially toxic metals. Concentrations of organic carbon (indicator of humic acids) showed an inverse trend to these variables. Thus, on the basis of these unambiguous trends, it could be concluded that the severe acidity associated with high metal concentrations that cause fish kills in the Larsmo and Öja Lake are mainly caused by sulfur oxidation in the sulfide-bearing sediments, not by soils discharging humic acids.

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