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

Toivonen, Janne; Österholm, Peter; Fröjdö, Sören

Published in:
Journal of Hydrology

DOI:
10.1016/j.jhydrol.2013.02.034

Published: 01/01/2013

Document Version
Final published version

Journal of Hydrology 487 (2013) 60–69

Contents lists available at SciVerse ScienceDirect

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

Janne Toivonen *, Peter Österholm, Sören Fröjdö

Åbo Akademi University, Geology and Mineralogy, Domkyrkotorget 1, 20500 Åbo, Finland

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.

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; Kortelainen 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

* Corresponding author. Present address: Västergränd 2 bost. 18, 68620 Jakobstad, Finland. Tel.: +358 (0)503610682.

E-mail addresses: janne.toivonen@abo.fi (J. Toivonen), peter.osterholm@abo.fi (P. Österholm), soren.frojdo@abo.fi (S. Fröjdö).

0022-1694/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhydrol.2013.02.034

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 Åström, 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

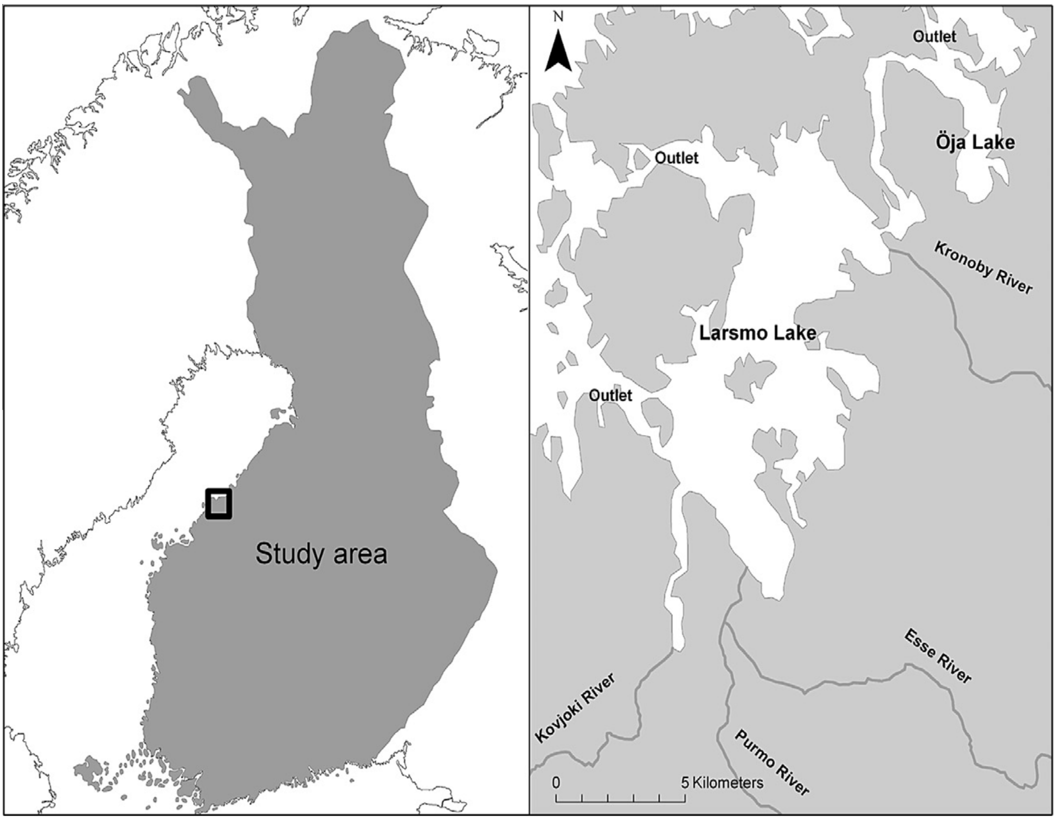

Fig. 1. The Larsmo-Öja Lake system in Midwestern Finland. Embankments not visible in this scale.

salinity. Instead, from numerous studies it is well established that in areas with a significant occurrence of a.s. soils, the large amount of ions leached from these soils is generally strongly dominating the budget of ions in stream water. This leads to very strong correlations between electric conductivity (EC) and a.s. soil-related elements (r_s commonly 0.90–0.99) in this region (e.g. Åström and Åström, 1997; Roos and Åström, 2005a; Österholm and Åström, 2008). On the basis of results in a recent study from the streams, rivers and the recipient lake in the current study area, it is obvious that this also applies for the study area; EC correlates very strongly with sulfate (typically 10–1000 mg/L) and other a.s. soil-related elements (data in Toivonen and Österholm (2011)). Moreover, in the same study it was also clearly shown that the typical low pH values in the area are strongly associated with sulfide oxidation (high sulfate concentrations) and not humic acids from the forested areas in the catchment. To further investigate the suitability of EC to represent impact from a.s. soils, an additional analysis of pH, EC, sulfate (SFS-EN ISO/IEC 17025:2005) and dissolved Al (ICP-MS, filtered through 0.45 μm membrane filter) was performed on 22 water samples taken in Esse River from December 2007 to May 2008. The samples represented both high and low runoff conditions. This resulted in excellent correlations between sulfate and EC (r_s = 0.98), dissolved Al and EC (r_s = 0.89) and pH and EC (r_s = −0.89). However, it is notable that the ratios between EC, pH and different elements are somewhat site specific, i.e. they vary to some extent between different catchments due to different soil types (e.g. grain size and mineralogy) and land use (depth of drainage). Consequently, together with pH, the impact of a.s. soils can be estimated by relative variations in EC in the current study area. As pH and EC are relatively easily measured and the laboratory methods have not changed over time, the risks of inhomogeneities are small in the available long and continuous records. Thus, in this study, we focus mainly on pH and EC in order to describe the impact from a.s. soils on stream water geochemistry.

Aluminum is considered to be the most abundant potential toxic metal released from a.s. soils (Österholm and Åström, 2004), and a wide range of pH and Al concentrations (pH 4–6 and Al concentrations 0.025–0.9 mg/L) have been shown to cause increased disturbance and mortality in the eggs, juveniles and adult fish of many species (e.g. Brown, 1983; Vuorinen et al., 1993; Waring and Brown, 1995). However, different species, life stages and populations show different sensitivities to low pH and high metal concentrations, and the toxicity of metals vary, among other things, with pH (Brown, 1983; Driscoll, 1985; Nystrand et al., 2012). Thus it is difficult to establish overall harmful pH and EC threshold values. Nevertheless, national threshold values of pH below 5.5 and 5.0 have been widely adapted to roughly indicate moderate and poor ecological status, respectively (Vuori et al., 2009). Therefore, in this study we put particular focus on these pH thresholds and term pH below 5.5 as very acidic, and pH below 5.0 as extremely acidic. In terms of EC, we consider values above 12 mS/m as harmful because they represent a rough threshold when pH decreases below 5.5 and dissolved (0.45 μm) Al concentrations increase above 0.8 mg/L in rivers discharging into Larsmo-Öja Lake (Toivonen and Österholm, unpublished data).

For long- and short-term trend analysis, data on water quality from the main river, Esse River (48% of all discharge to Larsmo-Öja Lake), was provided by Jakobstad water plant, whose water intake lies close to the outlet. The data from Esse River contain almost daily pH-analyses beginning from 1963, total aluminum concentrations since 1985 and EC beginning from 1987. Aluminum has been analyzed with ICP-OES (ISO 11885:2007) on unfiltered samples. Temperature measurements have been performed regularly since 1969.

Because the analysis of Al was performed on unfiltered samples, it is likely to include some eroded Al-bearing silicate particles unrelated to leaching from a.s. soils (Nystrand et al., 2012). However, the flat topography and the lack of the typical color of the eroded clay particles in the water would suggest that erosion is not a dominating source of Al. Also, total Al concentrations was found to correlate with pH (r_s = −0.78). Previous studies from other catchments in the region suggests that the particulate fraction of Al, calculated as the difference between filtered and unfiltered samples, is normally 0–30% (Åström and Björklund, 1995; Nystrand and Österholm, 2013).

In addition, data on pH and EC for all four rivers discharging into Larsmo-Öja Lake, Esse, Purmo, Kronoby and Kovjoki Rivers, was obtained from the HERTTA database (OIVA-environment and geographic information service, Finnish Environment Institute). An equal amount of data was selected from winter, spring, summer and autumn. The data on Esse-, Purmo- and Kronoby Rivers extend from the early 1960s to 2010, with some gaps, while information on Kovjoki River was only available from 1976 to 1981 and 2006 to 2008.

Sampling of the four rivers discharging into Larsmo-Öja Lake was done during a 2-day period of high runoff in December 2007 for pH (measured with an electrode *in situ*) and acidity analysis (potentiometric titration within 24 h). Instead of the standard titration up to pH 8.3, titration up to pH 5.5 was performed because, as mentioned above, this was used as a threshold value to very acidic water.

Specific runoff was based on the daily measurements made in the unregulated Pahkaoja stream (catchment size 23.5 km^2) in the nearby Lestijärvi municipality, and the data was obtained from the HERTTA database. Due to a very flat and similar terrain and a short distance between sites, Pahkaoja stream represents the general hydrological conditions in the area well. The total runoff for each river was obtained by multiplying the specific runoff for Pahkaoja with the drainage area of each river.

2.2. Statistical methods

Data from the HERTTA database was used in order to describe water quality variations (pH and EC) in the four rivers. Because the sampling has not been performed regularly, there is data missing from many years, and the sampling dates do not match every year. Therefore, to give more robust and comparable results, mainly medians and the 10th and 90th percentiles from each river were used. Nevertheless, the comparison between rivers should still only be considered as indicative.

The vast data on Esse River provided by the water plant was used in six different ways in order to study the impact from a.s. soils, and to describe trends in water quality through time, based on years, months and hydrological conditions:

1. Data on pH, EC, Al and temperature from the fifteenth of every month (or nearest date when data not available) was used in detecting monthly changes. The fifteenth reflects the typical water quality for the month, and this approach enables the use of specific runoff for the same date for the study of impact of runoff on water quality, and also for the creation of runoff-corrected data (see below). Data selected from fifteenth of every month was used in all trend tests and water quality descriptions unless otherwise mentioned.
2. To ensure that no important data that possibly could cause trends was excluded (as is the risk in the previous method), median pH and EC from every month was also tested for trends.
3. To detect trends connected to different seasons and hydrological conditions, the data was divided into four seasons (winter, spring, summer and autumn) following Österholm and Åström (2008): Winter is characterized by temperatures below zero and low flow (base flow), and was defined to begin at 1 January

each year. The spring period (and end of winter) was set when the specific runoff reached 10 L s^{-1} km^{-2}. In most cases this increase in flow occurred suddenly (easy to define) as a result of snowmelt. Summer was set to begin on 1 June. Because of high temperatures and crop growth, evapotranspiration in most cases exceeds precipitation. This results in a low groundwater level (down to about 2 m) enabling oxidation of a.s. soils. Autumn was set to begin in September, the first day when specific runoff exceeds 1 L s^{-1} km^{-2}, which is an indication of a rising groundwater level. Median pH and EC from every season was used to detect trends based on seasons.

4. In order to obtain knowledge about the short-term effect of dry spells on water quality, average specific runoff during summer (defined in item 3) was tested for correlation with median pH and EC during the following autumn and spring (defined in item 3).
5. Days per year (%) when pH < 5.5 and <5.0, and EC > 12 mS/m was used in detecting yearly trends. The data on EC representing base flow (runoff <1 L s^{-1} km^{-2}) was excluded in these calculations, because during dry periods, EC may be significantly raised due to evaporation or a high proportion of non-acidic deep ground water.
6. The last method to describe water quality considers the frequency of acidic events; that is the number of times when pH was below 5.5 and 5.0 for at least 1 day during the month in question. This accounts for the frequency of acidic events rather than the actual number of acidic days or actual pH (used in methods 1–5). The period after the severe drop in pH (1970 and forward) was also divided into 10-year periods (1970–1979, 1980–1989, 1990–1999 and 2000–2009) in order to describe the frequencies of acidic events during different decades. Data from 1963 to 1967 was used as background information representing a period of better water quality.

The non-parametric Kendalĺs tau and seasonal Kendalĺs trend tests were used for detecting trends in time in the data series mentioned above. The level of confidence was set to 95% ($p = 0.05$). Non-parametric regression (Lowess, $f = 0.67$) was used in modeling the effect of runoff on water quality. The residuals acquired from the Lowess curve were used for detecting runoff-corrected trends over time (Hirsch et al., 1991). Spearman rank correlation (r_s) was used for determining the correlation between summer droughts and water quality, and the level of confidence was set to 95% ($p = 0.05$).

3. Results and discussion

3.1. General water quality in the streams discharging into Larsmo-Öja Lake

Based on the long-term data acquired from the HERTTA database, medians, 10th and 90th percentiles of pH and EC indicate that Kovjoki River has the greatest impact of a.s. soils, followed by Purmo, Kronoby and Esse Rivers (Table 1). In terms of e.g. acidity, EC, sulfate and metal concentrations, this ranking is also similar to results in studies where more short-term data was used (Palko and Alasaarela, 1988; Palko and Yli-Halla, 1993; Toivonen and Österholm, 2011). However, in terms of extremely acidic events (minimum and 10th percentile pH and EC) there is little difference between Purmo and Kronoby Rivers, also indicated by Roos and Åström (2005b). The better water quality in Esse River compared to the other rivers is because a large part of the catchment of Esse River lies above the highest level of the Littorina Sea, thus having a smaller proportion of a.s. soils (perhaps less than 2%; Palko and Alasaarela, 1988). However, since Esse River also regularly experience bad water quality shows that even small areas of a.s. soils are able to cause severe acidity.

Table 1
pH and electric conductivity (EC) in the four rivers discharging into Larsmo-Öja Lake (1962–2010 for Esse and Purmo Rivers, 1964–2010 for Kronoby River, and 1976–1981 and 2006–2008 for Kovjoki River, HERTTA database).

	Esse River	Purmo River	Kronoby River	Kovjoki River
pH				
Min	4.3	4.2	4.2	4.2
10 percentile	5.4	4.6	4.8	4.4
Median	6.4	5.7	6.1	5.2
90 percentile	6.8	6.5	6.8	6.2
Max	7.3	6.9	7.2	6.9
Electric conductivity				
Min	3.7	5.7	5.6	13
10 percentile	6.3	8.4	9.2	13
Median	7.8	13	13	21
90 percentile	12	18	20	37
Max	21	33	30	56

The different level of impact from a.s. soils in the four rivers is also reflected by the theoretical need of limestone ($CaCO_3$) in order to raise pH to 5.5: Kovjoki River (field-pH 4.6) needed 11 g/m^3, Purmo River (field-pH 4.5) 8.0 g/m^3, and Kronoby River (field-pH 5.0) 2.4 g/m^3. During this sampling, Esse River displayed a field-pH above 5.5, and was therefore not in need of liming. When the runoff was taken into consideration (about 15 L s^{-1} km^{-2}), the total amount of required limestone was about 16 t/day divided by the three smaller rivers. However, it is notable that during more extreme events (when pH in Esse River also drops below 5.5) and higher runoff, this amount will also be significantly higher. In addition, low-order streams not included in the calculations above contribute about 25% of the acidic load to Larsmo-Öja Lake (Toivonen and Österholm, 2011), and will raise the limestone requirement significantly in case all discharge water to Larsmo-Öja Lake is to be limed.

The pH and EC in all four rivers vary with somewhat the same magnitude based on 90th percentiles/10th percentiles (1.3–1.4 for pH and 2.0–2.4 for EC) (Table 1). When comparing the data on Esse River from the HERTTA database (1962–2010; Table 1) with the more extensive data on Esse River (1963–2009) acquired from the water plant, practically the same 10th percentile (5.6), median (6.5) and 90th percentile (6.9) and variation (90th percentiles/10th percentiles: 1.2) in pH can be found. As the catchment of Esse River roughly equals the combined catchments of the three smaller rivers, variation of water quality in this river is expected to be of greatest importance for the lake as a whole. Under normal conditions, the river will act as an important dilutant, but during acidic events it will, together with other rivers, have a negative effect on the water quality in the lake. Therefore, the more extensive and coherent data on the water quality in Esse River obtained from the water plant used below is well suited for detecting trends in impact from a.s. soils associated with changes in land use, hydrology and climate in this region. The data is also expected to reflect changing conditions in the Larsmo-Öja Lake over the past four decades.

Because of irregular sampling and the varying choice of analyzed parameters, the possibilities for statistically valid trend analysis on data found in the HERTTA database, especially for the smaller rivers, was limited. Unfortunately, this is typical of many monitoring programs, and highlights the importance of having well planned and consistent sampling schemes in future monitoring programs.

According to the data acquired from the water plant, pH in Esse River during the study period (47 years) has decreased to less than

5.5 at least once in 89% of the years, and to less than 5.0 at least once in 62% of the years. During the worst period in the early 1970s between 20% and 30% of the days per year displayed a pH less than 5.5, and 10–20% of the days per year displayed a pH less than 5.0.

3.2. Role of runoff on water quality

The highest runoff and lowest pH typically occur in spring and autumn: May and November displayed the highest average specific runoff in spring (24 L s^{-1} km^{-2}) and autumn (11 L s^{-1} km^{-2}), while the overall lowest median pH in Esse River was found in April and May (pH 6.0) and November (pH 6.2). February and July showed the lowest average runoff in winter (1.9 L s^{-1} km^{-2}) and summer (2.3 L s^{-1} km^{-2}), and a generally high median pH (6.4 and 6.7, respectively). The difference in pH between seasons is also visible in Fig. 5. Based on this, the months of February, May, July and November were chosen to represent the four seasons and display the role of runoff on water geochemistry in Esse River during different hydrological conditions.

pH decreases with increasing runoff in May and November, but the decrease is neither linear nor exactly similar for the two seasons (Fig. 2): pH tends to decrease below 6.0 in November at a specific runoff above 10 L s^{-1} km^{-2}, while pH below 6.0 in May is still rare at 10 L s^{-1} km^{-2}; it typically occurs when runoff is >20 L s^{-1} km^{-2} and the lowest pH values are found when the runoff is >25 L s^{-1} km^{-2}. Although pH is somewhat lower during the spring than in the autumn, it seems that there is a higher proportion of dilution by discharge from non-a.s. soils and melting snow during the spring.

pH during February and July shows no clear correlation with runoff since these seasons are dominated by a buffered base flow (Fig. 2). The relatively high pH in winter can be explained by frozen soil, preventing the percolation of water through the acidic soil layers. Even though rainy spells occur during the summer, the ground water during the summer in a.s. soils is often low, and the complete lack of correlation between runoff and pH is difficult to explain. This lack of correlation was also found by Österholm and Åström (2008) who studied long-term trends in a small catchment. Because the main discharge from a.s. soils on farmlands occur through subsurface pipe drainage at a depth of 1.0–1.4 m (no discharge through the pipe if ground water level is below this), one potential explanation is that the proportion of discharge from farmlands is relatively low during summers. When the ground water is occasionally above this, during prolonged heavy rains, there is relatively little time for the water percolating through macro pores to interact with the soil. A study on the quality of the undiluted water running directly from the drain pipe, together with monitoring of ground water from the same field, during a very wet summer would be needed to test this hypothesis in the field. Eventually, it would also be possible to simulate such conditions on a smaller scale in the lab, but this would require relatively large samples so that the large cracks (macro pores), typical for a.s. soils and responsible for most of the water percolation, would be preserved.

No clear increase in EC with runoff can be observed in May, indicating that dilution effects on EC in spring, in accordance with pH, are prominent (Fig. 3). In November EC increases with runoff up to between 5 and 10 L s^{-1} km^{-2} after which there is no clear trend of a further increase in EC. In February and July, a slight increase in EC with increasing runoff can be observed up to 5 and 2 L s^{-1} km^{-2}, respectively, but no general increase in EC occurs during higher runoff. As with the corresponding trends for pH, the reasons for this are not fully understood, but may be related to inhibited percolation in the frozen ground in winter and more dilution from other areas during the summer.

3.3. Effects of summer droughts on water quality

Dry summers are expected to cause enhanced acidic events the following autumn due to increased sulfur oxidation. However, using the whole data set, no correlation was seen between average

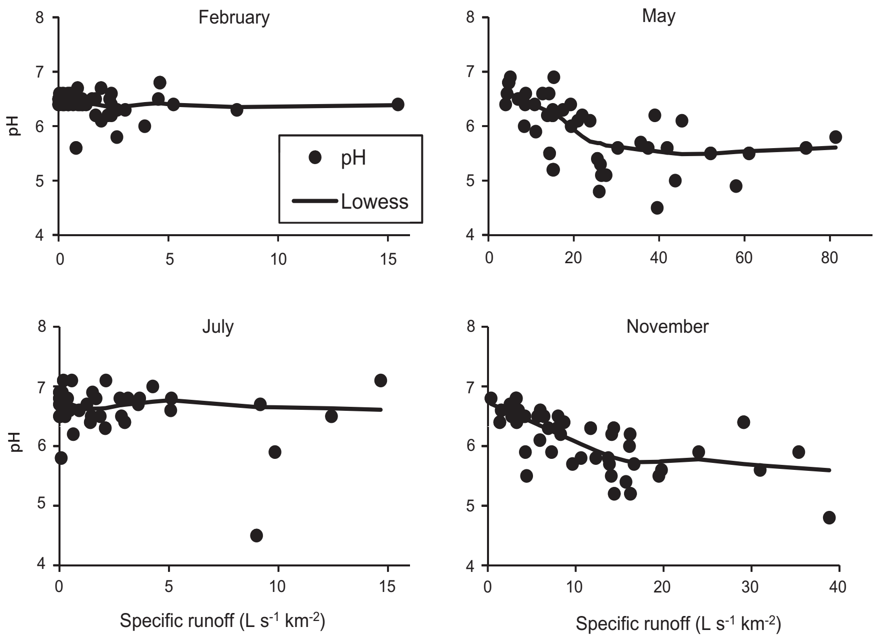

Fig. 2. Lowess curve (f = 0.67) indicating the potential relationship between specific runoff and pH for winters (February), springs (May), summers (July) and autumns (November) in Esse River 1963–2009.

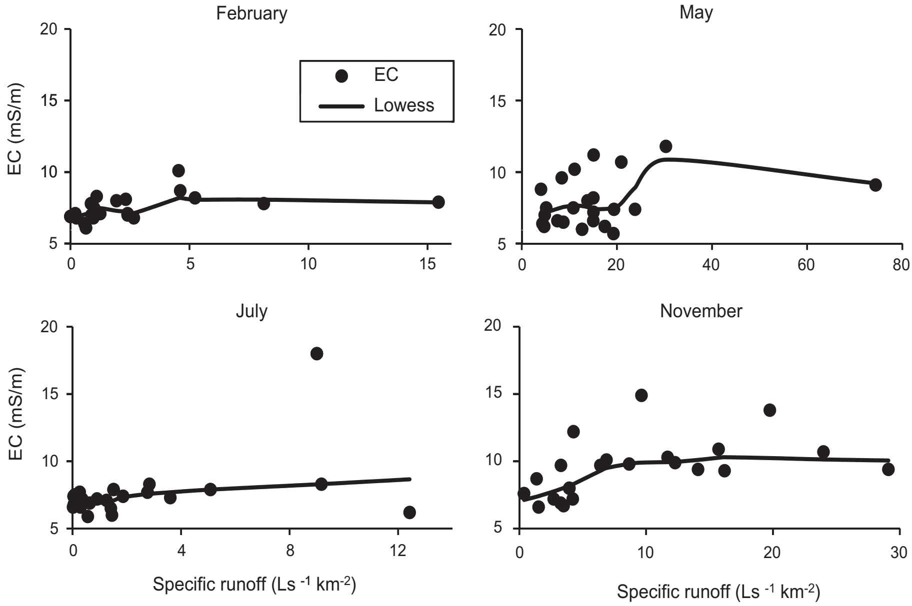

Fig. 3. Lowess curve (f = 0.67) indicating the potential relationship between specific runoff and EC for winters (February), springs (May), summers (July) and autumns (November) in Esse River 1987–2009.

runoff during summers and median pH or EC the following autumn. However, as shown in Section 3.2, high specific runoff is needed for low pH and high EC. Therefore, by excluding days in the autumn with low and moderate runoff (runoff <10 L s^{-1} km^{-2}) from the calculations, the correlation became significant (r_s = 0.55 for pH and −0.65 for EC) (Fig. 4). Consequently, the hydrological condition during the summer is not the only factor controlling the acidic load; high runoff during the autumn is also required for the increased pool of acidity and metals to be flushed to water courses. This was shown in an exceptional way in 2006 and 2007, when a very dry summer followed by a very rainy autumn and winter caused an acidic event containing the lowest pH and highest EC ever recorded in Esse River (pH 4.1 and EC 28 mS/m). If a change in climate causes an increase in the frequency of similar extreme weather conditions, the frequency of severe acidic metal surges, like the one that occurred in 2006 and 2007, will also increase in the near future.

For spring seasons a significant correlation was found between average runoff preceding summer and median pH (r_s = 0.36), but not median EC. This indicates that while part of the acidity pool created during a dry summer prevails through the winter, in line with Österholm and Åström (2008) who studied a small catchment, dilution effects caused by the low-ionic melt water seem to be more important in explaining variations of spring time EC in larger catchments with a lower proportion of a.s. soils. The calculations were done without excluding any data as the runoff is generally high in the spring.

3.4. Trends in impact from a.s. soils

A remarkable decrease in pH took place in the late 1960s and early 1970s, and many years since then were characterized by low pH values (Figs. 5 and 7). The same pattern can be found in many other water courses in western Finland (Anonymous, 1973; Åström et al., 2005; Saarinen et al., 2010). In the previous sections it was shown that the impact from a.s. soils on water quality is highly dependent on hydrological conditions that, in turn, vary greatly between seasons and years. The great variation in water quality between seasons and years is also visible in Figs. 5 and 6. The hydrological conditions are also dependent on changes in climate. However, the increasing acidity in the late 1960s was most likely a direct result of increased drainage because (1) drainage is

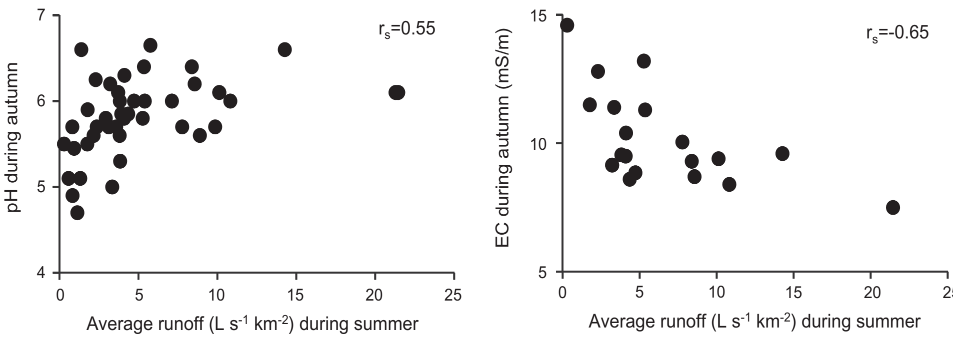

Fig. 4. Correlation between average runoff during summer and pH (left) and EC (right) during the following autumn (autumn days with runoff <10 L s^{-1} km^{-2} are excluded).

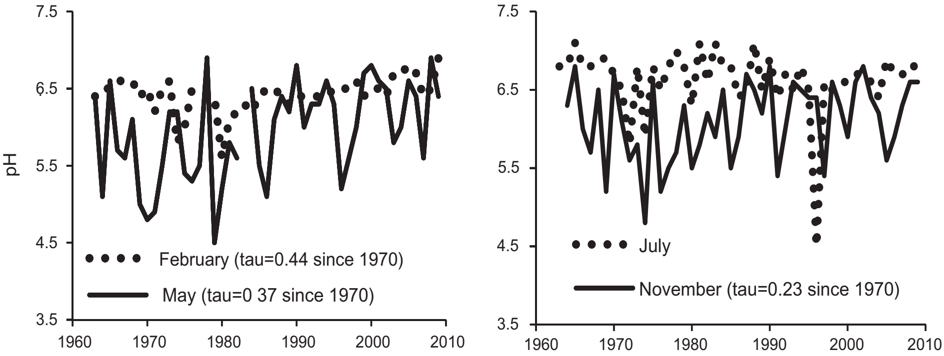

Fig. 5. pH in Esse River in February and May (left), and July and November (right) 1963–2009.

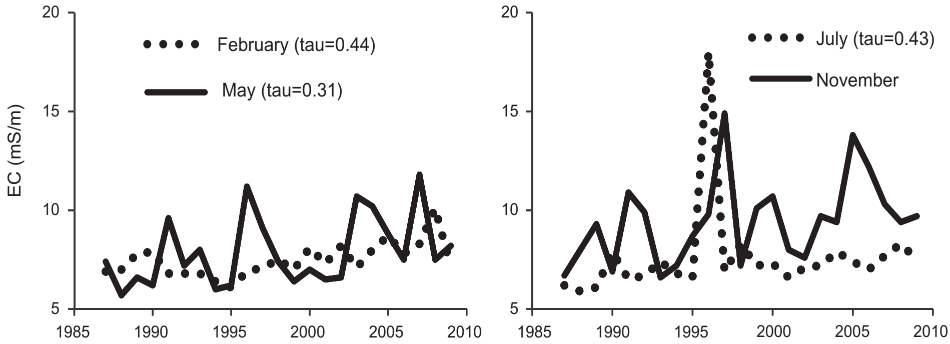

Fig. 6. EC in Esse River in February and May (left), and July and November (right) 1987–2009.

necessary for significant leaching of acidity to occur (Österholm and Åström, 2004); (2) increased drainage rather than long-term changes in weather conditions coincided with the pH-drop; and (3) the low pH conditions prevailed for many consecutive years.

Since 1970 pH is recovering (Seasonal Kendall: tau = 0.23, Fig. 5 shows pH during four seasons). This increase in pH was also visible according to statistical tests on the other types of data; e.g. percentage of days with pH < 5.5 (tau = −0.36, data not shown), frequency when pH has dropped to 5.5 and 5.0 at least once per year (Fig. 7), median pH every month (Seasonal Kendall: tau = 0.24, data not shown) and median pH every season (Seasonal Kendall: tau = 0.27, data not shown). The rising trend was statistically significant for the months of November, April, September, October, May and February (tau = 0.23–0.44, Fig. 5). As compared to the period of 1970–1979, median pH 2000–2009 based on data from February, May and November was 0.2, 1.0 and 0.6 units higher, respectively, while median pH based on data from July has remained practically the same (−0.1 units lower). Moreover, a weak but significant trend was found for runoff-corrected data (Seasonal Kendall: tau = 0.08, data not shown). Consequently, the increasing pH that can be observed is not a result of changes in climate related runoff changes, but may instead be due to the fact that the pool of oxidizable sulfides in a.s. soils decrease very rapidly upon efficient drainage, and the sulfide pool can be halved within a few decades (Österholm and Åström, 2004). There has also been a weak but significant decreasing trend in total Al since 1985 (Seasonal Kendall: tau = −0.09). Thus, the older a.s. soils created many decades ago will slowly become relict a.s. soils with less environmental impact. A change in climate can, however, prolong the time of bad water quality to some extent by increasing the oxidation depth (today typically 2.0 m; Toivonen and Österholm, 2011) in a.s. soils. Electric conductivity has been increasing with time since 1987 (Seasonal Kendall: tau = 0.35, Fig. 5 shows EC during four seasons). As with pH, the increase was significant in all types of data, e.g. the percentage of days in a year with EC > 12 mS/m (tau = 0.40, data not shown). Median EC based on data from February, May, July and November in 2000–2009 was 1.2, 1.0, 0.7 and 1.3 mS/m, respectively, higher than in 1987–1996. There was also a rising trend for runoff-corrected data (Seasonal Kendall: tau = 0.34, data not shown), showing that the increasing EC is unrelated to changes in runoff, consistent with the lack of clear trends in Fig. 3. The long-term rise in EC was relatively small and ions from a.s. soils (e.g. sulfate from sulfide oxidation) were still dominating EC at the end of the study period. Nevertheless, this trend may indicate a small increase of elements not primarily originating from a.s. soil oxidation/leaching. Possible explanations include increased evapotranspiration (increasing ion concentrations in the remaining soil water) and/or deeper flow paths (longer residence time for water) due to deeper drains, although it is not possible to explain the rising long-term trend from the available data.

A change in water temperature and the timing of high runoff has occurred that may relate to a change in climate; a weak but significant increase (Seasonal Kendall, tau = 0.14) in water temperature was found, but the only individual month that showed a significant increase was April (tau = 0.32). Specific runoff in February was increasing (tau = 0.20), while decreasing in May (tau = −0.32) since 1963. The timing of the spring flood seemed to vary more and occur earlier in later years (Fig. 8). This is in line with the expectation that global warming will cause increasing winter temperatures (Finlands National Strategy for Adaptation to Climate Change, Ministry of Agriculture and Forestry, 2009).

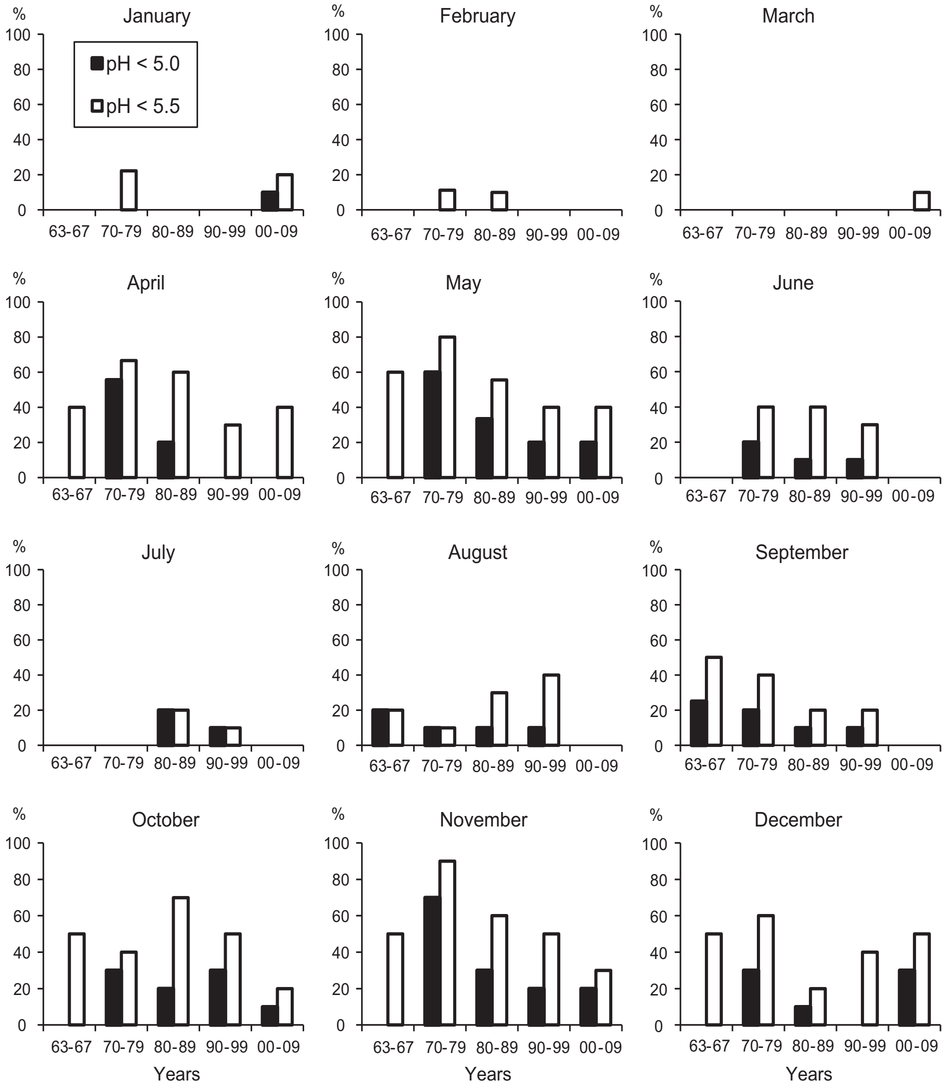

Fig. 7. Months (%) when pH has decreased for at least 1 day to less than 5.5 and 5.0 during different months during different decades.

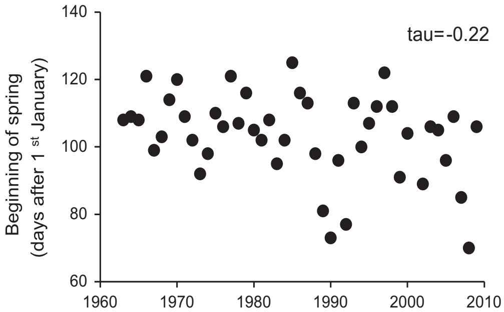

Fig. 8. Timing of the spring flood (days after 1st January when runoff exceeds 10 L s^{-1} km^{-2}).

As a result of the change in the timing of high runoff, indications were found that events when pH has dropped below 5.5 and 5.0 in 2000–2009 were increasing for the cold period (December, January, March and April) (Fig. 7). However, the overall improved pH may have partly masked changes in the timing of acidic events. Earlier springtime acidic events benefit species that reproduce in late spring, e.g. bream (*Abramis brama* L.), while species reproducing in autumn, winter or early spring, e.g. burbot (*Lota lota* L.) may be less affected (Hudd, personal communication).

A general decrease in acidic events was also visible in the summer months (Fig. 7). Notable is the complete lack of acidic events in July during the 1970s, which was probably due to differences in hydrological conditions. The frequent acidic events in August and September 1963–1967 compared to the 2000s may be related to the fact that most fields were drained by open drains in the 1960s, which caused the a.s. soils to be shallow and small in volume. Early autumn rains starting in August and September may have caused small acidic events originating from the shallow and therefore extremely hydrologically active a.s. soils, before the acidic events disappeared due to dilution effects later in autumn. Today, early autumn rains may cause less acidic discharge because the upper parts of a.s. soils are depleted of acidity, and acidic events occur mainly later in autumn when the deeper parts are being flushed.

4. Conclusions

This study shows that water quality in all four rivers discharging into Larsmo-Öja Lake have been heavily affected by discharge from acid sulfate (a.s.) soils during the last four decades. Even though Esse River is least affected by discharge from a.s. soils of the four studied rivers, pH during the 47-year study period has decreased to very acidic levels (pH < 5.5) in nine out of 10 years, and extremely acidic levels (pH < 5.0) in six out of 10 years. This shows that even a small proportion of a.s. soils in the catchment can cause serious problems with water quality.

It was shown that short- and long term trends in water quality in a.s. soil areas are strongly related to anthropogenic (land use and potential climate change) and natural (seasonal and meteorological variations) changes in hydrological conditions: (1) A severe and consistent drop in pH occurred in the late 1960s and early 1970s, coinciding with the building of efficient drainage networks. This enabled the ground water to drop significantly, thus oxidizing sulfidic sediments. The drains also function as an effective conduit for the transport of the acidic waters from the soil. (2) The impact from a.s. soils is greatest during seasons with high runoff (spring and autumn), when the proportion of discharge from a.s. soil areas is greatest. Due to significant dilution by melt water in spring, the relationship between water quality and runoff is, however, different than in autumn. (3) Years with severe summer droughts (low ground water level) increase sulfide oxidation, but extreme acidic events occur only if the droughts are followed by high runoff in the autumn. (4) Acidic events become more common in winters (higher flow) and acidic spring events occur earlier due to higher temperatures at the end of the study period. Consequently, potential changes in climate will most likely have effects on water quality in a.s. soil areas; if extreme hydrological conditions by todaýs standards (summer droughts followed by later periods with high runoff) become more common, the frequency of severe acidic events will increase, while changes in the timing of runoff events will have different effects on different water living species. Because acidic events are mainly associated with high runoff, in-stream neutralization of the acidity is extremely difficult. Instead, focus must be put on land use practices that prevent oxidation of sulfides, particularly during summers. The overall recovery in pH since the 1970s seems, however, not to be related to changes in hydrological conditions. Instead it indicates, in line with some recent studies, that the pool of acidity decreases, from a geological perspective, relatively fast in existing a.s. soils. Mitigation of large catchments with a.s. soils that would lead to short-term improvements is very difficult. However, by understanding the kind of conditions that cause acidic events, we can better utilize such water bodies, evaluate the kind of mitigation strategies that may be applicable and ultimately prepare ourselves for future changes.

Role of the funding source

Funding of this work has been provided by K.H. Renlunds stiftelse, Svenska Österbottens kulturfond, Svensk-Österbottniska samfundet, Maa-ja vesitekniikan tuki ry. and Suomen Kulttuurirahaston Etelä-Pohjanmaan rahasto. The funding sources had no role in the study design, collection, analysis or interpretation of data, in the writing of the report or in the decision to submit the paper for publication.

Acknowledgements

We thank Jakobstad water plant, in particular Jan Snellman, for supplying data on water quality. Comments by two anonymous reviewers helped to improve the paper.

References

Andriesse, W., van Meensvoort, M.E.F., 2006. Acid sulfate soils: distribution and extent. In: Lal, R. (Ed.), Encyclopedia of Soil Science, second ed. Taylor & Francis Group, New York, pp. 14–19 (electronic version).

Anonymous, 1973. Selvitys Kyrönjoen ja sen edustan merialueen kalakuolemien syistä. National Board of Waters in Finland (in Finnish).

Åström, M., Åström, J., 1997. Geochemistry of stream water in a catchment in Finland affected by sulphidic fine sediments. Appl. Geochem. 12, 593–605.

Åström, M., Björklund, A., 1995. Impact of acid sulfate soils on stream water geochemistry in western Finland. J. Geochem. Explor. 55, 163–170.

Åström, M., Björklund, A., 1997. Geochemistry and acidity of sulphate-bearing postglacial sediments of western Finland. Environ. Geochem. Health 19, 155–164.

Åström, M., Österholm, P., Bärlund, I., Tattari, 2007. Hydrochemical effects of surface liming, controlled drainage and lime-filter drainage on boreal acid sulfate soils. Water, Air, Soil Pollut. 179, 107–116.

Åström, M., Sundström, R., Holmberg, M., Storberg, K.-L., 2005. PH of streams in western Finland – a perspective from the middle ages into the mid 21st century. Agric. Food Sci. 14, 5–13.

Brown, D.J.A., 1983. Effect of calcium and aluminum concentrations on the survival of brown trout (*Salmo trutta*) at low pH. Environ. Contam. Toxicol. 30, 582–587.

Driscoll, C., 1985. Aluminum in acidic surface waters: chemistry, transport, and effects. Environ. Health Perspect. 63, 93–104.

Edén, P., Weppling, K., Jokela, S., 1999. Natural and land-use induced load of acidity, metals, humus and suspended matter in Lestijoki, a river in western Finland. Boreal Environ. Res. 4, 31–43.

HERTTA database, 2011. OIVA-Environment and Geographic Information Service. Finnish Environment Institute. <http://wwwp2.ymparisto.fi/tietoapalvelusta.html> (accessed 15.12.11).

Hildén, M., Rapport, D., 1993. Four centuries of cumulative impacts on a Finnish river and its estuary: an ecosystem health-approach. J. Aquat. Ecosyst. Health 2, 261–275.

Hirsch, R., Alexander, R., Smith, R., 1991. Selection of methods for the detection and estimation of trends in water quality. Water Resour. Res. 27, 803–813.

Hudd, R., Hildén, M., Urho, L., 1986. The effects of anthropogenic acidification on the stocks and fisheries of bream and burbot in the sea area influenced by the river Kyrönjoki in the Gulf of Bothnia. Publ. Water Res. Inst., Natl. Boards Waters, Finland 68, 134–138.

Hudd, R., Leskelä, A., 1998. Acidification-induced species shifts in coastal fisheries off the river Kyrönjoki, Finland: a case study. Ambio 27, 535–538.

Kortelainen, P., Mannio, J., Forsius, M., Kämäri, J., Verta, M., 1989. Finnish lake survey: the role of organic and anthropogenic acidity. Water, Air, Soil Pollut. 46, 235–249.

Kortelainen, P., Mannio, J., 1990. Organic acidity in Finnish lakes. In: Kauppi, P., Anttila, P., Kenttämies, K. (Eds.), Acidification in Finland. Springer-Verlag, Berlin, pp. 849–863.

Kortelainen, P., Saukkonen, S., 1995. Organic vs. minerogenic acidity in headwater streams in Finland. Water, Air, Soil Pollut. 85, 559–564.

Laudon, H., Köhler, S., Bishop, K.H., 1999. Natural acidity or anthropogenic acidification in the spring flood of northern Sweden? Sci. Total Environ. 234, 63–73.

Mattsson, T., Kortelainen, P., Räike, A., 2005. Export of DOM from boreal catchments: impacts of land use cover and climate. Biogeochemistry 76, 373–394.

Mattsson, T., Kortelainen, P., Lepistö, A., Räike, A., 2007. Organic and minerogenic acidity in Finnish rivers in relation to land use and deposition. Sci. Total Environ. 383, 183–192.

Ministry of Agriculture and Forestry in Finland, 2009. Finlandś National Adaptation Strategy. <http://www.mmm.fi/attachments/ymparisto/sopeutuminen/5lCSFc9Ts/Finlands_national_adaptation_srtrategy_julkaisu.pdf> (accessed 16.07.12).

Nystrand, M., Österholm, P., Nyberg, M., Gustafsson, J.P., 2012. Metal speciation in rivers affected by enhanced soil erosion and acidity. Appl. Geochem. 27, 906–916.

Nystrand, M.I., Österholm, P., Metal species in a Boreal river system affected by acid sulfate soils. Appl. Geochem. (2013), http://dx.doi.org/10.1016/j.apgeochem.2012.12.015.

Österholm, P., Åström, M., 2004. Quantification of current and future leaching of sulfur and metals from Boreal acid sulfate soils, western Finland. Aust. J. Soil Res. 42, 547–551.

Österholm, P., Åström, M., 2008. Meteorological impacts on the water quality in the Pajuluoma acid sulphate soil area, W. Finland. Appl. Geochem. 23, 1594–1606.

Österholm, P., Virtanen, S., Uusi-Kämppä, J., Rosendahl, R., Westberg, V., Mäensivu, M., Ylivainio, K., Yli-Halla, M., Turtola, E., 2012. Minimizing sulfide oxidation on acid sulfate farmlands by enhanced controlled drainage and subsurface irrigation. In: Österholm, Peter, Yli-Halla, Markku, Edén, Peter (Eds.), Proceedings of the 7th International Acid Sulfate Soil Conference, Vaasa, Finland, 2012. Geological Survey of Finland, Guide 56, 2012.

Palko, J., Alasaarela, E., 1988. Larsmo-Öjasjöns flodområde: Förekomst av sura sulfatjordar och deras inverkan på vattnets surhet. Valtion teknillinen tutkimuskeskus, Oulu (in Swedish).
Palko, J., Weppling, K., 1994. Lime requirement experiments in acid sulphate soils. Acta Agric. Scand. Sect. B, Soil Plant Sci. 44, 149–156.
Palko, J., Yli-Halla, M., 1988. Solubility of Co, Ni and Mn in some extractants in a Finnish acid sulphate soil area. Acta Agric. Scand. 38, 153–158.
Palko, J., Yli-Halla, M., 1990. Solubility of Al, Cr, Cu and Zn in soils from a Finnish acid sulphate soil area. Acta Agric. Scand. 40, 117–122.
Palko, P., Yli-Halla, M., 1993. Assessment and management of acidity release upon drainage of acid sulphate soils in Finland. Selected Papers of the Ho Chi Minh City Symposium on Acid Sulphate Soils, Wageningen, Netherlands, pp. 411–418.
Puustinen, M., Merilä, E., Palko, J., Seuna, P., 1994. Kuivatustila, viljelykäytäntö ja vesistökuormitukseen vaikuttavat ominaisuudet Suomen pelloilla. Summary: Drainage Level, Cultivation Practices and Factors Affecting Load on Waterways in Finnish Farmland. National Board of Waters and Environment, Research Report A 198.
Rask, M., Tuunainen, P., 1990. Acid-induced changes in fish populations of small Finnish lakes. In: Kauppi, P, Anttila, P, Kenttämies, K. (Eds.), Acidification in Finland. Springer, Berlin/Heidelberg, pp. 911–927.
Roos, M., Åström, M., 2005a. Seasonal and spatial variations in major and trace elements in a regulated boreal river (Esse River) affected by acid sulphate soils. River Res. Appl. 21, 351–361.
Roos, M., Åström, M., 2005b. Hydrogeochemistry of rivers in an acid sulphate soil hotspot area in western Finland. Agric. Food Sci. 14, 24–33.
Saarinen, T., Vuori, K.M., Alasaarela, E., Klove, B., 2010. Long-term trends and variation of acidity, COD_{Mn} and colour in coastal rivers of Western Finland in relation to climate and hydrology. Sci. Total Environ. 408, 5019–5027.
Toivonen, J., Österholm, P., 2011. Characterization of acid sulfate soils and assessing their impact on a humic boreal lake. J. Geochem. Explor. 110, 107–117.
Yli-Halla, M., Puustinen, M., Koskiaho, J., 1999. Area of cultivated acid sulfate soils in Finland. Soil Use Manage. 15, 62–67.
Vuori, K.-M., Mitikka, S., Vuoristo, H., 2009. Classification of the Ecological Status of Surface Waters in Finland. Environmental Guide, 3. Finnish Environment Institute.
Vuorinen, V., Vuorinen, P., Hoikka, J., Peuranen, S., 1993. Lethal and sublethal threshold values of aluminium and acidity to pike (*Esox lucius*), whitefish (*Coregonus lavaretus pallasi*), pike perch (*Stizostedion lucioperca*) and roach (*Rutilus rutilus*) yolk-sac fry. Sci. Total Environ. Suppl. 953–967.
Waring, C., Brown, A., 1995. Ionoregulatory and respiratory responses of brown trout, *Salmo trutta*, exposed to lethal and sublethal aluminium in acidic soft waters. Fish Physiol. and Biochem. 14 (1), 81–91.
Witters, H.E., van Puymbroeck, S., Vangenechten, J.H.D., Vanderborght, O.L.J., 1990. The effect of humic substances on the toxicity of aluminium to adult rainbow trout, *Oncorhynchus mykiss* (Walbaum). J. Fish Biol. 37, 43–53.