pH of streams in western Finland — a perspective from the Middle Ages into the mid 21st century

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In the central parts of western Finland, many streams are severely acidified as a result of land-use activities on overburden (soils) capable of producing and ultimately releasing extreme acidity. Consequently, the extent of the acidification problem is likely to have varied over time in response to the type and extent of contemporary land use. In this study, we have combined historical information on land use and knowledge on hydrogeochemical processes in order to assess the pH declines that are likely to have occurred in streams in this area since the Middle Ages. The results show that among several potentially acidifying activities, reclamation of mires for farmland (19th and 20th centuries) and subsurface drainage of acid sulphate soils (post-war times) are the major causes of the pH decline. Recent methods developed to combat the acidification and possible future changes in pH are discussed.

Key words: acid sulphate soil, hydrochemistry, acidification, ditching, land use

Introduction

In the central parts of western Finland (hereafter C-W Finland), many streams are severely acidified (e.g. Weppling 1993, Åström and Åström 1997, Edén et al. 1999) which has resulted in deterioration of the aquatic life in general and many serious sudden fish kills (Vuori 1995, Kjellman and Hudd 1996, Hudd and Kålax 1998). The overall reason for the poor water quality is extensive land-use activities on overburden (soils) capable of producing and ultimately releasing extreme acidity. Consequently, the extent of the acidification problem is...
likely to have varied over time in response to the type and extent of contemporary land use. In addition, in recent times there has been the additional effect of acid rain. Therefore, the acidification problem of the area is complex. The aim of this study was to assess how the pH of streams in this area has varied since the Middle Ages. The method consists of combining historical information on land-use and recently acquired knowledge on hydrogeochemical processes.

Area description

In C-W Finland (Fig. 1) the land surface extends up to 150 m above sea level (a few peaks reach 200–250 m a.s.l.) and it rises, due to post-glacial land uplift, at an overall rate of 7–9 mm per year. Since the land uplift increases from south-east (ca. 7 mm) to north-west (ca. 9 mm), the slope of the streams running in this direction continuously decrease and new land is exposed at a rapid rate along the shallow-water coast.

The bedrock dominated by Proterozoic granitoids, gneisses and schists is locally mineralised (metal sulphides) and contains scattered small limestone bodies/lenses. Thus, the bedrock is locally a source of sulphide-derived acidity (geogenic sulphuric acid) or carbonate-derived alkalinity. In general, however, it is inert as far as short-term acid-base reactions are concerned. The bedrock is overlain by a more or less continuous sheet of locally derived glacial till. In valleys and depressions in the terrain, the till is overlain by clay-silt sediments that were deposited during Holocene in brackish waters (Litorina Sea and Baltic Sea). These sediments contain secondary sulphides (ca. 0.5% on average) but are poor in carbonate (Åström and Björklund 1997). Two distinct types of areas in terms of geomorphology and Quaternary geology are thus recognised: (1) valleys and depressions covered with clay-silt sediments (hereafter for clarity referred to as “sulphide clay areas”, although not all of the clay horizons are sulphide-bearing and many layers are dominated by silt), and (2) elevations and ridges mainly covered with or consisting of till. While in many catchments the distribution of exposed sulphide clay and till is a mosaic, the most common pattern is that till dominates in the upper and distal parts and sulphide clay in the lower and central (around the main stem and tributaries) parts of the catchments. Bedrock outcrops, glaciofluvial deposits and peat layers also exist in the area.

The annual climatic and hydrological cycles in the area are characterized by four distinct seasons. The summer (June-August) is characterised by a mean temperature of about 15°C, high biological activity, and mainly baseflow conditions. During the autumn months (September-November), there is a gradual decrease in temperatures from ca. 15°C to ca. 0°C, a corresponding decrease in biological activity and evapotranspiration, and high-flow events of variable duration. The winter (December-April) is characterised by freezing tem-
temperatures and a snow cover ranging in maximum thickness from approximately 20 cm to 80 cm. Often there are, however, short periods of thaw and temporary snowmelt even in mid-winter. The snow cover melts in April, resulting in annual peaks in the hydrograph. A few weeks later the ground is commonly completely defrosted. The mean annual temperature in the area is ca. 4°C and precipitation ca. 500 mm. The growing season is 160–180 days.

Levels and controls of pH

“Natural-conditions”: prior to and in the 15th century

In C-W Finland at these times, mires covered a large part of the sulphide clay areas and certainly those parts of the till areas having a poor natural drainage. Peat deposits were thus widespread and from these humic substances (organic acids) were delivered to the aquatic environment. Also at present, when many of the peat deposits have been destroyed (see below), high concentration of humic substances (dissolved organic carbon: 15–60 mg l⁻¹) is typical of many streams in the area (Kortelainen and Saukkonen 1998). Many studies have shown that these acids can cause dramatic pH declines in natural waters, such as in forested areas in C-W Finland where low-order streams can have pH values between 4.5 and 5.5 throughout the year due to these acids (Aström et al. 2001). Hence, there is no question that both humic-rich and acidified streams existed in the area prior to extensive and serious human activities.

In the majority of the streams there certainly was, like today, substantial temporal pH variations controlled primarily by hydrology. In periods of high ground-water table after snow melting in spring and heavy rains in autumn, organic acids are efficiently mobilized in the near surface layers, resulting in natural episodic acidification of the runoff and recipient streams. During baseflow, organic acids are extracted less efficiently and the acid neutralizing capacity of the waters is increased, resulting in a higher pH of the outflow waters (Laudon and Bishop 1999, Bishop et al. 2000, Moiseenko et al. 2001).

Forest clear cutting and river dredging: 17th, 18th and 19th centuries

In the middle of the 18th century, several thousand hectares pine forest (Pinus sylvestris) per year was utilised in C-W Finland for the production of tar, which was both exported and utilised by local ship builders (Airola et al. 1998). In addition, wood was utilised for heating, and timber for the construction of houses and ships. Due to these activities, the proportion of easily available (reachable) wood steadily decreased and in the mid 19th century there was a lack of this raw material, in particular near the coast (Hallantie et al. 1998). Because of the excess cation uptake over anion uptake and subsequent excretion of protons to the soil, tree removal ultimately results in soil acidification (Olsson et al. 1993, Eriksson 1996, Sverdrup and Rosén 1998). Thus, it is possible that soil (and water) pH decreased, due to extensive tree removals, over this period.

In order to make the transport of wood and tar from the inland to the coast via the waterways more efficient and convenient, the rapids of many major streams were thoroughly dredged over this period. This gave the water an easier route to the coast, which resulted in decreased flooding at high-water flows and in a minor decrease in O₂ levels in the waters. None of these effects are likely to have had a significant impact on stream-water pH.

Expanding agriculture: 1800 – Second World War

While in C-W Finland permanent agriculture was established in several places in the 15th century and reclamation of mires for farmland was initiated in the 17th century, it was not until the beginning of the 19th century that agriculture expanded,
on a large scale, into new areas (Airola et al. 1998). In focus were the waterlogged and peat-covered sulphide-clay areas, and to some extent shallow-water lakes (the latter in particular in 1850–1940). After the waterlogged land had been drained by manually dug ditches, the peat dried up and was then burnt in order to expose the sulphide clays that consists productive farmland. As a consequence, the ground-water table dropped on many sulphide-clay areas thus exposing the inherent sulphides to penetrating $O_2$. When this occurs, sulphuric acid is formed through a complex sequence of chemical and biochemical processes (e.g. van Breemen 1973, Lowson 1982, Kelly 1982) and the soil, due to the release of this acid, is severely acidified (Kivinen 1938, Wiklander and Hallgren 1949). Many farmers were lucky, however, since when the peat was burnt, $CO_2$ and $SO_2$ and $NO_x$ were lost to the atmosphere, while the hydroxide-rich alkaline residue (ash) was left on the fields. Consequently, the sulphuric acid formed in the topsoil was efficiently neutralised by the basic chemical components in the ash, making cultivation possible. However, the subsoil was severely acidified by the sulphuric acid. In contrast, where the farmland was on non-sulphidic clays or coarse sediments, acidification did not occur.

In areas where the subsoil and locally the topsoil under the reclaimed agricultural land were acidified, the associated streams certainly were too. During high-water flow (snow melting or heavy rains), sulphuric acid was extensively leached from the fresh acidic soils, resulting in a substantial decrease in pH (see Palko and Yli-Halla 1993). In many main streams it is likely that pH dropped to values around or even below 4.0 and in a large number of ditch drains down to 3.0 (pH levels assessed based on present-day situation in similarly drained catchments). This is thus the period when the first unnatural and widespread acidification problems occurred in the area.

**Post war forest drainage**

Throughout Finland, forests on mires and waterlogged mineral-soil sites were extensively drained (ditched) during the latter half of the 20th century. The peak occurred in 1970 (Fig. 2). The forests in C-W Finland were no exception to this general trend. From a forestry point of view, these operations have been successful, since there is no question that part of the nationwide tree volume increment from 91 million $m^3$ in 1952 to 137 million $m^3$ in 1991 is due to these operations (Hallantie et al. 1998, Lauhanen and Ahti 2001). These drainage activities have, however, resulted in a considerable change in the pattern of natural forest drainage. In general, the ditches penetrate the upper peat cover and the underlying till and/or sand layers. Consequently, drainage of forest that grows on sulphide-rich till or sulphide clays (both quite rare) result in sulphide oxidation and a subsequent pH decline in soil and water.

In the majority of the catchments in C-W Finland, however, the bedrock and till are poor in sulphides. In these catchments, in contrast, the forest drainage results, by as yet poorly known mechanisms, in a pH increase of stream waters by up to one unit (Heikurainen et al. 1978, Ramberg 1981, Manninen 1998, Prevost et al 1999, Joensuu et al. 2001). Consequently, in C-W Finland forest ditching is not, in general, a proton-producing activity.
After the Second World War, there was a great need for more farmland in Finland, partly due to the delivery of land areas in the eastern part of the country (Karelia). Therefore, in C-W Finland, the reclamation of farmland on the sulphide clay areas continued and was particularly intensive in the 1960s. At the end of the 1950s subsurface drainage (drainpipes installed at a depth of ca. 1 m) grew in popularity (Fig. 3). The reasons for this are that the drainpipes more efficiently than open surface ditches drain the soils, and that they do not cut the farmland into small plots unpractical for modern machine-based agriculture. Both virgin fields and fields previously drained by open ditches were (and still are) converted to subsurfacially drained land. At present, more than half of the farmland in the C-W Finland is drained by this technique.

A negative side effect of these activities is that the oxidation of the soils increases, often to a depth of more than 2 m (Joukainen and Yli-Halla 2003). This, in turn, increases the production of sulphuric acid, which is efficiently leached through the subsurface pipes. In addition, Fe\(^{2+}\) released by the dissolution of sulphides and Al\(^{3+}\) by weathering of alminosilicates/Al-hydroxides, are efficiently leached through the drainpipes. Downstream, oxidation and hydrolysis of Fe\(^{2+}\) and hydrolysis of Al\(^{3+}\) produces additional in-stream acidity (Weppling 1993, Palko 1994). These processes accelerate the pH decline of the recipient streams. Hence, this is a period when the farmland runoff became even more acidic, while the forest runoff (after ditching) became less acidic.

In the 1970s and 1980s, there was a growing environmental concern of these acidic soils, not only in Finland but also elsewhere where similar soils were recognised, such as in Sweden, the Netherlands, W and E Africa, N South America, S North America, Australia, and S and SE Asia (Kawalec 1973, Dent 1980, Öborn 1989). These soils were at the time named ”acid sulphate soil” (AS soil) relating to the characteristic high acidity and sulphate concentrations (Dent and Pons 1995, Ritsema et al. 2000). At present, there is a worldwide awareness of the environmental impacts of these soils (e.g. van Breemen 1993, Sammut et al. 1996, Minh et al. 1997, Cook et al. 2000).

Palko (1994) estimates that AS soils at present cover 3360 km\(^2\) of the Finnish coastal agricultural land, and that approximately half of them are located in C-W Finland. Subsequent more rigorous classification work reveals that the AS soils are commonly Sulfic Cryaquepts and Typic Sulfaquepts (Yli-Halla 1997) and that the total area of these soils is less than Palko’s (1994) estimate (Yli-Halla et al. 1999).

**Acidic deposition**

Emissions of SO\(_2\) (energy production, industrial processes) and NO\(_x\) (traffic, energy production) contribute to the acidity of precipitation that ultimately infiltrates the ground. In Europe, acidifying sulphur emissions have been declining since 1980 (Vestreng 2003), and the role of nitrogen oxide emissions is expected to increase in the future (Jokhansson et al. 2001). In C-W Finland (Ähtäri), the deposition of SO\(_2\)\(^{2-}\)-sulphur decreased from 613 to 227 mg m\(^{-2}\) from 1973 to 1996, while the pH of the precipitation has been quite stable over the same period (4.61 in 1973, 4.50 in 1987 and 4.66 in 1996) (Kulmala et al. 1998).
The precise effect of the anthropogenic airborne compounds on stream-water pH in C-W Finland is difficult to determine, because in the 1960s, 1970s and 1980s when the precipitation had a low pH and a high S load, the forest drainage caused a pH rise of the forest runoff and the farmland subsurface drainage a pH decline of the farmland runoff. The effect of the airborne compounds is thus strongly masked by the variable and large effects of intensive land-use activities. However, the airborne compounds will not have had any detectable effect on the AS soil (farmland) waters, since such water is severely acidic (pH 3-4) and rich in sulphide-derived SO\textsubscript{4}\textsuperscript{2−} (up to 3000 mg l\textsuperscript{-1}). In contrast, anthropogenic airborne acidity is a significant, although not major, component of pH decline during snow melt episodes in forested catchments (Bishop et al. 2000).

**Efforts to combat acidification**

In order to reduce the chemical leaching of the AS soils, several techniques, based on chemistry and/or hydrology, have been developed and tested over the last two decades. While each technique has had recognisable positive effects, all of them have drawbacks: (1) calcitic (CaCO\textsubscript{3}) and dolomitic (CaMg(CO\textsubscript{3})\textsubscript{2}) limestone powder (< 2 mm) applied in large quantities on-field increases the topsoil pH thus making crop production possible (Purokoski 1959, Öborn 1993), but does not penetrate the subsoil where a large majority of the acidic runoff is generated (Weppling 1997, Österholm and Åström 2002), (2) in-stream application of powdered limestone or CaO can substantially increase the water pH (Björkqvist and Weppling 1987), but creates metal-rich precipitates (which may later dissolve) and needs sophisticated technical controls due to the episodic nature of the acidification (Weppling 1997), (3) controlled drainage is likely to work on well-drained AS soil, but cannot prevent substantial sulphide oxidation and generation of acidic runoff in S-rich near-surface horizons in poorly drained AS soils, (4) lime filter drains, constructed by mixing the soil material around and above the drainpipe with CaO, may increase the pH of runoff in the short term (Weppling 1997), but the long-term effects, including the fate of the fresh metal precipitates in the soil-CaO mixture, are unknown, and (5) SAPS (successive alkalinity producing systems) which are currently built on test sites are likely to work qualitatively but the quantitative problems are substantial due to the enormous increase in loadings on short high-flow episodes.

**The future**

As a result of continuous oxidation and leaching, the AS soils are gradually loosing inherent sulphide-bound acidity. Thus, active AS soils will ultimately become relict AS soils, and will by then be less of an environmental concern. Consequently, both the rate and duration of this process are important long-term environmental factors in catchments affected by active AS soils. The existing hydrochemical data for streams in C-W Finland is, however, too sparse, both in temporal and spatial dimension, to reveal any reliable historical trends and likely (near) future scenarios. This has resulted in a need to develop models for future predictions. Palko and Weppling (1995) use both a static and a dynamic black-box approach to predict the runoff acidity from catchments containing AS soils. They applied the model on data from three catchments and two rivers in Finland, and obtained good estimates of the river water acidity. The static model can be used to classify rivers and river basins according to state of acidification and neutralisation demand under varying hydrological conditions. The dynamic model can contribute to the planning of mitigation strategies including estimates of feasibility and expenses of river liming measures. The HAPSU model (Hutka et al. 1996) describes, on basis of the key principles of the chemical part of the SMASS (Simulated Model for AS Soils) model, the fluxes of heat, water, oxygen and solutes (SO\textsubscript{4}\textsuperscript{2−}, H\textsuperscript{+}, Ca\textsuperscript{2+}, Fe\textsuperscript{2+}/Fe\textsuperscript{3+}, Al\textsuperscript{3+}) in boreal AS soils. The calculation procedure is based on redox chemistry, precipitation/dissolution of hydroxides, cation exchange and ion associations. In a long-term simulation based on data from two catchments in C-W Finland, the HAPSU model
predicted that: (1) there will be a weak but significant decrease in runoff pH over a three-decade-period, (2) ponding, by preventing oxidation of the lower soil layers, will reduce the runoff acidity, and (3) extensive application of lime on the fields will not neutralise the water discharging from the soil.

In addition to focusing on the current active AS soils, it is important to consider the fresh sulphide-rich sediments (potential AS soils) that are continuously exposed along the shallow shores as a result of postglacial isostatic land uplift. If those sediments are reclaimed by present-day agricultural practices (deep ditching), they will develop into new active AS soils which will be at least as hazardous as those currently active. If they are not drained, they will remain reduced and thus chemically inert and environmentally friendly. Another important point to consider is the fact that many agricultural fields are depressing at a rate of ca. 1–2 cm per year which leads to a continuous need of extending the ditches into as yet unoxidised sulphide-rich layers.

Whereas ‘pristine’ forest land in Finland is no longer drained, ditch cleaning and supplementary ditching in previously drained forests are increasing in order to improve the drainage of the overgrown and old ditch-networks (Fig. 2). Since the aquatic effects of ditch cleaning-supplementary ditching are similar to those of first-time drainage (Manninen 1998), in the (near) future there will be a continuous supply of additional alkalinity from the forested areas. However, while pushing the pH towards more neutral values, the forest-ditching operations have several other clearly negative aquatic and ecological impacts (Heikurainen et al. 1978, Vuori et al. 1998, Ahtiainen and Huttunen 1999, Joensuu et al. 1999) and can therefore not be recommended as an acid-combating tool.

Conclusions

In the central parts of western Finland, several human activities over the latest centuries have resulted in pH decline in soil and water. These include: (1) reclamation of farmland on waterlogged sulphide clays, (2) subsurface drainage of farmland located on AS soils, (3) acidic deposition, and (4) extensive wood removal for various purposes. Of these, the first two are by far the most important. Other activities, however not of the same quantitative importance, have resulted in a pH increase. These are: (1) the burning of peat on widespread lowlands and (2) drainage of typical forests underlain with Proterozoic granitoids and gneisses.

Based on what we now know about hydrogeochemical processes in the area, we can explain why mass fish kill occurred in unusually clear stream waters in Merikart village in Lillkyrö in 1834 (Sevola 1979). After drainage of sulphide clays, AS soil develops and ultimately releases water that has low pH, high metal concentrations (Al, Cd, Ni, Co, Be, Mn) and low concentrations of dissolved humic substances and particulates (Edén and Björklund 1993, Edén et al. 1999, Åström and Åström 1997). Hence, such waters are clear, but their low pH and high metal levels are lethal. Such waters, to the surprise of the local people, killed the fish in Merikart 170 years ago, and today still kills fish from time to time in many streams in C-W Finland.

While the overall pH controls and reasons for fish kills in streams in C-W Finland are thus recognised, both the qualitative and quantitative pH controls for many individual streams in the area remain as yet to be determined. In order to carry out such assessments on a meaningful level of precision, more detailed maps of the occurrences of actual and potential AS soils are required and more knowledge on the relative contribution of anthropogenic and organically derived acidity in forested catchments is needed. From a remedial point of view, the most important task would be to find and develop new environmentally friendly ways of draining the actual AS soils, and to stop all sort of drainage of potential AS soils.

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