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Organic and minerogenic acidity in Finnish rivers in relation to land use and deposition

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Abstract

The role of organic and minerogenic acidity in controlling pH levels in Finnish rivers was studied by measuring total organic carbon (TOC) and non-marine sulphate ($*SO_4$) concentrations in river water of the main river basins and their sub-basins. The basins are located along a latitudinal gradient (60°N to 69°N) and cover 297,322 km^2, 88% of the total area of Finland. The basins are predominately covered by coniferous forests and peatlands, and are located in areas with low sulphate deposition (80–430 mg S m^{-2} a^{-1}). The proportion of the basin covered by forests on mineral soils ranges from 29 to 64% and the proportion of peatlands from 3 to 60%. The percentage of peatland is highest in northern Finland (28–60%), whereas the proportion of forests on mineral soils increases towards the south. The majority of the agricultural land is located in southern and western Finland. $*SO_4$ concentrations were positively correlated with the proportion of agricultural land in the basin. Moreover, the percentage of peatlands had a positive correlation with the concentrations of TOC and organic anion. High peatland proportion and high TOC and organic anion concentrations decreased pH values in the river water, whereas no correlation between $*SO_4$ concentrations and pH was observed. The average organic anion concentration exceeded the average $*SO_4$ concentration in river water in 17 basins out of the 86 studied basins. The organic anion-dominated areas were situated in northern basins, reflecting the high extent of peatlands in these areas. $*SO_4$ dominated in southern Finland and in western coastal areas, where the extent of agricultural land, acid sulphate soils and the deposition of sulphate is highest.

Keywords: Acidity; Agriculture; Land use; Organic carbon; pH; Rivers; Sulphate

1. Introduction

Over wide regions in Finland, lake water acidity has been shown to be dominated by organic acids, and the pH of lakes has a significant negative correlation with total organic carbon (TOC) concentrations. In southernmost Finland, where sulphate deposition is highest, minerogenic acidity is more important (e.g. Kortelainen and Mannio, 1988; Kortelainen et al., 1989). Sulphate deposition in Finland is relatively low but has a rather wide range, from 430 mg S m^{-2} a^{-1} in the south to 80 mg S m^{-2} a^{-1} in the north (Leinonen, 2001). Similarly, the concentration of sulphate decreases in headwater streams from the south to the north, reflecting higher deposition and more fertile soils in southern Finland (Finér et al., 2004).

Several studies have shown increasing trends of organic carbon concentrations (Freeman et al., 2001; Worral et al., 2004; Evans et al., 2005; Skjelkvåle et al., 2005; Vuorenmaa et al., 2006) and decreasing trends of sulphate concentrations (Skjelkvåle et al., 2005;

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Watmough et al., 2005) in lakes and streams in Europe and North America during the last 10–15 years. These increases and decreases induced by one or more external drivers (e.g. acid deposition, temperature, hydrology, rising atmospheric CO_2 and land use) probably affect the balance of organic and minerogenic acidity in surface waters. Moreover, Hongve et al. (2004) reported that in Norway, natural organic matter (NOM) in runoff water has become more acidic and coloured as a result of changed water pathways due to increased total precipitation and extended periods of very intensive rain, which may further enhance the role of organic acidity in lakes and rivers.

Land use-induced variations of organic carbon and sulphate (SO_4) can have a significant effect on the acidity and the pH of river water. Land use has been shown to have strong relationships both with organic carbon (e.g. Correll et al., 2001; Mattsson et al., 2005) and sulphate (e.g. Williams et al., 2005) export/concentrations in rivers. Concentrations of SO_4, the base cations and acid neutralizing capacity (ANC) in stream water had significant positive relationships with the percentage of urban and agricultural land use (Williams et al., 2005). As the percentage of urban and agricultural land use had positive correlation with both SO_4 and base cation concentrations (and ANC), the pH of stream water remained relatively invariant. Peatlands and wetlands have been shown to be important contributors to organic carbon concentrations and export (e.g. Dillon and Molot, 1997; Aitkenhead et al., 1999; Mattsson et al., 2005) and thus to affect the pH of the river water. Moreover, elevated organic carbon concentrations and fluxes have been reported from catchments dominated by agricultural land (Correll et al., 2001; McTiernan et al., 2001).

In Finland, the study of organic and minerogenic acidity in surface waters has focused on forested headwater streams and lakes (Kortelainen and Mannio, 1988; Kortelainen et al., 1989; Kortelainen and Saukkonen, 1995). In the Finnish Lake Survey of 1987, 26% of the variation in lake water pH was explained by TOC concentration, 23% by base cation concentrations and only 12% by sulphate concentrations, indicating the dominating role of TOC and base cation in determining the pH of lake water (Kortelainen et al., 1989). Moreover, stream water acidity was dominated by organic acids in the majority of the forested first-order streams, and 67 to 82% of the variability in stream water pH could be explained by base cation and organic carbon concentrations (Kortelainen and Saukkonen, 1995). Considerably less information exists about organic acids and SO_4 from river basins with mixed land use. This study provides an assessment of the organic and minerogenic acidity, and TOC concentrations in the major Finnish rivers in relation to land use and sulphate deposition.

2. Material and methods

2.1. River basins and sub-basins

We studied 36 river basins in Finland flowing to the Baltic Sea. The rivers with their sub-basins, altogether 86 catchments, situate between latitudes 60°N and 69°N and cover 297,322 km^2, 88% of the total area of Finland (Fig. 1). The areas of the river basins and their sub-basins range from 73 to 56,000 km^2 (Tables 1 and 2). For each basin, the different land use classes were derived from satellite image-based land cover and forest classification data (25×25 m grids). The basins are predominately covered by coniferous forests and peatlands. The percentage of peatland is highest in northern Finland, whereas the proportion of forests on mineral soils increases towards the south. The majority of the agricultural land in Finland is located in the southern and western coastal zone. By contrast, in the northernmost basins the proportion of agricultural land is minor. Agricultural land in Finland is mostly cropland, but also includes some grassland. The proportion of agricultural land varies from 7–44% in the southern and western coasts to 0.6–3.4% in the north. The surface water area of the basins ranges from 0.5 to 26%. Urban areas (range 0–6.5%) are concentrated in southern Finland, whereas

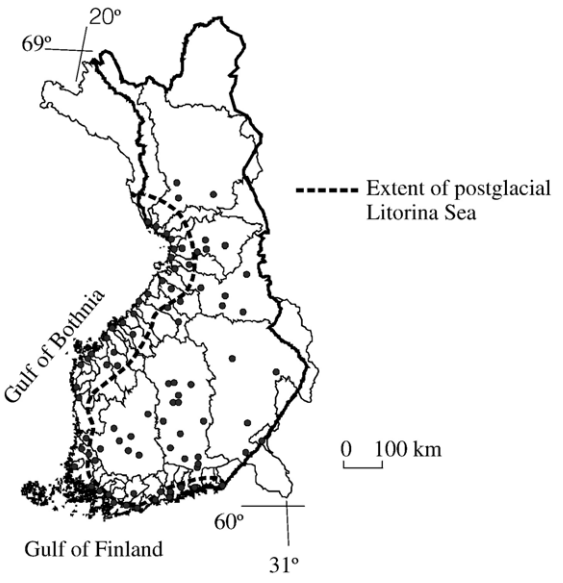

Fig. 1. The Finnish river basins included in the study and water sampling points. Finland is outlined in black.