

## Links between river water acidity, land use and hydrology

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In western Finland, acid leaching to watercourses is mainly due to drainage of acid sulphate (AS) soils. This study examined how different land-use and land-cover types affect water acidity in the northwestern coastal region of Finland, which has abundant drained AS soils and peatlands. Sampling conducted in different hydrological conditions in studied river basins revealed two different catchment types: catchments dominated by drained forested peatlands and catchments used by agriculture. Low pH and high electric conductivity (EC) were typical in rivers affected by agriculture. In rivers dominated by forested peatlands and wetlands, EC was considerably lower. During spring and autumn high runoff events, water quality was poor and showed large spatial variation. Thus it is important to ensure that in river basin status assessment, sampling is carried out in different hydrological situations and in also water from some tributaries is sampled.

### Introduction

Fine-grained sulphide-bearing sediments are found in different parts of the world (Asia, Africa, Australia, Europe and Latin America), covering in total about 17 million ha (Andriess and van Mensvoort 2006). In Europe, the largest occurrence is in Finland, but these sediments have not yet been fully mapped. The estimated area of acid sulphate (AS) soils in cultivation in Finland is 60 000–130 000 ha according to the criteria of Soil Taxonomy and FAO Unesco system, where the diagnostic properties of AS soil classes have to be met within 150 cm and 125 cm of the soil surface, respectively (Yli-Halla *et al.* 1999). The sulphide-bearing sediments were formed during the Littorina period of the Baltic Sea 7500–4000

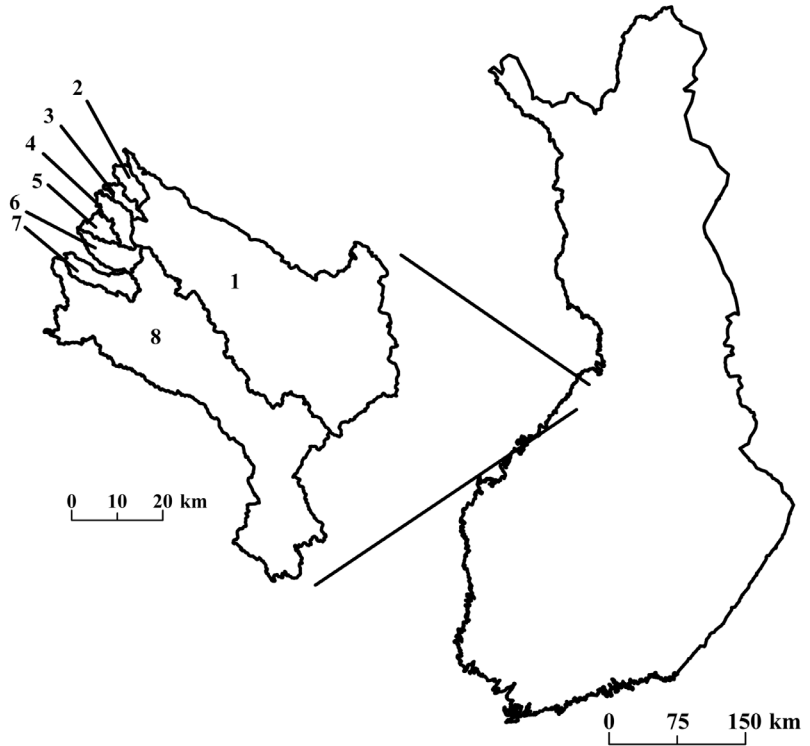
years ago (Sternbeck and Sohlenius 1997), and emerged above the sea level after postglacial isostatic land uplift. The sulphides they contain remain in reduced form under anoxic conditions but are oxidised to sulphuric acid as the groundwater level is lowered, mainly because of intensive drainage for agriculture (Kivinen 1938, Hartikainen and Yli-Halla 1986, Palko 1994, Joukainen and Yli-Halla 2003). Low pH allows mobilisation of different trace metals (Cd, Co, Mn, Ni, Zn) from soil matrix (Sohlenius and Öborn 2004). Oxidation of sulphides has been found to occur even at 2–3 m depth during dry periods in summer (Joukainen and Yli-Halla 2003). Droughts followed by rainfall cause leaching of huge amounts of acidity and soluble metals from soil pore water, posing a significant threat to watercourses.

The environmental impacts of acid leaching from AS soils during high runoff periods are well-known all over the world (MacDonald *et al.* 2007, Fältmarsch *et al.* 2008, Saarinen *et al.* 2010). In western Finland, a number of rivers suffer from episodic acidification and high metal concentrations (Åström and Björklund 1995, Roos and Åström 2005, Nordmyr *et al.* 2008, Saarinen *et al.* 2010). Increased acid leaching is the main reason for deterioration of water chemical and ecological quality in rivers situated below the 60-m isoline in western Finland (Ministry of Agriculture and Forestry and Ministry of Environment 2011). It has been estimated that the metal leakage from Finnish AS soils is 10–100 times higher than the effluent discharges from the entire Finnish industrial sector (Sundström *et al.* 2002). Abundant leaching of acidity and metals to watercourses, especially during high runoff periods in autumn after long dry summers, causes severe chemical and ecological effects (Hudd 2000). The most obvious effect of increased acidity is fish kill, which can in some cases be extensive after summer droughts. The most recent extensive fish kill in Finland was observed in a high proportion of rivers along the west coast in autumn 2006, after an extremely dry summer (Nyberg *et al.* 2011). It has been estimated that in future dry and warm summers with droughts will become more common, and as a consequence acidification problems may increase and probably be prolonged (Österholm and Åström 2008).

In addition to the severe acidification effects caused by AS soils, leaching of humic acids from peatlands also causes acidity in rivers (Mattsson *et al.* 2007). As peatlands are common in Finland, a large proportion of Finnish rivers and streams are brown-coloured and slightly acidic (median pH 5.9) (Lahermo *et al.* 1996). Organic carbon in surface waters is estimated to be mainly in dissolved form (DOC) (Mattsson *et al.* 2005). Due to the low amount of carbonate minerals in bedrock in northwestern Finland, surface waters are also poorly buffered (Kortelainen 1993). Concentration and export of total organic carbon (TOC) are related mainly to the proportion of peatlands in the catchment and, for example, precipitation (Sarkkola

*et al.* 2009). Approximately 50% of Finnish peatlands have been drained for agriculture and forestry, which may increase leaching of humic substances, metals, suspended solids and nutrients. The increased leaching of DOC will probably cause organic acidification of watercourses, especially in areas with abundant peat cover (Sallantausta 1986). Humic acids play a significant role as a buffer against acidification because they are characterised as weak acids (Hruška *et al.* 2003, Evans *et al.* 2008). In colloidal form, they also bind metals and chemicals, which decreases their bioavailability by decreasing their concentrations in water. Declining concentration of organic carbon substances in water sometimes coincides with high acidity due to precipitation of humic substances (Åström and Björklund 1995, Åström and Corin 2000).

A number of previous hydrochemical studies examined leaching of acidity and metals from AS soils due to artificial drainage and/or climate variations (Åström and Åström 1997, Åström 1998, Eden *et al.* 1999, Roos and Åström 2005, Saarinen *et al.* 2010, Nyberg *et al.* 2011, Saarinen and Kløve 2012). However, only few of these studies were focused on spatial variation in water acidity in large areas with different land-use characteristics. In classification of river basins based on water quality, it is important to take into account the catchment as a whole system in order to obtain reliable estimates of chemical and ecological quality. According to the Finnish national strategy for AS soils, the most important areas of these soils and the leaching risks should be mapped by 2015 (Ministry of Agriculture and Forestry and Ministry of Environment 2011). In the present study, the spatial variation in water acidity was studied in eight watercourses in north-western Finland. In smaller river basins extensive monitoring was conducted, while in two large rivers (Siikajoki and Pyhäjoki) the downstream area was monitored. The main aims of the study were: (1) to determine how different land cover and land use types affect water acidity in different parts of a river basin, and (2) to take different hydrological conditions into account when estimating leaching from catchment areas.



**Fig. 1.** Locations of the eight river basins studied. 1 = Siikajoki, 2 = Majavaoja, 3 = Olkijoki, 4 = Pattijoki, 5 = Haapajoki, 6 = Piehinginjoki, 7 = Liminkaoja, 8 = Pyhäjoki. © Maanmittauslaitos permission no. 7/MML/09.

## Materials and methods

### Study area

The study was conducted in river basins of different sizes in northwestern Finland (Fig. 1). Basic information on the land cover and land use in each catchment area is presented in

Table 1. According to the Finnish river typology system, the Siikajoki (4318 km<sup>2</sup>) and Pyhäjoki (3712 km<sup>2</sup>) are large rivers. We also studied medium-sized rivers: Pattijoki (141 km<sup>2</sup>), Piehinginjoki (176 km<sup>2</sup>) and Liminkaoja (187 km<sup>2</sup>); and small rivers: Majavaoja (97 km<sup>2</sup>), Olkijoki (68 km<sup>2</sup>) and Haapajoki (90 km<sup>2</sup>). All these rivers flow into the Gulf of Bothnia. In all

**Table 1.** Summary of land cover and land use in the catchment area of the eight Finnish river basins studied. CORINE 2006 land cover data.

River basin	Drainage area (km <sup>2</sup> )	Urban areas (%)	Agriculture (%)	Forests on mineral soils (%)	Forests on peatlands (%)	Wetlands (open stands in peatlands (%)	Peat harvesting areas (%)	Watercourses (%)
Siikajoki	4318	2.0	10.2	33.6	33.5	18.2	0.2	2.3
Majavaoja	97	1.0	8.2	47.6	31.4	11.5	0.2	0.1
Olkijoki	68	3.4	12	45.8	27.2	9.5	1.6	0.5
Pattijoki	141	8.5	13.7	52.0	18.4	6.9	0.3	0.2
Haapajoki	90	3.5	9.2	53.4	23.3	5.2	0.4	5.1
Piehinginjoki	176	1.3	2.4	47.8	30.6	17.2	0.2	0.6
Liminkaoja	187	1.9	6.3	54.6	28.7	7.7	0.2	0.7
Pyhäjoki	3712	3.2	11.8	45.1	26.2	8.4	0.2	5.2

the river basins, proportions of peatlands are > 25%; in case of the Siikajoki and Piehingin-joki, ~50% of their catchments is covered by peatlands. The proportion of agriculture is highest in the Pattijoki basin (13.7%) and lowest in the Piehinginjoki basin (2.4%). The proportion of watercourses is > 5% only in the Haapajoki and Pyhäjoki basins (Table 1). Mean annual air temperature at the Siikajoki meteorological station during the period 1960–2010 was 2.4 °C and precipitation was 522 mm.

### Water samples and hydrological data

Water samples were collected in different hydrological conditions from a total of 71 sites during 2009–2011 (sampling frequency is shown in the Appendix). Sampling was conducted during all seasons except winter. During high runoff periods, sampling was conducted at least once per month, but during summer the frequency was lower. Samples were taken from the middle of cross-section of each river from 20–40 cm depth, depending on the depth of the water. The sampling points were located at two sites in the main stream (downstream and upper part of river basin) of each river basin and the most important tributaries located between sampling points in the main streams. In the Siikajoki and Pyhäjoki, sampling was conducted in the lower part of the river basin. Water quality data were obtained partly from the HERTTA database of the Finnish Environment Institute. Most of the data are based on water sampling from the 71 sampling points included in the study (*see* Appendix).

Samples from the main river sites, were analysed for alkalinity, acidity, sulphate ( $\text{SO}_4^{2-}$ ), aluminium (Al), cadmium (Cd), iron (Fe), manganese (Mn), nickel (Ni), chemical oxygen demand ( $\text{COD}_{\text{Mn}}$ ) and colour according to SFS standards, at the Centre for Economic Development, Transport and the Environment of Northern Ostrobothnia (ELY Centre). Alkalinity was analysed using the potentiometric titration method involving titration to pH 4.5 and 4.2. Acidity was analysed with titration methods up to pH 8.3 according to SFS 3005:1981.  $\text{SO}_4^{2-}$  was analysed from filtered samples with the ISO 10304-1:2007 method using ion chromatography. Titrimetric method

following oxidation with  $\text{KMnO}_4$  was used for  $\text{COD}_{\text{Mn}}$  determination (SFS 3036). TOC analyses were conducted with according to SFS-EN 1997 SFS 3005. Water colour analyses were conducted according to SFS-EN ISO 7887:1995, section 4. Metals were analysed with the method ISO 1185:2007 from unfiltered samples, indicating both dissolved and particulate concentrations. During sampling, pH and electric conductivity (EC) of water were measured in the field with a Mettler Toledo MP120 meter. In tributaries, only pH and EC were determined, except in some of the most important tributaries related to acidity in the Pyhäjoki (Tähjänjoki, Talusoja and Toholanoja) and the Siikajoki basins (Luohuanjoki, Rukkisenoja and Levänoja). In Siikajoki and Pyhäjoki, continuous measurements of pH (half-hourly intervals) were made from September 2009 using pH sensors connected to an EHP-QMS data logger with internal modem, which sends data via the internet twice a day. Daily mean pH values were calculated using these data.

Daily data on the discharge of the Siikajoki and Pyhäjoki were obtained from the HERTTA database of the Finnish Environment Institute. These data refer to the lower reaches of the rivers. The relationship between pH and discharge was studied during peak discharge periods in autumn 2010 and in spring 2011. The discharge sampling periods were 23 Sep.–8 Oct. 2010 and 4 Apr.–5 May 2011, and 23 Sep.–10 Oct. 2010 and 5 Apr.–16 May 2011, in the Pyhäjoki and Siikajoki, respectively. Using the measured discharge, discharges of one tributary of the Siikajoki (Luohuanjoki) and one tributary of the Pyhäjoki (Talusoja) were calculated as  $Q_1 = F_1 / F_2 \times Q_2$ , where  $Q_1$  is the discharge of the river basin,  $F_1$  is the area of the river basin,  $F_2$  is the area of the nearest river basin (Siika/Pyhäjoki),  $Q_2$  is the discharge of the Siika/Pyhäjoki.

Because of limitations in the pH data from these two tributaries, the relationship between pH and discharge was studied for spring and autumn pooled together.

### Data analyses

Before the analyses, the year was divided into

four seasons according to the amount of runoff: (1) winter (January–March) with snow accumulation and low runoff, (2) spring (April–May) with snowmelt and high runoff, (3) summer (June–September) with low runoff due to high evaporation, and (4) autumn (October–December), characterised by low evaporation and moderate runoff. Sampling points were also classified according to their proportion of peatlands: (1) < 25%, (2) 25%–40%, (3) 40%–50% and (4) > 50%. The size classes used for the river basins were: 10–50 km<sup>2</sup>, 50–100 km<sup>2</sup>, 100–500 km<sup>2</sup> and > 500 km<sup>2</sup>.

The relationships between water quality parameters and land-use types in the catchment area were analysed using the Spearman correlation because of a non-normal distribution of the data. Least-squared regression analysis was used to study relationships between pH and discharge of the rivers. The differences in water quality between sampling points at the main stream sites were studied using the Mann-Whitney *U*-test.

## Results

### General water quality in 2009–2011

According to whole data (HERTTA database of the Finnish Environment Institute, and the conducted water analyses) minimum daily pH varied between 5.4 and 6.1, maximum EC between 9 and 22 mS m<sup>-1</sup>, minimum alkalinity between 0.02 and 0.11 mmol l<sup>-1</sup>, and maximum acidity between 0.2 and 0.29 mmol l<sup>-1</sup> (Table 2). Maximum Fe concentration varied between 4200 and 9600 µg l<sup>-1</sup>, maximum Mn between 79 and 860 µg l<sup>-1</sup>, maximum Cd between 0.02 and 0.11 µg l<sup>-1</sup> and maximum Ni between 1.3 and 9.5 µg l<sup>-1</sup>. Maximum COD<sub>Mn</sub> value was 20–34 mg l<sup>-1</sup> and colour 260–500 mg l<sup>-1</sup> (Table 2). The highest sulphate concentration was found in the Haapajoki (65 mg l<sup>-1</sup>) and the lowest maximum concentration in the Pichinginjoki and Liminkaoja (13 mg l<sup>-1</sup>) (Table 2). There were no statistically significant differences in variables between downstream and upstream sites (*U*-test: *p* > 0.05).

The acidity situation was better in the main rivers than in the tributaries. Among the tributaries studied, the highest sulphate concentration

(240 mg l<sup>-1</sup>) was recorded in the tributary of the Luohuanjoki (Rukkisenoja upstream, SI3F), where also low pH (even pH 3), high EC (89.6 mS m<sup>-1</sup>), high acidity (1.76 mmol l<sup>-1</sup>), and high concentrations of Fe (21 000 µg l<sup>-1</sup>) and other metals (Al 2500 µg l<sup>-1</sup>, Mn 680 µg l<sup>-1</sup>) were encountered. In the tributaries of the Pyhäjoki (Talusoja, PY3C and Toholanoja, PY3F), high metal concentrations were found (Al 4700 µg l<sup>-1</sup>, Cd 0.15–0.16 µg l<sup>-1</sup>, Mn 770–870 µg l<sup>-1</sup>, Ni 16–18 µg l<sup>-1</sup>). High sulphate concentrations (120–160 mg l<sup>-1</sup>) were also encountered in these rivers.

### Spatial variation of pH and EC in the study area

Some low pH and high EC values were recorded in different parts of the study area. Low pH (< 4.5) was measured at four sites in the Luohuanjoki sub-basin (SI3B, SI3E, SI3F, SI4B), where EC values were above 40 mS m<sup>-1</sup> (Fig. 2).

The lowest pH value (pH 3) was recorded in Rukkisenoja, which is a tributary of the Luohuanjoki. At two sites in the Pyhäjoki region minimum pH was below 4.5 (PY3C and PY4H), and the EC values were above 40 mS m<sup>-1</sup> (Fig. 3). There were also several sites at which pH was between 5.1 and 5.5. In the Pichinginjoki basin, some low pH values were measured, but there were no indications of high EC values. Similar findings were made for the Majavaoja basin. In the Haapajoki basin, high EC values were measured, but pH was not very low.

### Seasonal variations in water quality in streams of the Pyhäjoki and Siikajoki river basins

Water quality was poor during high-flow periods in spring and autumn as compared with that in the other seasons. Iron concentrations peaked in spring, with high peak values in the Pyhäjoki (5000–1600 µg l<sup>-1</sup>) and Siikajoki (20 000 µg l<sup>-1</sup>), and then decreased after summer toward a steady minimum of around 2000 µg l<sup>-1</sup>. Changes in aluminium concentrations were usually similar seasonal variations in Fe, with peak values in spring

and autumn (Pyhäjoki ~4000  $\mu\text{g l}^{-1}$ , Siikajoki 2000  $\mu\text{g l}^{-1}$ ). Colour and  $\text{COD}_{\text{Mn}}$  values peaked at the beginning of summer (colour 150–500  $\text{mg Pt l}^{-1}$ ,  $\text{COD}_{\text{Mn}}$  50–60  $\text{mg l}^{-1}$ ).  $\text{SO}_4^{2-}$  and EC were at their minima in spring, with values then increasing steadily during the year. In summer,  $\text{SO}_4^{2-}$  concentration in the Pyhäjoki increased to 150  $\text{mg l}^{-1}$ , while in Siikajoki it reached 240  $\text{mg l}^{-1}$ . During the same season, pH slightly increased and varied from 4 to 8 in the Pyhäjoki and from 3 to 8 in Siikajoki. In smaller rivers, water quality parameters were quite similar to

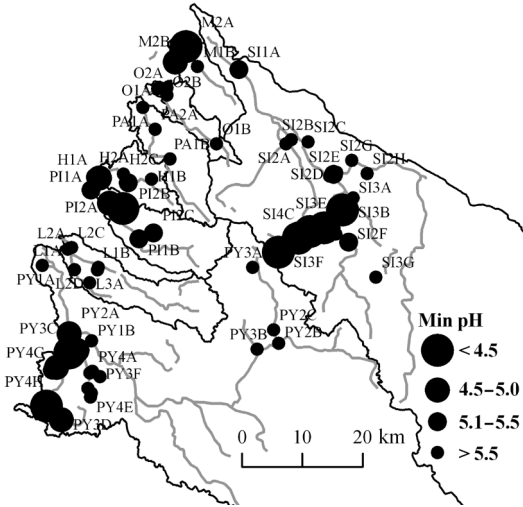
those in the streams of the Siikajoki and Pyhäjoki river basins.

### Correlations between water quality variables and land use types

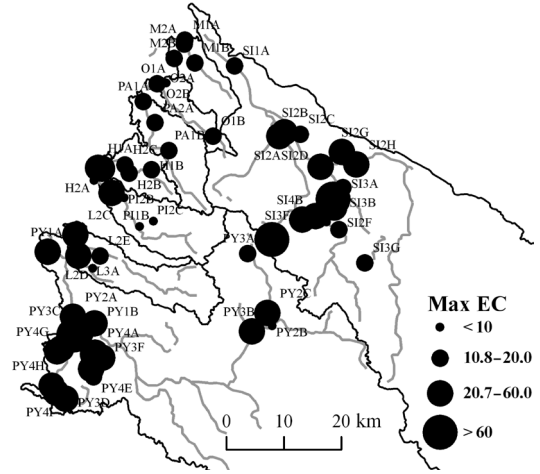
Concentrations of sulphate correlated negatively with pH and alkalinity (see Table 3), while colour and  $\text{COD}_{\text{Mn}}$  did not correlate with pH. Positive correlations between EC and  $\text{SO}_4^{2-}$ , Al, Cd, acidity and Ni were found. An increase in

**Table 2.** Water quality variables in main streams.

Variable	Pyhäjoki	Liminkaoja	Piehinginjoki	Haapajoki	Pattijoki	Olkijoki	Majavaoja	Siikajoki
Alkalinity ( $\text{mmol l}^{-1}$ )								
Max	0.37	0.49	0.36	0.67	1.52	0.52	0.44	0.77
Median	0.21	0.16	0.08	0.15	0.29	0.24	0.17	0.15
Min	0.07	0.08	0.02	0.03	0.11	0.11	0.07	0.06
SD	0.08	0.16	0.11	0.2	0.31	0.12	0.13	0.13
Acidity ( $\text{mmol l}^{-1}$ )								
Max	0.17	0.2	0.24	0.29	0.19	0.24	0.2	0.25
Median	0.13	0.13	0.16	0.19	0.12	0.11	0.11	0.13
Min	0.05	0.05	0.09	0.06	0.09	0.08	0.08	0.07
SD	0.04	0.05	0.05	0.08	0.03	0.05	0.04	0.06
pH								
Max	7.6	7.4	7	7.2	7.1	7.1	7.2	7.8
Median	6.7	6.5	6	6.4	6.6	6.6	6.8	6.4
Min	5.8	5.8	5.3	5.4	6	5.7	6.1	5.4
SD	0.3	0.4	0.5	0.5	0.3	0.3	0.2	0.3
EC ( $\text{mS m}^{-1}$ )								
Max	21.1	11.1	9	22	19.7	12.4	11.6	10.8
Median	12.2	6.15	5.4	15.5	13.3	9	9.1	5.56
Min	4.4	3.8	3.2	9.6	7.2	6.6	7.8	4.1
SD	4.5	2	1.5	3.4	3.1	1.3	1.1	1.3
Al ( $\mu\text{g l}^{-1}$ )								
Max	1430	790	724	1800	679	590	416	1140
Median	598	610	430	1190	451	363	310	500
Min	71	200	210	120	66	96	100	32
SD	393	200	160	563	196	152	97	265
Fe ( $\mu\text{g l}^{-1}$ )								
Max	4200	5600	8500	9200	7100	6700	9600	7000
Median	2100	2450	3300	5150	3550	3900	3450	3300
Min	1200	1900	1700	3400	2600	2700	2800	2400
SD	524	1601	2057	2108	1395	1189	2633	856
$\text{SO}_4^{2-}$ ( $\text{mg l}^{-1}$ )								
Max	56	13	13	65	45	18	19	20
Median	25	7	7	42	22	13	17	8
Min	6	5	4	14	16	5	13	2
SD	15	3	2	14	10	3	2	17
Colour ( $\text{mgPt l}^{-1}$ )								
Max	330	300	390	300	300	260	300	500
Median	150	270	270	180	200	160	180	245
Min	60	200	180	160	120	100	130	100
SD	65.4	42.2	58.9	57.6	49.9	41.2	65	59.1



**Fig. 2.** Minimum pH 2009–2011 in the eight river basins studied and their tributaries (for site codes see Appendix).



**Fig. 3.** Maximum EC 2009–2011 (mS m<sup>-1</sup>) in the eight river basins studied and their tributaries (for site codes see Appendix).

water colour was connected with an increase in metal concentrations.

Proportion of agricultural land in the catchment areas correlated positively with nearly all variables (Table 4), minimum pH, alkalinity, colour and COD<sub>Mn</sub> being the only exceptions. There was a slightly different pattern with percentages of wetlands and forested peatlands. Organic matter (colour and COD<sub>Mn</sub>) and SO<sub>4</sub><sup>2-</sup> correlated positively with percentage of wetlands, but not with percentage of forested peatlands (Table 4). A decrease in the area of peat harvest was resulted in increased concentrations of Al, Cd and Ni as well as colour. A decrease in

acidity was related to an increase in proportion of watercourses.

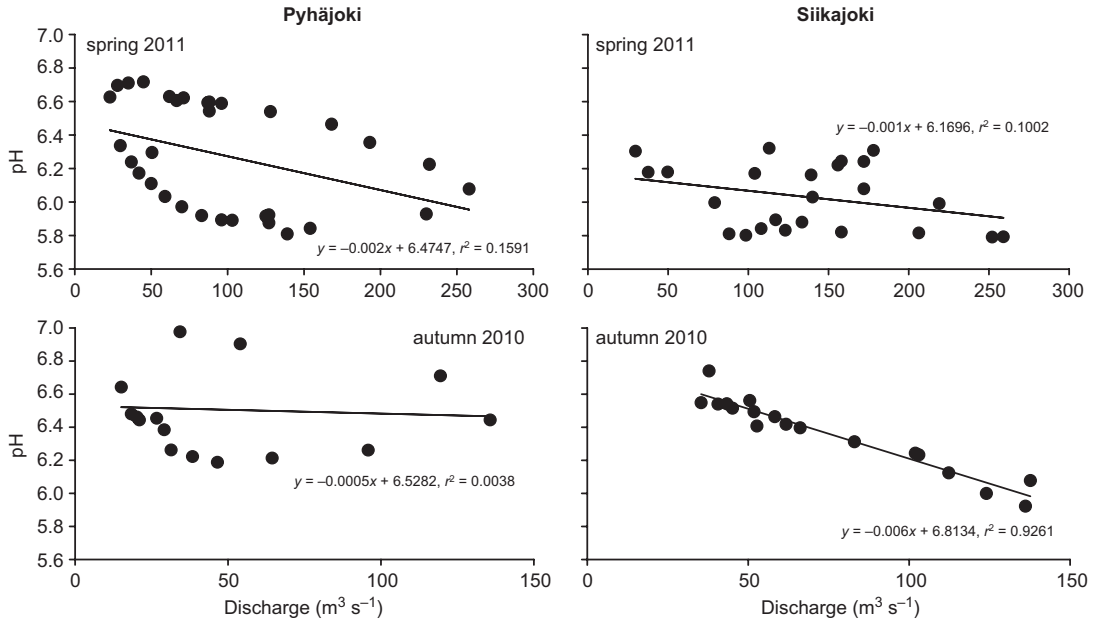
**Relationships between discharge and pH during flood periods**

In the Siikajoki, discharge and pH were strongly related only during the autumn runoff peak (Fig. 4). In the Pyhäjoki, there were no such relationships (Fig. 4).

In both rivers, spring was generally associated with lower pH values and higher discharge. During high runoff in spring, a small increase

**Table 3.** Correlations (*r<sub>s</sub>*, only significant (*p* < 0.05) values are given) between water quality variables. Samples sizes are given in Appendix.

	Min pH	Alkalinity	Al	Acidity	Cd	COD <sub>Mn</sub>	Ni	Fe	SO <sub>4</sub> <sup>2-</sup>	EC	Colour
Alkalinity	0.71										
Al	-0.44	-0.36									
Acidity	-0.85	-0.63	0.44								
Cd	-0.40	-0.18	0.70	-							
COD <sub>Mn</sub>	-	-	-	-	-						
Ni	-	-	0.55	0.35	0.86	-					
Fe	-0.53	-	-	0.56	-	-	-				
SO <sub>4</sub> <sup>2-</sup>	-0.51	-0.42	0.64	0.67	0.59	-	0.57	0.61			
EC	-0.25	-	0.63	0.53	0.55	-	0.44	-	0.81		
Colour	-	-	0.42	-	0.60	0.71	0.46	0.40	-	-	
Mn	-0.45	-	0.65	0.42	0.66	-	0.59	0.62	0.85	0.73	-



**Fig. 4.** Relationships between pH and discharge during the spring and autumn runoff peaks in the Siikajoki and Pyhäjoki.

in pH was recorded in the Pyhäjoki. When discharge exceeded  $50 \text{ m}^3 \text{ s}^{-1}$ , the pH value started to decrease, reaching a minimum three days after the runoff peak. After this, an increase in pH could be found. During autumn, minimum pH was reached four days after the maximum discharge. In the Siikajoki, the minimum pH was reached simultaneously with the runoff peak in both spring and autumn.

## Discussion

### Evaluation of catchment acidity sources from water samples

In rivers in western Finland, increased leaching of acidity from river basins is closely related to extensive drainage of AS soils, which increases oxidation of sulphides in the subsoil as the

**Table 4.** Correlations ( $r_s$ , only significant ( $p < 0.05$ ) values are given) between water quality parameters and land use (%) in the catchment area.

	Urban areas	Agriculture	Forest on mineral soils	Forested peatlands	Wetlands	Areas of peat harvest	Watercourses	Peatlands
Min pH	–	–	–	–	–	–	–	–
Alkalinity	–	–	–	–	–	–	–	–
Al	–	0.38	–	–0.40	–0.40	–0.35	–	–0.37
Acidity	–	0.35	–	–	–	–	–0.43	–
Cd	–	0.54	–	–0.49	–	–0.46	–	–0.46
COD <sub>Mn</sub>	–	–	–	–	0.43	–	–	–
Ni	–	0.51	–	–0.50	–0.42	–0.40	–	–0.48
Fe	–	0.40	–	–	–	–	–	–
SO <sub>4</sub> <sup>2-</sup>	–	0.56	–	–	–0.35	–	–	–
EC	0.46	0.63	–	–0.35	–0.38	–	–	–0.45
Colour	–	–	–0.36	–	0.36	–0.36	–	0.37
Mn	0.44	0.72	–0.38	–	–	–	–	–



groundwater level is lowered (e.g. Åström and Björklund 1995, Åström 1998, Fältmarsch *et al.* 2008). In some cases, the increase in acidity results mostly from leaching of organic acids from peatlands (Mattsson *et al.* 2007, Sarkkola *et al.* 2009). In the present study, the difference between acidity derived from peatlands and that from agricultural AS soils can be clearly seen because a decrease in pH was associated with an increase in  $\text{SO}_4^{2-}$  concentrations but not with an increase in concentrations of organic matter (Table 3). In particular, EC differences between peatlands (forested peatlands and wetlands) and agricultural land were found, with EC being clearly higher in streams with higher proportion of agriculture in the catchment area (Fig. 3 and Table 4).

According to the preliminary results of the AS soil mapping conducted by the Geological Survey of Finland (GTK), some of the study area is covered by drained agricultural AS soils, which can be clearly seen in water quality in adjacent streams. Most problematic sites concerning acidity leaching were the tributaries of the Siikajoki (the Luohuanjoki and especially the sub-basin Rukkisenoja) and the tributaries of the Pyhäjoki (the Tähjänjoki and the sub-basins Talusoja and Toholanoja). In all these rivers, minimum pH was occasionally below 4.5 and EC was high ( $> 40 \text{ mS m}^{-1}$ ). Intensive agriculture is practised in all these sub-basins and the proportion of agriculture in the catchment area varies from 13% to 17%. Also alkalinity was sometimes completely lost in these rivers, which contributed low pH values. In Finnish streams, median EC is  $4.4 \text{ mS cm}^{-1}$  (Lahermo *et al.* 1996), but measurements in this study exceeded this limit, especially in rivers probably affected by AS soils. It can be concluded that acidity problems in these streams are thus mostly related to leaching of acidity from agricultural soils, which are classified as AS soils according to the mapping survey by GTK. It has been estimated that the concentration of sulphate in AS soils may be 1.5- to 5-fold higher in subsurface drains than in open drains because of the depth (2 m in some cases) of the drainage effect in subsurface drainage (Palko 1988).

In smaller rivers between Siikajoki and Pyhäjoki, low pH values were measured, but EC

values were lower than in the tributaries of the Pyhäjoki and Siikajoki, which can be related to the occurrence of AS soils indicated by preliminary GTK mapping. Among others, Åström (2001) reported similar results. Substantial proportions of these river catchments are covered by forested peatlands and wetlands (Table 2). Thus, it can be estimated that most of the acidity is leached from peatlands. Lower EC values of the rivers whose catchment areas were dominated by peatlands are the result of limited dissociation of humic substances to water and thus they do not increase EC in water (Niemi and Raatela 2007). In addition, the amount of easily mobilised elements in peatlands is considerably lower than in AS soils and thus an increase in EC cannot be found (Åström 2001). According to Kortelainen and Saukkonen (1995), TOC is a good explanatory factor related to low pH values (explaining 67%–83% of the pH variation in that study, where the lowest pH values were recorded in peatland-dominated rivers). These results support previous findings that pH alone is not a relevant indicator of AS soils and instead, additional parameters are needed to confirm the presence of AS soils. Thus for example EC can potentially be a relevant indicator of AS soils as it showed a high positive correlation with sulphate (Table 3). Åström (2001) found a high positive correlation between pH and EC in AS soil-affected streams and suggested that leaching of acidity and ions is much greater from AS soils than from other soil types such as till and peat. However, EC is sum of the conductance caused by several anions and cations and thus sulphate is not the only ion, which affects electric conductivity of the river water. According to Cook *et al.* (2000), analyses of acidity and/or metals are required to give a relevant estimate of the incidence of AS soils. Nyberg *et al.* (2011) also concluded that organic acids derived from peatlands are responsible for low pH values in some cases and thus that pH is not a suitable method for detecting the occurrence of AS soils.

### Variation in acidity-related variables

In rivers on the southwestern coast of Finland (Laajoki and Sirppujoki), the minimum and

median pH values are approximately at the same level as those in the main rivers analysed in this study, but the EC values are about 2.5-fold higher than those in our study (HERTTA database of the Finnish Environment Institute, Nyberg *et al.* 2011). During 2009–2011, a clear spatial trend of minimum pH values was found on the coast of Finland (HERTTA database of the Finnish Environment Institute). In the mid-western coast (Vaasa region), the minimum pH values were generally below 5 (in some rivers even under 4.5), and the maximum EC values exceeded  $50 \text{ mS m}^{-1}$ , while in the main streams of the rivers included in the present study the minimum pH values never decreased below 5, and the maximum EC values never exceeded  $25 \text{ mS m}^{-1}$ . In the Kyrönjoki and Lapuanjoki, occasional low pH is an annual phenomenon in the long-term data. In these rivers, alkalinity has been lost and even pH 4 was recorded during high-runoff periods (Saarinen *et al.* 2010). These river basins are extensively used for agriculture (about 25% of catchment area is covered by farmland) (Saarinen *et al.* 2010). According to Roos and Åström (2005), in the Sulvanjoki median pH was approximately one pH unit lower than median pH of the Piehinginjoki. In addition, EC increased above  $60 \text{ mS m}^{-1}$  in the Sulvanjoki, which is situated in the middle of an estimated hotspot area for Finnish AS soils.

In the large rivers studied here (Kyrönjoki, Lapuanjoki, Pyhäjoki and Siikajoki), whose catchment were quite similar in size, the maximum Al concentrations differed widely during 2009–2011 (Saarinen and Kløve 2012). The Al concentrations were on average 50% higher in the Kyrönjoki and Lapuanjoki than in the Pyhäjoki and Siikajoki. Al is often estimated to exist as colloidal of particulate fraction, binding to humic substances (organic complexes) as well as to clay minerals (Nystrand *et al.* 2012). High Al concentrations in these catchments intensively used by agriculture may thus be a consequence of increased erosion of metal-bearing suspended solids (e.g. phyllosilicates) and organic matter. For example, in the Kyrönjoki, the concentration of suspended solids in 2009–2011 was about 0.6 times higher than in the Siikajoki (HERTTA database of the Finnish Environment Institute). In the Kyrönjoki basin, extensive flood protection

works (dredging) and drainage have significantly increased erosion (Heikkilä 1991). In contrast, the colour values were on average 40% higher in the Pyhäjoki and Siikajoki than in the Kyrönjoki and Lapuanjoki. This is clearly connected to the larger proportion of drained forested peatlands and wetlands in the basins of the Pyhäjoki and Siikajoki and to higher abundance of agricultural land in the Kyrönjoki and Lapuanjoki basins.

### Seasonal variation in acidity in the studied rivers

In general, river water acidity produced moderate water quality status, as the average annual pH minima were below 5.5 (Vuori *et al.* 2009). This situation occurred in our rivers during flood periods, but during low runoff in summer and winter the water acidity situation was better. During spring, dilution effects of poorly-buffered snow-melt waters are reported to play a major role in decreasing the buffering capacity of rivers and thus lowering pH (Laudon and Bishop 2002). In addition, Finnish rivers are usually poorly buffered because of lack of carbonates in the soil. During autumn, acidity runoff is very common. Drought in the preceding summer is mostly responsible for this situation, as sulphide minerals are oxidised during dry, warm periods, which lowers pH in soils (e.g. Palko and Weppling 1995, Österholm and Åström 2008). This enables mobilisation of several metals in the soil. The compounds formed during oxidation then leach to watercourses during high precipitation events in autumn. The latest acidity runoff event in autumn related to intensive drought in summer occurred during 2006, when most Finnish coastal rivers suffered from occasional acidification (Nordmyr *et al.* 2008). Intensity of the summer drought is strongly correlated with water quality, because when leachable reserves of oxidised compounds are large, water quality is notably lower during autumn (Österholm and Åström, 2008). The situation may not normalise until after several wet summers if the leachable pool is large.

Many studies of hydrological parameters concluded that abundant runoff is mostly responsible for episodic acidity in rivers (Saarinen

*et al.* 2010, Nyberg *et al.* 2011, Saarinen and Kløve 2012). Because of the huge variation in concentrations of acidity-related variables in different hydrological conditions, either reported in the literature or in this study, it would be very useful to take into account hydrological conditions when sampling river water. This would increase reliability and representativeness when studying water quality and determining the ecological status of rivers. In some most strongly acidified rivers affected by AS soils, high acidity may be found even during low-runoff periods, as upstream in the Rukkisenoja in this study.

### **Impacts of catchment land use on water quality**

According to the results of this study, leaching of acidity and metals (Cd, Ni, Fe and Mn), as well as EC and  $\text{SO}_4^{2-}$ , strongly increases with an increasing proportion of agricultural land in the catchment area (Table 4). This is certainly related to AS soils, which deliver acidity and metals released as a result of oxidation processes of sulphidic material (e.g. Boman *et al.* 2008, 2010). However, no correlations between minimum pH and proportion of agriculture were found. Roos and Åström (2005) also concluded that there was no significant correlation between river pH and percentage of arable land in the catchment area. Many different sources produce reductions in river pH, and thus it is not directly the result of AS soil impact only, but also organic acids derived from peatlands. From the end of the 1950s, subsurface drainage started and during the 1960s it became very common everywhere in Finland. At the same time, forest ditching was intensive. From the beginning of the 1960s, low alkalinity values have been recorded in several rivers, even in the Siikajoki (Saarinen *et al.* 2010). Extensive subsurface drainage has increased oxidation of sulphidic materials, which has worsened the acidity situation. According to Österholm and Åström (2004), the rate of oxidation of soil sulphides will decrease over time, because of the lower pool of leachable sulphur in soil. Yet leaching will still continue for several decades and will thus have negative effects on water quality. Drainage operations in agriculture

are thought to be the most important source of acidic load to watercourses (Maa- ja metsätalousministeriö 2009).

### **Conclusions**

There was huge variation in acidity-related variables in the eight studied rivers. At some sites in the tributaries (Rukkisenoja, Levänoja, Talusoja), water quality did not improve even during low runoff periods. The results identify two catchment types in the study area; catchments dominated by drained forested peatlands and catchments used by agriculture. Both land use and hydrological conditions had impacts on water quality, especially on acidity-related variables. In catchments dominated by drained forested peatlands and wetlands, occasional low pH values being a consequence of organic acids derived from peatlands were measured in 2009–2011. However, the EC values remained close to the national average for peatland-dominated rivers in Finland. In contrast, in agriculture-dominated catchments, low pH and high EC values in rivers were common and sulphate concentrations were also higher than the national average. Thus low pH together with high EC can be a reliable indicator of the occurrence of AS soils, because EC directly increases due to the oxidation of sulphidic materials in AS soils. There are also major seasonal variations in acidity-related variables, with the episodic acidification occurring during spring and autumn high runoff. The main north-western rivers analysed in this study were not in as poor condition in terms of acidity as rivers located in southwestern coastal areas, a hotspot for AS soils (Vaasa region). However, some tributaries can be classified as being of poor or even bad quality. Our results suggest that when evaluating the condition of river basins, more reliable estimates can be obtained by ensuring that sampling is conducted in different hydrological situations and also in some tributaries potentially affected by AS soils.

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**Appendix.** Number of water samples taken for each parameter at different sampling sites during the period 2009–2011. Alk = alkalinity, Acid = acidity.

Site	Code	pH	EC	Alk	Acid	Al	Fe	Mn	Cd	Ni	SO <sub>4</sub> <sup>2-</sup>	COD	Colour
Ahmaoja	PY3A	3	3				3					3	3
Haapajoki													
downstream	H1A	22	22	9	8	9	10	4	1	1	10	5	5
upstream	H1B	9	9	8	7	8	5	3	1	1	8	1	4
Hanhioja	SI2C	4	4									4	4
Huopakinojan mittapato	PA2A	5	4										
Ispinäoja	PI2C	4	4				4	4			1	4	
Jahtavisneva, 787-tie	PY4C	1	1										
Jouttioja	H2C	1	1										
Järvinevan laskuoja	SI2G	1	1										
Kaartisoja	M2A	17	16	1	1	1	1	1			1		1
Karkulahdenoja	PY4D	3	3										
Kauniinkorvenoja	L2D	10	9										
Kettusaarenoja	SI4A	1	1										
Kilpuanoja	PY3B	3	3				3					3	3
Kipsuanoja	SI3A	16	12	1	1	1	1	1			1		1
Koiraoja	SI3C	6	6										
Kotakankaan kanava	SI3B	1	1										
Levänoja	SI4B	227	16	4	4	4	4	4			4		4
Liminkaoja													
downstream	L1A	19	18	9	8	9	6	4	1	1	9	1	5
upstream	L1B	12	11	8	7	8	5	3	1	1	8	1	4
Luohuanjoki													
downstream	SI2E	320	82	46	22	42	25	33	33	33	22	30	45
upstream	SI2F	226	34	9	8	9	6	4	1	1	9	14	18
Majavaoja													
downstream	M1A	36	16	9	8	9	6	4	1	1	9	1	5
upstream	M1B	51	6	6	6	6	3	1	1	1	6		2

continued

## Appendix. Continued.

Site	Code	pH	EC	Alk	Acid	Al	Fe	Mn	Cd	Ni	SO <sub>4</sub> <sup>2-</sup>	COD	Colour
Murkonaavan oja	O2A	2	2										
Mäntyoja	PI2B	8	8				4				1	4	
Niemenrämenoja	PY5A	1		1	1	1	1						
Nälkäneva	SI4C	1		1	1	1	1						
Ohtuanoja	SI2B	39	35	1	1	1	1	1			1	23	24
Olkijoki													
downstream	O1A	37	33	24	17	10	21	5	1	1	17	15	20
upstream	O1B	11	8	8	7	8	5	3	1	1	8	1	4
Pahapuro	PY4J	1	1										
Parhalahdenoja	L2A	4	3										
Pattijoki													
downstream	PA1A	37	35	25	8	9	22	4	1	1	9	15	21
upstream	PA1B	9	9	8	7	8	5	1	1	1	1	1	4
Pesuanoja	SI2H	17	17				8					16	16
Peuraoja	SI3G	4	4									4	4
Piehinginjoki													
downstream	PI1A	35	33	24	17	9	21	4	1	1	17	15	20
upstream	PI1B	17	13	9	8	9	9	3	1	1	9	5	8
Piipsanjoki	PY2B	4	4				3					5	4
Poikajoki													
Haapajoki	H2A	4	4										
Piehinginjoki	PI2A	10	10				4				1	4	
Pyhäjoki													
downstream	PY1A	820	85	60	12	58	56	46	45	45	45	57	62
upstream	PY1B	19	15	8	6	8	8	1	1	1	1	5	7
Riitaoja	SI3D	10	10	2	2	2	2	2			2		2
Rukkisenoja													
downstream	SI3E	321	46	12	12	12	7	4	1	1	10	9	14
upstream	SI3F	423	27	9	9	9	5	5	1	1	9		5
Ruonaoja	M2B	2	2										
Saarilampioja	PY4E	4	4										
Sarpaoja	PY4G	3	3										
Saukonoja	PY4F	5	5										
Siikajoki													
downstream	SI1A	810	88	75	27	69	59	49	41	41	60	58	66
upstream	S1B	69	63	42	22	41	9	33	33	33	22	37	41
Sivupuro													
Kopistontie	L2E	4	4										
Koskela	O2B	3											
Sortinoja	L2B	1	1										
Sysilampioja	PY4A	1	1										
Talusoja													
downstream	PY3C	372	23	8	8	8	5	5	1	1	8		5
upstream	PY3D	302	20	8	8	8	5	4	1	1	7		4
Toholanoja													
downstream	PY3E	407	23	8	8	8	5	5	1	1	8		5
upstream	PY3F	12	9	2	2	2	2	1	1	1	2		1
Tuohikorvenoja	PY4I	1	1										
Tuoreenmaanoja	H2B	9	9				8				2	8	
Tyypäkinoja	L2C	1	1										
Tähjänjoki	PY2A	26	24	4	4	4	11	1	1	1	3	9	10
Uitonoja	PY4B	2	2										
Vaihoja	L3A	1	1										
Vesinevanoja	SI2D	4	4										
Vihanninjoki	PY2C	12	12				9					12	12
Vuolunoja	SI2A	17	16	1	1	1	1	1			1	6	7
Vähäoja	PY4H	9	5	4	4	4	4						