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Tuomas Saarinen

TEMPORAL AND SPATIAL VARIATION IN THE STATUS OF ACID RIVERS AND POTENTIAL PREVENTION METHODS OF AS SOIL-RELATED LEACHING IN PEATLAND FORESTRY

UNIVERSITY OF OULU GRADUATE SCHOOL;
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Abstract

This thesis examines temporal and spatial variations in the status of different rivers and streams of western Finland in terms of acidity and sources of acid load derived from the catchment area. It also examines the monitoring of acid runoff water derived from maintenance drainage in peatland forestry and suggests potential mitigation methods.

A total of 17 river basins of different sizes in western Finland were selected for study, including rivers affected by both drainage of agricultural AS soils and forested peatlands. Old data from 1911–1931 were available, but most data were from the 1960s onwards and were taken from the HERTTA database. During 2009–2011, pH and conductivity measurements and water sampling were conducted. Biological monitoring for ecological classification was conducted in the Sanginjoki river system during 2008 and 2009. Three peatland forestry sites were selected to study acid leaching via pH and EC measurements and water sampling. Fluctuations in groundwater level in different drainage conditions were simulated and acid leaching was investigated in laboratory experiments in order to replicate a situation where the groundwater level drops and allows oxidation of sulphidic materials.

It was found that river pH decreased and metal concentrations increased with runoff. The highest acidity observed coincided with periods of intense drainage in the 1970s and after dry summers in the past decade. Together with pH, electric conductivity and sulphate in river water were identified as suitable indicators of AS soils in a catchment, because they directly respond to acid leaching derived from AS soils. Acidity derived from organic acids was clearly observed in catchments dominated by forested peatlands and wetlands. Temporal and spatial variations in ecological status were observed, but monitoring at whole-catchment scale and during consecutive years is needed to increase the reliability of the results.

Simulations on the potential effects of maintenance drainage in peatland forestry on runoff water quality showed a clear risk of oxidation of sulphidic materials during dry summers. This can be prevented mainly by avoiding too deep drainage. Knowledge of the hydrochemical impacts of acidic load derived from AS soils and drained peatlands is necessary for land use planning and sustainable water management of river basins affected by these soils.

Keywords: acid sulphate soils, acidity, drainage, ecological status, leaching, peatlands

Saarinen, Tuomas, Happamien jokivesistöjen tilan ajallinen ja paikallinen vaihtelu sekä kunnostusojituskohteilta huuhtoutuvan happamuuden ehkäisy suldifipitoisilla turvemailla.
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Tiivistelmä

Tutkimuksessa tarkastellaan Suomen länsirannikon happamuudesta kärsivien jokivesistöjen tilan ajallista ja paikallista vaihtelua. Tutkimuskohteena on sekä happamien sulfaattimaiden että ojitettujen turvemaiden jokivesistöjä. Tutkimuksessa tarkastellaan myös sulfidipitoisilta metsäojitetuilta turvemailta valuvaa happamuutta sekä ehdotetaan tällaisille kohteille soveltuvia keinoja huuhtouman ehkäisemiseksi.

Tutkimukseen valittiin 17 erikokoista jokivesistöä, joiden valuma-alueella on sekä happamia sulfaattimaita että metsäojitettuja turvemaita. Varhaisin väitöskirjaan sisällytetty aineisto on vuosilta 1911–1931. HERTTA-tietokannasta poimittiin aineistoa happamuusmuuttujista 1960-luvulta alkaen. Vuosina 2009–2011 suoritettiin pH- ja sähkönjohtavuusmittauksia sekä otettiin vesinäytteitä Siika- ja Pyhäjoen valuma-alueen joista sekä näiden välissä sijaitsevien pienempien valuma-alueiden joista. Ekologisen tilan selvittämiseksi otettiin biologiset näytteet Sanginjoen valuma-alueen joista ja puroista vuosien 2008 ja 2009 aikana. Kunnostusojituskohteilla seurattiin pH:n ja sähkönjohtavuuden muutoksia kokoojaojissa sekä otettiin vesinäytteitä. Pohjaveden pinnan vaihtelua selvitettiin sekä kenttämittauksilla että mallinnuksen avulla. Laboratoriokokeen avulla selvitettiin sulfidien hapettumista.

Metallipitoisuudet nousivat ja pH laski valumien kasvaessa. 1970-luvulla toteutetut salaojitukset heijastuivat jokien happamuuden kasvuna. Myös viime vuosikymmenen kuivat kesät näkyivät veden happamuuden lisääntymisenä syksyn ylivirtaamatilanteissa. Veden pH, sähkönjohtavuus sekä sulfaatti ilmensivät happamien sulfaattimaiden esiintymistä valuma-alueella. Orgaanisista hapoista peräisin olevaa happamuutta havaittiin valuma-alueilla, joilla on runsaasti ojitettuja turvemaita. Ekologisen tilan ajallisen ja paikallisen vaihtelun vuoksi seurantaa tulisi toteuttaa peräkkäisinä vuosina sisällyttäen tarkasteluun valuma-alueen eri jokia ja puroja.

Kunnostusojitukset voivat aiheuttaa happamuutta, jos ojitus ulottuu sulfidikerrokseen. Riski on olemassa poikkeuksellisen kuivina kesinä. Sulfidien hapettumista voidaan ehkäistä välttämällä liian syvien ojien kaivamista. Maatalouskäytössä olevilta happamilta sulfaattimailta ja ojitetuilta turvemailta peräisin olevan huuhtouman vaikutukset tulee tuntea, jotta valuma-alueiden maankäyttöä ja vesiensuojelua voidaan toteuttaa tehokkaasti.

Asiasanat: ekologinen tila, happamat sulfaattimaat, happamuus, huuhtoutuminen, kuivatus, turvemaat

To my lovely family

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Laukaa, March 2013 Tuomas Saarinen

List of symbols and abbreviations

Al	Aluminium
AS soil	Acid sulphate soil
Ca	Calcium
Cd	Cadmium
Co	Cobalt
COD_{Mn}	Chemical oxygen demand
Cr	Chromium
Cu	Copper
DOC	Dissolved organic carbon
EC	Electrical conductivity
EQR	Ecological quality ratio
ET	Evapotranspiration
Fe	Iron
FMI	Finnish Meteorological Institute
GW	Groundwater
HERTTA	Database of Finnish Environment Institute
Ksat	Saturated hydraulic conductivity
Mn	Manganese
Ni	Nickel
P	Precipitation
RBMP	River basin management planning
S	Sulphur
SD	Standard deviation
SO_4^{2-}	Sulphate
SYKE	Finnish Environment Institute
TOC	Total organic carbon
WFD	EU Water Framework Directive
Zn	Zinc

List of original publications

This thesis is based on the following original publications, which are referred to in the text by their Roman numerals.

I Saarinen T, Vuori K-M, Alasaarela E & Kløve 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. Science of the Total Environment 408(21): 5019–5027.

II Mykrä H, Saarinen T, Tolkkinen M, McFarland B, Hämäläinen H, Martinmäki K & Kløve B (2012) Spatial and temporal variability of diatom and macroinvertebrate communities: How representative are ecological classifications within a river system? Ecological Indicators 18: 208–217.

III Saarinen T & Kløve B (2012) Past and future seasonal variation in pH and metal concentrations in runoff from river basins on acid sulphate soils in Western Finland. Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering 47(11): 1614–1625.

IV Saarinen T, Celebi A & Kløve B Links between river water acidity, land use and hydrology. Boreal Environment Research (In press).

V Saarinen T, Mohämmädighävam S, Marttila H & Kløve B (2013) Impact of peatland forestry on runoff water quality in areas with sulphide–bearing sediments; how to prevent acid surges. Forest Ecology and Management 293: 17–28.

The author's contribution to publications

I: Designed the study with co-authors, conducted the data analyses and wrote the paper. Kari-Matti Vuori and Bjørn Kløve critically commented on all versions of the manuscript.

II: Conducted the field work with Heikki Mykrä and Mikko Tolkkinen and data analyses together with co-authors. Heikki Mykrä mainly wrote the paper.

III: Designed the study based on the comments of Kari-Matti Vuori, conducted field work and data analyses and wrote the paper. Bjørn Kløve critically commented on all versions of the manuscript.

IV: Designed the study with Bjørn Kløve, conducted the field work and data analyses together with Ahmet Celebi and wrote the paper.

V: Designed the study, conducted the field work and data analyses with co-authors and wrote the paper with co-authors.

Contents

1 Introduction

1.1 Background of the study

High loading of acidity is one of the key factors together with increased nitrogen and phosphorus loading which has degraded the ecological status of a number of rivers in Finland (Åström & Björklund 1996, Niemi & Raateland 2007). Several rivers in western Finland are classified as having moderate or even poor ecological status, as the mean annual pH minimum is often below 5.5, which is the boundary between moderate and good status in the national guidance for River Basin Management Planning (RBMP) based on the EU Water Framework Directive (EU WFD) (Vuori *et al.* 2009). Increased episodic acidification of rivers, especially during high runoff periods, has a number of negative effects on the quality and function of the whole river ecosystem (Urho *et al.* 1990, Sammut *et al.* 1995, Hudd & Kjellman 2002, Åström *et al.* 2005, Roos & Åström 2005a, 2005b, Sutela *et al.* 2010). Thus it also has significant impacts on recreational use of water bodies. This increased acidity of rivers mainly derives from drained agricultural and forested peatlands and acid sulphate (AS) soils in the catchments (Edén *et al.* 1999, Mattson *et al.* 2007). After the Second World War, Finland needed industrial growth and a major programme was begun to drain peatlands in order to improve forest growth and to dredge Finnish rivers for timber transport purposes. By the year 2000, about 50% (5.7 million ha) of the total peatland area in Finland had been drained for agriculture, forestry and peat mining (Turunen 2008). Drainage operations on pristine peatlands were most intensive during the 1960s and 1970s, with the peak occurring in the late 1960s (Ylitalo 2011). Nowadays no drainage of pristine peatlands is conducted, but only maintenance drainage operations.

Achieving and maintaining good ecological status of the water in streams and rivers is the key issue in the EU WFD. The assessment of the chemical and ecological quality of surface waters should be based on sufficient and representative information on watersheds. More environmentally sustainable planning of land use in catchments influenced by AS soils and prevention methods of acid loading are needed. The effects of a changing future climate (predicted warmer and drier summers) should also be taken into account when assessing preventative actions against river acidification.

The main reason for episodic acidification of a number of rivers in western Finland is intensive drainage of sulphidic soils in their catchment areas (Roos & Åström 2005b). These sediments can be found all over the world (total area approximately 17 million ha) (Andriesse & Menswoort 2006). There are about 4.5 million ha of sulphidic soils in Africa, 6.5 million ha in Asia, 3 million ha in Australia and 2.8 million ha in Latin America. Within Europe, Finland has the highest incidence of sulphide-bearing sediments. Aarnio (1928) was first noticed the presence of black iron sulphide-rich sediments during geological soil mappings in agricultural area of Ostrobothnia in Western Finland. Local mappings of acid sulphate soils have been carried out by Purokoski (1959), Erviö (1975) and Palko (1994). Yli-Halla *et al.* (1999) estimated the area of cultivated AS soils in Finland that meets the criteria of US Soil Taxonomy or the FAO Unesco classification (pH < 3.5 or < 4 and/or sulphidic materials within 150 or 125 cm, respectively), to be 60 000–130 000 ha, while using broader national criteria, Puustinen *et al.* (1994) suggested there are probably about 336 000 ha of AS soils in coastal areas of Finland. These sediments (mainly consisting of iron (Fe) sulphides) are rich in sulphur (S) (up to 3% of dry weight) and were formed naturally during the Holocene (8000–4000 years ago), in the brackish Litorina period of the Baltic Sea. Due to the drop in groundwater (GW) level as a consequence of postglacial isostatic land uplift, these sediments have emerged above sea level. According to Johansson *et al.* (2004), absolute land uplift varies between 3.1–9 mm $year^{-1}$, being highest in the middle of the western coast (the Vaasa region). Thereafter, contact with atmospheric oxygen has ultimately led to the formation of AS soils with extremely low pH (below 4) as a consequence of oxidation processes (van Breemen 1973). The end-products of these oxidation processes are Fe (II) and sulphuric acid, which cause a severe increase in acidity in the soil (van Breemen 1973, Hartikainen & Yli-Halla 1986, Ritsema *et al.* 2000). Acidic conditions contribute to the dissolution of various metals (e.g. Al, Cd, Co, Ni and Zn), which ultimately leads to the formation of acid-rich and metal-rich pore water in the soil. During high runoff, this leaches to watercourses (Palko 1994, Åström & Björklund 1997, Joukainen & Yli-Halla 2003, Sohlenius & Öborn 2004). According to present knowledge, human–derived drainage operations (e.g. subsurface drainage) are mainly responsible for fast and intensive oxidation of sulphidic materials because of deep field drainage (down to 2 m) and oxidation may occur even down to near 3 m (Joukainen & Yli-Halla 2003, Boman *et al.* 2010). Similar effects are produced by black schists, which are sulphur-rich deposits (median S concentration 5–11%) in bedrock. These can be found at higher altitudes than sulphidic materials and are thus a problem in inland areas of Finland (Airo & Loukola-Ruskeeniemi 2004, Herranen 2010).

Increased dissolved organic carbon (DOC) concentrations are mainly derived from peatlands in catchment areas (Kortelainen & Saukkonen 1995). The natural organic acids leached from the catchment area have been found to contribute strongly to increased river acidity (Kortelainen & Saukkonen, 1995, Mattsson *et al.* 2007). Thus, because of the significant proportion (about 30% of land area) of peatlands in their catchment areas, Finnish watercourses are naturally acidic (median pH 5.9) (Kortelainen & Mannio 1988, Lahermo *et al.* 1996, Turunen 2008). The proportion of peatlands in forestry areas is 34% in the country as a whole but is higher in some regions, for example in Northern Ostrobothnia the proportion is 52% (Ylitalo 2011). In this inventory, there was no criterion for the minimum depth of the peat layer, but mire plants as a proportion of the whole surface vegetation comprised 75%. In addition, the overall storage of alkalinity in the catchment areas is quite poor because of the lime-poor composition of the mineral base (Kortelainen 1993).

In addition to the above-mentioned acidity sources, the increase in sulphur and nitrogen deposition following the rapid growth of industrialisation in the 1960s caused surface water acidification, which damaged aquatic ecosystems throughout Northern Europe (Wright *et al.* 1976, Rosenqvist 1978, Rosseland & Henriksen 1990, Kämäri *et al.* 1991, Gorham 1998). Since the early 1980s, atmospheric pollution has had a considerable impact, especially in lakes. As a result of emission reduction policies in the 1990s deposition declined markedly, which contributed to rapid recovery of previously acidified Finnish lakes (Forsius *et al.* 2003, Vuorenmaa 2004). Due to the geological characteristics (peatlands, AS soils and black schist) of catchments in addition to atmospheric deposition, it is sometimes challenging and complex to distinguish the sources of acidification.

Since the 1990s, more attention has been paid to research into river water protection from acidification due to the significant effects of drainage activities in catchment areas. It is important to know the exact sources and leaching mechanisms of acidic loading in boreal streams so that restoration methods can be targeted accurately and cost-effectively. Hydrochemical studies have been conducted related to leaching of acidity and metals from AS soils due to drainage and/or climate variations (e.g. Alasaarela & Heinonen 1984, Åström & Åström 1997, Edén *et al.* 1999, Roos & Åström 2005b, Nyberg *et al.* 2012). However, only few studies have focused on long-term seasonal and spatial variations in water acidity and metals in large areas with different land use characteristics.

Furthermore, little research has been concentrated into the potential effects of climate on leaching of acidity-related elements from AS soils. Some studies have been carried out in small catchments in Finland, but only rarely in large river basins. River pH and metal concentrations will probably be different in future because of increased leaching owing to the predicted climate change.

The function of river ecological communities is strongly influenced by habitat characteristics and water quality, which is dependent on, among other factors and land cover and land use in the catchment area (Liljaniemi *et al.* 2002, Soininen & Könönen 2004). For accurate evaluation of the ecological status of rivers, it is important to have reliable and representative results of ecological classification from the whole catchment scale, including tributaries. There are some sources of uncertainties which have to be taken into account in classification. There have only been few studies of the temporal variability in river communities in streams altered by human disturbances, whereas pristine streams have been better studied (Feio *et al.* 2010, Nichols *et al.* 2010, Smuckler & Vis 2011). The ecological classification system used in RBMP is mainly suitable for large and medium-sized rivers, but there is currently a lack of an equivalent system for smaller streams. There is also a lack of empirical parameters that take better account of different stressor factors, such as increased acidity.

Drainage of AS soils for agriculture is thought to be mainly responsible for the acidification of rivers with AS soils in their catchment area (Maa- ja metsätalousministeriö 2009). Thus most studies to date have concentrated on the effects and potential prevention of acid loads in agriculture. However, in some cases maintenance drainage for peatland forestry may have severe local impacts on water quality if the drained area comprises a significant proportion of the catchment area and if there are sulphidic materials in the mineral soil fraction. Despite the importance of massive peat drainage operations in risk AS soil areas and their clear potential links to acid leaching, studies on the role and impacts of maintenance drainage on the acid load from drained peatland areas with sulphidic materials in subsoil are lacking.

1.2 Leaching processes and environmental impacts of acidic load

The acidification of rivers is dependent on a number of factors. These include soil characteristics and land use, since the intensity of drainage operations and the proportion of AS soils and peatlands in the catchment area strongly affect the acidification status of rivers (e.g. Edén *et al.* 1999, Roos & Åström 2005b). The natural buffering capacity owing to e.g. geological factors (amount of lime minerals in bedrock) can counteract the acidification of river water (Lahermo 1991). Another important group is climatological factors (amount of precipitation and evapotranspiration), which affect the intensity of sulphide oxidation processes in the soil and thus directly have effects on water acidification (Green *et al.* 2006, MacDonald *et al.* 2007, Österholm & Åström 2008).

Sulphide-bearing sediments were originally formed by microbial sulphate reduction processes in anaerobic conditions in seawater sediments (Connell & Patric 1968, Berner 1984). This sulphate reduction process can be presented with following reaction: $8SO_4^{2-} + 2Fe_2O_3 + 15C + 7H_2O \rightarrow 4FeS_2 + 14HCO_3^{-} + CO_3^{2-}$. Bacteria used organic carbon as their energy source and as a consequence of these reactions, sulphate (SO_4^{2-}) in seawater was reduced to sulphide (S^{2-}). Sulphide sulphur (S^{2-}) reacted with several metals, mainly with Fe, and various metal sulphides were produced, e.g. mackinawite (FeS), greigite (Fe_3S_4) and pyrite (FeS_2) (Boman 2008). Sulphide-bearing sediments usually have a fine-grained texture, a black colour indicating the presence of metastable iron sulphide (FeS), a high concentration of sulphide sulphur (about 1% of dry weight) and a high amount of organic matter (> 6% of dry weight) (Palko 1994, Åström & Björklund 1997). In anaerobic, waterlogged conditions, the sediments stay in reduced form and thus are called potential acid sulphate soils with circumneutral pH (van Breemen 1973). Because of the contact with atmospheric oxygen resulting from isostatic land uplift, sulphidic materials were oxidised with complex oxidation reactions and AS soils were formed. The overall reaction of oxidation of monosulphide can be presented as: $4FeS + 9O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 4H_2SO_4$ and oxidation of pyrite as: $4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4$. O_2 is primary oxidant at circumneutral pH values, because Fe^{3+} usually precipitates as Fe–hydroxides [$Fe(OH)_3$] (van Breemen 1973). However, the Fe^{3+} ion can be an oxidant in extreme acidic conditions (pH < 3.5) because of high Fe(III) solubility in low pH and favourable conditions for the catalysing bacterial species *Thiobacillus ferrooxidans* (van Breemen 1982). Following these oxidation processes, a dramatic drop in pH from 6–7 to less than 4.5 or even 3.5 has been observed (e.g. Joukainen & Yli-Halla 2003). Oxidation of FeS produces Fe^{2+} ions and increased acidity of soil promotes dissolution of metals in the soil matrix (metal sulphides and metal-bearing minerals such as aluminosilicates) into pore water. The colour of the soil also becomes lighter (brownish or light grey). Oxidation processes mainly take place during summer, when the GW level drops and allows penetration of atmospheric O_2 into soil and the soil temperature is favourable for soil microbes.

Leaching of the compounds produced causes deterioration in water quality (low pH and high metal concentrations) and ecological damage during high runoff conditions, especially during autumn and spring (e.g. Palko 1994, Åström & Björklund 1995, Hudd & Kjellman 2002, MacDonald *et al.* 2007, Fältmarsch *et al.* 2008, Sutela *et al.* 2010). Metal leaching from AS soils during the period 1978–2002 is estimated to be 10–100 times greater than the entire load produced by Finnish industry (Sundström *et al.* 2002). Occasional high acidity periods in rivers may become common in future due to predicted climate change. Groundwater levels may potentially drop due to higher evapotranspiration in summer and reduced spring snowmelt (Okkonen & Kløve 2010). During summer droughts, oxidation of sulphides may increase and thus also mobilisation of metals and acidity in AS soils (Österholm & Åström 2008).

Coniferous forests and peatlands are important contributors of organic acidity to watercourses in boreal catchments because of the large export of organic acids (Kortelainen *et al.* 1989, Mattsson *et al.* 2005, 2007). Climate change and changes in land use may increase the leaching of humic acids and thus contribute further to surface water acidification (Mattsson *et al.* 2009). However, the ability to increase the buffering capacity against acidification of humic substances in water system is well known (e.g. Hruška *et al.* 2003, Evans *et al.* 2008). When bicarbonate buffering is depressed due to the input of strong acids, the role of organic anions in controlling buffering reactions becomes more important.

In peatland forest areas, the peat layer is usually thicker than in agricultural areas but the peat density is usually lower. Forestry is usually situated in upland areas, where sulphidic materials are found in deeper soil horizons compared with coastal agricultural soils (Palko & Ruokanen 1994). The actual impacts of acidity are thus probably minor in peatland forestry compared with those of drainage in agriculture, especially owing to the lower drainage intensity (lower GW level) in forestry. Faster leaching has also been observed for subsurface drains than for open ditches (Palko & Weppling 1994). However, peatland forestry may have significant local impacts if the drained area comprises a significant proportion of the catchment area and sulphidic materials are located close to the soil surface. Especially after dry summers, runoff water acidification may occur because of increased oxidation processes.

Drainage operations can increase runoff water pH, according to several studies (e.g. Prévost *et al.* 1999, Åström *et al.* 2001b, Joensuu *et al.* 2002). This is the situation in soils with a shallow peat layer (< 80 cm of soil surface) and no sulphidic materials in the underlying mineral soil because of intensive flushing effects of groundwater to the ditches. However, drainage operations cause increasing acidity because of increased leaching of humic acid in areas with thick *Sphagnum* peat, where drainage depth does not extend to the mineral layer (Sallantaus 1986). Furthermore, if there are sulphidic materials in the mineral soil under the peat layer, these can potentially be oxidised, causing a dramatic drop in the pH of runoff water (Sallantaus 1986).

Acid sulphate soils are suitable for cultivation because of their fine-grained texture. However, problems related to plant growth have begun to arise since the early 1900s, when acid salts first emerged in the plough layer of the soil (Kivinen 1938, Erviö & Palko 1984). Deep drainage has been suggested to prevent this rise of acid salts into surface soil layers (Purokoski 1959). In addition, liming of the soil to safeguard crop production activities has been recommended. Nowadays, it is well-known that during high flow periods the combined effects of low pH (< 5.5) and high metal concentrations induce both direct and indirect toxic responses in several species of fish (Urho *et al.* 1990, Vuorinen *et al.* 1993, Vuorinen *et al.* 1998, Sutela *et al.* 2010). These responses include disturbances of ion balance, unsuccessful reproduction and even massive fish kills. In particular, dissolved aluminium (Al^{3+}) can easily precipitate onto the alkaline surface of fish gills as $Al(OH)_3$, disturbing respiration (Driscoll *et al.* 1980). The most vulnerable organisms to acidity are newly hatched fish and spawning usually overlaps with runoff peaks during spring and autumn (Vuorinen *et al.* 1993, Hudd & Leskelä 1998). In an early study conducted by Kivinen (1944), acid leaching from AS soils was recognised as the reason for fish kills. In the river Kyrönjoki, the first extensive fish kill event was recorded in 1834 (Suupohja *et al.* 1973). However, because of intensive drainage of AS soils, massive fish kills have occurred more regularly since the 1970s. The most recent high acidity period, in late autumn 2006 and early winter 2007, caused extensive fish kills in several rivers in western Finland. High acidity also disturbs other aquatic taxa and some decline in species richness, biomass and depletion of sensitive species of macroinvertebrates has been reported (Fältmarsch *et al.* 2008). Morphological deformation, disruption of ion regulation and damage to the respiratory organs of caddis larvae because of increased acidity have been reported (Vuori 1995). In addition to these ecological impacts, high water acidity can cause damage to infrastructure (corrosion of metals) and human exposure to metals via the food web (Roos & Åström 2006, Fältmarsch *et al.* 2008).

1.3 Mitigation practices to reduce the effect of acid leaching

For rivers likely to be affected by acid leaching from AS soils, there are generally two main strategies for mitigation of acid leaching: 1) Prevention of acid leaching by having environmentally safe drainage practices in the catchment area, thus avoiding contact between atmospheric oxygen and sulphidic materials, and 2) Use of treatment methods to counteract any negative environmental impacts that have already occurred (Ministry of Agriculture and Forestry and Ministry of Environment 2011). Most of the acidity is derived from artificial drainage practices in the catchment area, when oxidation can be exceptionally fast (Österholm 2005, Boman *et al.* 2008, 2010). Thus the development and implementation of environmentally sustainable methods in forestry, agriculture and peat harvesting is necessary for reaching or maintaining good status of watercourses. Drainage of AS soils for farming purposes potentially significantly affects acidification of rivers in AS areas because of the deeper drainage potential of subsurface drainage, but drainage practices for peatland forestry may also be important and are the main focus of this thesis.

Using environmentally safe drainage practices to avoid oxidation of sulphidic materials in the subsoil may be challenging in future, especially because of predicted drier summers due to climate change. In agriculture, subsurface drainage is a more efficient drainage method than open ditches, because of greater benefits relating both to crop growth (deeper drainage potential) and reduced leaching of suspended solids and nutrients (Turtola & Paajanen 1995). However, it has been estimated that leaching acidity is about five-fold higher for subsurface drainage than for open drainage during the first eight years after drainage (Palko 1994). In controlled drainage, it is possible to control the GW level of the field by using control wells. This means that during dry periods in summer, GW level can be maintained as high as possible, while during autumn and spring the GW level can be lower because of the lower risk of oxidation (Österholm *et al.* 2005). Good maintenance of controlled drainage is necessary for optimal functioning, but potentially drier summers in future pose a challenge because of increased evapotranspiration, which lowers GW level (Vehviläinen & Huttunen 1997). Thus, controlled drainage alone may not be sufficient to achieve less acidic runoff water, and pumping of supplementary water into control wells may be needed during dry summer periods (Joukainen & Yli-Halla 2003). However, the availability of supplementary water may be problematic in some cases, and thus the costs may be relatively high.

In peatland forestry, the effective mitigation practices to avoid the negative effects of acid runoff are mainly unknown. During maintenance drainage operations (ditch clearing and supplementary ditching), it can be assumed that it is important not to exceed the original drainage depth in areas with sulphidic materials in mineral soil. Lowering of the GW level into mineral soil and further oxidation of sulphidic materials can thereby be prevented (Dent & Pons 1995, Indraratna *et al.* 1995, Minh *et al.* 1998). The risks of oxidation of sulphidic materials may be high in areas with a thin peat layer. Thus some water protection methods, such as detention basins, might be impracticable in these risk areas because they have to be dug deep into mineral soil and thus may create a risk of oxidation of sulphidic materials (Maa- ja metsätalousministeriö 2009). Intensive ditching should be avoided in the most risky areas to minimise the leaching of acidity and metals into watercourses. In theory, controlled weirs installed in the main ditch network outlet could be used to prevent GW level drops into sulphidic materials during dry summer periods. According to simulations by Blunden & Indraratna (2000), formation of acidity in soil decreased by 75% even at 10 m distance from the drain when a weir was used for maintaining higher water levels in the drain. However these simulations were conducted for an agricultural area. In peatland forestry, runoff control methods have successfully been used to decrease concentrations of suspended solids and nutrients (N and P) (Marttila & Kløve 2010).

Lime-filter dams have been tested in practice at peatland forestry sites in the Sanginjoki catchment area, which is located close to the city of Oulu (Tertsunen *et al.* 2012). The objective was to neutralise runoff waters derived from drained peatland forestry sites. These acid waters are mainly derived from organic acids of peat. According to analyses of samples taken from the lower and upper part of the dam structures, the pH increase was 0.8 units on average, with alkalinity of 0.29 mmol L^{-1} and a decrease in acidity of 0.16 mmol L^{-1} on average. No detectable changes in pH were observed during the second monitoring year, but monitoring has only been running for two years. Thus, this method should be tested during different runoff periods (also in high runoff) to ensure optimal functioning of the structures. The function of pipe dams in decreasing the velocity of runoff water has also been tested in the Sanginjoki area by using constructed and unconstructed areas. The purpose of these structures is to limit and smooth runoff peaks by increasing the water storage capacity of drained peatland areas. The results showed that the concentration of acidity-related variables was not significantly different between the unconstructed (normal drainage) and constructed (drainage with pipe dams) peatland areas (Tertsunen *et al.* 2012). However, that study was conducted in peatland areas with no AS soil impact and the effects of retention of runoff waters in AS soil-affected areas remain to be determined.

Liming of soil and/or of acidified waters is one of the most debated remedial methods. It may not solve the real underlying problem, but can be used as a first aid tool to increase the buffering capacity of watercourses. The purpose of liming in this case is to improve water buffering capacity and thus elicit positive responses in fish populations (Henrikcson *et al.* 1995). However, liming has been documented to decrease concentrations of inorganic aluminium, which is very toxic to fish (Andrén *et al.* 2001). In streams, liming can potentially be used only in some limited cases of ecological importance. For example, in Norway successful liming of surface waters has observed as positive chemical and biological responses of the surface waters and catchment (Rosseland & Hindar 1988). In AS soils, the effects of adding agricultural lime are limited because the lime is rapidly consumed by the high acidity of these soils. As a result of aluminium hydrolysis (Al is transported upwards via capillary forces), H^+- ions are released in limed layer with higher pH. If there are high amounts of acidity and low amounts of buffering agents in the soil, it would also be very difficult to achieve the target effects of soil liming in such cases (Åström *et al.* 2007). According to Palko & Weppling (1994), the liming effect is better in subsoil (20–40 cm) than in the plough layer (0–20 cm), because the high content of organic matter in the plough layer reduces the neutralisation effect. However, according to Österholm & Åström (2002), liming does not significantly contribute to decreasing the acidity of subsoil because of the limited leaching of lime below the plough layer.

1.4 Objectives of the study

The main objective of this thesis was to estimate temporal and spatial variations in the status of different rivers and streams in western Finland (from south-western Finland to Lapland) in terms of acidity and sources of acid load derived from the catchment area. Other objectives were to examine monitoring of acid runoff water derived from maintenance drainage in peatland forestry and to devise potential mitigation methods.

Acidity-related variables of rivers affected by different land cover and land use characteristics were studied. These included long-term seasonal changes (temporal variation), spatial variations and the effects of hydrological, climatological and land cover and land use characteristics on acidic load derived from the catchment area. Rivers other than those affected by AS soils were also included, to obtain new information of the acidity of these rivers in a broader scale (acidity derived from organic acids from peatlands). One main focus for the investigation of spatial variation in acidity-related variables was to estimate how these results could be used as a supportive method in mapping of AS soils. Whole catchment-scale analysis was related to ecological classification and the effects of different stressors in ecological communities in river suffering from episodic acidification during high runoff periods. In addition, the impacts of maintenance drainage in peatland forestry and ways to prevent acidic load from drained peatland area were investigated. Similar investigations of runoff water acidity in peatland forestry related to areas of sulphidic materials in subsoil have not been published previously.

Estimation of the influence of past and present climate and land use (drainage) on acidic load was the main aim, and this was achieved by investigating long-term and seasonal variations in acidity-related variables. Variations in pH, alkalinity, COD_{Mn} and colour values in Finnish coastal rivers during the period 1961–2007 were studied in relation to land use and climate–related variables and different proportions of AS soils in the catchment area. In addition, variations in alkalinity, COD_{Mn}, were studied in the period 1913–1931, to examine the potential impacts of drainage on river alkalinity and pH. River pH was also compared against runoff, precipitation and temperature (Paper I).

In investigations of ecological classification, assessments were made of temporal (inter-annual) and spatial variations (main channel and tributaries) in classification results and predictable relationships to gradients in major stressors (e.g. pH) were determined. Variations in the status classification of stream biological communities were assessed in a whole–catchment analysis. The study was conducted in a medium-sized boreal humic river, Sanginjoki, which suffers from episodic acidification derived from different sources (drained peatlands, AS soils, black schist in bedrock) resulting from drainage actions in the catchment area (Paper II).

Past and future trends in metal concentrations and pH in rivers affected by AS soils were investigated. In this study, the role of climate-related variables (precipitation, temperature, runoff and evaporation) in explaining temporal and seasonal variations in pH and metals (Al, Cd, Cr, Fe, Ni and Zn) was determined in some major rivers affected by AS soils. Estimates of future changes in these acidity–related variables were made using regression models according to the calculated discharge scenarios (Paper III).

The contribution of different land cover and land use types to water acidity in different parts of the river basin was investigated. The study was conducted in eight different watercourses in north-western Finland. Other rivers that were not potentially affected by AS soils were included in this study. In two large river basins (Siikajoki and Pyhäjoki), the downstream area was monitored, while extensive monitoring was carried out in smaller river basins. Different hydrological situations were also taken into account when estimating the leaching processes from catchment areas (Paper IV).

The quality of runoff water (acidity-related variables) derived from maintenance drainage areas in peatland forestry was determined in areas affected by sulphidic materials in subsoil. In addition, potential impacts on GW level of different drainage practices and/or of extremely dry conditions when the GW level falls to the mineral layer, promoting oxidation of sulphidic materials in subsoil, were studied. This study was conducted in three peatland forestry sites situated in north-western Finland (Luohuanjoki river basin). Runoff water was studied by using both manual and automated measurement data. In addition, the potential effects of maintenance drainage were estimated in laboratory leaching experiments and in theoretical simulations using the DRAINMOD model. The reason for these investigations was to take into account the situation when the GW level falls below the peat layer (Paper V).

2 Description of study areas

2.1 River basins

A total of 17 river basins of different sizes in Finland, from the south-west coast up to Lapland, were selected for the study (Fig. 1). The Sanginjoki river is the lowermost tributary of the River Oulujoki (Paper II), while all other rivers studied flow into Gulf of Bothnia.

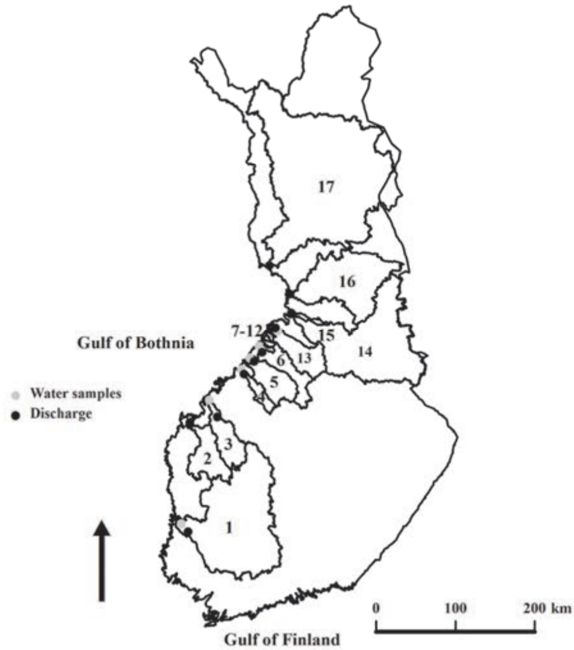

Fig. 1. Locations of the river basins studied in this thesis (©Maanmittauslaitos permission no. 7/MML/09). Code numbers for each river are presented in Table 1.

The river basins studied vary in terms of size, land cover and land use characteristics (Table 1). Because of the lack of accurate mapping of AS soils, their proportion was roughly estimated by using mapping carried out by Puustinen (1994). The proportion of agricultural land is highest in the Kyrönjoki and Lapuanjoki river basins, where 22.7–25.6% of the total catchment area is covered by agricultural land. The Kokemäenjoki and Oulujoki river basins have the highest proportion of watercourses of all river basins studied.

Table 1. Land cover and land use in the 17 river basins studied.

River basin	Code	Drainage area, km^2	Constructed areas, %	Agriculture, %	Forests in mineral soil, %	Forests in peatlands, %	Wetlands, open stand, %	Peat harvesting areas, %	Water-courses, %
Kokemäenjoki	1	27046	6.4	16.2	53.2	10.1	3.1	0.2	10.1
Kyrönjoki	2	4923	5.4	25.6	43.3	15.4	8.6	0.2	1.4
Lapuanjoki	3	4122	5	22.7	44.6	16.8	7.8	0.2	2.8
Lestijoki	4	1373	2.6	11.3	44.2	20.5	15.3	0.1	6.1
Kalajoki	5	4247	3.5	17.1	46.9	22.7	7.5	0.2	1.9
Pyhäjoki	6	3712	3.2	11.8	45.1	26.2	8.4	0.2	5.2
Liminkaoja	7	187	1.9	6.3	54.6	28.7	7.7	0.2	0.7
Piehinginjoki	8	176	1.3	2.4	47.8	30.6	17.2	0.2	0.6
Haapajoki	9	90	3.5	9.2	53.4	23.3	5.2	0.4	5.1
Pattijoki	10	141	8.5	13.7	52.0	18.4	6.9	0.3	0.2
Olkijoki	11	68	3.4	12	45.8	27.2	9.5	1.6	0.5
Majavaoja	12	97	1	8.2	47.6	31.4	11.5	0.2	0.1
Siikajoki	13	4318	2	10.2	33.6	33.5	18.2	0.2	2.3
Oulujoki	14	22515	1.9	2.7	47.3	21.4	14.4	0.2	12.1
Sanginjoki	15	400	1.8	2.1	41.6	28.4	23.1	0.09	2.9
Iijoki	16	14191	1.2	1.8	49.3	17.5	24.1	0.1	6
Kemijoki	17	49467	0.8	0.9	57.1	13.7	23	0.06	4.5

The size of the river basins varies between 68 and 49 467 km^2, so that each size class according to river typology used in RBMP was represented in the studies. The river basins are mainly characterised by substantial peatlands (proportion of peatlands > 25%), but the river Kokemäenjoki has been typified as a mineral soil river according to the river typology of Finland (Vuori *et al.* 2006). A significant proportion of each river basin is situated below the 80 m isoline above sea level, which is the approximate boundary of the former Litorina seashore. AS soils are located within several of these river basins, including the hot–spot area of Central Western Finland (river basins Kyrönjoki and Lapuanjoki). Further details of land use and hydrology in the different river basins can be found in Papers I–IV.

Annual mean temperature ranges between 4.4 °C in the south and 1.2 °C in the north, while the sum of precipitation is 581 mm yr^{-1} in the south and 517 mm yr^{-1} in the north. Annual maximum water equivalent of snow is 95 mm in the south and 179 mm in the north. During the period 1980–2011, mean discharge in the large rivers Kokemäenjoki, Oulujoki, Iijoki and Kemijoki varied between 171–569 m^3 s^{-1}, being highest in Kemijoki and lowest in Iijoki. In other rivers mean discharge varied between 12–43 m^3 s^{-1}, being highest in Kyrönjoki and lowest in Lestijoki. In the small river Pattijoki, mean discharge was 1.5 m^3 s^{-1}. In other small rivers no discharge data were available.

2.2 Peatland forestry sites

The peatland forestry sites investigated in this study are located in the Luohuanjoki river basin (area 352 km^2), which is one of the tributaries of the River Siikajoki in north-west Finland. Three study sites were selected based on mapping of potential sulphide–bearing sediments using aerogeophysical data (aerogeophysical mapping of resistivity) and soil data produced by the Geological Survey of Finland (GTK). All three sites were situated in downstream areas of the Luohuanjoki river basin (Fig. 2).

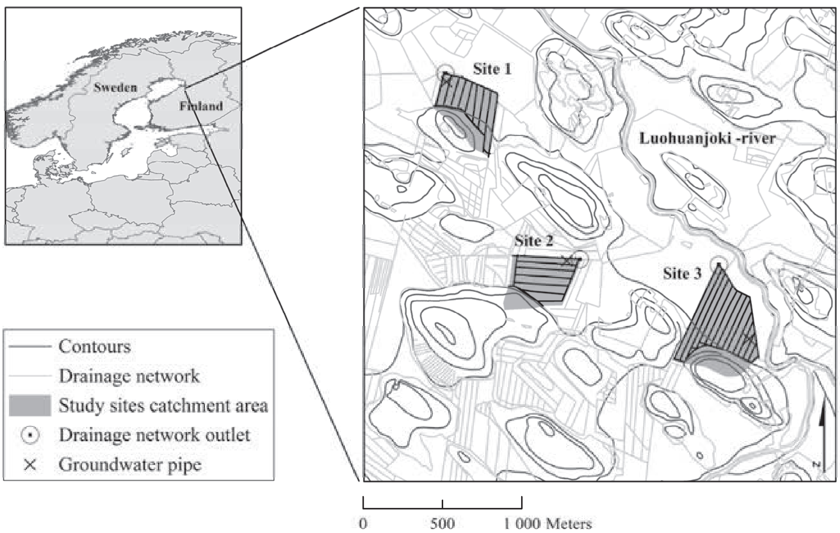

Fig. 2. Location of peatland forestry sites 1–3 in the Luohuanjoki river basin. © Maanmittauslaitos permission no. 7/MML/09 (V, published by permission of Elsevier).

Initial drainage (open ditches) of these peatland forestry areas was carried out in 1971–1972 (sites 1 and 2) or 1974–1976 (site 3). The area drained and the total catchment area was 10 and 13.8 ha, respectively, at site 1, 8.5 and 12.1 ha at site 2, and 13 and 18.7 ha at site 3. In all areas, maintenance drainage (ditch clearing) was carried out in autumn 2006 (sites 2 and 3) or spring 2007 (site 1). Surface drainage at the sites follows a systematic pattern, with open ditches at 40 m spacing and a mean drainage depth of approximately 1 m in lateral ditches, which are connected to the ditch network outlet. All the ditches are connected to a major outlet that discharges into a ditch network outlet connected to the Luohuanjoki river. All sites are pine mires with good or moderately productive forest dominated by Scots pine (*Pinus sylvestris* L.) and occasional admixture of downy birch (*Betula pubescens* Erhr.) and Norway spruce (*Picea abies* L.). At site 1, the proportion of Scots pine was 59% and the proportion of Norway spruce 41% and total stem volume was 131 m^3 ha^{-1}. At site 2, Scots pine was the dominant species and total stem volume was 13 m^3 ha^{-1}. At site 3, where the stand consisted of 44% Norway spruce, 33% Scots pine and 23% downy birch, total stem volume was 167 m^3 ha^{-1}. Mean annual temperature in the study region is 2.3 ºC and mean annual precipitation 522 mm in the reference period 1960–2010 (FMI).

The thickness of the peat layer is 80, 160 and 90 cm at site 1, 2 and 3, respectively (Fig. 3). Immediately below the peat layer there is a reduced mineral layer containing black-coloured iron monosulphide (FeS)-rich clay or silt at sites 1 and 2. The total sulphur concentration increases immediately below the peat layer and at sites 1 and 2 it was 1.26% and 1.06%, respectively. According to Soil Taxonomy (Soil Survey Staff 2010), sulphidic material starts from 90, 160 and 160 cm below soil surface level at site 1, 2 and 3, respectively. The diagnostic criterion for this is that the pH of incubated sample (8 weeks) should decrease by 0.5 units to a value 4 or less. According to WRB (FAO 1998), sulphur percentage should be at least 0.75% of dry mass and pH of incubated samples at least 4. According to Soil Taxonomy, site 1 can be classified as a Typic Sulfisaprist having sulphidic materials within 100 cm of the soil surface. Sites 2 and 3 are Typic Cryosaprists with sulphidic material at 160 cm below the soil surface. The saturated hydraulic conductivity of the peat layer varies from 259.2 down to 0.06 cm hr^{-1} at site 1, from 180 to 0.43 cm h^{-1} at site 2, and from 129.60 to 0.02 cm hr^{-1} at site 3.

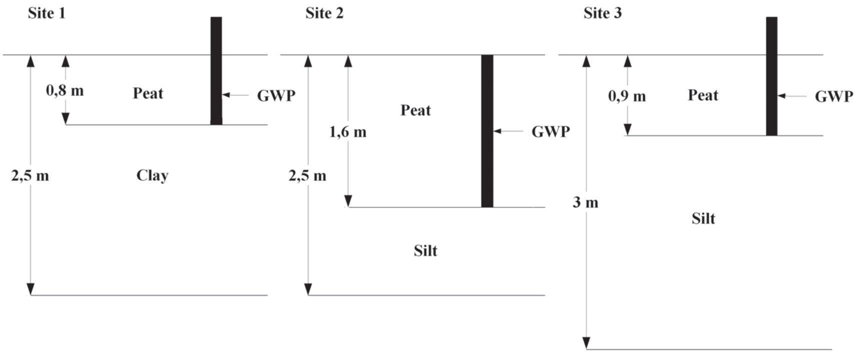

Fig. 3. Schematic diagram of soil layers and location of groundwater pipes (GWP) at peatland forestry sites 1–3 (V, published by permission of Elsevier).

3 Materials and methods

3.1 Water sampling and analyses of acidity-related variables (I, III–IV)

Data on acidity-related variables (pH, electric conductivity, alkalinity, acidity, SO_4^{2-}, COD_{Mn}, colour, total concentrations of metals: Al, Cd, Cr, Ni, Zn, Fe, Mn) were taken from the database of the Finnish Environment Institute (HERTTA) for Papers I, III and partly IV (Table 2). These variables were selected in order to determine the effects of leaching from drained agricultural AS soils, as well as the leaching of organic matter from drained forested peatlands and wetlands. Similar variables have been used e.g. by Åström & Björklund (1995) in a study of AS soil–affected rivers.

Table 2. Different water quality variables studied in Papers I–V.

Variable	Paper I	Paper II	Paper III	Paper IV	Paper V
Alkalinity, mmol L^{-1}	X	X		X	X
Acidity, mmol L^{-1}				X	X
SO_4^{2-}, mg L^{-1}				X	X
pH	X	X	X	X	X
EC, mS m^{-1}		X		X	X
Colour, mg Pt L^{-1}	X	X		X	X
TOC, mg L^{-1}					X
CODMn, mg L^{-1}	X	X		X	
Al, µg L^{-1}		X	X	X	X
Fe, µg L^{-1}		X	X	X	X
Mn, µg L^{-1}				X	X
Cd, µg L^{-1}			X	X	
Cr, µg L^{-1}			X		
Ni, µg L^{-1}			X	X	
Zn, µg L^{-1}			X		X

Data on alkalinity and COD_{Mn} were available for the period 1911–1931 (Holmberg 1935) and from the 1960s on, while data on pH and colour were available from the 1960s (Paper I). Data on metals since the 1990s were taken from HERTTA, because of more frequent sampling. During 1911–1931, the Hydrographic Bureau conducted the first river water quality monitoring in most significant rivers discharging to the Gulf of Bothnia, including Kokemäenjoki, Kyrönjoki, Lapuanjoki, Lestijoki, Kalajoki, Siikajoki, Oulujoki, Iijoki and

Kemijoki, approximately monthly from downstream of each river (Holmberg 1935). Since the 1960s, river water quality has been monitored regularly throughout Finland by the Regional Environment Centres and their predecessors. Since 2010 sampling is conducted by the regional Centres for Economic Development, Transport and the Environment (ELY Centres). Frequency of sampling has varied between years and rivers and more frequent sampling has been conducted during high-flow periods in spring and autumn. The average number of sampling occasions ranges typically between 5 and 20 per year. Sampling has been conducted downstream in each river.

For Paper IV, water sampling (alkalinity, acidity, SO_4^{2-}, COD_{Mn}, TOC, colour, total concentrations of metals: Al, Cd, Cr, Ni, Zn, Fe, Mn) and manual measurements (pH and EC) were conducted in different hydrological conditions at 71 sites in eight river basins of different sizes, including those of Pyhäjoki and Siikajoki and smaller river basins between those (numbers 6–13, Fig. 1, Table 1) during the period September 2009–November 2011. All these variables indicate acid leaching derived from drainage flushes of AS soils and peatlands (see Section 1.2). Analyses of TOC, COD_{Mn} and colour were conducted in this study to distinguish the leaching from agricultural AS soils more clearly.

All analyses were carried out according to SFS standards in an accredited laboratory of the Finnish Environment Institute. Measurements of pH were carried out with electrometric or ion-selective electrodes in the laboratory or in field conditions. Analyses of alkalinity were conducted by HCl-titration. Methyl orange was used as an indicator during the period 1911–1931. From the beginning of the 1960s until 1972, methyl orange was again used as an indicator if alkalinity value was above 0.1 mmol L^{-1} (Alasaarela & Heinonen 1984). From 1972 on, the potentiometric titration method was used involving titration to pH values of 4.5 and 4.2. At the beginning of the 1990s, metal analyses were mainly conducted with atomic absorption spectroscopy methods (AAS: graphite furnace and flame). Since 1994, inductively coupled plasma techniques (ICP-MS and/or ICP-OES) have been more common. In this thesis, results indicating total metal concentrations (unfiltered samples) were taken from the HERTTA database (Paper III). Water colour analyses were conducted by following method: SFS-EN ISO 7887:1995; Section 4. During 1913–1931 chemical oxygen demand (COD_{Mn}) results were expressed as permanganate consumption ($KMnO_4$). These results were changed to be comparable to present–day results COD_{Mn} with the following formula: $COD_{Mn} = KMnO_4/3.95 + 0.17$ (Niemi & Rekolainen 2009). After this earliest period, titrimetric methods following oxidation with $KMnO_4$ have been used in COD_{Mn} determination (SFS 3036).

In addition to the above-mentioned methods, in Paper IV acidity was analysed with titration methods up to pH value 8.3 according to SFS 3005:1981. SO_4^{2-} was analysed from filtered samples by the ISO 10304-1:2007 method using ion chromatography. TOC analyses were conducted with method SFS-EN 1997. Metal were analysed with method ISO 1185:2007 on unfiltered samples. Manual measurements of the pH and electric conductivity (EC) were made using a Mettler Toledo MP120 meter (Paper IV). Furthermore, in the rivers Siikajoki and Pyhäjoki, continuous measurements of pH (half-hourly intervals) were carried out 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 (Papers III and IV).

Annual maximum, median, minimum and percentiles of alkalinity and pH were calculated for the period 1913–1931, based on data of Holmberg (1935), and for 1961–1970, 1971–1980, 1981–1990, 1991–2001 and 2001–2007 based on data in the HERTTA database (SYKE). For COD_{Mn} and colour, previously mentioned statistical parameters were calculated for 1961–2007 and metal concentrations for 1990–2011. In addition, the monthly medians of alkalinity and pH were calculated for the whole study period (I). Before the analyses, the year was divided into four different 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 (Papers I, III & IV).

3.2 Sampling and analyses of river ecological status (II)

In Paper II, water samples were collected from different streams in the Sanginjoki river basin during October 2008 and 2009 and analysed with methods presented in Section 3.1. Samples of diatom and macroinvertebrates were taken at 10 sites in the main channel of the Sanginjoki river and at nine sites in its main tributaries. These samples were preserved in 70% ethanol in the field. Simultaneously during sampling, stream environmental characteristics were determined. Furthermore, river channel depth and current velocity at 0.6×depth were measured using a velocity meter at 40 random locations along the same transects, during sampling.

The results for biological samples (diatoms and macroinvertebrates) from the Sanginjoki river basin were compared with results from Finnish reference streams (pristine streams with no obvious signs of human impact in the stream channel and riparian zone). The ecological status of each study site was described by calculating the Ecological Quality Ratio (EQR). The EQR values of the different parameters (stressor-specific or community composition) were then compared with environmental characteristics (e.g. water chemistry, pH and land use) for each sampling site. EQRs of type-specific taxa were calculated for diatoms (O/E_{DI}) and macroinvertebrates (O/E_{MI}), which describe taxonomic richness and composition (Hämäläinen *et al.* 2002, Aroviita *et al.* 2008). For diatoms, EQRs were calculated also for Index of Pollution Sensitivity (IPS) (Coste in CEMAGREF 1982) and acidity index for diatoms (ACID) (Andrén & Jarlman 2008). ACID is based on the ratio of acid-sensitive and acid-tolerant diatom taxa (Andrén & Jarlman 2008). For macroinvertebrates, EQRs were calculated also for Average Score Per Taxon (ASPT) (Armitage *et al.* 1983) and Acid Water Indicator Community (AWICsp) (Murphy *et al.* 2013). AWICsp is a new species level acidity index. For each index, the mean values of the EQRs of the reference sites in each river type were used as an expected value. Each site was classified according to EU WFD, the ecological condition classification based on five different quality classes. Details of calculations and analyses are presented in Paper II.

3.3 Hydrological and climatological factors (I, III–IV)

Data on daily river discharge and evaporation for each river was obtained from the HERTTA database (Papers I, III–IV). The discharge data related to the lower reaches of rivers, before they reach the Gulf of Bothnia, and comprised annual and seasonal (spring: April–May and autumn: October–November) means and maximums of discharge at each monitoring site for the period 1961–2007.

The database of the Finnish Meteorological Institute was used to calculate annual and seasonal means and maximum values for temperature, precipitation and water equivalent of snow for each river basin. If there was no weather station in the study catchment, data from a weather station in a neighbouring river basin were used.

Estimation of impacts of climate change on water quality variables (pH, Al, Cd, Ni, Zn) for the rivers Lapuanjoki and Siikajoki used monthly discharge scenarios (2011–2099) provided by the Finnish Environment Institute (SYKE).

The main hypothesis was to study if there is a potentially increase in metal concentrations and decrease in pH when discharges increase in future. Regression equations were calculated where discharge was the explanatory factor and these relationships were used to estimate potential effects in future. Water quality (pH and metal concentrations) in the future was estimated based on regression equations between relationships of discharge and relevant variables (pH, metals). The SYKE discharge scenarios are calculated using future climate predictions (precipitation and temperature). The future climate is an average of 19 global climate model outputs calculated by the Finnish Meteorological Institute using 1971 to 2000 as a reference period and based on the A1B emission scenario.

3.4 Analysis of land use of river basins (IV)

Land cover of each catchment area was determined using CORINE 2006 land cover and land use data produced by the Finnish Environment Institute (resolution 25 m x 25 m). Land cover classes were reclassified into different types (constructed areas, agricultural soils, forests in mineral soil, forests in peat soil, mires and wetlands, peat harvest areas and watercourses) using a GIS programme. Based on the land cover data, each sampling point was classified according to the proportion of peatland as: 1) < 25%, 2) 25–40%, 3) 40–50% and 4) > 50% peatlands. In this classification peatlands included both forests on peat soil and mires and wetlands, but not peatlands in agricultural use. In addition, the river basins were classified according to size as follows: 10–50 km^2, 50–100 km^2, 100–500 km^2 and > 500 km^2. For more details of land use analyses, see Paper IV.

3.5 Peatland forestry sites (V)

3.5.1 Measurements and analyses of water acidity and water level

Water sampling was conducted in the ditch network outlet and groundwater was also sampled (pH and EC) at each peatland forestry site in different hydrological conditions. Simultaneously during sampling, pH and EC in water from the ditch network outlet and groundwater were measured using a Mettler Toledo MP120 meter. The following analyses were carried out according to SFS standards in an accredited laboratory of the Finnish Environment Institute: alkalinity, acidity, SO_4^{2-}, Al, Fe, Mn, Zn, TOC and colour. Loggers for monitoring pH (TruTrack pH–HR Data Logger), electrical conductivity (EC) (Solinst LTC-Levelogger-JUNIOR, model 3001-LTC) and water level (TruTrack WT-HR-1500 Water Height) were installed in the ditch network outlet at each site in spring 2010 to monitor water quality and quantity continuously at 15-minute intervals. In addition, plastic groundwater pipes (diameter 5.7 cm and length of sieve part 1 m) were inserted to the boundary between the peat and mineral layers (Fig. 3). Loggers for monitoring pH and water level were installed into each groundwater pipe. For more details of sampling and measurements, see Paper V.

3.5.2 Soil samples and laboratory experiments

Soil samples were taken using a spiral auger at 10–20 cm intervals from the centre area between two ditches, to a depth of 2.8 m at site 2 and 2.9 m at sites 1 and 3. The soil profile was divided into three layers in each area; peat layer, mineral layer and impermeable layer. Samples were taken from the peat and mineral layers, with 10, 13 and 12 samples at site 1, 2 and 3, respectively. In the transition zone between the peat and mineral layers, samples were taken from both fractions, with the boundaries of different layers estimated with 5 cm accuracy. The pH was measured in the laboratory within 24 hours of sampling and again after 8 weeks of incubation in open plastic jars (SFS-EN 13037). This was done to detect whether there are sulphidic materials in mineral soil, because according to criterion of Soil Taxonomy (Soil Survey Staff 2010) pH value should drop at least 0.5 pH units to a value of 4.0 or less within 8 weeks. Total concentration of sulphur was analysed in each soil sample at an accredited laboratory using the HNO_3/HCl solvent and ICP-OES-method. The saturated hydraulic conductivity (K_{sat}) of the peat layer at each site was measured in situ by a direct–push piezometer (volume 50 cm^3), using the falling head method, at intervals of 0.1 m to a depth of 1.0 m. Information on soil saturated hydraulic conductivity was needed as input data for DRAINMOD modelling (see Section 3.4.3). In addition, undisturbed peat samples were taken in plastic tubes at neighbouring points in two layers, 0.2–0.3 m and 0.4–0.5 m. The centre area between two ditches was used for sampling and a total of two peat profiles were taken per site. In the laboratory, pF curve, water content and unsaturated hydraulic conductivity were determined using the evaporation method (Tamm 2002). In the pF curve, the water storage capacity of different soil types can be observed and this information was needed in DRAINMOD calculations (see Section 3.5.3). To determine the pF curve for subsoil layers beneath the peat deposits, undisturbed soil samples were taken from three depths, 0 m, 0.5 m and 1 m, starting from the interface between peat and subsoil. The soil pF curve was also measured in the laboratory using standard pressure cells.

Oxidation of sulphidic materials and leaching of acid water and metals were tested in laboratory conditions (T = 20 °C). Undisturbed mineral soil samples (4 controls and 4 treatments) were taken from fully saturated soil in plastic columns (diameter 10 cm, height 50 cm) from the edge of the ditch network outlet at site 1. The experiment consisted of three phases: stabilisation, drainage and irrigation. Values of pH and EC were determined in infiltrated water during whole experiment. In the stabilisation phase, soil water was replaced with deionised water so that the conditions were constant (pH and EC values were stabilised) in each sample. Deionised water was used in this experiment because its pH and EC values are relatively close to those of rain water. During drainage, the treatment samples were drained and the volumetric water content of samples was monitored using a Degacon EC-H_2O Soil Moisture Sensor EC-5. During irrigation, samples were taken 1–3 times per week and analysed for pH, EC and following variables: Al, Ca, Cd, Co, Cu, Cr, Fe, Mn, Ni and Zn and SO_4^{2-}. Metals were analysed from unfiltered samples. For more details of these analyses, see Paper V.

3.5.3 Modelling the impacts of drainage

The DRAINMOD model (Skaggs 1980) was used to simulate the effects of drainage and groundwater level in the peatland forestry areas on GW level fluctuations. The model inputs included soil properties, infiltration parameters, drainage system parameters, surface storage, daily maximum and minimum temperature, and daily precipitation. Most important output data of the DRAINMOD model related to this study were included: infiltration for day (cm), evapotranspiration for day (cm) depth of the groundwater at the end of the day (cm), runoff for the day (cm) and total water loss for the day (cm). DRAINMOD was manually calibrated by comparing observed and modelled GW level. Calibration parameters were adjusted on a trial and error basis using daily GW level data. In order to validate the model, the field measurements were divided into two periods. The 2011 data were used to calibrate GW level, while the 2010 data were used to validate GW level. The validated model was used for scenario studies. The impact of drainage intensity was studied for values of 50, 80, 100, 120 and 150 cm depth for lateral ditches and 20, 30, 35, 40, 45 and 50 m spacing between lateral ditches. The aim of this was to estimate environmentally sound options while maintaining sufficient forest growth in the peatlands. In addition, simulations with different depths of controlled weir installed into the ditch network outlet were conducted for site 1 using data from a dry year (2006). The main function of the controlled weir is that it prevents a drop in GW level during dry summers so that sulphidic materials are not exposed to atmospheric oxygen.

3.6 Statistical methods

3.6.1 River water acidity, ecological status and catchment characteristics (I–IV)

Trends in alkalinity and pH during the period 1961–2007 were analysed with the non-parametric Seasonal Kendall trend test, which is robust for outliers and missing data in time series (Hirsch *et al.* 1982). Relationships between the climate- and acidity-related variables were studied using least square regression analysis and curve fit regression method (Papers I & III). Spearman rank correlation was used rather than Pearson correlation to analyse relationships between water quality parameters, climate-related variables and land cover parameters because of the non-normal distribution of the data. The differences between sampling points in main streams were studied using the Mann-Whitney non-parametric U-test.

Pearson correlation was used to calculate agreement of the EQR metrics data (Paper II). Partial regression was used to calculate the relationship between EQR of the parameters measured and environmental parameters. Because of the independency of sampling years, regressions were conducted using redundancy analysis (RDA). Only those variables which explained statistically significantly variation of metrics were selected in the final analysis. This RDA analysis was used to examine the influence of a set of significant variables (in-stream habitat and catchment characteristics, as well as water chemistry and land use) on variations in diatom and macroinvertebrate metrics.

3.6.2 Analyses in peatland forestry sites (V)

Non-parametric Spearman rank correlation was used to analyse relationships between water quality variables and GW level and water level in ditch network outlets, because of the non-normal distribution of the data. Linear regression was used to study relationships between observed and simulated GW level data, in order to estimate the match of the modelled data to the observed data. Weekly means of the replicates (controls and treatments) were calculated from the irrigation phase of the experiment. The Mann-Whitney non-parametric U-test was used to test for differences between controls and treatments in the laboratory experiment, because of the non-normal distribution of the data.

Objective evaluation of the DRAINMOD model was performed by calculating statistical parameters including: average deviation (AD) (James & Burges 1982), average absolute deviation (AAD) (Janssen & Heuberger 1995), Relative Root Mean Square Error (RRMSE) (El-Sadek *et al.* 2003), coefficient of determination (R^2) (El-Sadek *et al.* 2001, 2003, Singh *et al.* 2001, Fernandez *et al.* 2006), and coefficient of efficiency (E) (Nash & Sutcliffe 1970). The E value, a statistical index, was used to judge model performance.

4 Results and discussion

4.1 Rivers studied: Status and trends (I–IV)

4.1.1 Acidity status of the rivers (I–IV)

Certain river basins in Western Finland suffer extensively from episodic acidification derived especially from drainage of AS soils, which is clearly seen also in the results presented in Papers I–IV. In general, alkalinity and pH were highly variable between the rivers. General results (range and median values) for each river studied are presented in the Appendix. Median alkalinity varied between 0.08 and 0.29 mmol L^{-1} and median pH between 5.3 and 6.9. Median EC varied between 4.2 and 15.5 mS m^{-1}. Current analytical methods for alkalinity are in most cases comparable with those studied in 1911–1931, except that usage of methyl orange may provide too high results at very low alkalinity values (Alasaarela & Heinonen 1984). In all rivers median Fe concentration varied between 1800–5150 µg L^{-1}, Al 301–1600 µg L^{-1}, Mn 56–160 µg L^{-1}, Cd 0.02–0.1 µg L^{-1} and Ni 1.6–17 µg L^{-1}. Median concentration of Cr varied between 1.3–1.8 µg L^{-1} and Zn 4–31 µg L^{-1}. Overall, the rivers Kyrönjoki and Lapuanjoki had several–fold higher metal concentrations than other rivers, indicating flushing effects derived especially from AS soils.

When putting new analytical devices into operation, results with old and new devices have been compared and usually those results have been quite consistent in laboratory of Finnish Environment Institute. Thus, results of this thesis conducted during different decades are also reliable in most cases. In metal analyses the newer ICP-MS technique is more sensitive than ICP-OES. This means that the detection limit of ICP-MS is lower than in the ICP-OES technique. When concentrations of metals are lower than the detection limit of ICP-OES, then analyses are repeated with ICP-MS.

In clay soil catchments in particular, metal-bearing phyllosilicates may also increase metal concentrations in river water because of increased runoff of suspended solids (Nyberg *et al.* 2012). In River Paimionjoki, where there was no AS soil impact and high proportion of clay soils in the catchment area, relatively high metal concentrations were observed, and a significant proportion of the metals were estimated to occur in colloidal or particulate form (Nystrand *et al.* 2012). For example, almost 80% of Ni was observed to occur as particulate form, while in some other sites even about 60% of Ni was estimated to occur as dissolved form (Nystrand *et al.* 2012). In this study, only total concentrations of metals were analysed. Mean concentrations of suspended solids (filtered with 0.45 µm filter) were generally higher in the rivers Kyrönjoki (23.5 mg L^{-1}) and Lapuanjoki (21.4 mg L^{-1}) than in Pyhäjoki (14.8 mg L^{-1}) and Siikajoki (18.5 mg L^{-1}) during the period 1990–2011 (HERTTA database). Thus part of the high metal concentrations in the rivers Kyrönjoki and Lapuanjoki is the consequence of the erosion of clay particles (phyllosilicates) and is not directly related to leaching of AS soils. Small clay particles can bind and transport several metals, because of their high adsorption capacity and specific surface area which allows longer reaction time between soil pore water and soil matrix (Parker & Rae 1998). Most of the metal analyses conducted by environmental authorities are on unfiltered samples and thus ecological effects of metals may potentially be overestimated. Median values of COD_{Mn} were 10–34 mg L^{-1} and colour 60–270 mg L^{-1}. Median sulphate concentration was highest in the river Haapajoki (42 mg L^{-1}) and lowest in the rivers Liminkaoja (7 mg L^{-1}) and Piehinginjoki (7 mg L^{-1}), indicating clearly less significant effects of AS soils in latter two river basins (Paper IV).

The largest of the rivers studied can be classified into one of three classes according to the potential occurrence of AS soils in their catchment as estimated by Puustinen *et al.* (1994). The southernmost river, Kokemäenjoki, and the northernmost rivers, Oulujoki, Iijoki and Kemijoki, displayed minor or no effects of AS soils on their water quality. Their pH status was classified as good in the national classification system used in RBMP (Vuori *et al.* 2009), as the pH never decreased below 5.5, which was used as the boundary value between good and moderate ecological status The rivers with minor or moderate AS soil impact (Lestijoki, Kalajoki, Pyhäjoki and Siikajoki) suffered not very often from pH values below the critical level of 5.5. The small streams (Majavaoja, Olkijoki, Pattijoki, Haapajoki, Piehinginjoki and Liminkaoja) also showed low values only occasionally and the pH never decreased below 5. In larger rivers, the pH was generally higher than in tributaries, because of dilution effects in larger amounts of water. In the rivers Kyrönjoki and Lapuanjoki, which are known to be severely affected by AS soils, the pH very frequently decreased below the threshold level used for pH in ecological classification and several-fold higher metal concentrations were observed than in the rivers Pyhäjoki and Siikajoki. Alkalinity was also sometimes completely lost in these rivers. The Sanginjoki river was affected mainly by drained forested peatlands, but probably also by AS soils and black schist, and the pH showed critical decreases, down to even 4.0. It has been observed that if pH decreases below a value of 6, there are significant decreases in fish assemblages (fish species composition and numbers) (Sutela *et al.* 2010). Extensive fish deaths were observed in some of the rivers studied in Papers I–IV during autumn runoff in 2006 after an extremely dry summer.

4.1.2 Variations in ecological status and impacts of acidity (II)

Tributaries generally displayed worse ecological conditions than main channel sites of the Sanginjoki river, although there were temporal variations in the parameters studied. The results of ecological classification were strongly affected by both spatial (differences between sampling sites) and temporal (differences between studied years) factors. In the main channel, measured mean cover of mosses (53%) was higher than in tributaries (20%), indicating better habitat characteristics. The concentrations of organic solids were higher in tributaries (maximum 47 mg L^{-1}) than in the main channel (maximum 6.6 mg L^{-1}). Variations in the classification results were also observed between the two taxonomic groups studied (diatoms and macroinvertebrates). In general, diatoms indicated worse ecological conditions than macroinvertebrates. The main reason for this was differences between the life cycles of these organisms. In contrast to macroinvertebrates, diatoms undergo a rapid life cycle, which contributes to their adaptation to changing environmental conditions (Soininen & Eloranta 2004, Lavoie *et al.* 2008).

One of the significant explanatory factors for the ecological classification was pH, which was generally the leading factor determining species composition in communities in the Sanginjoki river system. As regards measurements of macroinvertebrates in particular, pH best explained variation in stress-related variables (Table 3). Overall, 40–92.5% of the total amount of variation (TVE %) in each parameter was explained by factors where pH was also included. The highest explanatory power was observed in tributaries (TVE = 92.5%).

Table 3. Results of partial Redundancy Analysis (pRDA) showing percentage variation in diatom and macroinvertebrate counts explained by natural (habitat characteristics) and stress-related (water chemistry, land use) variables, and shared component of variation explained by interaction of the two sets of variables, for sites in the main channel and tributaries of the river Sanginjoki. See abbreviations in Section 3.2. SD = standard deviation (II, published by permission of Elsevier).

	TVE (%)	Natural (%)	Stress (%)	Shared (%)
O/E_{DI}				
Main channel	40.0	13.9	13.8	12.3
Velocity				
Depth				
Mean pH				
Tributaries	44.8	44.8	–	–
Depth				
SD particle size				
ACID				
Main channel	50.3	4.1	38.8	7.4
Velocity				
Depth				
Min pH				
COD_{Mn}				
Tributaries	69.5	19.8	33.8	15.9
Depth				
SD macrophytes				
Mean pH				
Organic solids				
O/E_{MI}				
Main channel	40.0	12.8	18.0	9.2
SD depth				
Mean pH				
Tributaries	92.5	27.4	4.8	60.3
% shading				
Mean pH				
AWICsp				
Main channel	18.0	3.8	7.6	6.6
% shading				
Mean pH				
Tributaries	73.9	73.9	–	–
Depth				
Velocity				

In addition to pH, variation in diatom measurements was explained by COD_{Mn} (ACID in main channel) and organic solids (ACID in tributaries). The relationships between pH-specific indices (ACID, AWIC) and pH in the study years showed only weak correlations, which may be explained by the fact that there was annual variation in the acidity responses, while community-scale responses can be long-lasting (Sommer & Hoewitz 2009). This means the latter responses may still reflect the conditions in previous years. Thus in the Sanginjoki river system, pH is not the only regulating factor for ecological communities. Leaching of suspended solids and nutrients (N and P) derived from peatland forestry may also have contributed to the results of ecological classification by causing e.g. eutrophication. The ecological impacts of increased leaching of suspended solids from catchment areas are diverse (e.g. changes in community structure and reduced diversity). These effects have been widely reported and reviewed, e.g. by Wood & Armitage (1997). Complementary information may be limited by using stressor-specific indices in general ecological classification of river systems with multiple stressor variables, because these indices are calibrated against a certain water chemistry variable. To increase the reliability of the ecological classification, it is important to take into account the spatial and temporal variability of the biological communities. Thus, when assessing the conditions of a river, it would be good to allocate resources for sampling the whole river system and not a single affected site in the main channel. In addition, it is important to conduct monitoring during several years in order to get reliable results for classification.

4.1.3 Trends in acidity-related variables in the rivers (I)

Alkalinity was significantly higher in all rivers studied during the period 1913–1931 than from the 1960s onwards. Only the river Kokemäenjoki showed a statistically significant increasing trend for alkalinity and pH since the 1960s, although there was a slightly significant increasing trend in the river Oulujoki as well. However, in the other rivers studied no significant trends were observed and pH status has been quite constant over the decades (Fig. 4).

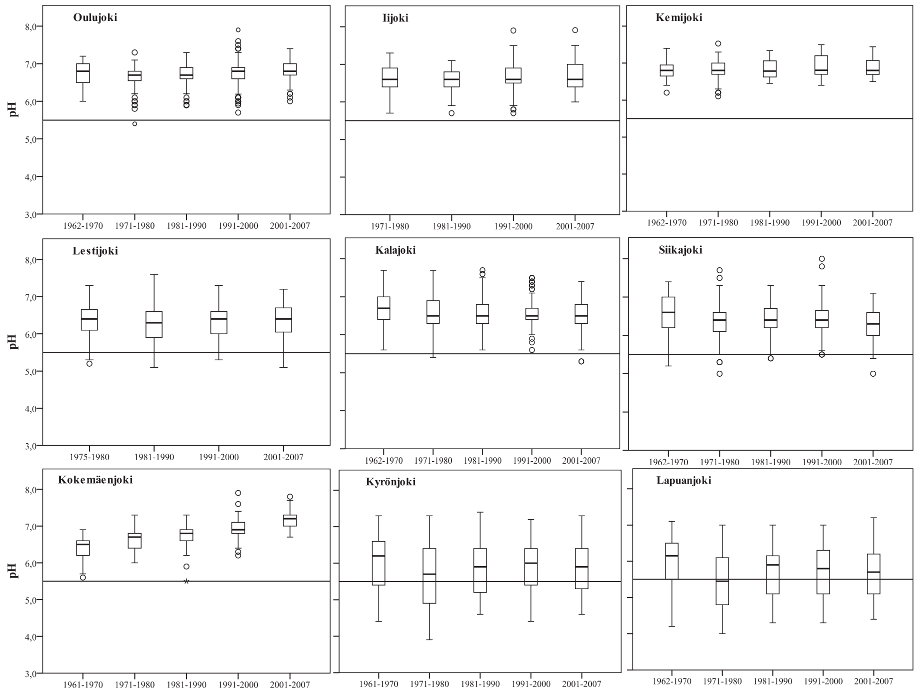

Fig. 4. Median, upper and lower 25th percentiles and minima and maxima for pH in the nine rivers studied in Paper I, 1961–2007. The critical value of pH in ecological classification, 5.5 is indicated by a horizontal line (I, published by permission of Elsevier).

In the 1960s, some low pH values occurred in the highly AS soil-affected rivers Kyrönjoki and Lapuanjoki, with the minimum pH reaching 4 during this time. This is a clear consequence of the dramatic increase in the drainage of AS soils for agriculture since the early 1970s (Hildén & Rapport 1993). Subsurface drainage in particular has increased the leaching rate of acidity and metals because of its extremely high drainage potential, which has increased the oxidation of soil sulphidic materials several-fold compared with open ditches (Palko 1988, Palko & Weppling 1994). Drainage potential can be detected by measuring redox potential of the soil profile. Transition layer is the point when redox potential decreases below zero, where there are anaerobic conditions in soil (Palko 1994). Mainly during the last decade (2000–2011), pH values below 5 have occurred frequently, probably as a result of some extremely dry summers causing intensive oxidation of sulphidic materials in soil (e.g. Österholm &

Åström 2008). This has influenced the runoff water quality during the following winter and even subsequent years, when low pH values have been observed.

4.2 Impacts of catchment characteristics on water acidity (I–IV)

Leaching of acidity from drained agricultural AS soils and peatlands is the main reason for the high acidity and metal concentrations in the rivers studied (Papers I–IV). A large proportion of the river basin areas studied here is drained, which lowers the groundwater level and thus increases the oxidation of sulphidic materials in subsoil several-fold.

In the Kyrönjoki river basin, the proportion of drained arable land with sub-surface drainage techniques increased four-fold from the 1950s to the 1970s (Hildén & Rapport 1993). This is mostly related to increased subsurface drainage in Finland since the 1960s (Åström *et al.* 2005). Land use development in other rivers has probably been similar. During the 1960s and 1970s, river dredging and construction for flood protection and to enable agriculture also contributed to oxidation of sulphidic materials, with increased leaching of acidity and sulphate from the catchment area (Alasaarela 1982, Hildén & Rapport 1993). In the Kyrönjoki river basin, dredging was intensive during the 1930s, 1950s and 1970s (Heikkilä 1991). Excavation of river sediments increases the risk of mobilisation of toxic metals from bottom sediments (Roos & Åström 2005b, Nordmyr *et al.* 2008).

The lowest alkalinity and pH values were observed in the rivers Kyrönjoki and Lapuanjoki, which have a significant proportion of AS soils in their catchment area. Erviö (1975) estimated that about 22% of the total agricultural area is classified as AS soils (classification criterion: pH < 5 at about 40–50 cm below soil surface) in the basin of the river Kyrönjoki. The values of electric conductivity (EC) in the rivers examined in Papers I–IV and the concentrations of SO_4^{2-} and metals (Cd, Ni, Fe and Mn) strongly increased with an increasing proportion of agricultural area in the catchment areas and thus a significant positive correlation was observed (Table 4). This means that leaching is more abundant, especially from agricultural AS soils. Only pH, alkalinity and organic matter (colour/COD_{Mn}) did not show any significant positive correlation with proportion of agriculture in the catchment area.

There was a slightly different pattern for wetlands and forested peatlands (Table 4). Organic matter (colour/COD_{Mn}) was positively correlated with inclusion of wetlands, but not with forested peatlands. This is probably because of increased flushing of groundwater and subsurface water from peatland forestry areas and because of ditching not being carried out in peat but in mineral soil (Åström *et al.* 2001a, 2001b). Between SO_4^{2-} and wetlands, a significant negative correlation was observed. Cadmium concentration was negatively correlated with forested peatland area, but not with wetland area, suggesting that Cd is strongly bound in humic matter and thus only labile in well-oxidised soil (Sohlenius & Öborn 2004). Aluminium, cadmium and nickel concentrations were observed to be negatively correlated with proportion of peat harvesting sites, as was colour. Manganese concentration and EC were positively correlated with proportion of constructed area. High EC is explained by increased human impact in the catchment area (Niemi & Raateland 2007). A negative correlation was observed between acidity and proportion of watercourses, which is probably the reason for the diluting effects of lakes. Due to the varying proportion of lakes in the catchment areas, the variations in alkalinity and pH were great between the rivers studied in Papers I–IV.

Table 4. Correlation coefficients correlations (r_s, only significant ($p < 0.05$) valus are given) between water quality variables and land cover and land use in the catchment area (data on 71 sampling points included, see details in Paper IV) (IV, published by permission of Boreal Environment Research Publishing Board).

	Constructed areas, %	Agri-culture, %	Forests on mineral soil, %	Forests on peatland, %	Wetlands, %	Peat harvest, %	Water courses, %	Peat-lands, %
MinpH	–	–	–	–	–	–	–	–
Alkalinity	–	–	–	–	–	–	–	–
Aluminium	–	0.38	–	-0.40	-0.40	-0.35	–	-0.37
Acidity	–	0.35	–	–	–	–	-0.43	–
Cadmium	–	0.54	–	-0.49	–	-0.46	–	-0.46
COD_{Mn}	–	–	–	–	0.43	–	–	–
Nickel	–	0.51	–	-0.50	-0.42	-0.40	–	-0.48
Iron	–	0.40	–	–	–	–	–	–
SO4	–	0.56	–	–	-0.35	–	–	–
EC	0.46	0.63	–	-0.35	-0.38	–	–	-0.45
Colour	–	–	-0.36	–	0.36	-0.36	–	0.37
Manganese	0.44	0.72	-0.38	–	–	–	–	–

In some cases, leaching of organic acids mainly contributed to water acidification and TOC concentration is reported to explain up to 67–83% of low pH values

(Kortelainen & Saukkonen 1995). Similar conditions have been reported in other studies with a high proportion of peatlands and low proportion of lakes in the catchment area (e.g. Buffam *et al.* 2008). EC was significantly lower in rivers dominated by peatland forests and wetlands than in rivers with a significant proportion of agriculture and thus probably more risky areas related to leaching of acidity (Paper IV). Humic substances usually have limited dissociation to water and thus do not contribute to EC in water (Niemi & Raateland 2007). This suggests that pH alone is not a sufficient indicator of the occurrence of AS soils, but that EC or sulphate concentration should also be measured, because they readily respond to oxidation processes. Similar conclusions have been reached by Roos & Åström (2005a) and Nyberg *et al.* (2012).Water quality data can thus be used as additional supporting information in AS soil mapping.

4.3 Impacts of climate-related variables on water acidity (I, III–IV)

River water pH and metal concentrations (Al, Cd, Cr, Fe, Ni and Zn) were strongly dependent on the discharge during each season in the four rivers studied (Table 5). Discharge was the most relevant factor to explain the variation in water acidity. The correlation was weak with other climate–related variables. During spring and autumn high runoff periods, the most obvious acidity was observed, and episodic acidification was an annual phenomenon caused by snowmelt in spring and high precipitation in autumn in all rivers studied. This has also been reported in previous studies (e.g. Roos & Åström, 2005a, Nyberg *et al.* 2012).

Table 5. Correlation coefficients (r_s, only significant ($p < 0.01$) valus are given) for the relationships between different variables (concentrations) and discharge (III, published by permission of Taylor & Francis Group).

River	Period of discharge	Al	Cd	Cr	Ni	Zn	Fe	pH
Kyrönjoki	Winter	0.88	0.85	–	0.85	0.84	-0.5	-0.64
Lapuanjoki	Winter	0.87	0.78	–	0.73	0.81	-0.48	-0.68
Pyhäjoki	Winter	0.57	0.58	–	0.56	0.49	0.42	-0.56
Siikajoki	Winter	0.47	0.44	–	0.69	0.46	-0.24	0.38
Kyrönjoki	Spring	0.65	–	0.67	–	–	0.70	-0.28
Lapuanjoki	Spring	0.65	–	0.69	–	–	0.55	-0.29
Pyhäjoki	Spring	0.54	0.37	0.52	0.2	0.34	0.47	-0.68
Siikajoki	Spring	0.51	0.40	0.54	–	0.28	–	-0.69
Kyrönjoki	Summer	0.56	0.63	–	0.57	0.65	-0.41	-0.57
Lapuanjoki	Summer	0.67	0.59	–	0.55	0.65	-0.44	-0.70
Pyhäjoki	Summer	0.81	0.63	0.71	0.62	0.53	0.45	-0.68
Siikajoki	Summer	0.84	0.47	0.55	0.70	0.58	-0.33	-0.71
Kyrönjoki	Autumn	0.75	0.67	–	0.65	0.64	–	-0.59
Lapuanjoki	Autumn	0.70	0.63	–	0.58	0.57	–	-0.69
Pyhäjoki	Autumn	0.80	0.48	0.59	0.32	0.56	0.64	-0.37
Siikajoki	Autumn	0.63	0.38	0.50	0.46	0.39	–	-0.52

4.3.1 High runoff periods

During autumn, median discharge varied between 18.7 and 37 $m^3\ s^{-1}$ in the four rivers studied (Kyrönjoki, Lapuanjoki, Pyhäjoki and Siikajoki) based on 1962–2010 data. When discharge increased, minimum pH decreased, so there was a negative relationship between these two parameters in each river ($R^2 = 0.26$–0.52, $P < 0.001$) (Fig. 5). In the autumn 2010 peak runoff period, there was strong significant negative relationship between pH and discharge in Siikajoki ($R^2 = 0.93$, $P < 0.001$). More acidic water was thus closely related to increased discharge in high runoff periods.

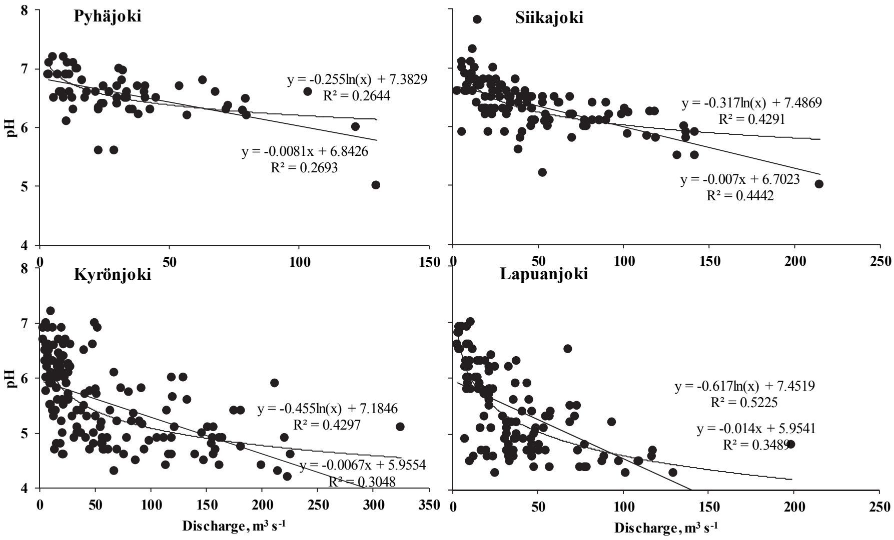

Fig. 5. Relationship between monthly maximum discharge and monthly minimum pH in four Finnish rivers in autumn, based on 1962–2010 data. Linear and logarithmic fittings are presented (III, published by permission of Taylor & Francis Group).

Metal concentrations also increased with discharge and thus significant positive relationships were observed, except for Cd in Siikajoki and Cr in Kyrönjoki and Lapuanjoki. During summer low runoff periods, when GW level lowering allows penetration of atmospheric O_2 into soil, oxidation of iron sulphides in soil begins and redox potential increases. This results in the formation of a large pool of acidity (H_2SO_4 and easily leachable metals) during summertime (Österholm & Åström 2008). This leachable pool of acidity and metals is easily flushed to watercourses, causing increasing acidity. The first runoff peak caused by increased precipitation is usually the most acidic because of high concentrations of acid salts concentrating into the plough layer during the previous long-lasting dry period (Green *et al.* 2006). Dry periods followed by high runoff have been estimated to increase acidity in streams affected by AS soils (e.g. Laudon & Bishop 2002, MacDonald *et al.* 2007, Österholm & Åström 2008). It has been observed that after several moist summers, water acidity may not recover if the preceding summer is extremely dry. This is because of the larger pool of leachable ions in the soil contributing acidity than during normal hydrological years (Österholm & Åström 2008). In Papers I and III, there were no significant relationships between precipitation, temperature and evaporation in the preceding summer and pH and metal concentrations. This can be explained by the infrequent occurrence of dry summers during the study period (mainly in the 2000s). Furthermore, many of the rivers studied are large, with high water volume, and thus the effects of increased oxidation were not clearly apparent in river water acidity. It has been observed by Roos & Åström (2005a) that even when the proportion of AS soils is only 2% of catchment area, there may still be some severe impacts on water quality, especially increasing concentrations of some metals, but not pH. In the northernmost rivers studied in Paper I, with no or minor AS soil impact and low lake percentage, hydrology explained a large proportion of the variation in COD_{Mn} levels during the autumn-winter period. This was indicated by the significant increase in leaching of organic matter from the catchment with increasing river discharge. Previous studies have also found that rivers with catchments dominated by peatlands have increased concentrations of TOC, and thus organic acidity, during autumn (Kortelainen & Saukkonen 1995, Laudon *et al.* 2004).

The relationships between runoff and the variables studied in the 1960–2010 data (pH) and 1990–2010 data (metals) were not as clear in spring as in autumn. Simultaneously with peak runoff (median discharge above 50 m^3 s^{-1}) between mid–April and early May, minimum pH (between 5.3–6) was observed. In Lestijoki, Pyhäjoki and Siikajoki, pH decreased with increased discharge and thus there was a significant negative relationship (R^2 = 0.42, 0.42 and 0.48, respectively, $P < 0.001$), but not e.g. in Kyrönjoki and Lapuanjoki. There was no significant regression between monthly maximum discharge and minimum pH in spring in data for the rivers Kyrönjoki and Lapuanjoki. On the contrary, Al concentrations increased with discharge and thus there was a significant positive correlation only in Kyrönjoki and Lapuanjoki (R^2 = 0.26 and 0.28, respectively). In Finnish coastal area non–AS clay soils are common, which means that the erosion of metal–bearing phyllosilicates may be partly responsible for high Al concentrations (Nyberg *et al.* 2012). Effects of erosion may thus be obvious in these rivers because of higher concentrations of suspended solids than in the rivers Pyhäjoki and Lapuanjoki (see Section 4.1.1). Acidification of soil during oxidation processes causes mobilisation of aluminium from aluminosilicates and in acidic conditions (pH < 4.5) it is more mobile (Fältmarsch *et al.* 2008). There was a clear significant correlation between pH and aluminium, suggesting that abundant Al is leached from AS soils during high runoff (e.g. Åström 1998). High concentrations of toxic soluble Al (i.e. Al^{3+} or $Al(H_2O)_6^{3+}$) forms in acidic water highly contribute to ecological damage (Driscoll *et al.* 1980). During spring, river water acidity is strongly dependent on the conditions in snowmelt waters and frost conditions (Åström & Åström 1997). High amounts of snowmelt waters cause dilution effects and thus leaching water is not as acidic in spring as during autumn after a dry summer (Edén *et al.* 1999). After the melting of soil frost, the acidity of runoff water generally increases because of increased rate of infiltration and flushing out of oxidised compounds (Åström & Björklund 1995). Soil frost conditions have high annual variation and thus the proportion of infiltration in spring runoff compared with surface runoff can be difficult to predict. In some cases, the degree of spring acidification is dependent on the intensity of oxidation in the preceding summer and the amount of precipitation in the autumn (Österholm & Åström 2008).

4.3.2 Low runoff periods

Low discharge (median 10.6–20.0 m^3 s^{-1}) was observed in the rivers Kyrönjoki, Lapuanjoki, Pyhäjoki and Siikajoki during winter and only on a few occasions did discharge exceed 50 m^3 s^{-1} based on 1962–2010 data. In an aerobic incubation experiment Hartikainen & Yli-Halla (1986) measured much lower sulphide oxidation at 5 °C than at room temperature, probably caused by lower microbial activity at lower temperature. On this basis, it was concluded by Palko & Weppling (1995) that only minor oxidation occurs in winter-time. However, according to the results presented in this thesis, high runoff periods may occur even in winter, which may cause increased runoff water acidity. Statistically significant negative relationships between discharge and pH were observed in winter ($R^2 = 0.41$–0.59, $P < 0.001$) (Fig. 6).

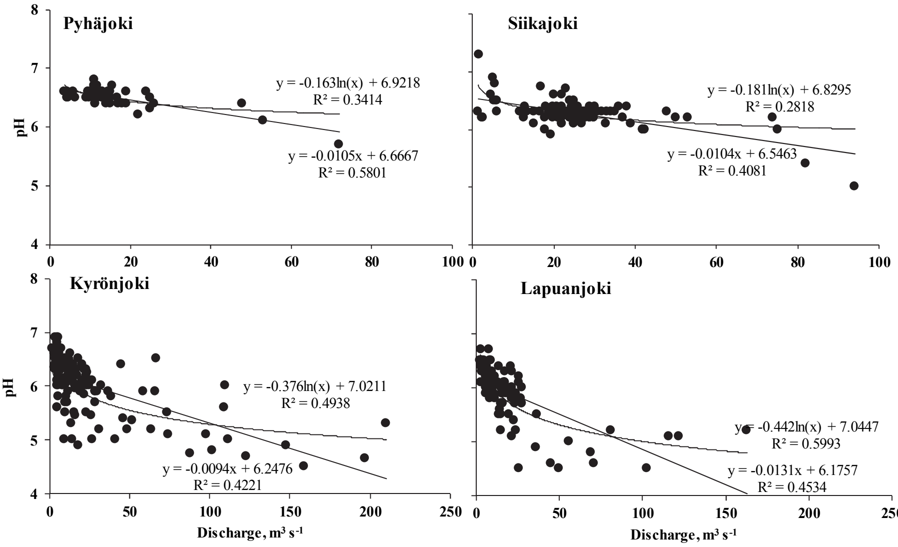

Fig. 6. Relationship between monthly maximum discharge and monthly minimum pH in four Finnish rivers in winter, based on 1962–2010 data. Linear and logarithmic fittings are presented (III, published by permission of Taylor & Francis Group).

During low runoff, several metal concentrations increased with discharge and thus a statistically significant positive relationship was observed in all rivers studied (Kyrönjoki, Lapuanjoki, Pyhäjoki and Siikajoki). Only the river Kyrönjoki displayed a relationship between discharge and Cr concentration (R^2 = 0.6, $P < 0.001$). Increased Cr concentrations during summer are probably a consequence of increased erosion of catchments, which may give high background concentrations of metals (Nyberg *et al.* 2012). Chromium is not easily mobilised in AS soils and when it occurs in dissolved form it usually forms complexes with humic and fulvic acids and thus Cr concentrations are closely related to DOC concentrations of river (Lahermo *et al.* 1996). However, in extremely acid conditions (pH 2.5–3.5), Cr may become mobile (Åström 2001). In all rivers studied in this thesis, there was a significant relationship between maximum discharge and Cd concentration except in Siikajoki. Cadmium, Ni and Zn occur as trace in components and are released upon oxidation of sulphidic materials and remain rather mobile in acid conditions and thus are suitable indicators of the occurrence of AS soils (e.g. Åström 1998, Sohlenius & Öborn 2004). These metals are mobile in AS soils due to increased acidity of the soil and occur mainly in cationic forms in river water (Åström & Corin 2000). Extremely enriched concentrations of these metals in water have been reported in the rivers Teuvanjoki and Maalahdenjoki (Roos & Åström 2005b).

During summer, leaching of acidity and metals from AS soils is minor because of the low precipitation and high evapotranspiration. In the rivers studied in Papers I–IV, median discharge varied between 11.1 and 18.6 $m^3 s^{-1}$ during summer. However, in some cases during summer when precipitation exceeds evapotranspiration, runoff and acid leaching from the catchment area may increase. Thus also during summer acid peaks have been observed. In addition, there was a significant positive relationship between metal concentrations and discharge except for Cd in Siikajoki, Cr in Kyrönjoki and Lapuanjoki, and Zn in Siikajoki. These findings are probably a consequence of increased mobility of metal-bearing phyllosilicates from catchments, because analyses were conducted on unfiltered samples.

4.3.3 Future trends for acidity (III)

It has been concluded that the rate of oxidation of sulphidic materials in soil will decrease over time, because of the lower pool of oxidisable sulphur in soil (Österholm & Åström 2004). However, leaching will continue for several decades and thus have a negative impact on water quality (Österholm & Åström 2002). This can be explained by the decreasing reserves of reduced inorganic sulphur compounds in soil, which would also increase soil pH and result in less efficient dissolution of metals. However, increasing precipitation and temperature as a consequence of climate change may dramatically alter hydrological processes and thus river water quality. According to current climate change scenarios, summer droughts and increased precipitation during autumn are expected to occur in future (Vehviläinen & Huttunen 1997, Jylhä *et al.* 2004). Increased summer droughts can lower GW levels (Okkonen & Kløve 2010) and thus expose reduced sulphidic materials to atmospheric oxygen, enabling intensified acid leaching from AS soils. Increased mobilisation and export of TOC from peatlands to watercourses may also become more common in future (Hongve *et al.* 2004, Vuorenmaa *et al.* 2006, Worrall & Burt 2007, Österholm & Åström 2008, Mattsson *et al.* 2009). According to Sarkkola *et al.* (2009), precipitation is the most important factor to increase TOC export from catchment areas via increased runoff. At present, winter runoff is minor part of the total annual runoff, but in future increased winter runoff will also become common because of increased precipitation in winter due to warmer temperatures (Venäläinen *et al.* 2001, Jylhä *et al.* 2004). In addition, the duration of soil frost will shorten (Vehviläinen *et al.* 2001). These effects will probably result in reduced spring snowmelt, and thus lower summer groundwater levels during summer base flow.

According to the regression model in Paper III, there will probably be a decreasing trend in pH and an increasing trend in metal concentrations in the four Finnish rivers studied during winter. In other seasons, no clear trend was apparent. These results suggest that high autumn runoff with increased acidity will probably be prolonged in future due to warmer winters and limited soil frost conditions in the beginning of winter. Changes in land use practices in AS soil areas will have to be taken into account more carefully when building models, because land use type in AS soil areas is the most important driving factor of the incidence and severity of water acidification. Higher estimated future metal concentrations may also reflect increased erosion with increased runoff from catchment areas. Thus using only climate- and runoff-related variables does not give sufficiently reliable estimates of the future acidic leaching situation. The leaching rate of several metals and sulphur is estimated to increase in future, and it will be a number of years until this leaching reaches environmentally safe level (Österholm & Åström 2004).

Several sources of uncertainty can be encountered when modelling future leaching according to climate change scenarios. Different runoff scenarios may be obtained by using different scenarios for CO_2 emissions. There may also be differences between forecast precipitation and temperature depending on the scenario used. Limited knowledge is available on the effects of evapotranspiration (ET) in a changing climate. Increased atmospheric CO_2 will probably result in reduced stomata opening and thus less transpiration (Penuelas & Matamala 1990). The regression model used in Paper III was not verified, but the purpose was mainly to show potential future trends. Some validation is provided, because all rivers showed similar trends. The exact future trends are not yet well understood, but if drainage and predicted climate change continue as forecast, the recovery of river acidity will be very slow or non-existent. The rivers studied here also differed in their acidity status.

4.4 Leaching of acidity from peatland forestry sites (V)

In order to maintain optimum growth of trees in wet peatland soils, it is necessary to carry out ditch maintenance operations to remove excess water from the root zone. However, if there are sulphidic materials in the soil within ditching depth, increased leaching of acidity and metals may be observed in runoff water during dry periods. This is due to the exposure and oxidation of new sulphidic materials during drainage operations.

During the study period for Paper V (2010–2011), groundwater level, pH and water quality analyses did not show any oxidation of sulphidic materials. The observed GW level remained in the peat layer and thus maintained reduced conditions in the mineral soil (Fig. 7). Overall, pH increased with higher water level and thus probably indicated the buffering capacity of humic substances (Wieder & Lang 1986). However, the individual lowest pH values were measured during high runoff periods. Increased runoff water acidity occurred during autumn high runoff, when pH values in water at the ditch network outlets varied between 4.4 and 7.8. However, in groundwater the median pH was between 4.9 and 5.9 at all study sites and did not show any temporal variation between seasons and years. The low acidity and high alkalinity values at all sites did not indicate increased acid runoff. Furthermore, relatively low sulphate concentrations (median 4–29 mg l^{-1}) were observed at all sites compared with previous findings on AS soils. In small streams in the Larsmo and Öja areas in central western Finland, the median concentration of sulphate is 134 mg L^{-1} (Toivonen & Österholm 2011) and in streams in western Finland 85 mg L^{-1} (Åström & Björklund 1995). According to Lahermo *et al.* (1996), the median concentration of sulphate in 1161 headwater streams in Finland is 3.5 mg L^{-1}, which is lower than in this thesis, perhaps partly because of the different size of streams studied. In contrast, organic matter indicator variables (TOC and colour) were high at all sites, as also reported by Kortelainen & Saukkonen (1995). There was a significant negative correlation between organic matter and pH ($r_s = -0.58$, $P < 0.05$), but not between pH and SO_4^{2-} using all runoff water quality data. There was also a significant correlation ($r_s = 0.82$, $P < 0.001$) between TOC and acidity. This relationship between TOC and/or colour and pH has also observed in many other studies (e.g. Åström & Spiro 2005, Mattsson *et al.* 2007). These results suggest that acidity is derived mainly from humic acids from peat and not from AS soils in these areas. During high runoff periods (spring and autumn), water usually moves in the peat layer and leaching of oxidised humic substances and a simultaneous drop in pH may be observed (McDowell & Likens 1988, Mattsson *et al.* 2005).

The potential effects of drainage operations at peatland forestry sites were estimated using the DRAINMOD model, which measures fluctuations in GW level. The model simulated the pattern of GW level fluctuations with a good degree of accuracy (average deviation < 5 cm) (Fig. 7). The R^2 values were in the range 0.63–0.74 and 0.57–0.68 at site 1 and 3, respectively. At site 2, predicted daily GW level during the validation year did not show good agreement with the observed values ($R^2 = 0.38–0.69$). The most significant source of uncertainty and the sensitivity of the model was the difference between vertical saturated hydraulic conductivity and parameter interactions. Some errors with functioning of water level loggers were also observed at site 2. Missing values for observed GW level were replaced by interpolation.

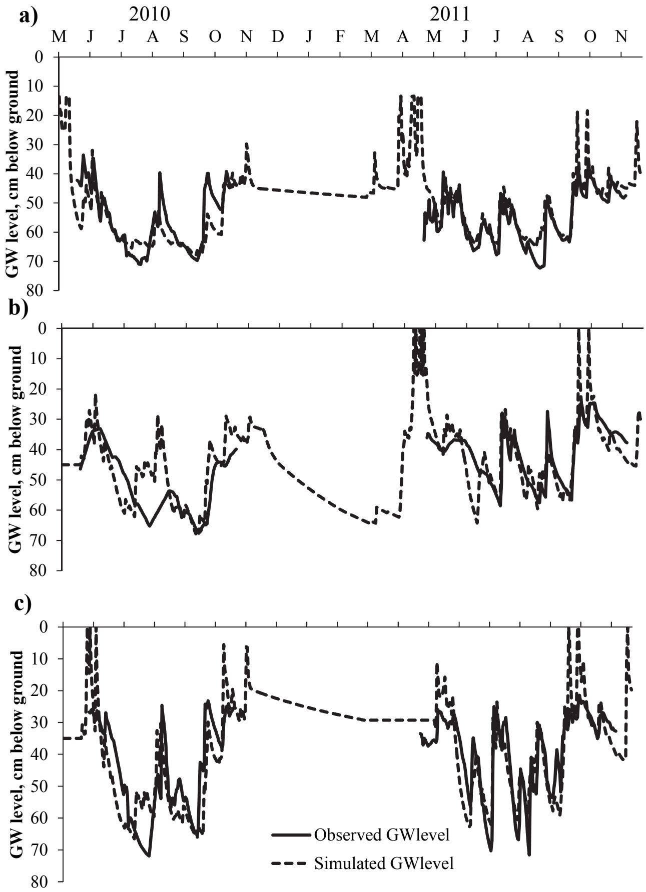

Fig. 7. Observed and simulated GW level at sites 1 (a), 2 (b) and 3 (c) in the period 2010–2011. Boundary between peat and mineral horizons at site 1 80 cm, site 2 160 cm and site 3 90 cm (V, published by permission of Elsevier).

Historical simulations (back to the 1960s) were used to evaluate whether there was a risk of oxidation of sulphidic materials over time. According to these results, the GW levels reached the sulphidic soil materials at site 1 during dry periods in summer on several occasions; in the late 1960s (1968–1969), in the mid-1990s (1995–1996) and in 2006 (Fig. 8). On each occasion, the GW level dropped down to almost 100 cm depth. The pattern of GW level fluctuations at site 3 was quite similar to that at site 1, although it did not fully drop into the sulphidic horizon, except during the dry summer of 2006. At site 2, simulations show that GW level has not dropped down to sulphidic materials. The water balance of forest peatland is strongly regulated by water usage by the tree stand during summer. In central and northern parts of Finland, transpiration by trees during summer is estimated to represent approximately 50% of total evapotranspiration (Sarkkola *et al.* 2012).

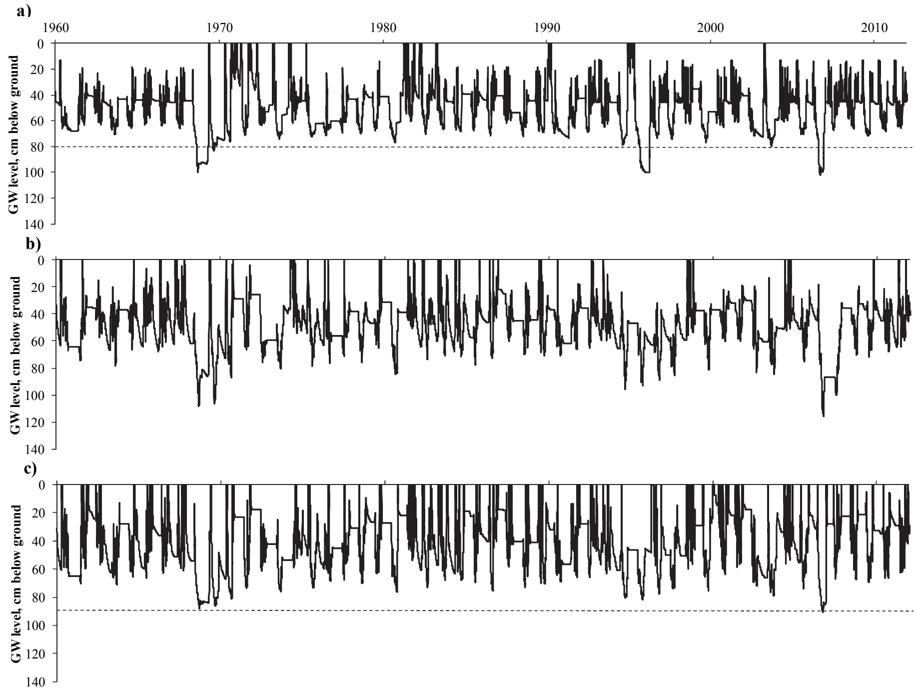

Fig. 8. Simulated GW level at (a) site 1, (b) site 2 and (c) site 3 in the period 1960–2011. Boundary between peat and mineral horizons marked as a horizontal dashed line. At site 2, the boundary is at 160 cm depth (V, published by permission of Elsevier).

According to the results of laboratory experiments, oxidation of sulphidic materials can be remarkably fast, which may happen if the GW level drops into the sulphide layer (Paper V). In Table 6, median and range values are presented for each variable measured in infiltrate water during different phases of the experiment. Infiltrated water was mainly clear during the irrigation phase. In soil samples taken from site 1 (Paper V) in all treatments, the pH dropped down to 2.5 and the concentrations of elements and SO_4^{2-} increased several-fold during the irrigation phase of the experiment. Median concentrations of Cr and Cd were higher (25% and 50%, respectively) in infiltrated water in the irrigation phase compared with the pre-irrigation phase (stabilisation and drainage).

Table 6. Water quality parameters analysed in infiltrated water in the laboratory experiment. Number of samples (n), median and range values are presented. T = treatment (n = 4), C = control (n = 4). Units: elements, µg L^{-1}, SO_4^{2-}, mg L^{-1} and EC, µS cm^{-1} (V, published by permission of Elsevier).

	Stabilisation and drainage						Irrigation					
	n		Median		Range		n		Median		Range	
	T	C	T	C	T	C	T	C	T	C	T	C
Al	8	8	0.5	0.37	0.2–1.4	0.2–0.9	9	9	34.95	0.33	0.5–1010	0.1–1.0
Ca	8	8	1.65	0.86	1.3–2.8	0.6–1.2	9	9	45.15	1.05	6.1–331	0.5–1.8
Cd	8	8	0.002	0.002	0.002–0.002	0.002–0.002	9	9	0.004	0.002	0.002–0.04	0.002–0.002
Co	8	8	0.003	0.003	0.003–0.003	0.003–0.003	9	9	0.155	0.003	0.007–2.0	0.003–0.003
Cu	8	8	0.11	0.02	0.03–0.3	0.01–0.07	9	9	9.46	0.08	0.05–257	0.01–0.8
Cr	8	8	0.01	0.01	0.01–0.01	0.01–0.01	9	9	0.04	0.01	0.01–1.3	0.01–0.01
Fe	8	8	0.94	0.54	0.1–3.6	0.2–1.3	9	9	22.2	0.75	0.03–1630	0.1–2.8
Mn	8	8	0.065	0.028	0.01–0.2	0.005–0.06	9	9	4.39	0.04	0.3–63	0.005–0.2
Ni	8	8	0.076	0.019	0.04–0.3	0.005–0.1	9	9	1.145	0.031	0.14–40.6	0.005–0.3
Zn	8	8	0.16	0.03	0.02–0.9	0.02–0.08	9	9	12.85	0.21	0.32–186	0.02–5.4
SO_4^{2-}	8	8	13.4	5.2	4.3–24.7	4.5–6	9	9	705.5	6.2	60.3–3275	2.6–13.3
pH	116	120	5.7	5.8	4.7–6.1	5.1–6.1	152	152	2.8	5.7	2.5–4.0	3.8–6.6
EC	116	120	48	22	16–130	15–34	152	152	1800	29	201–9820	12–238

As a consequence of artificial drainage, rapid oxidation of metastable iron sulphides will take place and this is estimated to be several-fold faster than oxidation caused by isostatic land uplift (Boman *et al.* 2010). During oxidation processes, Al^{3+} is mobilised and displaces Ca and Mg cations at negatively charged soil sites and thus soil acidity will increase rapidly (Hartikainen & Yli-Halla, 1986). According to e.g. Sohlenius & Öborn (2004), mobility of Cd, Ni, Mn, Co, Zn and to some extent Cu is high in AS soils mostly due to low pH in soil. These metals move down in the oxidised mineral layer and re-precipitate just above the reduced horizon where pH is higher (Åström 1998). Mobility of Cr and Fe is more limited from AS soils (Österholm & Åström 2002, Sohlenius & Öborn 2004). Organic matter content strongly controls mobilisation of Cu, which forms complexes with organic matter (Österholm & Åström 2002). Temperature strongly affects the microbial activity of the soil and thus according to Hartikainen & Yli-Halla (1986) the oxidation rate of sulphides is higher at warmer temperatures. At 20 °C, leaching of sulphur in initially saturated soil conditions was 68% greater than at 5 °C (Hartikainen & Yli-Halla 1986). Leaching of Fe was also greater at warmer temperature, but in samples taken from the oxidised surface horizon temperature had no impact on leaching.

In the laboratory experiment presented in this thesis, the initial conditions of soil samples were fully saturated with potentially no prior oxidation. The experiment was conducted at room temperature (20 °C), and the results for infiltrated water may be different if the experiment is repeated in field conditions (in lower temperature) because of slower oxidation processes in soil. At Ruukki (about 15 km away from the study sites), the mean soil temperature has been only 9.2 °C in 100 cm below ground during June–August for the period 1976–1990 (Heikinheimo & Fougstedt 1992), but if ditches will be dug into mineral soil, the temperature may be higher, which increases oxidation of sulphidic materials. During summer months (June–August) the soil temperature at 20 cm depth from the soil surface has varied between 10.9–14.2 °C (Heikinheimo & Fougstedt 1992). The results of the modelling and leaching experiment suggest that peatland forestry areas with sulphidic materials under the peat layer pose a potential risk of acid leaching in dry summers, even in areas with a thick peat layer.

4.5 Prevention of AS-related acid leaching in peatland forestry by drainage practices (V)

Some general suggestions can be made for mitigating the effects of ditch maintenance on the oxidation of sulphidic materials. The most important precaution is to avoid the oxidation of sulphidic materials in mineral soil. In Paper V, different simulations were made of several drainage practices (drain depth and drain spacing) at different sites. According to the simulations conducted using 2011 data, the GW level at one of these sites (site 1) dropped to the depth of sulphidic materials when conditions exceeded the threshold level (drain spacing 20 m, drain depth 100 cm; drain spacing 30 m, drain depth 120 cm). If the thickness of the peat layer is between 30–80 cm, the recommended drainage depth in peatland forestry varies between 80–100 cm according to general national recommendations (Pohjois–Pohjanmaan metsäkeskus 2005).

According to these recommendations, the distance between lateral ditches should be 40 m and if the original drain spacing is 50 m, new drains should be installed between these. The risk of oxidation of sulphidic materials and further acidification of runoff water should be minor if these recommendations are taken into account. However, if the distance between drains is 25 m, then drain depth should be less than 100 cm to avoid lowering the GW level to the mineral soil and causing sulphide oxidation. Despite these precautions, if extreme droughts similar to that observed in summer 2006 are repeated, soil sulphide oxidation will occur for all different drainage practices according to simulations of the GW level. Thus, when renewing existing ditches or making new ditches in peatland forestry, it is important to ensure that ditch depth does not extend into the mineral soil if sulphidic materials are present. The simulations regarding installing a controlled weir in the ditch network outlet showed that this can shorten the period of low GW level during dry summers. If the controlled weir is equal to the depth of the peat layer, it can shorten the time of oxidation by one month according to simulations made using data for the dry summer 2006. No significant effect on GW level was observed in simulations when weir depth was less than the thickness of the peat layer.

Due to drainage, loss and subsidence of the peat layer as a consequence of increased decomposition of organic matter can be observed. Thus, in risky areas with a thin peat layer and sulphidic materials in mineral soil, oxidation of sulphidic materials might be inevitable if drainage continues. Restoration of these kinds of areas might be the most suitable method for prevention of sulphide oxidation.

5 General conclusions and suggestions for future research

Knowledge of the hydrochemical impacts of acidic load derived from AS soils and ditched peatlands is necessary for land use planning and sustainable water management of river basins affected by these soils. High acidity caused by AS soils is among the most serious factors impairing the ecological status of Finnish rivers and is thus among the major challenges facing water protection in Finland. Potential impacts of future climate change related to leaching of acidity from AS soils should be taken into account in river basin management.

Based on the key results of this study, the following conclusions were drawn:

Land use (drainage) and hydrological conditions (high runoff) both contribute acidity from catchments in AS soil areas. High acidity and metal concentrations have been a frequent phenomenon during spring and autumn high runoff in rivers in Western Finland during past decades. According to trend analyses, the acidity has not changed significantly since the 1960s in several rivers. In some rivers studied during the earliest monitoring period, the situation has even improved. In future, after dry summers and rainy autumns, pH and metal peaks may be expected to occur even during winter because prolonged high runoff in autumn and a shorter period of frost are predicted. This should be taken into account by better planning of environmentally sustainable land use practices in AS soil areas. The higher total metal concentrations observed in the rivers Kyrönjoki and Lapuanjoki partly indicate a potentially higher contribution of erosion (non-AS clay soils) to metal concentrations in these rivers. Thus, dissolved concentrations of metals should be analysed instead of total concentrations to get better estimates of ecological impacts.

Spatial and temporal variations in acidity-related variables and ecological conditions were also observed in individual river systems. In general, acidity and ecological conditions were worse in tributaries than in the main river channel. In catchments used more widely for agriculture, low pH and high EC values in rivers were common. In catchments dominated mainly by forested peatland and wetlands, the EC values of the river water were close to the national average. Thus, pH alone is not a reliable variable to indicate the presence of oxidising sulphidic materials in the catchment and EC at least should be measured, because it directly responds to oxidation of sulphidic materials. To improve the reliability and representativeness of chemical and ecological classifications of river basins, sampling should be conducted at catchment scale and if possible for several years (ecological monitoring), to minimise temporal and spatial variations in the results. The most distinctive tributaries at least, with their human impacts, should be included in the evaluation. In addition, hydrochemical sampling should be conducted in different hydrological conditions to indicate the situation during different runoff periods, because acidity is strongly related to runoff conditions.

Studies on leaching of acidity in peatland areas containing sulphidic materials below the peat showed that any acidity observed in runoff water was derived from organic acids in the peat. This suggests that the risks of acid surges are minor during normal hydrological years, when GW level does not drop below the peat layer down to sulphidic materials. However, maintenance drainage operations in peatland forestry can increase the risk of oxidation of sulphidic materials during dry summers if such minerals occur above drainage depth. Oxidation of sulphidic materials in the subsoil can be extremely fast and can produce large amounts of acid leaching (low pH and high metal concentrations of runoff water).

According to simulations, the best method to minimise oxidation of sulphidic materials is to control the GW level in risk areas with peatland forestry land by adapting drainage practices (avoiding deep drainage). This means that the re-drainage depth should not exceed the original drainage. Another way is to use specific control weirs in ditch network outlets to maintain the GW level above the sulphidic materials during dry summer months. The main aim of these kinds of weirs is to prevent a drop in GW level so that oxidation of sulphides is as minor as possible. In catchments where peatland forestry is a major land use practice, maintenance drainage should include a risk assessment and methods for preventing acid leaching. This means particularly that investigations of the presence of sulphidic materials in subsoil should be conducted when planning drainage. In the most risky areas (sulphidic materials < 80 cm from the soil surface), maintenance drainage should be avoided or a risk assessment should be carried out for each site to ensure that the leaching risks in such areas are minor.

This thesis provides knowledge of past, present and potential situations of future acidity in agricultural AS soil-related rivers and in rivers affected by drained forested peatlands. In addition, practical information on actual acid runoff derived from peatland forestry and potential recommendations on drainage practices are suggested. In future studies, the potential effects of climate change should be studied more precisely in small catchment areas where hydrological processes can be taken into account more accurately. The uncertainty in climate change predictions is high, and must be considered in future studies. The natural variability in weather conditions should be better investigated. More studies related to the ecological impacts of AS soils in watercourses are needed for evaluating the impacts more precisely. More precise whole-catchment studies related to ecological classifications are needed in areas comprising AS soils. The simulations reported in this thesis showed the potential impacts of oxidation of sulphidic materials on runoff water derived from peatland forestry. However, recommendations on drainage practices are based solely on simulation results and thus various drainage and GW control methods need to be tested in practice. More controlled, large-scale studies are also needed to estimate the proportion of peatland forestry in acidity. Furthermore, new water protection methods must be developed to mitigate the effects of acid leaching.

References

Aarnio B (1928) Agrogeologiska Kartor N:o 5. Syd-Österbotten. Statens Markforskningsinstitut.

Airo M-L & Loukola-Ruskeeniemi K (2004) Characterization of sulfide deposits by airborne magnetic and gamma-ray responses in eastern Finland. Ore Geol Rev 24: 67–84.

Alasaarela E (1982) Acidity problems caused by flood control works of the river Kyrönjoki. Publications of the Water Research Institute 49: 3–16. National Board of Waters. Helsinki, Finland.

Alasaarela E & Heinonen P (1984) Alkalinity and chemical oxygen demand in some Finnish Rivers during the periods. Publications of the Water Research Institute, 57: 3–13. National Board of Waters and the Environment. Helsinki, Finland.

Andrén C, Andersson P & Fröberg E (2001) Temporal variations of aluminium fractions in streams in the Delsbo area, Central Sweden. Water Air Soil Poll 130: 1715–1720.

Andrén C & Jarlman A (2008) Benthic diatoms as indicators of acidity in streams. Fund Appl Limnol 173: 237–253.Andriesse W & Van Mensvoort M (2006) Acid sulfate soils: distribution and extent. In: Lal R (ed) Encyclopedia of Soil Science, second ed. New York, Taylor and Francis Group: 14–19.

Armitage PD, Moss D, Wright JF & Furse MT (1983) The performance of a new biological water quality score system based on macroinvertebrates over a wide range of unpolluted running–water sites. Water Res 17: 333–347.

Aroviita J, Koskenniemi E, Kotanen J & Hämäläinen H (2008) A priori typology based prediction of benthic invertebrate fauna for ecological classification of rivers. Environ Manage 42: 894–906.

Åström M (1998) Mobility of Al, P and alkali and alkaline earth metals in acid sulphate soils in Finland. Sci Total Environ 215: 19–30.

Åström M (2001) Effect of widespread severely acidic soils on spatial features and abundance of trace elements in streams. J Geochem Explor 73: 181–191.

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, Aaltonen E & Koivusaari J (2001a). Impact of ditching in a small forested catchment on concentrations of suspended material, organic carbon, hydrogen ions and metals in stream water. Aquat Geochem 7: 57–73.

Åström M, Aaltonen E & Koivusaari J (2001b) Effect of ditching operations on stream–water chemistry in a boreal forested catchment. Sci Total Environ 279: 117–129.

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 (1996) Hydrogeochemistry of a stream draining sulfide–bearing postglacial sediments in Finland. Water Air Soil Poll 89: 233–246.

Åström M & Björklund A (1997) Geochemistry and acidity of sulphide–bearing postglacial sediments of western Finland. Environ Geochem Health 19: 155–164.

Åström M & Corin N (2000) Abundance, sources and speciation of trace elements in humus–rich streams affected by acid sulphate soils. Aquat Geochem 6: 367–383.

Åström M & Spiro B (2005) Sources of acidity and metals in a stream draining acid sulphate soil, till and peat, western Finland, revealed by a hydrochemical and sulphur isotope study. Agr Food Sci 14: 34–43.

Åström M, Sundström R., Holmberg M & Storberg K (2005) pH of streams in western Finland-A perspective from the Middle Ages into the mid 21st century. Agr Food Sci 14: 5–13.

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

Berner RA (1984) Sedimentary pyrite formation: an update. Geochim Cosmochim Ac 48: 605–615.

Blunden BG & Indraratna B (2000) Evaluation of surface and groundwater management strategies for drained sulfidic soil using numerical simulation models. Aust J Soil Res 38: 569–590.

Boman A (2008) Sulphur dynamics in boreal potential and actual acid sulphate soils rich in metastable iron sulphide. PhD thesis. Åbo Akademi University, Dept of Geologi and Mineralogy.

Boman A, Åström M & Fröjdö S (2008) Sulfur dynamics in boreal acid sulfate soils rich in metastable iron sulphide-The role of artificial drainage. Chem Geol 255: 68–77.

Boman A, Fröjdö S, Backlund K & Åström M (2010) Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulphide. Geochim Cosmochim Ac 74: 1268–1281.

Buffam I, Laudon H, Seibert J, Mörth C & Bishop K (2008) Spatial heterogeneity of the spring flood acid pulse in a boreal stream network. Sci Total Environ 407: 708–722.

CEMAGREF (1982) Etude des méthodes biologigues quantitatives d'appréciation de la qualité des eaux. Rapport Division Qualité des Eaux Lyon. Agence financiére de Bassin Rhône – Méditerranée – Corse. Pierre–Bénite, 218 p.

Connell WE & Patric WH (1968) Sulphate reduction in soil: effects of redox potential and pH. Science 159: 76–89.

Dent DL & Pons LJ (1995) A world perspective on acid sulphate soils. Geoderma 67: 263–276.

Driscoll C, Baker J, Bisogni J & Schofield C (1980) Effect of aluminium speciation on fish in dilute acidified waters. Nature 284: 161–164.

Edén P, Weppling K & Jokela (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.

El–Sadek A, Feyen J, Radwan M & El-Quosy D (2003) Modeling water discharge and nitrate leaching using drainmod– GIS technology at small catchment scale. J Irrig Drain 52: 363–381.

El–Sadek A, Radwan M & Feyen J (2001) Numerical analysis of the transport and fate of nitrate in the soil and nitrate leaching to drains. The Scientific World 1: 170–180.

Erviö R (1975) Cultivated sulphate soils in the drainage basin of river Kyrönjoki. Journal of the Scientific Agricultural Society of Finland 47: 550–561.

Erviö R & Palko J (1984) Macronutrient and micronutrient status of cultivated acid sulphate soils at Tupos, Finland. Ann Agric Fenn 23: 121–134.

Evans C, Monteith D, Reynolds B & Clark J (2008) Buffering of recovery from acidification by organic acids. Sci Total Environ 404: 316–325.

FAO (1998) World reference base for soil resources. World soil resources report No. 84. Rome.

Fältmarsch R, Åström M & Vuori K–M. (2008) Environmental risks of metals mobilised from acid sulphate soils in Finland: A literature review. Boreal Environ Res 13: 444–456.

Feio MJ, Coimbra CN, Craca MAS, Nichols, SJ & Norris RH (2010) The influence of extreme climatic events and human disturbance on macroinvertebrate community patterns of a Mediterranean stream over 15 years. J N Am Benthol Soc 29: 1397–1409.

Fernandez GP, Chescheir GM, Skaggs RW & Amatya DM (2006) DRAINMOD–GIS: A lumped parameter watershed scale drainage and water quality model. Agr Water Manage 81: 77–97.

Forsius M, Vuorenmaa J, Mannio J & Syri S (2003) Recovery from acidification of Finnish lakes: regional patterns and relations to emission reduction policy. Sci Total Environ 310: 121–132.

Gorham E (1998) Acid deposition and its ecological effects: a brief history of research. Environ Sci Policy 1: 153–166.

Green R, MacDonald B, Melville M & Waite T (2006) Hydrochemistry of episodic drainage waters discharged from an acid sulphate soil affected catchment. J Hydrol 325: 356–375.

Hämäläinen H, Koskenniemi E, Kotanen J, Heino J, Paavola R & Muotka T (2002) Benthic invertebrates and the implementation of WFD: sketches from Finnish rivers. Tema Nord 566: 55–58.

Hartikainen H & Yli-Halla M (1986) Oxidation-induced leaching of sulphate and cations from acid sulphate soils. Water Air Soil Poll 27: 1–13.

Heikinheimo M & Fougstedt B (1992) Tilastoja maan lämpötilasta Suomessa 1971–1990. Meteorologisia julkaisuja 22, Ilmatieteen laitos, Helsinki, 75s.

Heikkilä R (1991) The influence of land use on the sedimentation of the river delta in the Kyrönjoki drainage basin. Hydrobiologia 214: 143–147.

Henrikcson L, Hindar A Thörnelöf E (1995) Freshwater liming. Water Air Soil Poll 85: 131–142.

Herranen T (2010) Turpeen rikkipitoisuus Suomen soissa - tuloksia laajasta turveinventoinnista. (Summary: Sulphur concentration of peat in Finland - results of wide scale peat inventories) Suo 61: 49–56.

HERTTA database. Environmental Information System at the Centre for Economic Development, Transport and the Environment in Finland http://wwwp2.ymparisto.fi/tietoapalvelusta.html.

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, Slack J & Smith R (1982) Techniques of trend analysis for monthly water quality data. Water Resour Res 18: 107–121.

Holmberg L (1935) Ergebnisse optischer und chemischer Wasseranalysen 1911–31. Hydrografisen toimiston tiedonantoja 5. Helsinki, Finland.

Hongve D, Riise G & Kristiansen J (2004) Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water -a result of increased precipitation? Aquat Sci 66: 231–238.

Hruška J, Köhler S, Laudon H & Bishop K (2003) Is a universal model of organic acidity possible: Comparison of the acid/base properties of dissolved organic carbon in the boreal and temperate zones. Environ Sci Technol 37: 1726–1730.

Hudd R & Kjellman (2002) Bad matching between hatching and acidification: a pitfall for the burbot, *Lota lota*, off the river Kyrönjoki, Baltic Sea. Fish Res 56: 153–160.

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

Indraratna B, Sullivan J & Nethery A (1995) Effect of groundwater table on the formation of acid sulphate soils. Mine Water Environ 14: 71–84.

James LD & Burges SJ (1982) Selection, calibration, and testing of hydrologic models. In: Hanns CT, Johnson HP & Brakensiek DL (eds). Hydrologic modeling of small watersheds. ASAE, St. Joseph, Missouri, USA.

Janssen PHM & Heuberger PSC (1995) Calibration of process–oriented models. Ecol Model 83: 55–66.

Joensuu S, Ahti E & Vuollekoski M (2002) Effects of ditch network maintenance on the chemistry of runoff water from peatland forests. Scand J Forest Res 17: 238–247.

Johansson MM, Kahma KK, Boman, H & Launiainen J (2004) Scenarios for sea level on the Finnish coast. Boreal Environ Res 9: 153–166.

Joukainen S &Yli-Halla M (2003) Environmental impacts and acid loads from deep sulphidic layers of two well–drained acid sulphate soils in western Finland. Agric Ecosyst Environ 95: 297–309.

Jylhä K, Tuomenvirta H & Ruosteenoja K (2004) Climate change projections for Finland during the 21 st century. Boreal Environ Res 9: 127–152.

Kämäri J, Forsius M, Kortelainen P, Mannio J & Verta M. (1991) Finnish lake survey: present status of acidification. Ambio 20: 23–27.

Kivinen E (1938) Uber die Eigenschaften der Gyttjaböden. Bodenkunde und Pflanzenernährung 9: 122–134.

Kivinen E (1944) Aluna – Eli sulfaattimaista. Maataloustieteellinen Aikakauskirja 16: 147–161.

Kortelainen P (1993) Contribution of organic acids to the acidity of Finnish lakes. Publications of the water and environment Research Institute, 13. National Board of Waters and the Environment. Helsinki, Finland.

Kortelainen P & Mannio J (1988) Natural and anthropogenic acidity sources for Finnish Lakes. Water Air Soil Poll 42: 341–352.

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

Kortelainen P & Saukkonen S (1995) Organic vs. minerogenic acidity in headwater streams in Finland. Water Air Soil Poll 85: 559–564.

Lahermo P (1991) Hydrogeochemistry and sensitivity to acidification of streamwaters in crystalline areas of northern Fennoscandia. Environ Geol 18: 57–69.

Lahermo P, Väänänen P, Tarvainen T & Salminen R (1996) Suomen geokemian atlas. Osa 3: Ympäristögeokemia–purovedet ja –sedimentit. Geologian tutkimuskeskus, Espoo.

Laudon H & Bishop K (2002) Episodic stream water pH decline during autumn storms following a summer drought in northern Sweden. Hydrol Process 16: 1725–1733.

Laudon H, Köhler S & Buffam I (2004) Seasonal TOC export from seven boreal catchments in northern Sweden. Aquat Sci 66: 223–230.

Lavoie I, Campeau S, Darchambeau F, Cabana G & Dillon P (2008) Are diatoms good indicators of temporal variability in stream water quality? Freshwater Biol 53: 827–841.

Liljaniemi P, Vuori K–M, Ilyashuk B & Luotonen H (2002) Habitat characteristics and macroinvertebrate assemblages in boreal forest streams: relations to catchment silvicultural activities. Hydrobiologia 474: 239–251.

Maa- ja metsätalousministeriö (2009) Kohti happamien sulfaattimaiden hallintaa. Ehdotus happamien sulfaattimaiden aiheuttamien haittojen vähentämisen suuntaviivoiksi. Työryhmämuistio 8.

MacDonald B, White I, Åström M, Keene A, Melville M & Reynolds J (2007) Discharge of weathering products from acid sulphate soils after a rainfall event, Tweed River, eastern Australia. Appl Geochem 22: 2695–2705.

Marttila H & Kløve B (2010) Managing runoff, water quality and erosion in peatland forestry by peak runoff control. Ecol Engin 36: 900–911.

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.

Mattsson T, Kortelainen P, Laubel A, Evans D, Pujo–Pay M, Roke A & Conan P (2009). Export of dissolved organic matter in relation to land use along a European climatic gradient. Sci Total Environ 407: 1967–1976.

McDowell WH & Likens GE (1988) Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook valley, Ecol Monogr 58: 177–195.

Minh LQ, Tuong TP, van Mensvoort MEF & Bouma J (1998) Soil and water table management effects on aluminum dynamics in an acid sulfate soil in Vietnam. Agr Ecosyst Environ 68: 255–262.

Ministry of Agriculture and Forestry and Ministry of Environment (2011) Guidelines for mitigating the adverse effects of acid sulphate soils in Finland until 2020. Julkaisuja 2/2011. Tampereen Yliopistopaino Oy – Juvenes Print, Tampere 2012.

Murphy JF, Davy–Bowker J, McFarland B & Ormerod SJ (2013) A diagnostic biotic index for assessing acidity in sensitive streams in Britain. Ecol Indic 24: 562–572.

Nash JE & Sutcliffe JV (1970) River flow forecasting through conceptual models: Part I – a discussion of principles. J Hydrol 10: 282–290.

Nichols SJ, Robinson WA & Norris RH (2010) Using the reference condition maintains the integrity of a bioassessment program in a changing climate. J N Am Benthol Soc 29: 1459–1471.

Niemi J & Raateland A (2007) River water quality in the Finnish Eurowaternet. Boreal Environ Res 12: 571–584.

Niemi J & Rekolainen S (2009) Pohjanmaan jokien orgaanisen aineiden pitoisuuksista vuosina 1913–1931 ja 1962–2006. Vesitalous 2/2009.

Nordmyr L, Österholm P & Åström M (2008) Estuarine behaviour of metal loads leached from coastal lowland acid sulphate soils. Mar Environ Res 66: 378–393.

Nyberg ME, Österholm P & Nystrand MI (2012) Impact of acid sulfate soils on the geochemistry of rivers in south–western Finland. Environ Earth Sci 66: 157–168.

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

Okkonen J & Kløve B (2010) A conceptual and statistical approach for the analysis of climate impact on ground water table fluctuation patterns in cold conditions. J Hydrol 388: 1–12.

Österholm P (2005) Previous, current and future leaching of sulphur and metals from acid sulphate soils in W. Finland. PhD Thesis, Åbo Akademi University. Dept of Geology and Mineralogy.

Österholm P & Åström M (2002) Spatial trends and losses of major and trace elements in agricultural acid sulphate soils distributed in the artificially drained Rintala area, W. Finland. Appl Geochem 17: 1209–1218.

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 area, W. Finland. Appl Geochem 23: 1594–1606.

Österholm P, Åström M & Sundström R (2005) Assessment of aquatic pollution, remedial measures and juridical obligations of an acid sulphate soil area in western Finland. Agr Food Sci 14: 44–56.

Palko J (1988) Happamien sulfaattimaiden kuivatus ja kalkitus Limingan koekentällä 1984–1987. Vesi- ja ympäristöhallituksen julkaisuja 19.

Palko J (1994) Acid sulphate soils and their agricultural and environmental problems in Finland. PhD thesis. Acta Univ Oul C 75. University of Oulu.

Palko J & Ruokanen I (1994) Siika-Pattijoen uusjakoalueen metsäojitus: arvio happamien sulfaattimaiden esiintymisestä alueella ja toimenpide-ehdotus happamuushaittojen ehkäisemiseksi. Oulun vesi- ja ympäristöpiiri & Pohjois-Pohjanmaan metsälautakunta.

Palko J & Weppling K (1994) Lime requirement experiments in acid sulphate soils. Acta Agric Scand 44: 149–156.

Palko J & Weppling K (1995) Modelling the effects of acid sulphate soils on river acidity in Finland. Nordic Hydrol 26: 37–54.

Parker A & Rae JE (1998) Environmental interactions of clays: Clays and the environment. Springer-Verlag, Berlin and Heidelberg GmbH & Co.

Penuelas J & Matamala R (1990) Changes in N and S leaf content, stomatal density and specific leaf area of 14 plant species during the last three centuries of CO_2 increase. J Exp Bot 41: 1119–1124.

Pohjois–Pohjanmaan metsäkeskus (2005) Kunnostusojituksen työvaatimukset. Työohje. Pohjois–Pohjanmaan metsäkeskus.

Prévost M, Plamondon A & Belleau P (1999) Effects of drainage of a forested peatland on water quality and quantity. J Hydrol 214: 130–143.

Purokoski P (1959) Rannikkoseudun rikkipitoista maista. Agrogeologisia Julkaisuja 74: 1–23.

Puustinen M, Merilä E, Palko J & Seuna P (1994) Kuivatustila, viljelykäytäntö ja vesistökuormitukseen vaikuttavat ominaisuudet Suomen pelloilla. Series A 198. National Board of Waters and the Environment, Helsinki, Finland.

Ritsema CJ, van Mensvoort MEF, Dent DL, Tan Y, van den Bosch H & van Wijk ALM (2000) Acid sulfate soils. In: Sumner ME (ed.) Handbook of soil science. CRC Press, Boca Raton: 121–150.

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) Hydrochemistry of rivers in an acid sulphate soil hotspot area in western Finland. Agr Food Sci 14: 24–33.

Roos M & Åström M (2006) Gulf of Bothnia receives high concentrations of potentially toxic metals from acid sulphate soils. Boreal Environ Res 11: 383–388.

Rosenqvist I (1978) Acid precipitation and other possible sources for acidification of rivers and lakes. Sci Total Environ 10: 271–272.

Rosseland B & Henriksen A (1990) Acidification in Norway - loss of fish populations and the 1000-lake survey 1986. Sci Total Environ 96: 45–56.

Rosseland B & Hindar A (1988) Liming of lakes, rivers and catchments in Norway. Water Air Soil Poll 41: 165–188.

Sallantaus T (1986) Soiden metsä- ja turvetalouden vesistövaikutukset–kirjallisuuskatsaus. Luonnonvarajulkaisuja 11. Maa- ja metsätalousministeriö, Helsinki, Finland.

Sammut J, Melville M, Gallinan L & Fraser G (1995) Estuarine acidification: impacts on aquatic biota of draining acid sulphate soils. Aust Geogr Stud 33: 89–100.

Sarkkola S, Hökkä H, Nieminen M, Koivusalo H, Laurén A, Ahti E, Launiainen S, Marttila H & Laine J (2012) Can tree stand water use compensate for maintenance of ditch networks in peatlands? Implications from water balance measurements. Extended abstract No. 53. 14th International Peat Congress, Peatlands in Balance. Stockholm, Sweden June 3–8 2012.

Sarkkola S, Koivusalo H, Laurén A, Kortelainen P, Mattsson T, Palviainen M, Piirainen S, Starr M & Finér L (2009) Trends in hydrometeorological conditions and stream water organic carbon in boreal forested catchments. Sci Total Environ 408: 92–101.

Singh J, Kalita PK, Mitchell JK Cooke RAC & Hirschi MC (2001) Tile water quality predictions using DRAINMOD–N and RZWQM, Paper # 01–2089 Presented at the ASAE Annual International Meeting Sacramento, California.

Skaggs RW (1980) Methods for design and evaluation of drainage–water management systems for soils with high water tables. DRAINMOD reference report. USDA–SCS South National Technical Center, Fort Worth, Texas.

Smuckler NJ & Vis ML (2011) Diatom biomonitoring of streams: reliability of reference sites and the response of metrics to environmental variations across temporal scales. Ecol Indic 11: 1647–1657.

Sohlenius G & Öborn I (2004) Geochemistry and partitioning of trace metals in acid sulphate soils in Sweden and Finland before and after sulphide oxidation. Geoderma 122: 167–175.

Soil Survey Staff (2010) Keys to Soil Taxonomy (11th edition). United States Department of Agriculture. Natural Resources Conservation Service.

Soininen J & Eloranta P (2004) Seasonal persistence and stability of diatom communities in rivers: are there habitat specific differences? Eur J Phycol 39: 153–160.

Soininen J. & Könönen K (2004) Comparative study of monitoring South–Finnish rivers and streams using macroinvertebrate and benthic diatom community structure of rivers benthic macroinvertebrate using South–Finnish streams monitoring study. Aquat Ecol 38: 63–75.

Sommer B & Hoewitz P (2009) Macroinvertebrate cycles of decline and recovery in Swan Coastal Plain (Western Australia) wetlands affected by drought–induced acidification. Hydrobiologia 624: 191–203.

Sundström R, Åström M & Österholm P (2002) Comparison of the metal content in acid sulfate soil runoff and industrial effluents in Finland. Environ Sci Technol 36: 4269–4272.

Sutela T, Vehanen T & Jounela P (2010) Response of fish assemblages to water quality in boreal rivers. Hydrobiologia 641: 1–10.

Suupohja O, Erviö R, Pälikkö E, Sumari O & Vuoristo H (1973) Selvitys Kyrönjoen ja sen edustan merialueen kalakuolemien syistä. Työryhmän selvitys Vesihallitukselle 2.3.1973.

Tamm T (2002) Effects of meteorological conditions and water management on hydrological processes in agricultural fields: Parameterization and modelling of Estonian case studies. PhD thesis. Water Resources Publications TKK–VTR–5, Espoo, Finland.

Tertsunen J, Martinmäki K., Heikkinen K, Marttila H, Saukkoriipi J, Tammela S, Saarinen T, Tolkkinen M, Hyvärinen M, Ihme R, Yrjänä T & Kløve B (2012) Happamuuden aiheuttamat vesistöhaitat ja niiden torjuntakeinot Sanginjoella. Suomen Ympäristö 37/2012, Suomen Ympäristökeskus, Helsinki, Finland.

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.
Turtola E & Paajanen A (1995) Influence of improved subsurface drainage on phosphorus losses and nitrogen leaching from a heavy clay soil. Agric Water Manage 28: 295–310.
Turunen J (2008) Development of Finnish peatland area and carbon storage 1950–2000. Boreal Environ Res 13: 319–334.
Urho L, Hildén M & Hudd R (1990) Fish reproduction and the impact of acidification in the Kyrönjoki River estuary in the Baltic Sea. Environ Biol Fishes 27: 273–283.
van Breemen N (1973) Soil forming processes in acid sulphate soils. In: Dost H (ed) Acid sulphate soil, vol 1. ILRI Publ 18: 66–130
van Breemen N (1982) Genesis, morphology, and classification of acid sulfate soils in coastal plains. In: Kittrick, J.A., Fanning, D.S. and Hossner, L.R. (eds.). Acid sulphate weathering, SSSA Special Publication 10. Soil Science Society of America: 95–108.
Vehviläinen B & Huttunen M (1997) Climate change and water resources in Finland. Boreal Environ Res 2: 3–18.
Venäläinen A, Tuomenvirta H, Heikinheimo M, Kellomäki S, Peltola H, Strandman H & Vaisänen H (2001) Impact of climate change on soil frost under snow cover in a forested landscape. Clim Res 17: 63–72.
Vuorenmaa J (2004) Long-term changes of acidifying deposition in Finland (1973–2000). Environ Pollut 128: 351–362.
Vuorenmaa J, Forsius M & Mannio J (2006) Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. Sci Total Environ 365: 47–65.
Vuori K-M (1995) Species- and population-specific responses of translocated hydropsychid larvae (Trichoptera, Hydropsychidae) to runoff from acid sulphate soils in tin River Kyrönjoki, western Finland. Freshwater Biol 33: 305–318.
Vuori K-M, Bäck S, Hellsten S, Karjalainen S-M, Kauppila P, Lax H-G, Lepistö L, Londesborough S, Mitikka S, Niemelä P, Niemi J, Perus J, Pietiläinen O–P, Pilke A, Riihimäki J, Rissanen J, Tammi J, Tolonen K, Vehanen T, Vuoristo H & Westberg V (2006) Suomen pintavesien tyypittelyn ja ekologisen luokittelujärjestelmän perusteet. Suomen Ympäristö 807. Suomen ympäristökeskus. Yliopistopaino, Helsinki, Finland.
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 M, 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 134: 953–967.
Vuorinen PJ, Keinänen M, Peuranen S & Tigerstedt C (1998) Effects ofiron, aluminium, dissolved humic material and acidity on grayling (Thymallus thymallus) in laboratory exposures, and a comparison of sensitivity with brown trout (*Salmo trutta*). Boreal Environ Res 3: 405–419.
Wieder RK & Lang GE (1986) Fe, Al, Mn, and S chemistry of Sphagnum peat in four peatlands with different metal and sulfur input. Water Air Soil Poll 29: 309–320.

Wood PJ & Armitage PD (1997) Biological effects of fine sediment in the lotic environment. Environ Manage 21: 203–217.

Worrall F & Burt T (2007) Trends in DOC concentration in Great Britain. J Hydrol 346: 81–92.

Wright R, Dale T & Gjessing E (1976) Impact of acid precipitation on freshwater ecosystems in Norway. Water Air Soil Poll 6: 483–499.

Yli-Halla M, Puustinen M & Koskiaho J (1999) Area of cultivated acid sulphate soils in Finland. Soil Use Manage 15: 62–67.

Ylitalo E (2011) (ed). Metsätilastollinen vuosikirja 2011 Metsäntutkimuslaitos. Vammala, Finland.

Appendix

Table. Number of samplings (N), range and median values of each variable in the rivers studied. Units: Alkalinity and acidity mmol L^{-1}, elements µg L^{-1}, SO_4^{2-} and CODMn mg L^{-1}, Color mg Pt L^{-1} and EC, mS m^{-1}.

River	Parameter	Alkalinity	Acidity	pH	EC	SO_4^{2-}	Al	Fe	Mn	Cd	Cr	Ni	Zn	COD_{Mn}	Colour
Kokemäenjoki	N	609	–	725	–	–	–	–	–	–	–	–	–	927	544
	Range	0.1–0.88	–	5.5–7.9	–	–	–	–	–	–	–	–	–	5–71	10–450
	Median	0.26	–	6.9	–	–	–	–	–	–	–	–	–	14	70
Kyrönjoki	N	822	–	2027	–	–	231	332	–	255	253	259	259	902	967
	Range	–0.04–0.6	–	3.9–7.4	–	–	272–4360	300–9600	–	0.01–0.36	0.41–24	1–47.1	3.3–94	10–450	40–480
	Median	0.11	–	5.9	–	–	1600	2100	–	0.1	1.78	17	31	25	200
Lapuanjoki	N	626	–	681	–	–	240	287	–	272	269	267	278	720	621
	Range	–0.07–0.6	–	4–7.2	–	–	145–9000	580–28000	–	0.01–9	0.1–139	0–53	0.5–114	2–75	35–568
	Median	0.1	–	5.8	–	–	1405	2170	–	0.1	1.3	12.9	31	24	200
Lestijoki	N	505	–	577	–	–	–	–	–	–	–	–	–	523	540
	Range	0.1–0.4	–	5.1–7.6	–	–	–	–	–	–	–	–	–	4–51	20–400
	Median	0.11	–	6.3	–	–	–	–	–	–	–	–	–	25	200
Kalajoki	N	745	–	745	–	–	–	–	–	–	–	–	–	809	720
	Range	0.04–0.69	–	5.3–7.7	–	–	–	–	–	–	–	–	–	5–49	87–650
	Median	0.21	–	6.5	–	–	–	–	–	–	–	–	–	26	200
Pyhäjoki	N	68	18	1689	100	46	353	444	46	339	337	319	341	62	69
	Range	0.07–0.37	0.05–0.17	4.6–8.2	4.4–21.1	6–56	24–5180	150–4200	11–900	0–0.4	0.3–8.6	0.4–9	0.5–130	1–45	60–330
	Median	0.19	0.13	6.6	12.2	25	675	1800	100.5	0.03	1.43	2.08	11	19	150
Liminkaoja	N	17	15	31	29	15	17	11	6	2	–	2	8	2	9
	Range	0.08–0.49	0.05–0.2	5.8–7.4	3.8–11.1	5–13	200–790	1900–5600	18–110	0.01–0.02	–	1.3–2.5	3–7	21–34	200–300
	Median	0.16	0.13	6.5	6.2	7	610	2450	73	0.02	–	1.9	3.95	27	270

River	Parameter	Alkalinity	Acidity	pH	EC	SO_4^{2-}	Al	Fe	Mn	Cd	Cr	Ni	Zn	COD_{Mn}	Colour
Piehinginjoki	N	33	25	46	46	26	18	30	7	2	–	2	9	14	28
	Range	0.02–0.36	0.09–0.24	5.3–7	3.2–9	4–13	210–724	1700–8500	33–79	0.02–0.03	–	1.4–1.8	3–8	17–38	180–390
	Median	0.08	0.16	6	5.4	7	430	3300	56	0.03	–	1.6	6	30	270
Haapajoki	N	17	15	31	31	18	17	17	7	2	–	2	9	6	9
	Range	0.03–0.67	0.06–0.29	5.4–7.2	9.6–22	14–65	120–1800	3400–9200	85–310	0.02–0.11	–	2.4–9.5	6–29	15–32	160–300
	Median	0.15	0.19	6.4	15.5	42	1190	5150	120	0.07	–	5.95	9.6	21	180
Pattijoki	N	33	15	46	44	10	17	17	5	2	–	2	9	12	25
	Range	0.1–1.52	0.09–0.19	6–7.1	7.2–19.7	16–45	66–679	2600–7100	82–300	0.02–0.06	–	1.4–5.5	3–34	5–38	120–300
	Median	0.29	0.12	6.6	13.3	22	451	3550	160	0.04	–	3.45	8	16	200
Olkijoki	N	32	25	50	41	25	18	26	7	2	–	2	9	13	24
	Range	0.11–0.52	0.08–0.24	5.7–7.1	6.6–12.4	5–18	96–590	2700–6700	78–180	0.02	–	2.6–3.2	3–17	5–20	100–260
	Median	0.24	0.11	6.6	9	13	363	3900	96	0.02	–	2.9	6	14	160
Majavaoja	N	16	14	87	22	15	16	9	6	2	–	2	9	1	8
	Range	0.07–0.44	0.08–0.2	6.1–7.2	7.8–11.6	13–19	100–416	2800–9600	55–140	0.02–0.03	–	3.1–3.9	4–11	20	130–300
	Median	0.166	0.11	6.8	9.1	17	310	3450	84.5	0.03	–	3.5	5.4	20	180
Siikajoki	N	786	49	1689	151	82	320	483	49	265	263	264	269	1245	1461
	Range	–0.022–22	0.07–0.25	4.7–8	4.1–10.8	2–20	1–18000	370–22000	0–660	0.01–2.3	0.1–9.5	0.6–13	0.5–44	7–224	10–2500
	Median	0.152	0.13	6.4	5.6	8	609	3300	130	0.02	1.3	2.5	8	22	200
Oulujoki	N	643	–	721	–	–	–	–	–	–	–	–	–	784	700
	Range	0.01–0.38	–	5.4–7.9	–	–	–	–	–	–	–	–	–	1–25	20–200
	Median	0.14	–	6.8	–	–	–	–	–	–	–	–	–	11	60
Sanginjoki	N	3	–	50	10	–	20	39	–	–	–	–	–	38	39
	Range	0.02–0.12	–	4–6.7	2.9–7.4	–	168–441	2000–5900	–	–	–	–	–	25–47	200–450
	Median	0.09	–	5.3	4.2	–	301	3300	–	–	–	–	–	34	270

River	Parameter	Alkalinity	Acidity	pH	EC	SO_4^{2-}	Al	Fe	Mn	Cd	Cr	Ni	Zn	COD_{Mn}	Colour
Iijoki	N	620	–	532	–	–	–	–	–	–	–	–	–	676	525
	Range	0.02–0.6	–	5.7–7.9	–	–	–	–	–	–	–	–	–	0.1–29	5–280
	Median	0.18	–	6.6	–	–	–	–	–	–	–	–	–	12	100
Kemijoki	N	636	–	520	–	–	–	–	–	–	–	–	–	657	481
	Range	0.07–0.74	–	6.1–7.5	–	–	–	–	–	–	–	–	–	1–25	5–200
	Median	0.29	–	6.8	–	–	–	–	–	–	–	–	–	10	75

Original publications

I Saarinen T, Vuori K-M, Alasaarela E & Kløve B (2010) Long term trends and variation of acidity, CODMn and colour in coastal rivers of Western Finland in relation to climate and hydrology. Science of the Total Environment 408(21): 5019–5027.

II Mykrä H, Saarinen T, Tolkkinen M, McFarland B, Hämäläinen H, Martinmäki K & Kløve B (2012) Spatial and temporal variability of diatom and macroinvertebrate communities: How representative are ecological classifications within a river system? Ecological Indicators 18: 208–217.

III Saarinen T & Kløve B (2012) Past and future seasonal variation in pH and metal concentrations in runoff from river basins on acid sulphate soils in Western Finland. Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering 47(11): 1614–1625.

IV Saarinen T, Celebi A & Kløve B Links between river water acidity, land use and hydrology. Boreal Environment Research (In press).

V Saarinen T, Mohämmädighävam S, Marttila H & Kløve B (2013) Impact of peatland forestry on runoff water quality in areas with sulphide-bearing sediments; how to prevent acid surges. Forest Ecology and Management 293: 17–28.

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