

Impact of acid sulfate soil catchments on water quality in a lake in western Finland; trends and total metal load

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Acid sulfate soils occur worldwide and can cause serious ecological damage by releasing acidity and toxic metals into watercourses. This study focused on short- and long-term changes to the water quality of a lake in western Finland. Here, a decline in water quality took place in the late 1960s. Since then, events concerning poor water quality have frequently occurred. The annual load of some potentially toxic metals varied from hundreds of kilograms to thousands of tons, depending on the metal. The proportion of low-order streams draining the nearest field to the lake is only 7% of the catchment area, while the share of the total metal load was estimated to be over 30%. This points to the importance of monitoring small coastal catchments. High runoff conditions were proven to be more important in terms of water quality than occasional summer droughts. During the past decade, acidic conditions have become more prolonged in the autumn, which is in line with a predicted scenario relating to climate change.

Introduction

Worldwide, more than 17 million ha of land is underlain with acid sulfate (a.s.) soils (Andriess and van Meensvoort, 2006). The origins of these soils are from fine-grained sediments, rich in iron sulfides; often referred to as potential a.s. soils (Boman *et al.* 2010, Wu *et al.* 2013). In many areas, these sediments are drained due to human activities. Aided by microbes (acidophilic oxidizers in Finnish a.s. soils; Wu *et al.* 2013), the sulfides oxidize to sulfuric acid, creating a.s. soils (pH < 4.0). The released acidity has been shown to cause potential toxic metals (e.g. Al, Cd, Ni and Zn) to leach from soil minerals into nearby watercourses during periods of high runoff (Åström and Björklund 1996, Green

et al. 2006, Maconald *et al.* 2007, Marttila *et al.* 2013). In western Finland, these soils exist mainly below the highest Litorina Sea stage (about 100 m a.s.l.). During the latter half of the 20th century, intensive land use in areas underlain with sulfidic sediments has caused the widespread formation of a.s. soils with detrimental effects on water quality (Suupohja 1973, Österholm and Åström 2004, Saarinen *et al.* 2010, Toivonen *et al.* 2013). The resulting acidic metal load has not only triggered occasional fish kills, but also a chronically poor chemical and ecological status in many watercourses (Hildén *et al.* 1982, Hudd and Leskelä 1998, Vuori *et al.* 2009, Wallin *et al.* 2015). The currently expected view of potential climate change is that the winters will become warmer, causing increased runoff

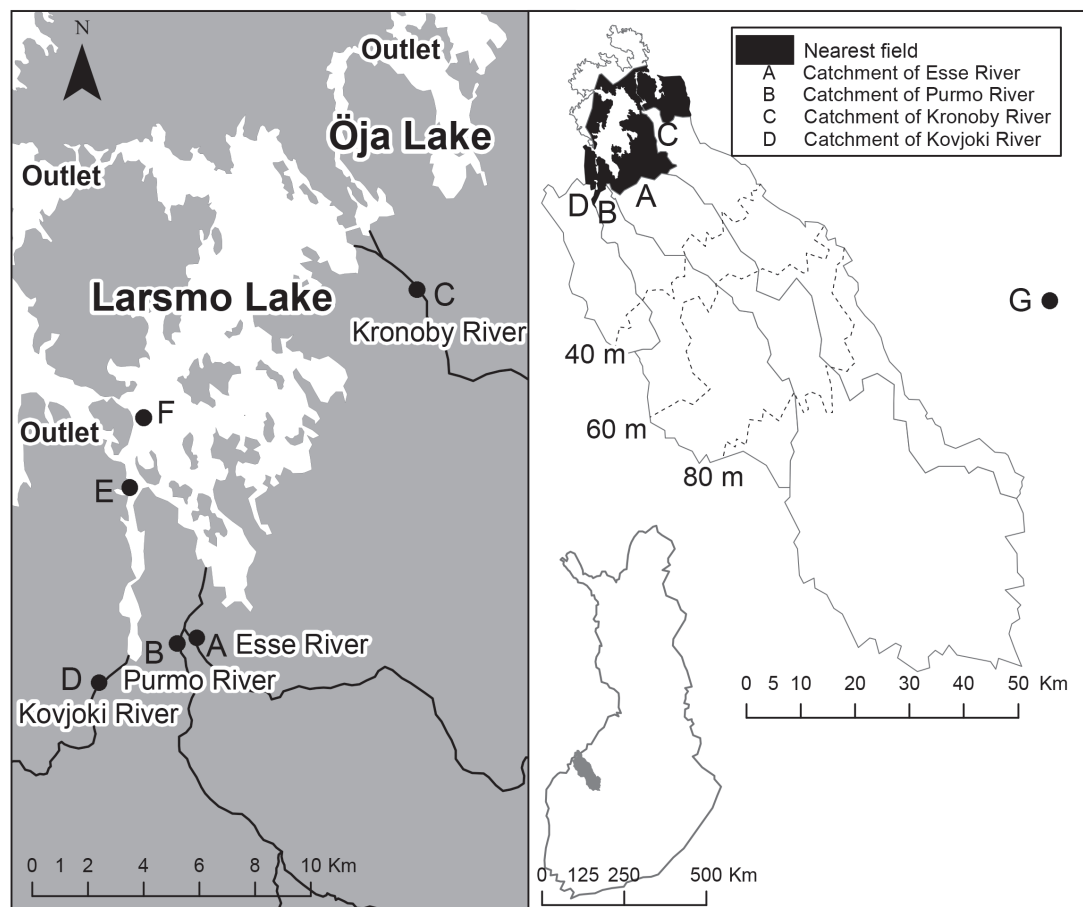


Fig. 1. Left: Sampling and monitoring points (A–F) in Larsmo-Öja Lake and inflowing rivers. Right: Catchments of the rivers and the nearest field discharging into Larsmo-Öja Lake, elevation lines, the location of Pakkajoki Stream (G) and the location of the catchment area on the Finnish west coast.

and the consequent increased leaching of acidity and metals in areas with a.s. soils (Saarinen *et al.* 2010). Regarding part of the current study area, this scenario, with notable consequences for the biota, has already taken place during the past decade (Toivonen *et al.* 2013).

Research area and aims of the study

Until the early 1960s, Larsmo-Öja Lake (85 km²; Fig. 1) was part of the inner archipelago of the Gulf of Bothnia before road embankments and dams were built to create a freshwater reservoir for industrial purposes. Larsmo Lake was created in 1962 and Öja

Lake in 1969. Four rivers discharge into the embanked lake (Esse, Purmo, Kronoby and Kovjoki; Fig. 1). The percentage of arable land in the catchments of the rivers is 14–19% and the percentage of peatland is 20–34% (Bonde *et al.* 2016). A canal allows water exchange between the lakes and a second canal allows part of the water from Kronoby River to discharge directly into Öja Lake. The main inflow of water occurs in the southeastern/eastern part of Larsmo Lake and the outflow from the lake takes place at three outlets. The main outflow from the lake occurs from the southwestern outlet. The main flow direction between the lakes is from Larsmo Lake to Öja Lake. The retention time is 53 days during an average discharge and 14 days during floods (Lauri 2014).

The two lake basins are often considered as one due to the canal between them. The lake is shallow (average depth of 2.3 m and a maximum depth of 10 m) with numerous islands (only the largest are visible in Fig. 1). The lake is important for fishing and recreation, and constructed fishways allow migration to and from the sea. Since the end of the 1960s, the lake and the rivers have suffered from acidity, mass kills of fish and continuously low ecological status due to discharge from a.s. soils (Palko *et al.* 1987, Snickars and Wistbacka 2000, Sutela *et al.* 2012). Acidic conditions in boreal environments are usually due to naturally occurring humic acids (Edén *et al.* 1999, Laudon *et al.* 1999, Mattsson *et al.* 2007). However, in many watercourses in western Finland, pH and acidity show an opposite relation to humic acids due to the acidic discharge from a.s. soils that overshadows the acidity caused by humic acids (Edén *et al.* 1999, Mattsson *et al.* 2007, Toivonen *et al.* 2011, Nystrand and Österholm 2013). The organic material has, instead, been found to reduce the acidity and toxicity of the metals by buffering and complexation reactions (Vuorinen *et al.* 1999, Pédrot *et al.* 2008). In contrast to most coastal areas in the world, tides at the Gulf of Bothnia are negligible and variance at the sea-water level is relatively small. Therefore, there is no intrusion of brackish water into watercourses. Consequently, the variance in electric conductivity (EC) and sulfate concentration in watercourses in areas with a.s. soils is due to leaching from a.s. soils (Åström and Åström 1997, Roos and Åström 2005, Österholm and Åström 2008, Toivonen and Österholm 2011). Even though the combined effects of the high concentrations of metals may increase the toxicity (e.g. Al and Fe; Vuorinen *et al.* 1999), the toxicity in acidic conditions is normally attributed to Al (Earle and Callaghan 1998, Gensemer and Playle 1999). Aluminum is also one of the most enriched elements in drainage water from a.s. soils (Fältmarsch *et al.* 2008). Since most of the data used in this study represent total Al concentration, eroded soils may affect the concentrations (Nystrand *et al.* 2012). However, studies in areas with a.s. soils in western Finland (Åström and Björklund, 1995, Nystrand and

Österholm 2013) and in the current study area (Roos and Åström 2005, Toivonen and Österholm 2011), together with the flat topography and the lack of the characteristic turbid water typical of erosion, have strongly indicated that erosion in areas with significant occurrences of a.s. soils is not an important source of Al. Hence, the data on pH, EC, sulfate and total Al were the main parameters used in this study, as they are considered to well represent the main impacts due to leaching from a.s. soils.

Studies of the water quality regarding the impact of a.s. soils on stream water in the area has previously been reported (e.g., Toivonen and Österholm 2011, Toivonen *et al.* 2013). These studies focused on the hypothesis that enhanced acidity with subsequent mass kills of fish in a river was caused by dry summers (dry summer-induced acidity-theory) and long-term trends related to changes in land use and hydrology. They also provided estimates on acidic load based on sulfate concentrations and acidity carried by the streams. In this study, we continued from previous studies by utilizing similar hydrological and geochemical data from Larsmo-Öja Lake. First, we studied the dry summer-induced acidity-theory in a lake environment and observed long-term trends. Second, we combined the stream and lake water data to study the interaction between the main river in the area and Larsmo-Öja Lake. Finally, we expanded the estimation of the load to the lake by including calculations of the amounts of potentially harmful metals carried to the lake. In particular, we focused on the load from the numerous, small unmonitored streams draining the nearest field and compared the results with data from more easily-monitored rivers.

Materials and methods

Data

Data set I (Esse River)

The main river discharging into the lake, Esse River, carries almost 50% of the water to the lake and acts as a source of drinking water to the

town of Jakobstad (water intake lies at point A in Fig. 1). The Jakobstad water plant provided data on daily pH (1975–2014) and weekly measurements of electric conductivity (EC; 1989–2014) from the river.

Data set II (Larsmo-Öja-Lake)

The Larsmo-Öja Lake acts as a source of fresh water for the UPM Kymmene paper mill in Jakobstad (water intake lies at point E in Fig. 1). Data on the pH and EC of the lake were available for every working day, as well as weekly total Al concentrations (photometric analysis of acid soluble Al), between 1975–2014. In addition, data on weekly sulfate concentrations were available for 1989–2014 (nephelometric determination and high performance liquid chromatography (HPLC)).

Data set III (national monitoring data on water quality and runoff)

Sparsen national monitoring data (www.syke.fi/avointieto) on pH and EC were available for 1962–2014 (point F in Fig. 1). Daily data on runoff from an unregulated nearby stream were obtained (Pahkaoja stream; point G, Fig. 1), as well as additional data on sulfate, Al and Mn from the four rivers (points A–D in Fig. 1) from the national monitoring database. The national monitoring data are largely irregular in terms of sampling time, sampling site and choice of analyzed parameters. The periods showing the most complete and comparable data on sulfate and metals from all four rivers are from: 2007–2014 (ion chromatography and inductively coupled plasma-optical emission spectrometry), 1976–1981 (sulfate and Mn, analysis methods unknown) and 1976–1977 (Al, analysis method unknown). The number of available analysis results during 2007–2014 (Appendix Fig. A1) from each river was 10–15 for sulfate, 24–26 (6 for Kovjoki River) for Al and 28–30 (2 for Kovjoki River) for Mn. The available analysis results for each river during the period from 1976–1981 was 51–57 for sulfate, 11–16 for Al and 63–74 for Mn.

Data set IV (water quality in streams during 2007)

In April 2007, additional sampling was performed by the authors during high flow in the rivers at sites A–D ($n = 4$; Fig. 1) for sulfate (HPLC), Al, Cd, Co, Ni, Mn, U and Zn ($0.45 \mu\text{m}$; inductively coupled plasma-optical emission spectrometry and inductively coupled plasma mass spectrometry). pH and EC were measured in situ with an electrode. Several low-order streams ($n = 29$) were also sampled and the chosen streams were estimated to represent the nearest field (drainage area drained by numerous small ditches and streams) both qualitatively and geographically (sampling sites not shown). The discharge was also estimated for the low-order streams by multiplying the water velocity with the cross-section area. The sampling of the rivers and low-order streams was also performed during August, November and December of the same year. For these latter samplings, the number of sampled low-order streams were reduced to ten.

Statistical methods

Percentiles and medians were used, in addition to non-parametric statistical methods because they have been shown to be robust against outliers, errors and skewed distributions (Helsel and Hirsch 2002, Reimann and Filzmoser 1999). Spearman rank correlation ($p = 0.05$) was used for correlations and Lowess smoothing ($f = 0.67$) was used for studying the effect of runoff on water quality and the residuals were used for detecting runoff-corrected trends over time (Hirsch *et al.* 1991). The non-parametric Mann-Kendall's tau (τ) and seasonal Kendall's trend tests (r_s) were used for trend testing and the level of confidence was set to 95% ($p = 0.05$).

Effects of short-term changes in hydrology

During the sampling of the four rivers and the lake in November 2007, a simple mixing test was performed in order to evaluate the vulner-

ability of the lake to acidic discharge. Water from the four rivers discharging into the lake (A, B, C and D; Fig. 1) was mixed in proportion to their catchment areas. The low-order streams that drain 7% of the drainage area were not included in the test. The pH in the combined river water was measured with an electrode. The river water was slowly added while stirring the water samples taken from the lake (one sample taken close to point F in Fig. 1, and one sample from the northern part of Larsmo Lake, close to the outlet) until the pH decreased below 5.5, which we considered was a coarse threshold value harmful to water due to the increasing concentrations and toxicity of Al (Witters 1998). The lake retention time (in days) was calculated by dividing the lake volume (227 million m³) with the total inflow (in m³) to the lake. The mixing test was also performed in December 2007. Data from the 15th of each month from 1975–2014 (data set II; $n = 38$, data on runoff from 2001 and 2012 was missing), was chosen to represent changes in pH and Al concentrations related to changes in runoff. Corresponding data on EC and sulfate was available from 1989–2014 (data set II; $n = 24$). Changes in water quality in Larsmo Lake in relation to the changes in Esse River were studied by correlating pH and EC on the 15th of every month in Esse River (data set I) with corresponding data on Larsmo-Öja Lake (data set II; $n = 40$). To take into consideration any delay of the changes in the lake, the previous 5-, 10-, and 30-day median of pH and EC from Esse River were also used. Even though the water quality was better in the Esse River than the three smaller rivers, variations in pH and EC were similar in all four rivers (Toivonen *et al.* 2013). Therefore, we considered the available river data as representative of short-term changes in water quality for all stream water discharging into the lake. In order to examine the short-term effect of dry spells on water quality, average runoff during summer (data set III) was tested for correlation at the 10th percentile and median pH for the lake during the following autumn and spring (data set II, $n = 38$). The autumn period was set to begin on the first day in September when runoff increased above $1 \text{ l s}^{-1} \text{ km}^{-2}$ (indi-

cation of rising ground water level) and end on the first of December. The spring was set to begin on the first day when runoff exceeded $10 \text{ l s}^{-1} \text{ km}^{-2}$ (indicating the beginning of snow melt) and end on the first of June (Österholm and Åström 2008, Toivonen *et al.* 2013). Both precipitation and runoff have previously been used to estimate the hydrological conditions responsible for water quality variations, including the intensity of summer droughts (Österholm and Åström 2008). Runoff has generally worked better than precipitation to describe the variations in the case of a.s. soil impact, which is largely dependent on the water content in the lower subsoil containing the highest sulfide content. The groundwater commonly drops below 1.5 m in the summer due to evapotranspiration; the ground-water level is not directly affected by precipitation in the summer (Österholm *et al.* 2015). Moreover, the cumulative amount of rainwater does not directly correlate with the amount of precipitation that is infiltrated or percolated because infiltration and percolation are largely dependent on the intensity of individual rain events. Under natural conditions, runoff is directly correlated with the groundwater level, i.e. the higher the groundwater level, the higher the hydraulic gradient and the higher the runoff. Consequently, as previous results have shown (Österholm and Åström 2008), runoff is a good way of determining the hydrologic conditions in the catchment. Runoff is probably a more robust measure of the general hydrological conditions of the subsoil in the catchment since it is responsible for causing most of the acidity in a.s. soils.

Effects of long-term-changes in hydrology

Data from the 15th of every month from data set II was used in our trend testing, which also enabled testing runoff-corrected pH, EC, sulfate and Al concentrations for trends. Additional trend tests were performed at the 10th percentile pH and median pH, as well as median and at the 90th percentile EC for every month. Data on pH and EC from Larsmo-Öja

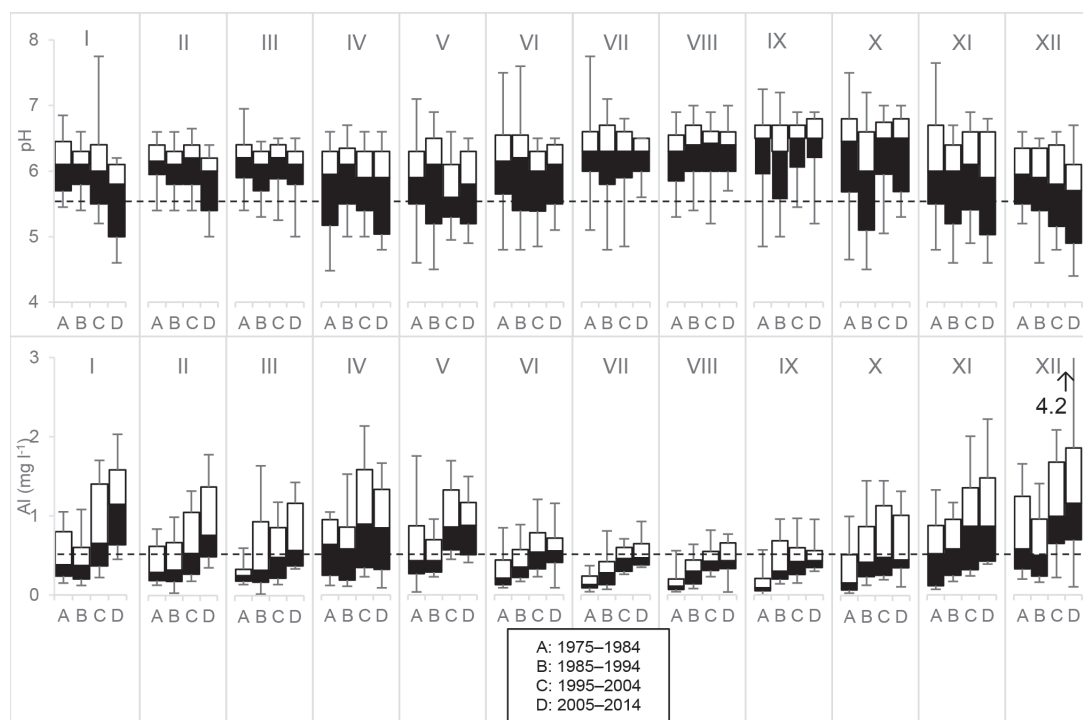


Fig. 2. Minimum, 10th percentile, median, 90th percentile and maximum pH and Al concentrations in Larsmo-Öja Lake (data set II). The data set representing each month is divided into four 10-year periods; **A:** 1975–1984, **B:** 1985–1994, **C:** 1995–2004 and **D:** 2005–2014. The dotted line indicates a rough threshold value to toxic water.

Lake (one sample/season) obtained from data set III were also tested for trends.

Quantification of the yearly acidic metal load on Larsmo-Öja Lake

The high concentrations of sulfate (indicator of sulfuric acid), Al, Cd, Ni, Mn, U and Zn are good indicators on the impact from a.s. soils (Åström and Björklund 1995). The quantity of each element discharging into Larsmo-Öja Lake during one year was estimated from data set IV by calculating a runoff-weighted average, where streams and sampling events with higher discharges are given greater significance, multiplied by the annual discharge to the lake. The results for the metals denote the dissolved (0.45 μm) fraction. To estimate the load for longer periods, data set III was used. Even though representative data from all four rivers was difficult to find, data on sulfate, Al and Mn analyzed from unfiltered samples were chosen from 1976–1981 and 2007–2014.

Results

Overall water quality and short-term changes

Based on data set II, median pH was below 6.0 and at the 10th percentile, it was approximately 5.0 during the spring and autumn months (i.e., months characterized by high runoff; Fig. 2). The median concentration of Al was about 1.0 mg l^{-1} . The median EC reached 13 mS m^{-1} and the sulfate concentrations were close to 35 mg l^{-1} during autumn and winter (Fig. 3). Only weak indications of decreasing pH and increasing EC, Al and sulfate concentrations during increasing runoff could be found during the autumn and winter months (Figs. 3 and 4, and Appendix Fig. A2–A5). There was a significant correlation between EC and sulfate for all months except August, while Al was mainly controlled by pH (Table 1). Acidic water ($\text{pH} < 5.5$) from 1975–2014 was found during nine out of ten years (93%). Very acidic water

(pH < 5.0) was found during four out of ten years (43%). Figure 4 visualizes the great effects of the hydrology on water quality during two years (data set I, II and III). Note the dry summer (July to mid-September) in 2006 and the following rainy period and extreme drop in pH from October 2006 to January 2007. Most of the year in 2007 was rainy with a corresponding poor water quality. The most extreme water quality in Larsmo-Öja Lake, from 1975–2014, was recorded during this event when pH dropped to 4.4 and Al-concentrations reached 4.2 mg l^{-1} in December 2006.

During January–February and July–August, (i.e., months characterized by low runoff) the river water (data set I) had no clear effect on the quality of the lake water (data set II; Table 2). Runoff was generally higher during the other months, and as expected, changes in pH in the river affected the lake water more during these months.

There was no clear impact from the river water in the lake in terms of EC during February and June–October (Table 2). For the remaining period of the year, EC in the lake tended to generally correspond better to the 1- and 5-day median EC in the river than the 10- and 30-day medians.

Based on the mixing tests, the combined pH of the four rivers during both sampling events (November and December; data set IV) in the autumn 2007 was 5.0. The different lake water samples used in the test had a pH from 5.9–6.5 and 50–67% of river water was needed to lower the pH to less than 5.5 in the samples. During both samplings, the runoff was $20\text{--}25 \text{ l s}^{-1} \text{ km}^{-2}$ and the theoretical lake retention time was therefore approximately 25–30 days.

No influence of average summer runoff (data set III) on pH (median and at the 10th percentile from data set II) or EC (median and at the 90th percentile from data set II) was found in the following autumn. Since high runoff during the autumns was found necessary for elevated acidity in Esse River (Toivonen *et al.* 2013), autumn days with low and moderate runoff ($< 10 \text{ l s}^{-1} \text{ km}^{-2}$) were excluded from the calculations. Despite this, no connection between summer droughts and water quality the fol-

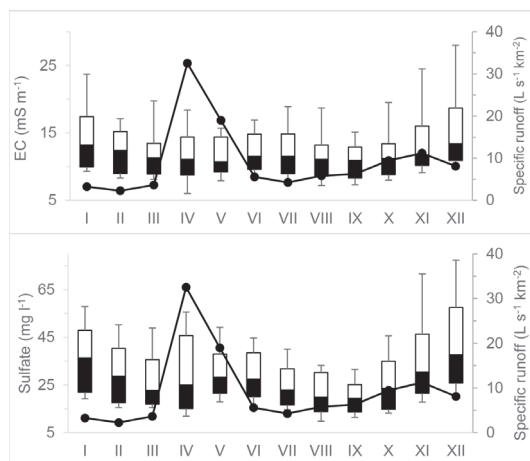


Fig. 3. Minimum, 10th percentile, median, 90th percentile and maximum electric conductivity (EC) and sulfate concentrations in Larsmo-Öja Lake 1989–2014 (data set II). The black line indicates average runoff for each month 1989–2014 (data set III).

lowing autumn was found. Instead, the average autumn runoff showed a significant negative correlation with pH at the 10th percentile ($R_s = -0.66$) and median pH ($R_s = -0.60$) during the autumn. In contrast, a low but significant correlation between summer runoff and at the 10th percentile and median pH the following spring was found ($R_s = 0.46$ and $R_s = 0.40$, respectively).

Table 1. Correlations (Spearman rank correlation, r_s) between electric conductivity, pH and Al concentrations in Larsmo-Öja Lake (data sampled on the 15th of every month; data set II). Values in bold are different from 0 with a significance level of $p = 0.05$.

Month	EC vs. sulfate $n = 25/\text{month}$	pH vs. Al $n = 40/\text{month}$	EC vs. Al $n = 25/\text{month}$
Jan	0.62	-0.61	0.53
Feb	0.82	-0.46	0.43
Mar	0.58	-0.42	0.39
Apr	0.51	-0.61	0.26
May	0.86	-0.26	0.35
Jun	0.72	-0.19	0.03
Jul	0.61	0.06	0.08
Aug	0.34	-0.27	-0.17
Sep	0.46	-0.21	-0.04
Oct	0.77	-0.56	0.05
Nov	0.78	-0.65	0.30
Dec	0.94	-0.62	0.72

Long-term trends

At the end of the 1960s and early 1970s, there was a steep decline in pH in the lake according to data set III (point F; Fig. 1 and Fig. 5). After that, pH increased (seasonal $r_{\tau} = 0.41$), during the spring ($\tau = 0.47$), summer ($\tau = 0.36$) and autumn ($\tau = 0.39$; data not shown). A high EC (40 mS m⁻¹) can be observed in 1962, indicating brackish water (data not shown). Although a decreasing EC was observed (seasonal $\tau = -0.21$), the only season showing a significant trend is the autumn ($\tau = -0.33$; data not shown). However, based on the more complete data set II (Point E; Fig. 1), starting in 1975, a small but statistically significant decrease in median and residual pH occurred (Table 3). This drop in pH occurred in January. EC showed a weak but significant decreasing trend, mainly during July–October (Table 3). Concentrations of Al showed an increase since 1975. No trend in sulfate concentrations was visible, except for October. No changes in runoff were detected, except for a decrease in May (Table 3).

Acidic metal load on Larsmo-Öja Lake

The discharge of sulfate to Larsmo-Öja Lake, based on data set IV, was in the order of 65 000 t (Table 4). Of this load, Esse River contributed

30%; Purmo River, 22%; Kronoby River, 16%; Kovjoki River, 10% and the small streams that drain the nearest field (area between the catchments of the rivers) and discharge into the lake, 23%. The same calculations performed on the concentrations of certain a.s. soil-related metals showed that Larsmo-Öja Lake received roughly 2300 t of Al, 450 t of Mn, 61 t of Zn, 19 t of Ni, 10 t of Co, 0.3 t of U and 0.2 t of Cd in dissolved form (0.45 µm); of which 24–34% originated from the low-order streams draining the nearest field.

Calculations based on data set III showed roughly the same amounts for the period from 1976–1981, but lower for the period from 2007–2014 (Table 4), which indicated a decreasing trend of the load via the rivers. These analyses were performed on unfiltered samples.

Discussion

Water quality and short-term trends

The water quality of Larsmo-Öja Lake, during the period from 1975–2014, revealed acidic metal discharge from a.s. soils. This was shown as rapidly changing water quality, with frequent, low pH values and a correspondingly high EC and Al and sulfate concentrations. In terms of pH and Al concentrations, the water quality com-

Table 2. Correlations (Spearman rank correlation, r_s) between water quality in Larsmo-Öja Lake (data set II) with corresponding data in Esse River (data set I) for pH (left) and EC (right) ($n = 40$ for pH and $n = 25$ for EC). The 1-day column indicates data from the same day. For Esse River, medians of the previous 5 days, 10 days and 30 days were also calculated for the correlations. Values in bold are different from 0 with a significance level of $p = 0.05$.

Month	pH				EC			
	1 day	5 day	10 day	30 day	1 day	5 day	10 day	30 day
Jan	0.18	0.30	0.25	0.27	0.73	0.64	0.64	0.64
Feb	0.00	0.02	0.03	0.15	0.38	0.40	0.41	0.58
Mar	0.38	0.43	0.47	0.48	0.77	0.83	0.76	0.65
Apr	0.62	0.59	0.64	0.54	0.70	0.61	0.46	0.52
May	0.39	0.49	0.49	0.52	0.59	0.65	0.68	0.67
June	0.05	0.12	0.18	0.35	0.55	0.50	0.29	0.69
July	0.02	-0.01	-0.11	0.00	-0.07	0.14	0.23	0.35
Aug	0.12	0.13	0.20	0.33	0.30	0.24	0.06	-0.17
Sep	0.34	0.35	0.48	0.61	0.13	0.09	0.35	0.19
Oct	0.61	0.61	0.64	0.68	0.02	0.01	0.01	0.01
Nov	0.43	0.45	0.61	0.61	0.61	0.41	0.58	0.45
Dec	0.69	0.70	0.67	0.51	0.85	0.75	0.72	0.65

Table 3. Mann-Kendall and seasonal Kendall trend tests on pH, EC, Al and sulfate concentrations in Larsmo-Öja Lake (data set II) and average runoff (Pahkaoja Stream, data set III) from 1975–2014. The 1-day column indicates the measurement on the 15th of each month (or nearest date where data was available), while the "percentile" and "median" columns represent median data of the whole month. Values in bold are significant ($p = 0.05$)

Month	pH ($n = 40$)			Residual	90th percentile	EC (mS m^{-1} ; $n = 26$)		Residual
	10th percentile	Median	1-day			Median	1-day	
Jan	-0.22	-0.25	-0.24	-0.20	0.24	0.24	0.28	0.09
Feb	-0.17	-0.21	-0.20	-0.21	0.03	0.07	-0.06	-0.04
Mar	-0.07	-0.10	-0.14	-0.16	-0.11	-0.06	-0.16	-0.12
Apr	-0.09	-0.06	0.14	0.18	0.07	0.04	0.07	-0.04
May	-0.01	-0.12	-0.17	-0.20	0.03	0.03	0.23	0.24
Jun	0.04	-0.01	-0.13	-0.22	-0.19	-0.12	-0.14	-0.07
Jul	0.05	0.05	0.10	0.05	-0.32	-0.16	-0.05	-0.16
Aug	0.20	0.13	0.09	0.04	-0.58	-0.47	-0.40	-0.38
Sep	0.14	0.05	0.08	-0.02	-0.45	-0.39	-0.16	-0.15
Oct	0.13	0.08	0.11	0.10	-0.34	-0.42	-0.40	-0.32
Nov	-0.03	-0.02	-0.13	-0.14	-0.13	-0.18	-0.25	-0.28
Dec	-0.19	-0.15	-0.15	-0.03	-0.02	0.01	0.11	0.01
Seasonal Kendall	-0.02	-0.08	-0.04	-0.07	-0.13	-0.12	-0.08	-0.10

Month	Al (mg l^{-1} ; $n = 38$)			Residual	Average Runoff	sulfate (mg l^{-1} ; $n = 24$)	Residual
	1-day	Residual	1-day				
Jan	0.36	0.35	0.28	0.14	0.02		
Feb	0.46	0.62	-0.02	0.06	-0.02		
Mar	0.36	0.42	-0.16	0.00	0.02		
Apr	0.12	0.14	-0.16	-0.12	0.19		
May	0.32	0.37	0.01	0.03	-0.33		
Jun	0.34	0.31	-0.07	-0.04	-0.20		
Jul	0.58	0.54	-0.19	-0.04	-0.04		
Aug	0.56	0.56	-0.04	-0.09	-0.01		
Sep	0.46	0.46	-0.26	-0.23	-0.16		
Oct	0.35	0.37	-0.32	-0.28	-0.16		
Nov	0.32	0.31	-0.01	-0.04	0.08		
Dec	0.31	0.28	0.13	-0.06	0.19		
Seasonal Kendall	0.45	0.39	-0.07	-0.05	-0.04		

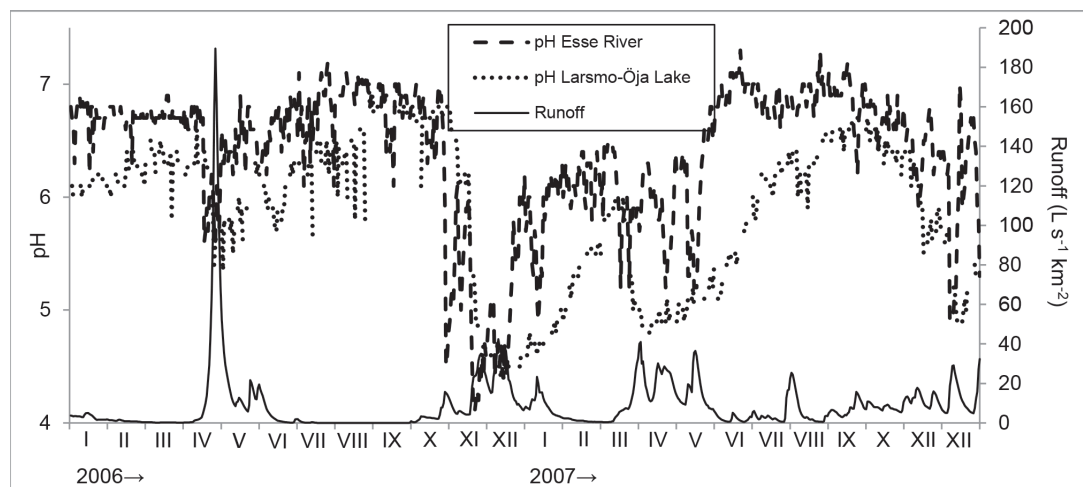


Fig. 4. Temporal variations of pH in Esse River (data set I), Larsmo-Öja Lake (data set II) and runoff (Pahkajoki stream; data set III) of years 2006 and 2007.

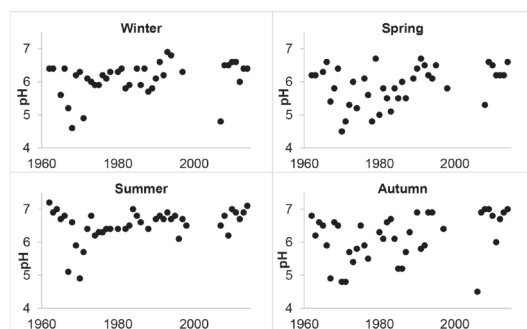


Fig. 5. Measured pH values in Larsmo-Öja Lake from 1962–2014 ($n = 39\text{--}41/\text{season}$; data set IV).

monly dropped below the threshold values that are considered toxic to the biota, e.g., $\text{pH} < 5.5$ (Witters 1998, Vuori *et al.* 2009). Even though these were small differences, changes in pH of the lake tended to occur with a delay in relation to the discharging river water, probably due to buffering reactions; while changes in EC generally occurred slightly quicker, due to the conservative sulfate ion, which is the main anion in water-courses affected by a.s. soils. The low pH and high EC, in addition to the high Al and sulfate concentrations found during the winter, indicated that acidic water tended to linger in the lake. In April, the faster drop in pH in the lake was due to a higher runoff, possibly also enhanced by a high input of low-buffered melt water that diluted the buffering capacity (Laudon and Bishop 1999). At the same time, the large amount of melt water

seemed to cause a dilution effect with increasing pH at runoff $> 20\text{--}30 \text{ l s}^{-1} \text{ km}^{-2}$.

The mixing tests and the theoretical lake retention time of 25–30 days in the autumn of 2007 indicated that at the time of sampling, the pH in the lake (5.9–6.5) would have dropped below 5.5 within a couple of weeks if the hydrological conditions had prevailed. This scenario, however, would require the discharging water to disperse evenly within the lake. The fact that the majority of the streams discharge in the southern and eastern part of the lake and the main outflow from the lake to the sea occurs in the southwestern part, together with the occurrence of numerous islands, bays, narrow straits and canals; there is an uneven spatial pattern of water quality in the lake (Fig. 1; Toivonen *et al.* 2011). Therefore, the results are only directional. It is also notable that the important, low-order streams that contributed with approximately 23% of the acidic load were, for practical reasons, not included in the test. This demonstrated that although mass kills of fish or other visible damage do not take place every year, the lake is very vulnerable and highly dependent on the extent of high runoff and spatial patterns of the dispersion of water in the lake.

Even though dry summers are expected to intensify acidic events the following autumn (Mayer *et al.* 2010., Palko and Yli-Halla 1993), no clear indication was apparent that a dry

Table 4. Sulfate and metal load to Larsmo-Öja Lake (t y^{-1}) from the four rivers and the nearest field (data set IV).

Catchment	km ²	2007					1976–1981					2007–2014			
		Sulfate	Al	Mn	Cd	Ni	Zn	U	Co	Sulfate	Al	Mn	Sulfate	Al	Mn
Esse	2048	19 509	455	126	0.05	2.5	16	0.09	2.3	21 050	548	196	12 823	325	92
Load/km ²		9.5	0.22	0.06	0.0	0.0	0.01	0.0	0.0	10	0.27	0.10	6.3	0.16	0.04
Purmo	866	14 201	537	95	0.04	4.9	14	0.04	2.0	10 920	579	102	7393	347	59
Load/km ²		16	0.62	0.11	0.0	0.01	0.02	0.0	0.0	13	0.67	0.12	8.5	0.40	0.07
Kronoby	767	10 297	267	78	0.03	3.8	8.7	0.03	1.3	9343	394	97	4555	190	44
Load/km ²		13	0.35	0.10	0.0	0.01	0.01	0.0	0.0	12	0.51	0.13	5.9	0.25	0.06
Kovjoki	292	6419	232	41	0.02	1.8	5.6	0.03	1.1	4170	244	45	3801	150	34
Load/km ²		22	0.79	0.14	0.0	0.01	0.02	0.0	0.0	14	0.83	0.16	13	0.51	0.12
Total (rivers)	3973	50 426	1491	340	0.14	13	44	0.19	6.6	45 483	1765	440	28 573	1012	229
Nearest field	320	15 183	772	105	0.06	5.8	17	0.09	3.3	—	—	—	—	—	—
Load/km ²		47	2.4	0.33	0.0	0.02	0.05	0.0	0.01						
Total (rivers + nearest field)	4293	65 609	2263	445	0.20	19	61	0.28	9.9	—	—	—	—	—	—

summer automatically causes increased acidity the following autumn in this study. Several dry summers with low average runoff ($0.29\text{--}3.8\text{ l s}^{-1}\text{ km}^{-2}$, in years of increasing order: 2009, 2002, 1995, 1975, 2014, 1982, 1983, 1976, 1979 and 1978) have occurred without causing any exceptional periods of acidity the following autumn (pH 5.5 or higher indicated at the 10th percentile). As a comparison, the average runoff was $5.5\text{ l s}^{-1}\text{ km}^{-2}$ during the summers from 1975–2014. The lack of direct causality is mainly because a high runoff is needed during the autumn for the acidic water to be flushed out (Toivonen *et al.* 2013) and the average runoff during some of these autumns was low to moderate from approximately $0.49\text{--}6.2\text{ l s}^{-1}\text{ km}^{-2}$ (as a comparison, the average runoff in the autumn was $10\text{ l s}^{-1}\text{ km}^{-2}$ from 1975–2014). Since a high runoff is important for the acidity and metals to leach from the soil, autumn days with a runoff $< 10\text{ l s}^{-1}\text{ km}^{-2}$ were excluded from the calculations according to Toivonen *et al.* (2013). However, this did not yield any better support to the hypothesis. This may indicate that the lake system is too large to react to high runoff in a similar way — as was found in the autumn river water in Toivonen *et al.* (2013).

The most severe acidic events in the autumn occurred in 1986, 1996 and 2006 and resulted in mass kills of fish (Palko *et al.* 1987, Sutela *et al.* 2012). This revealed to be, according to this study, the lowest 10th percentile (pH: 4.8, 5.1 and 4.5, respectively; with the average runoff at 18, 9.2 and $13\text{ l s}^{-1}\text{ km}^{-2}$, respectively). The summers of 1986 and 1996 were, in fact, dry (average runoff was 3.8 and $1.8\text{ l s}^{-1}\text{ km}^{-2}$, respectively), but were also preceded by dry summers in 1985 and 1995 (average runoff was 3.9 and $0.98\text{ l s}^{-1}\text{ km}^{-2}$, respectively), indicating a cumulative effect of two subsequent summer droughts. However, the very dry summer of 2006 ($1.1\text{ l s}^{-1}\text{ km}^{-2}$) was able to set off the acidic surge the following autumn, even though the runoff was close to normal ($5.3\text{ l s}^{-1}\text{ km}^{-2}$) in the summer of 2005.

Due to snowmelt and low evapotranspiration, the amount of runoff is always high in the spring and variations in the water quality were less dependent on runoff variations. Therefore, this represented well the geochemical processes

in the soil that may have occurred in the previous year, which included enhanced oxidation due to summer droughts (Österholm and Åström 2008). Moreover, due to the high runoff, there is a closer relationship between the current water quality in the streams and the lake during the spring. This highlighted the role of runoff patterns and explained why summer droughts had a clearer effect on water quality in the following springtime compared with the following autumn.

Long-term trends

The influence of brackish water in Larsmo-Öja Lake was visible in the early 1960s. As a comparison, EC is about 500 mS m^{-1} in the adjacent, open brackish sea. Before the embankments were built, the narrow straits prevented brackish water from dispersing effectively into the lake, at least during periods of high runoff (Bonde and Lax 2003). The observed clear drop in pH at the end of the 1960s (Fig. 5) occurred concurrently with the decline in pH in Esse River found in Toivonen *et al.* (2013). The drop in pH at that time was induced by intensified drainage on sulfidic sediments — a trend that can be found in many rivers in western Finland (Suupohja *et al.* 1973, Hudd *et al.* 1984, Hildén and Rapport 1993, Åström *et al.* 2005, Saarinen *et al.* 2010). As with the data on water quality in rivers (Toivonen *et al.* 2013), the timing of sampling and choice of analyzed parameters are inconsistent for the national monitoring data (data set III), which makes it difficult to obtain valid results from trend analysis. The data, however, indicated that after the drop during the late 1960s and early 1970s, the pH in the lake recovered somewhat during the following decades. This is somewhat contradictory to the more complete data set II, where the pH from 1975–2014 showed a small drop. This drop occurred in the winter during the last decade and was caused by the increased flushing of acidity and metals from a.s. soils due to increased runoff in the study area, which is also reported by Toivonen *et al.* (2013). This may cause notable consequences for the biota. Increasing temperatures causing rain instead of snow during wintertime, due to potential

climate change, is expected to increase discharge from a.s. soils (Saarinen *et al.* 2010). Controlled drainage, which is the standard mitigation method used today to improve water quality in areas with a.s. soils, has showed some potential toward preventing oxidation of sulfides deeper in the soil profiles (Österholm *et al.* 2015). However, the effect on the quality of the discharging water is moderate at most (Joukainen and Yli-Halla 2003, Åström *et al.* 2007, Virtanen *et al.* 2015). Also, the lack of detectable improved water quality in areas with a.s. soils (Saarinen *et al.* 2010, Saarinen and Kløve 2012) suggests that the mitigation strategy currently implemented is insufficient if the goals in the Water Framework Directive set by the EU are to be reached.

The small drop in pH in the lake indicated that the recovery in water quality in Esse River reported by Toivonen *et al.* (2013) and in the three smaller rivers was not enough to affect pH in Larsmo-Öja Lake. Another option is that acidic metal discharge from the low-order streams has increased. The observed increase in Al in the lake, without a comparable decrease in pH, may be related to the latter scenario. This is because Al has less of a chance to be removed from the water by precipitation or flocculation in the small streams due to a shorter transport distance, less input of well-buffered ground water and lower concentrations of organic matter. The detected increase in Al concentrations is also largely unrelated to any possible changes in runoff conditions due to the trend results from runoff-corrected Al.

Using water quality data one day per month (on the 15th of each month — or nearest date where data was available) proved to roughly provide the same results in long-term trend analysis when using 10th percentiles and medians (pH), and medians or 90th percentiles (EC, Al and sulfate); based on all data in the extensive data set (data set II). This indicates that sampling once per month (or once per season) could be sufficient in detecting long-term trends (decades) in watercourses, provided it is well planned and consistent in terms of timing and choice of parameters. However, it is important to bear in mind that the episodic nature of acidic metal discharge requires considerably

more frequent sampling or continuous monitoring to study any short-term changes.

Acidity and metal export to Larsmo-Öja Lake

The relative difference in water quality between the four studied rivers and the low-order streams is a result of the different distribution of a.s. soils in the catchment areas (Palko and Yli-Halla 1993). The discharge waters from a.s. soils are the most diluted in Esse River because a large part of its catchment lies above the highest coastline of the Litorina Sea stage (about 100 m above current sea level). The catchments of the three smaller rivers reach above the Litorina Sea coastline to a lesser extent and the low-order streams draining the nearest field have catchments exclusively below the highest coastline of the Litorina Sea stage (Fig. 1). An example of the differences in water quality between the rivers is visible in Appendix Fig. A1 (based on data set III), which also displays data on Larsmo-Öja Lake sampled on the 15th of every month for comparison (based on data set II). The proportion of the low-order streams draining the nearest fields is only 7% of the catchment area, but they contributed with almost one fourth of the total load of sulfate. This was only surpassed by the large Esse River (which accounts for almost 50% of the Larsmo-Öja Lake catchment), and equal to Purmo River. The different relative loads between the rivers and the nearest field becomes clear when comparing the load per km⁻² in Table 4. The metal load from the low-order streams was as high as about one third of the total load, generally larger than from any of the rivers. The fact that the combined load from small unmonitored catchments is larger than the load from many rivers may cause an underestimation of the total load of pollutants to the sea (Destouni *et al.* 2008). The relatively lower load of metals from the rivers was due to the higher extent of metal removal via precipitation, complexation and sedimentation when compared with the low-order streams. Sulfate, which is an indicator of sulfide oxidation and the amount of produced sulfuric acid, is a conservative ion and is not as

easily removed from the water by geochemical processes.

Since there was an acidic surge causing mass kills of fish in the autumn of 2006 and spring 2007 in western Finland, including the current study area, the metal load in the lake reported above, may have been larger than during a normal year. Comparing the river load from 2007 with more long-term data from 1976–1981 indicates roughly similar yearly loads. The data from 1976–1981, however, was based on unfiltered samples compared with filtered samples (0.45 µm) used in 2007, which suggest a somewhat lower yearly load from 1976–1981. The yearly load from 2007–2014 (also analyzed from unfiltered samples) seems to be roughly about half of that during 2007, which may indicate that the load from the rivers has decreased over time due to the ongoing depletion of the acidic pool in a.s. soils (Österholm and Åström 2004, Toivonen *et al.* 2013). The data on the four rivers from data set III were erratic; the sampling events were not necessarily evenly spread over the periods, but, for example, concentrated to the end of the periods (see Appendix Fig. A1 as an example for years 2007–2014). This caused uncertainties in the estimated loads and the comparability between the rivers. The obtained results should therefore only be regarded as directional. No reliable estimate for the load from the important low-order streams based on data set III could be made. The clear increase in Al concentrations in the lake shown in this study suggested, however, that the load from the low-order streams in the near-field was larger during 2007–2014 than during 1976–1981. Load calculations based on water samples may lead to errors due to rapidly changing water quality and the varying relation between discharge and concentrations (Valkama and Ruth 2017). Therefore, the total load carried to the lake reported in this study is only directional.

In addition to the four rivers and numerous low-order streams studied in this work, there are a total of approximately 30 rivers (and a vast number of low-order streams) found in western Finland that have been susceptible to elevated metal concentrations during the last 40–50 years, causing a permanently poor eco-

logical status with poor or absent fish stocks, for example. This study supports the results of Sundström *et al.* (2002) and Österholm and Åström (2004), who have concluded that discharge from a.s. soils is by far the most severe metal polluter of Finnish watercourses today.

Conclusions

Human land-use in areas with a.s. soils has caused an exceptional drop in water quality since the late 1960s and early 1970s. Low pH events with corresponding harmful elevated metal concentrations have occurred in Larsmo-Öja Lake during most years throughout the study period. The water quality showed rapid changes, typical in areas with a.s. soils. The total yearly load of sulfate (indicator of sulfuric acid) to the lake was in the order of tens of thousands of tons and the potential toxic metals in bio-available forms up to hundreds, or even thousands of tons. Even though summer droughts increased the risk of poor water quality the following autumn, the acidic metal discharge proved to be more dependent on high runoff conditions. Warmer winters with increased runoff during the last decade have increased the risk of acidic metal load during the winter. With the current predictions of potential climate change and warmer and rainier winters, the high dependence on hydrological conditions threatens to increase the risk of detrimental effects from a.s. soils in the future. Unfortunately, with the inconsistent sampling and the lack of sufficient data available for many watercourses, it is difficult to obtain valid results for long-term changes in water quality. The combined acid metal load to the lake from the numerous small streams in the nearest field was unexpectedly high, even though these streams cover only a relatively small portion of the drainage area. Due to the episodic nature of the acid metal load and the importance of small unmonitored coastal catchments, it is of uttermost importance to understand the full consequences of a.s. soils. This can be achieved through well-planned monitoring programs in combination with alternative tools such as bio-indicators.

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Appendix

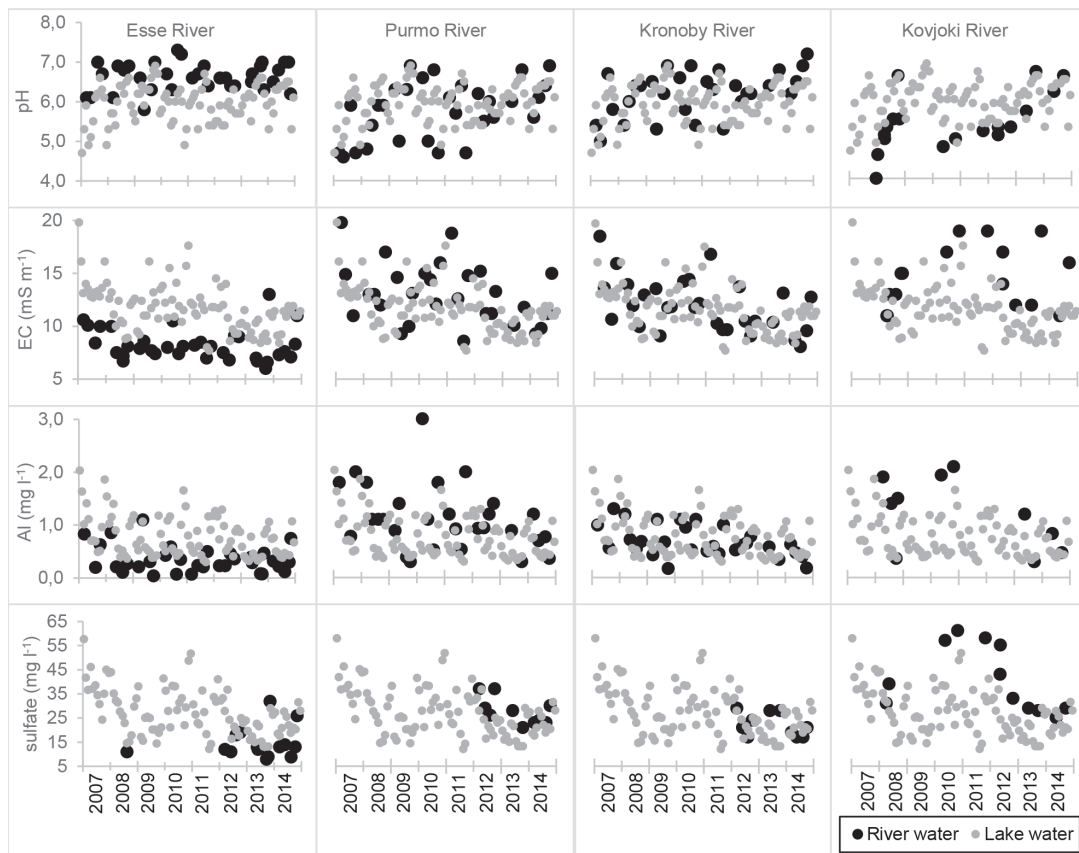


Fig. A1. Water quality in the rivers obtained from the national monitoring database (one sample/season; data set III) and Larsmo-Öja Lake, measured on the 15th day of every month from 2007–2014 (data set II).

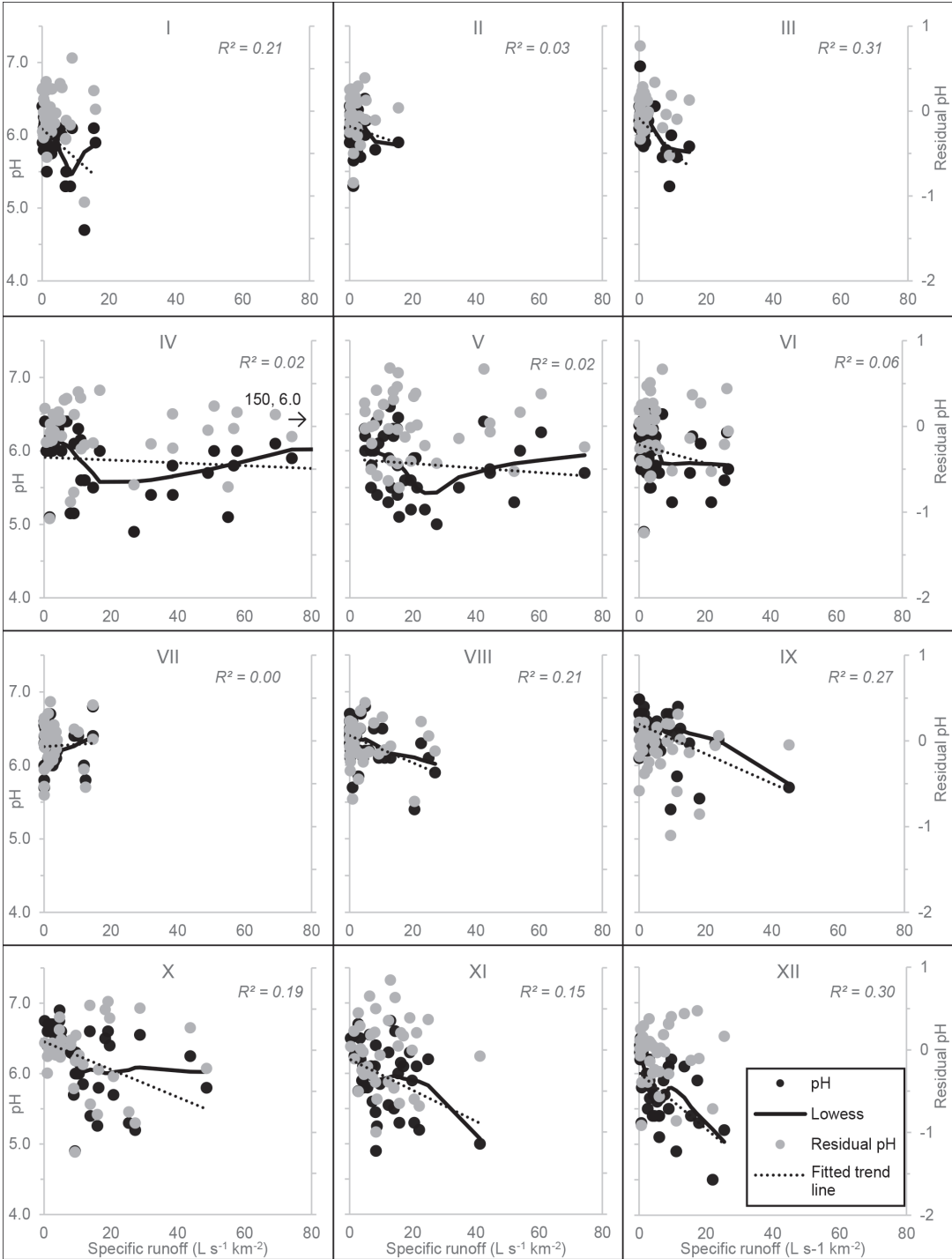


Fig. A2. The monthly potential relationship between runoff (Pahkaoja stream) and pH in Larsmo-Öja Lake, indicated by the trend line, Lowess curve ($f = 0.67$) and residual pH for data measured on the 15th day of every month from 1975–2014 (data set II).

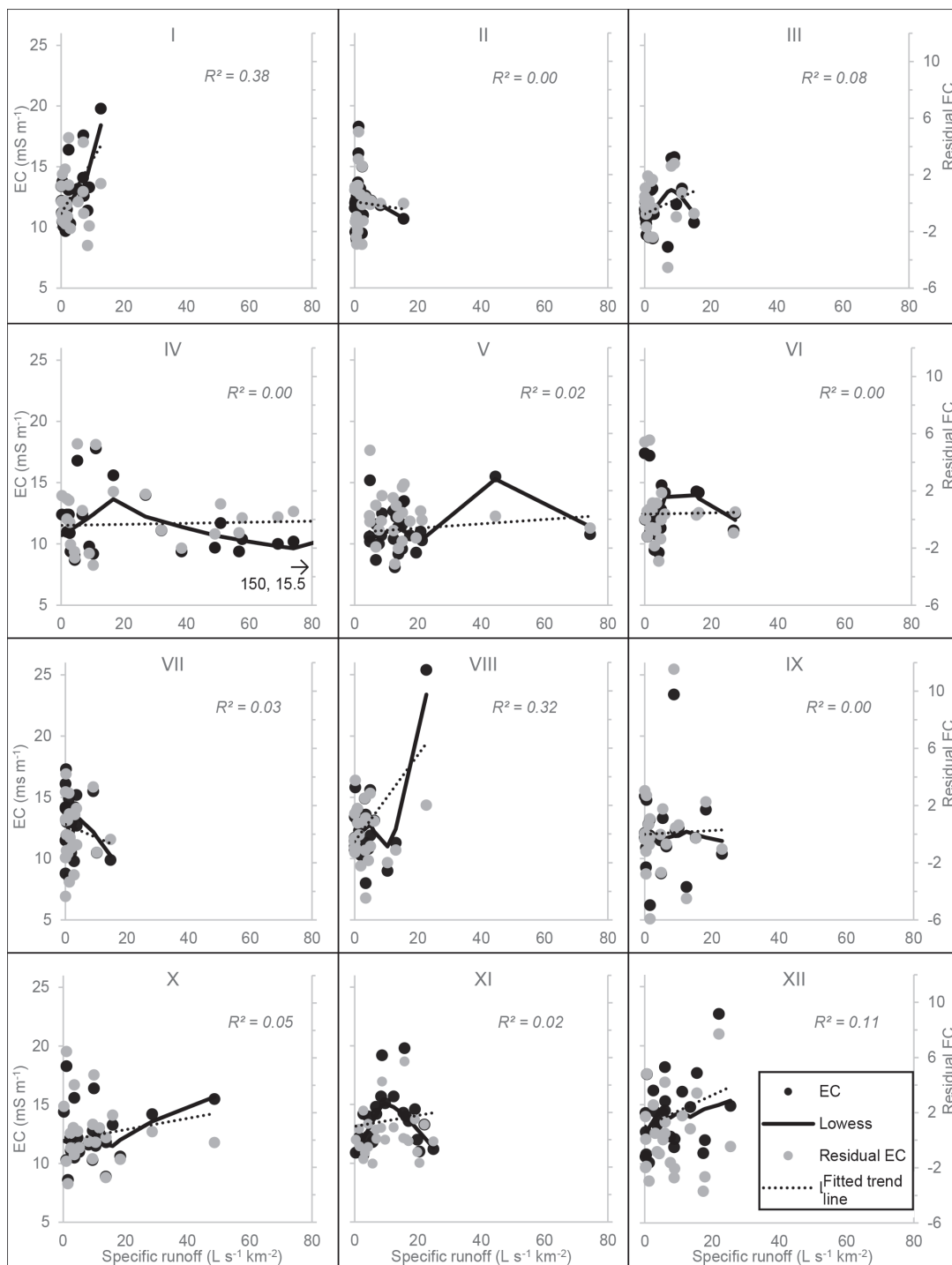


Fig. A3. The monthly potential relationship between runoff (Pahkajä stream) and EC concentrations in Larsmo-Öja Lake, indicated by the trend line, Lowess curve ($f = 0.67$) and residual EC for data measured on the 15th day of every month from 1989–2014 (data set II).

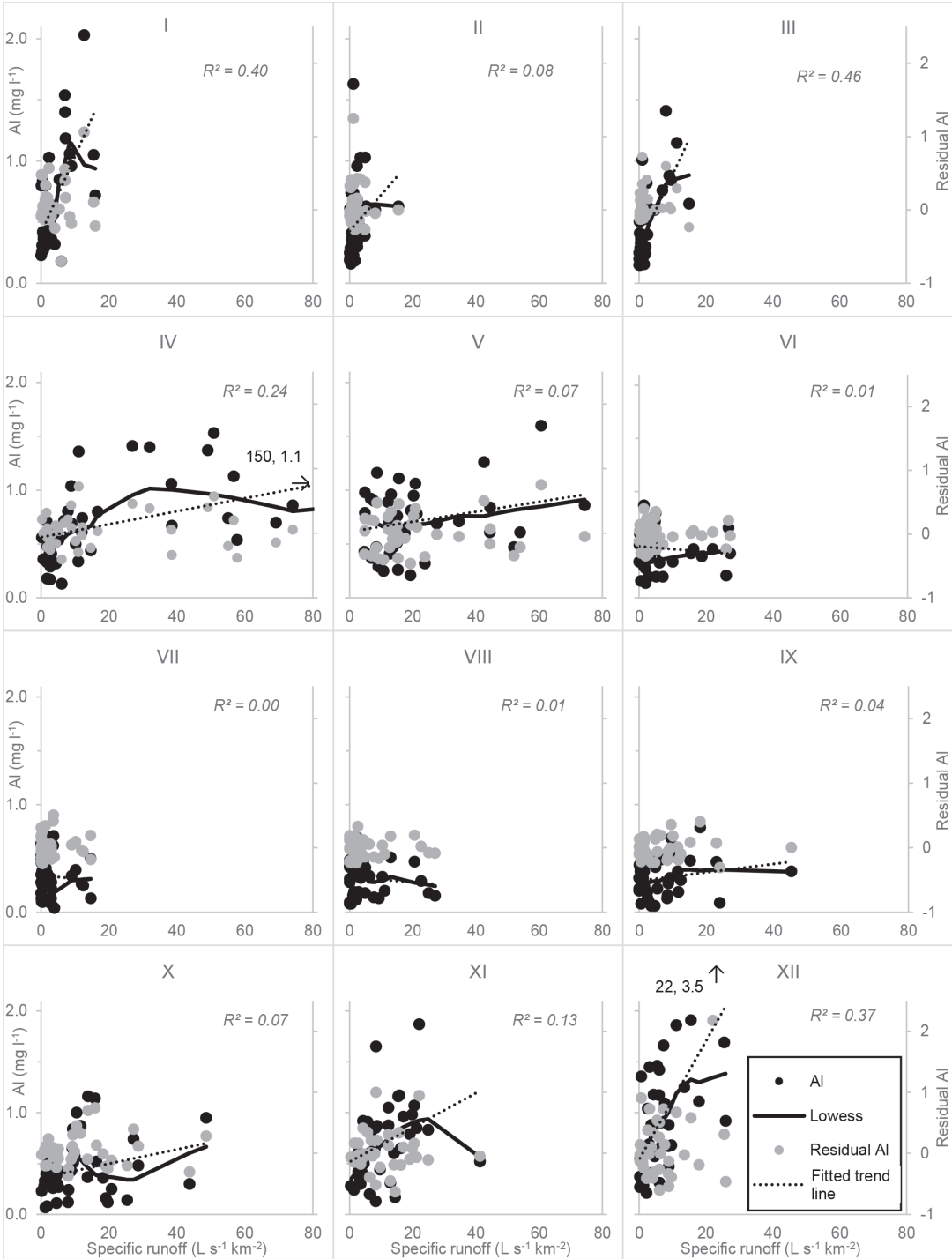


Fig. A4. The monthly potential relationship between runoff (Pahkajoki stream) and Al in Larsmo-Öja Lake, indicated by the trend line, Lowess curve ($f = 0.67$) and residual Al for data measured on the 15th day of every month from 1975–2014 (data set II).

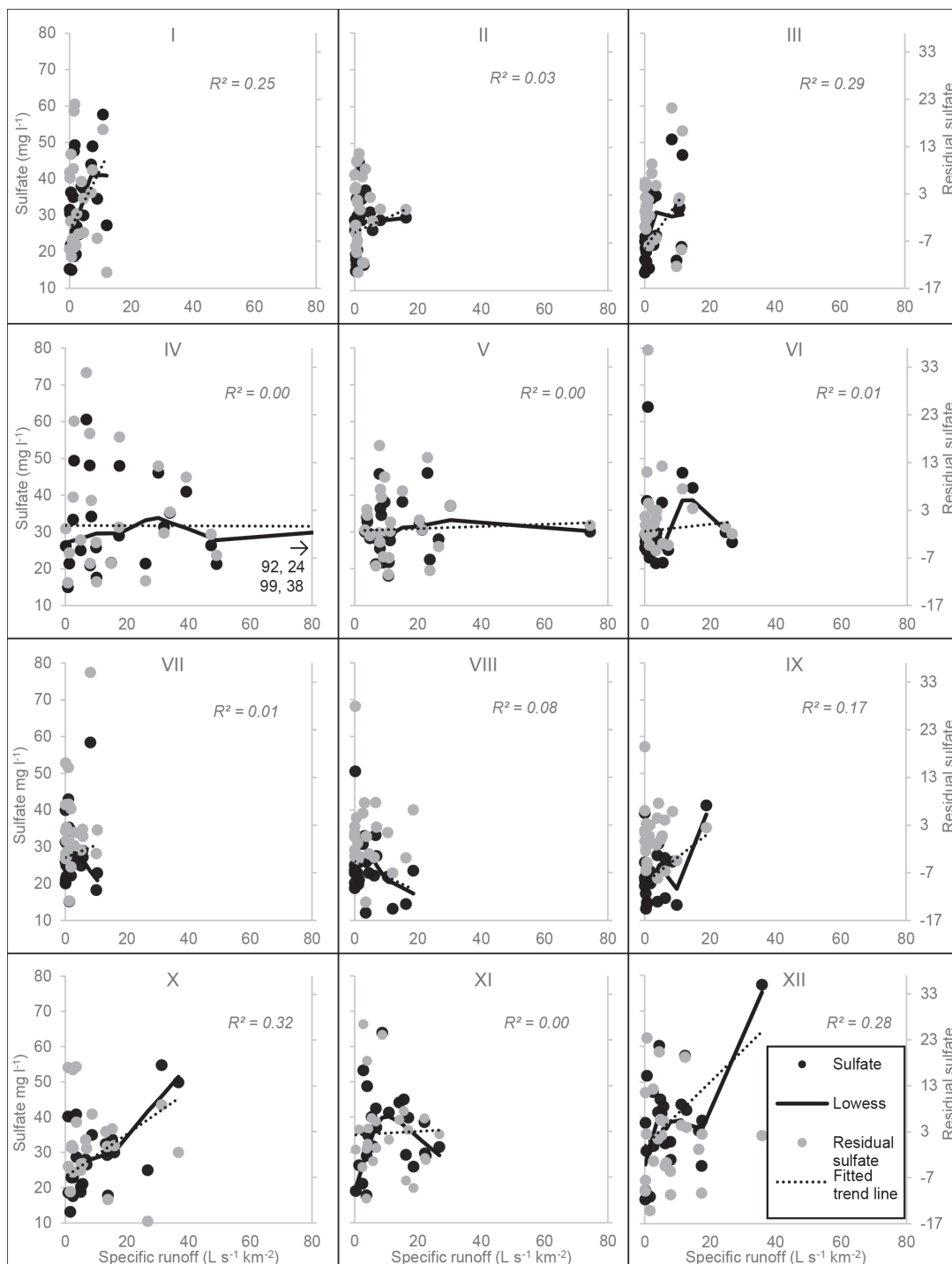


Fig. A5. The monthly potential relationship between runoff (Pahkaoja stream) and sulfate in Larsmo-Öja Lake, indicated by the trend line, Lowess curve ($f = 0.67$) and residual sulfate for data measured on the 15th day of every month from 1989–2014 (data set II).