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The geochemistry of podzol soils and its relation to lake water chemistry, Finnish Lapland

by Anne-Maj Kähkönen

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THE GEOCHEMISTRY OF PODZOL SOILS AND ITS RELATION TO LAKE WATER CHEMISTRY, FINNISH LAPLAND

by

ANNE-MAJ KÄHKÖNEN

with 47 figures and 15 tables in the text

ACADEMIC DISSERTATION

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The geochemistry and the importance of catchment surface area to lake-water chemistry and acid sensitivity were studied in the podzol soils and lakes of 90 catchments in Finnish Lapland. The study sites were selected from geochemically diverse provinces. Estimated annual total sulphur deposition was highest (1.0 g/m^2) in northeastern Lapland, and decreased gradually westwards (0.3 g/m^2).

Three different selective leaches were used to determine the solubility and of the main elements, cation exchange capacity, base saturation and pH in the different horizons of the catchment soils. The main chemical characteristics of the lake-water samples from corresponding catchments were determined as required by SF standards. The lakes were divided into headwater, drainage and closed types, and the surface areas of the lakes and catchments were determined, digitized and stored in databases.

Regionally, the geochemical properties of till in the catchments correlated with the lithological composition of the underlying bedrock. Hence, the chemical and mineralogical composition of parent material controlled the element concentrations of upper mineral soil and humus horizons to a considerable extent. For the acidification of soil and water courses, the relative abundances of aluminium and base cation fractions in different podzol horizons were more important than their absolute concentrations. The solubility of mafic, ultramafic, Ca-rich plagioclases and rare carbonate rock components in catchment soils were the chief factors controlling the buffer capacity, cation exchange reactions and BS of soils and were thus responsible for the high ANC values (> 150 µeq/l) of lakes, especially in the Central Lapland Greenstone Belt, the Peräpohja schist belt, and the Sokli and Angeli areas. Elsewhere in Finnish Lapland, till geochemistry, element concentrations and solubility showed a more mosaic-like pattern, and the acid-sensitivity of lakes was due to a complex combination of soil geochemistry, catchment size and runoff retention time.

The high natural variation in sulphur concentrations in soils was mainly due to the sulphide minerals, particularly in mineralized areas such as the Central Lapland Greenstone Belt. In northeastern Lapland, the relatively high sulphur concentrations in the humus horizons, and the sulphate concentrations in acidic and poorly buffered lakes indicate that sulphur deposition derive from the Cu-Ni smelters of Nikel-Zapolyarnyi on the Kola Peninsula. In addition, the geological features and the acid deposition patterns are superimposed by the extremely harsh climate.

Key words (GeoRef Thesaurus, AGI): environmental geology, drainage basins, soils, Podzols, till, geochemistry, sulfur, lakes, surface water, chemical properties, acidification, atmospheric fallout, Lapland, Finland.

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To Seppo and Janne

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INTRODUCTION

General

Grave concerns about the adverse effects of acidification processes on the environment in Europe were first expressed back in the 1960s (Oden 1968). The chemistry of forest-floor soils, surface waters and groundwaters has been studied intensively in Europe, Canada and the USA during recent decades, mainly due to growing anxiety about atmospheric acid deposition (Kenttämies 1973, Ugolini et al. 1977, Kenttämies 1979, Pätilä 1982, Matzner and Ulrich 1983, van Breemen et al. 1984, David and Driscoll 1984, Grenzius 1984, Cornan and Aiken 1985, Driscoll and Schecher 1985, Hallbäcken and Popovich 1985, Falkenberg-Grerip 1987, Henriksen et al. 1989, Räisänen 1989). Changes caused by acid deposition have been most distinct in clear lake waters in Europe and North America (Pätilä 1982, Kämäri 1984, 1985, Simola et al. 1985, Jeffries et al. 1986, Naturvårdsverket 1986, Henriksen and Brakke 1988a, Landers et al. 1988a, Neary and Dillon 1988, 1989, Schindler et al. 1989, Kelso et al. 1990).

In Finland, the first studies on lake acidification were conducted in the early 1970s (Kenttämies 1973, 1979, Pätilä 1982), when it was noticed that sulphur emissions were more than twice what they had been in the 1950s and 1960s (Buch 1960, Haapala 1972). During the 1980s the acidification of forest-floor soils, vegetation and surface and lake waters was studied at length in southern and central Finland (Tolonen and Jaakkola 1983, Kämäri 1985, Nuotio 1985, Simola et al. 1985, Kämäri 1986, Forsius 1987, Nysten 1988, Räisänen 1989, Kauppi et al. 1990). Studies concentrated on southern Finland, probably because northern Fennoscandia was still widely believed to be free of pollution. Details of industrial emissions on the Kola Peninsula were not available, and hence estimated annual sulphur deposition was thought to be lowest in Finnish Lapland (Kauppi et al. 1987). At the end of the 1980s, evidence began to accumulate that heavy-metal loads from Cu-Ni smelters on the Kola Peninsula were drifting over the Finnish-Norwegian and Russian borders (Kinnunen 1987, Rühling et al. 1987).

Air-quality monitoring was intensified, and additional monitoring stations were set up in Sør-Varanger in Norway, the Nikel area in Russia and in Finnish Lapland. Fresh evidence revealed the sensitivity of ecosystems to acidification and heavy-metal loads in northern Fennoscandia, northern Kola in particular (Henriksen et al. 1988a, Kinnunen 1990, Kinnunen and Varmola 1990, Pulkkinen 1991, Swedish Environmental Protection Agency 1991, Traaen et al. 1991, Tikkanen et al. 1992, Tikkanen et al. 1995). Unfortunately, however, there has been a lack of international collaboration in monitoring the acidification of soil and lake waters.

In Finland, lake density is highest in northernmost Lapland (> 800 lakes/100 km^2), where the bedrock-controlled topography favours the existence of numerous small lakes (Raatikainen and Kuusisto 1988). The detailed assessment

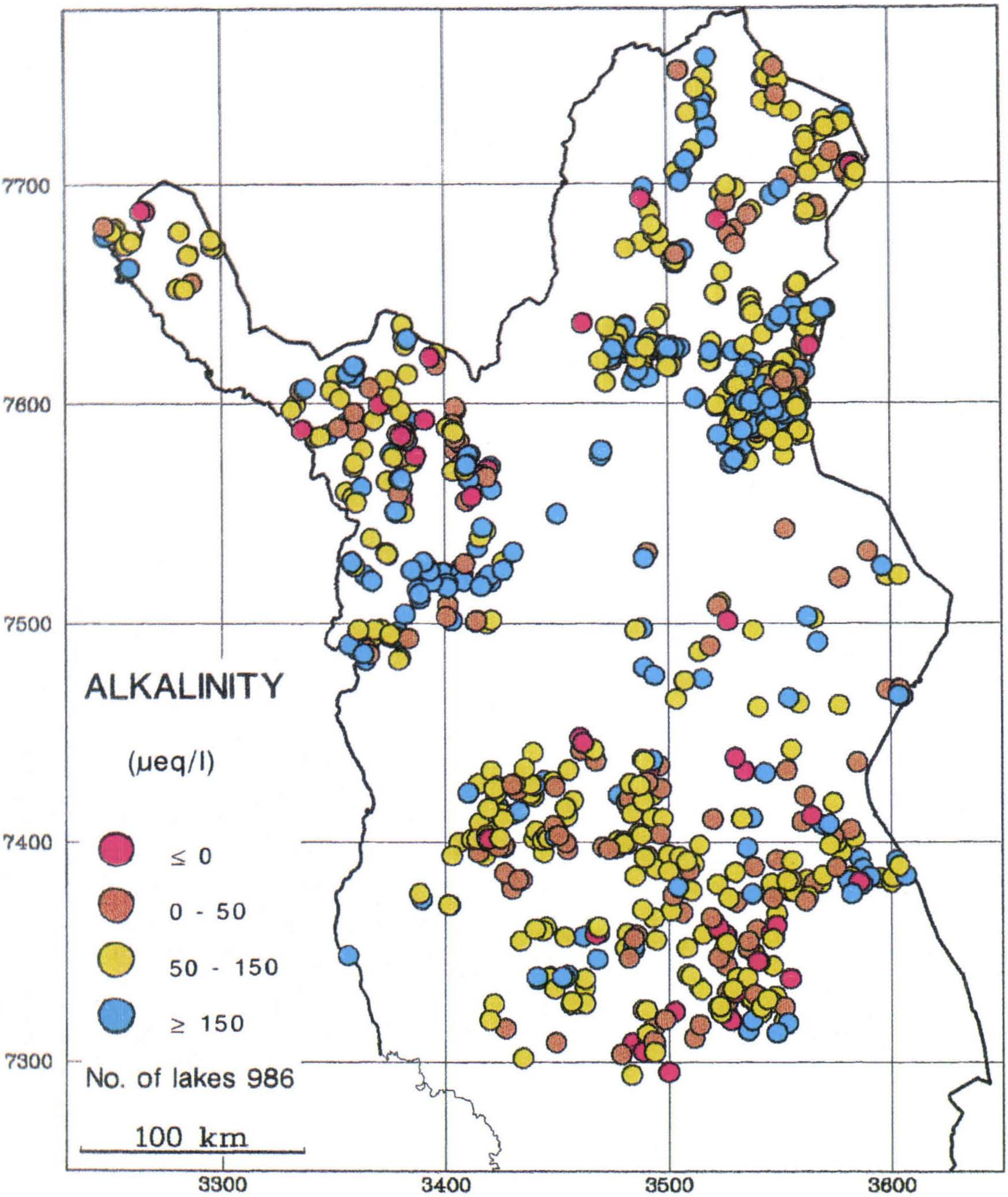


Fig. 1. The detailed small-lake assessment carried out by the Water and Environment District (now Regional Environment Centre) of Lapland in Finnish Lapland in 1987-1991 revealed that a substantial number of small lakes were acidic (ANC < 0.0 μeq/l) or that their alkalinity was critically low (ANC 0.0 - 50 μeq/l). Acid and acid-sensitive lakes were not, however, located in the area of heaviest sulphur deposition in northeastern Lapland but throughout Lapland, although mainly in northeastern, northwestern and southern Lapland (Kinnunen 1990, 1992, Kähkönen 1993).

of small lakes (0.01 - 10 km^2) in Finnish Lapland carried out by the Water and Environment District (now the Regional Environment Centre) of Lapland in 1987-1991 showed that a significant number of these lakes were acidic or that their alkalinity was critically low (Fig. 1) (Kinnunen 1990, 1992). The acid or acid-sensitive lakes were not, however, located within the area of heaviest sulphur deposition in northeastern Lapland but were scattered throughout the province, the majority nonetheless being concentrated in northeastern, northwestern and southern Lapland (Kinnunen 1992, Kähkönen 1993).

In many studies, lake-water quality has been used as an indicator of acid-sensitivity established by measuring either alkalinity (Omernik and Powers 1982) or base cation concentrations (e.g. Lachance et al. 1985, Forsius 1987, Sullivan et al. 1988, Forsius et al. 1990). The sum of base cation concentrations normally shows a good correlation with alkalinity in pristine, clear-water lakes (Henriksen 1980) and therefore both of these water-quality parameters provide an indication of increases in alkalinity within the catchment. The use of water quality as a sensitivity indicator is not, however, without problems. Surface waters in different regions receive, or have received, different amounts of acidifying and neutralizing compounds from catchment soils and anthropogenic sources, added to which, the high concentrations of organic acids in humic lakes lower alkalinity relative to the base cation concentrations (Brakke et al. 1987, Sullivan et al. 1989). The water quality of the lakes is thus no longer as it was initially.

Moreover, under harsh arctic climatic conditions (Fig. 2), large seasonal variations compounded by ice and frost prevent water circulation, and surface waters have a strong natural rhythm determined by solar radiation. In the northern boreal zone, the water of lakes, ponds and streams is frozen for many months in win-

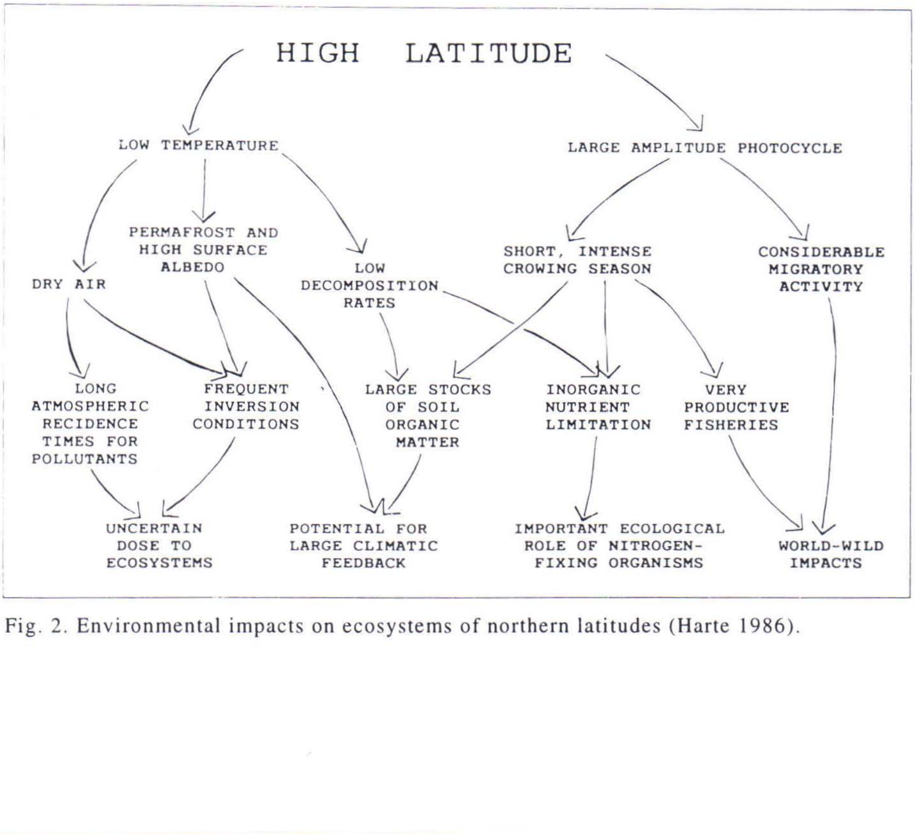


Fig. 2. Environmental impacts on ecosystems of northern latitudes (Harte 1986).

ter; only for a few months in summer are tundra and mountain-lake waters free of ice. Winter precipitation accumulates as snow, and during the rapid spring thaw much of the annual precipitation runs as water into lakes and rivers. Acid flood water mainly flows on the ground, unable to penetrate the frozen soil. Early spring - a period of sudden low pH values - is, therefore, a critical period for acid shock. Because the acidity of the snowpack has risen due to anthropogenic pollution, the buffer capacity of northern fresh water is put to a severe test every spring.

In Finland, the overburden is mainly composed of basal till with a wide variety of lithologies and particle sizes. According to an extensive Regional Geochemical Mapping programme conducted by the Geological Survey of Finland (GSF) with a sampling density of 1 sample/4 km^2 (Salminen 1995), the geochemistry of till soils in Finnish Lapland varies both regionally and locally. Over large areas, the soil is sensitive to acidification, which manifests itself as increased aluminium solubility, leaching of base cations, and low pH values in soil. Usually, however, podsolized till soils are extremely heterogeneous in chemical, mineralogical and physical properties (Kontio and Kähkönen 1991, Räisänen and Pulkkinen 1991, Kähkönen 1993). Comparison of soil acidification between different regions is difficult because acidification of forest-floor soils is related to a number of soil factors, and because acidification and the sensitivity of soil to acidification have been investigated on different soil types and grain sizes and using different analytical methods (e.g. van Breemen et al. 1984, Räisänen 1989, Bölviken et al. 1990, Chadwick and Kuylenstierna 1990, Kashulina 1991, Kontio and Kähkönen 1991, Öhlander et al. 1991, Räisänen and Pulkkinen 1991, Andersson 1992, Olsson 1992, Sutinen et al. 1994).

A lake with its catchment constitutes a dynamic hydrological entity in which the processes altering water quality take place in the course of the general water circulation. The main catchment factors controlling the acid sensitivity of Finnish lake waters are the physical, biological and chemical compositions of the catchment soil, organic matter derived from the catchment, sulphur deposition and the hydrological pathway of the runoff. However, the relationship between the chemistry of catchment soils and that of lake waters is complex. The equilibrium and buffering mechanisms between the soil and lake waters are controlled by various processes such as chemical and physical weathering of minerals and rocks, leaching and precipitation of elements and compounds, decomposition of organic matter, nutrient uptake, cation exchange, and aluminium, iron and silicate buffering. In water courses, too, many processes change and buffer water quality (Schindler et al. 1986, Kelly 1987, Schindler 1988). Thus, the proportion of acid and acid-sensitive lakes receiving similar amounts of organic and anthropogenic acids varies, depending on catchment factors (Chen et al. 1984, Kämäri 1985, Henriksen and Brakke 1988a, Landers et al. 1988, Sverdrup and Warfinge 1990, Kinnunen 1992, Kähkönen 1993). In Lapland, the sensitivity of soil and water courses to acidification is accentuated by features typical of northerly latitudes, that is, the cold and dark and the length of winter. As a consequence, the soil's ability to resist acidification is lower in Arctic regions than elsewhere (Räisänen and Pulkkinen 1991, Olsson 1992).

Objective

In the first part of a large cooperative project launched by the Water and Environment District (now Regional Environment Centre) of Lapland and the GSF in 1990 the concentrations of elements in parent till material soluble in aqua regia and their effect on the chemistry and acid-sensitivity of the water of about 1000 lakes were determined (Kähkönen 1993). The purpose of this thesis, a follow-up investigation, was to determine in greater detail the mineralogical and geochemical properties and processes, that is, weathering, leaching and precipitation of elements, cation exchange, aluminium buffer and sulphur concentrations, in 90 podzol till soils, in the humus, eluvial and illuvial horizons, the transition zone and the parent material, using three selective leaches. The geochemical effects and processes of the catchment soils were correlated with the water chemistry and acid-sensitivity of 90 lakes in these catchments, which received different amounts of natural and anthropogenic acid deposition. Attention also focused on the natural and anthropogenic concentrations of sulphur in the humus and mineral soils.

DESCRIPTION OF STUDY AREA

Bedrock

Finnish Lapland, which is part of the Precambrian Fennoscandian Shield, is bordered by Palaeozoic Caledonian rocks in its northwestern corner (Fig. 3) (Simonen 1980).

The largest schist areas are that of Peräpohja in the Kemi-Tornio-Tervola area and the Central Lapland Greenstone Belt, which is linked to the Kuusamo schist area in the southeast and the small Käsivarsi schist area in the northwest. The bedrock of these areas is mainly composed of quartzites, phyllites, mica schists, mafic and acid plutonic rocks and dolomitic limestones. The central Lapland schist area includes an extensive greenstone belt composed of mafic and ultramafic rocks sensitive to weathering. The chemical composition of the rocks of the greenstone belt are characterized by high concentrations of iron, magnesium and calcium and of heavy metals such as copper and nickel. Readily weathering dolomitic and calcium- and magnesium-rich limestones with interlayers occur in the Peräpohja and Kuusamo schist areas. The presence of mafic lithologies is reflected in the high concentrations of magnesium and calcium in the soil of these areas (Koljonen ed. 1992, Kähkönen 1993). In places, there are layers of black schist containing not only micas and quartz but regularly also pyrite and/or pyrrhotite (Simonen 1980).

There are three extensive granite gneiss areas: Pudasjärvi in southern Lapland, Koillis-Lappi in eastern Lapland and Taka-Lappi in northern Lapland. In the far northwest, there is the smaller area (Simonen 1980). The bedrock in all these areas is mainly composed of acid plutonic and metamorphic gneisses. Owing to their chemical composition, the major minerals of the rocks - quartz, potassium feldspar, micas and sodium-rich plagioclases - are highly resistant to weathering. Biotite is the most readily weathering mica. The granite gneiss areas include variable amounts of small mafic bodies and layers, intrusions, schist belts and diabase dykes. Locally, however, the rocks vary in composition both between and within gneiss-granite areas. Despite their small extent in the granite-gneiss areas, the mafic rocks have considerable impact on the soil owing to their readily weathering calcium- and magnesium-bearing minerals. The Iivaara alkali rock intrusive is located in the east of the eastern Finland granite gneiss area and the apatite-rich Sokli carbonatite deposit in the eastern part of the Koillis-Lappi granite gneiss area.

The arcuate Lapland granulite area extends northwestwards from between Nellimö and Korvatunturi in the east to Karigasniemi in the

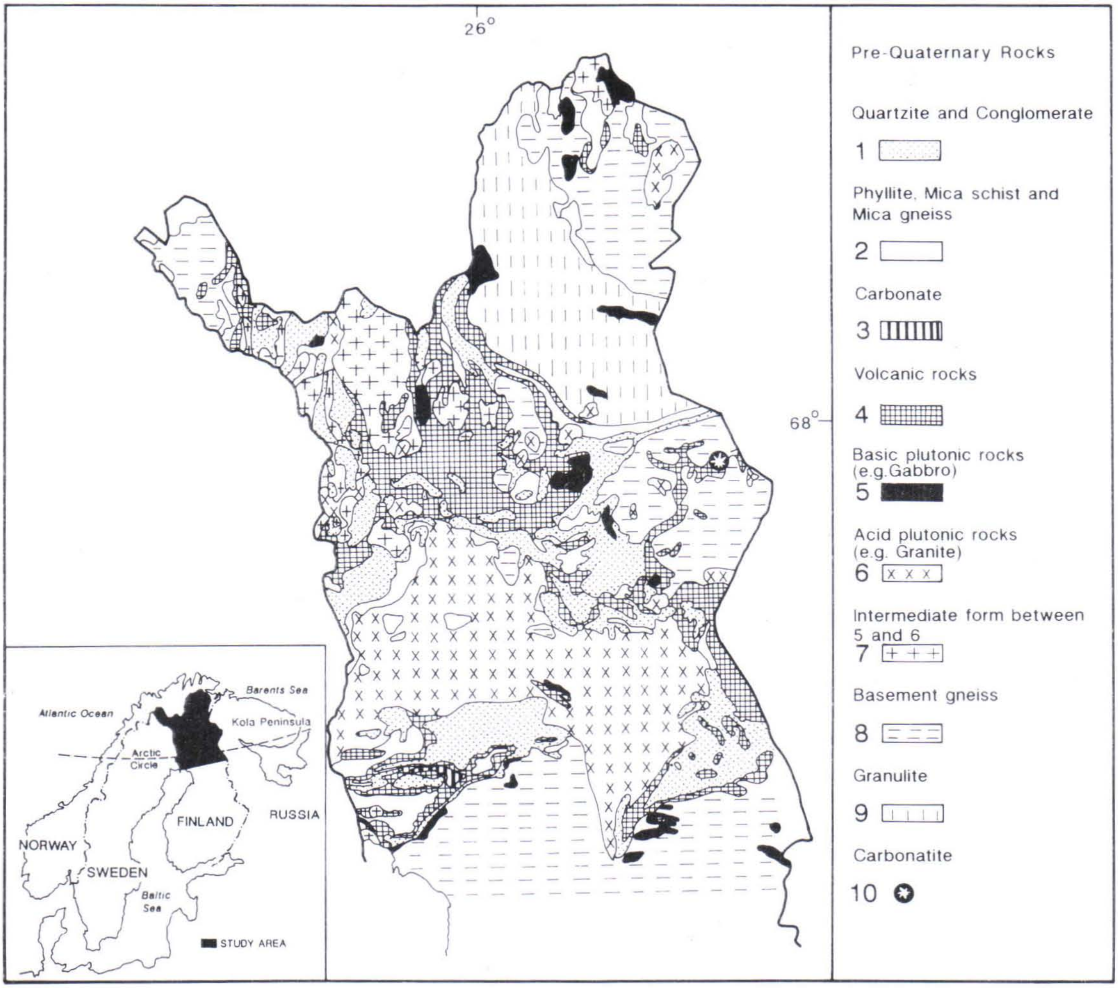


Fig. 3. Pre-Quaternary rocks of northern Finland. Modified after Simonen (1980) and Perttunen (1984).

west, and is bordered in the northeast by the Taka-Lappi granite gneiss area (Simonen 1980). The granulite is a metamorphic gneissose rock with plagioclase, quartz, garnet, micas and, in places, cordierite and sillimanite as major minerals. Garnet is an aluminium- and iron-rich mineral that is resistant to weathering (Bates and Jackson 1980). In places it has altered into easily weathering biotite.

The central Lapland granite area between Rovaniemi, Pello, Vaalajärvi and Salla is the largest area of acidic plutonic rocks. It is not, however, continuous but includes small schist and mafic rock areas (Mutanen 1991). Minor granite and granodiorite areas occur in western Lapland - in the Käsivarsi area, and in northern and northeastern Lapland. Plutonic areas composed of gabbros and peridotites are encountered in the central Lapland schist area, the Lapland granulite area and the Taka-Lappi granite gneiss area (Perttunen 1984).

Quaternary deposits

Covering about 50% of the land area, basal till is the most common soil type in Lapland (Fig. 4). Till covers a far greater area of bedrock, however, as other drift sediments rest on the basal till. In Lapland the average thickness of the till blanket is 5.8 m, but it varies greatly, even in adjacent areas; it is at its thinnest (0-2 m) on the summits of fells and hills, and thickest (10-15 m) in river valleys and other low-lying places (Mäkinen and Maunu 1884, Hirvas 1991).

In Finland, as in glaciated terrain elsewhere, there is usually a sharp contact between the bedrock and the overlying till, and the regional geochemical properties of till commonly coincide with those of the corresponding lithological areas (Koljonen ed. 1992). The lithological composition of till depends on the lithology and topography of bedrock, the erosion-resistance of the rocks, the variation in the direction of flow of continental ice sheets, and the type and amount of redeposited drift. The drift transported in basal parts of the ice sheet - the basal till - correlates better with the local composition of the bedrock than does the ablation till washed by meltwaters.

Most tills in Finland are of a fines-poor, sandy variety (Virkkala 1969a). In some areas, however, they are rich in fines, silt and clay fractions. According to Lintinen (1995), Finnish tills usually contain 20 - 55% fines. In Lapland, the abundance of till fines is highest (> 40%) in central Lapland (Fig. 5) (Lintinen 1995). Owing to its large reactive surface area, the fine till fraction has a considerable influence on the chemical and physical properties of till, as elements and compounds dissolve from it in abundance in chemical reactions. Therefore, it is chemically the most active fraction in mineral soil (Rose et al. 1979). The main constituents of Finland's till fines are quartz, feldspars, amphiboles, chlorite, illite, vermiculite and mixed-layer clay minerals (Soveri and Hyyppä 1966, Räisänen et al. 1992).

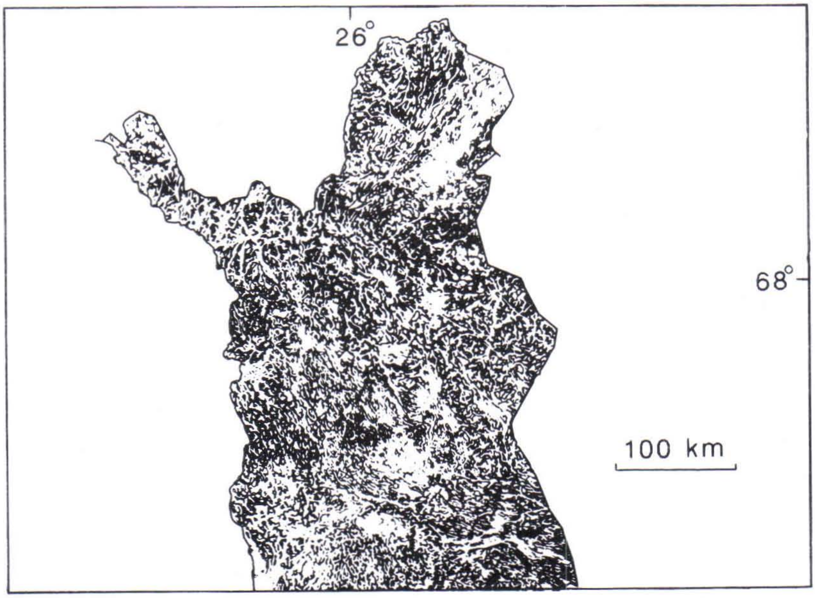


Fig. 4. Areas covered by basal till in Finnish Lapland (Kujansuu and Niemelä 1984).

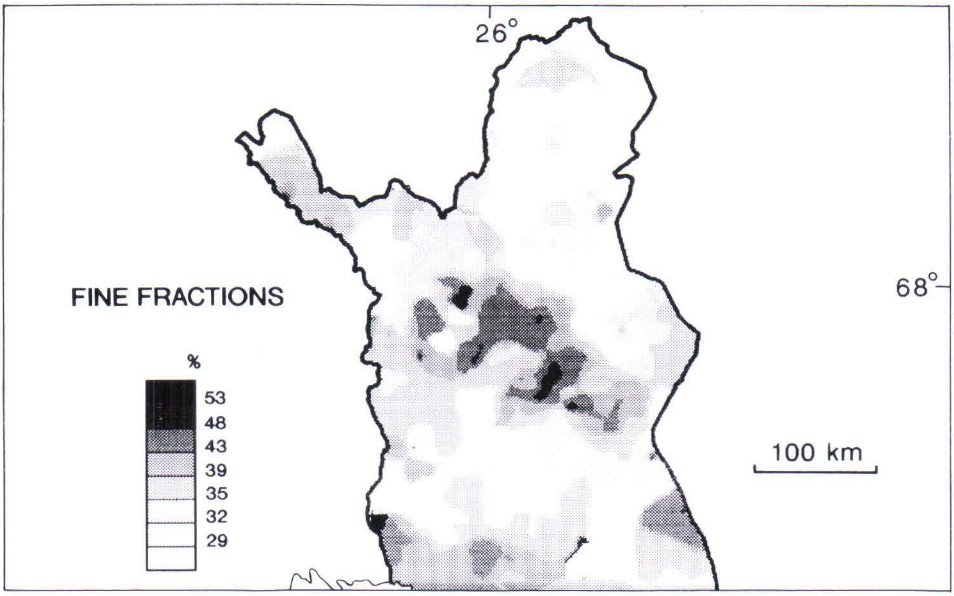


Fig. 5. Regional distribution of till fines (< 0.06 mm) in the < 2.0-mm till fraction in Finnish Lapland. White areas not sampled (Lintinen 1995).

According to Räisänen et al. (1992), the clay minerals in fines are mixed-layer types probably formed as alteration products of micas, mainly biotite. The alteration products include mica-vermiculite mixed-layer minerals. Some of the minerals exhibit polymerization of Al-hydroxide in interlayers of clay minerals. The formation of such interlayers is related to podzolization, in which mobilized Al migrates to and precipitates in lower horizons.

Rock exposures or rocky areas covered with overburden less than 1 m deep constitute less than 6% of the land area, occurring mainly in the mountainous areas of northernmost Lapland. Glaciofluvial and aeolian sediments cover about 10% of the land area; they are fairly evenly distributed, although the most extensive esker chains are located in northwestern Lapland. Major fluvial deposits occur mainly in river valleys. Aeolian deposits tend to be associated with large glaciofluvial formations (Atlas of Finland, 1990). Sorted sediments - sand and gravel - composed predominantly of quartz and feldspars reflect poorly the chemical composition, particularly the trace element composition, of the underlying bedrock.

Peatland covers about 22% of the land area in Lapland, accounting for about 40% of the total mire coverage in Finland (Fig. 6). The proportion of peatland is lowest in the Enontekiö area in northwestern Lapland, and in the Inari-Utsjoki area in northeastern Lapland, where it constitutes 10-20% of the land area. The proportion is highest in central Lapland and the Tervola, Ranua, Posio areas, where it accounts for over 40% of the land area. The largest mires are at Sodankylä and Kittilä in central Lapland (Mäkinen and Maunu 1984). Today many mires have been ditched and drained for forestry and agriculture, especially in southern Lapland (Paavilainen and Tiihonen 1988).

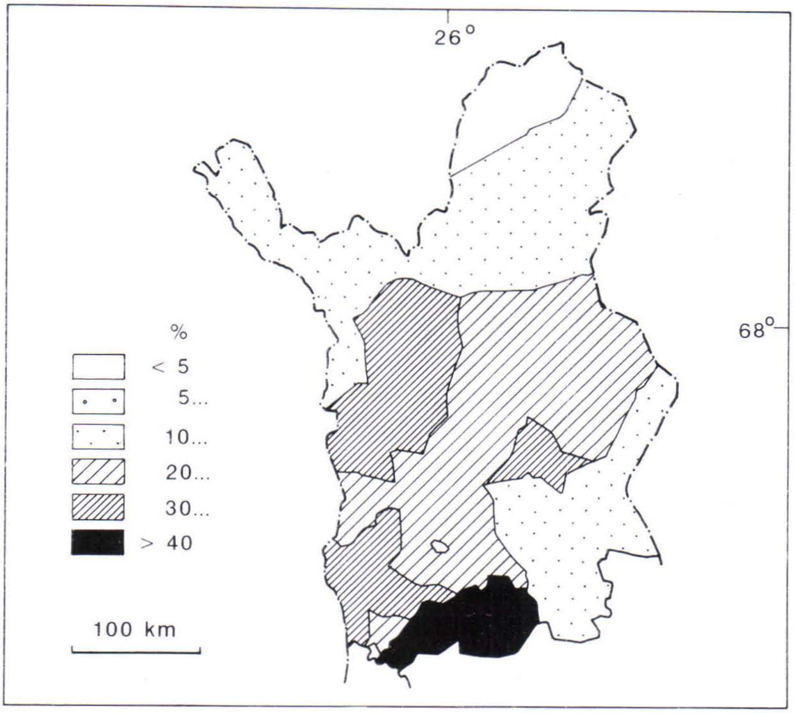


Fig. 6. The percentage of peatland in Finnish Lapland (Atlas of Finland 1990).

Preglacial regolith

A distinctive feature of Finnish Lapland is the in-situ occurrences of weathered bedrock. The largest known coherent occurrences of weathered rocks in Finland are in the ice divide in central Lapland, in a zone roughly 150 km wide and running from northwest to southeast (Salminen 1975, Saarnisto and Tamminen 1987, Hirvas 1991) (Fig. 7). Only random occurrences of weathered bedrock have been encountered outside this coherent zone (Hirvas et al. 1977). These occurrences were produced by intense weathering at a time when Finland's climate was much warmer and more humid than it is today, and when physical, and especially chemical, weathering of the bedrock was very intense. The weathering products are mixed with till to varying degrees, implying that weathering preceded glaciation. In eastern Lapland, the presence of marine diatoms in a secondary position suggests that this part of the land was covered by the sea in the early Tertiary (Hirvas and Tynni 1976, Tynni 1982). In Lapland the thickness of the weathered crust ranges from a few to a hundred metres (Mäkinen and Maunu 1984).

The weathered bedrock occurrences are not related to any particular rock type and have been met with in almost every lithological area (Salminen 1975). Their appearance, however, depends on the grain size of the parent rock and the degree of weathering. In western Lapland, the weathered crust is coarse grained and fragmented, but in eastern Lapland it contains fine, clayey material (Hirvas 1991). Although derived from the same bedrock, the till and weathered crust differ markedly from each other in

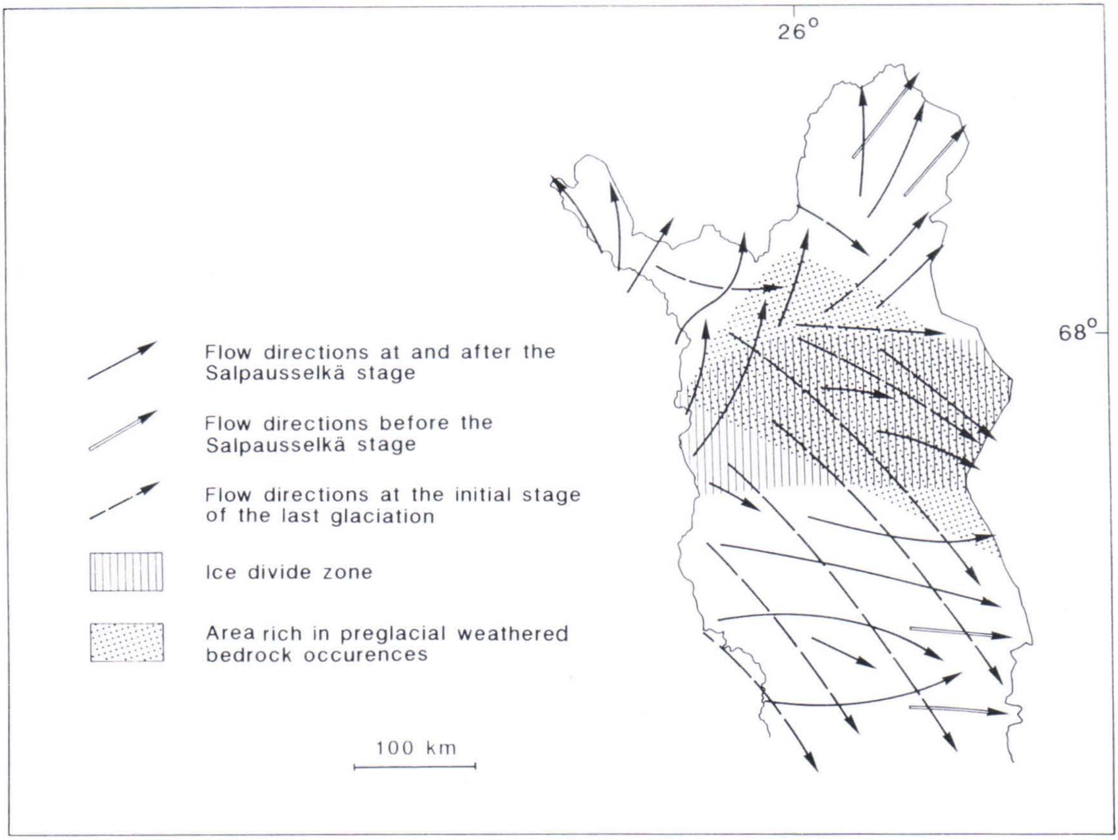


Fig. 7. Flow directions of the continental ice sheet during the Weichselian glaciation, the ice divide and the area with abundant occurrences of preglacial weathering crust (Koljonen 1992).

geochemical properties (Salminen 1975). The continental ice sheet and meltwaters mixed and homogenized the till, and weathering products were at least partly washed out. The weathered crust has preserved its original structure undeformed and largely in situ. The geochemical properties of the weathered rocks vary, depending on the underlying bedrock and their weathering properties. According to Simonen (1964), mafic rocks make up less than 10% and acidic rocks over 90% of the Finnish bedrock. In Lapland, the occurrences of weathering crust are far more common in mafic than in acidic rock areas owing to the poorer weathering-resistance of mafic rocks. In the mafic rock areas, the oxidation of sulphides into sulphuric acid in the course of weathering speeds up the weathering of mafic minerals (Salminen 1975).

In the event that chemical weathering has proceeded far enough, the weathering crust is enriched in clay minerals and oxides of silicon, aluminium and iron (Pulkkinen 1985, Räisänen 1989). Trace metal concentrations are usually substantially higher in the weathering crust than in till, where they increase as the abundance of weathering products in till increases (Salminen 1975, Hirvas et al. 1977). In some places the weathered bedrock occurrences have undergone intense chemical weathering and contain, for instance, vermiculite $(Mg,Fe, Al)_3$ $(Al,Si)_4O_{10}(OH)_2$ x $4H_2O$, kaolinite $(Al_2Si_2$

$O_5(OH)_4$ and other clay minerals (Pulkkinen 1985). As shown by the regional geochemical mapping programme, the high content of Al- and Fe-rich regolith in eastern Lapland makes the till more sensitive to acidification there than in other parts of Lapland, even at low levels of acid deposition (Räisänen and Pulkkinen 1991). Elevated concentrations of readily soluble aluminium have been encountered in the illuvial horizon and transition zone in areas of weathering crust (Räisänen 1989). However, there are places in which it is difficult to draw a boundary between weathering crust and till (Salminen 1975).

SOIL AND LAKE PROCESSES

Podzolization

The predominant soil-forming process in forested and treeless regions of Lapland is podzolization of mineral soils (Fig. 8). The main factors affecting the chemical, physical and biological properties of podzol soils are the mineralogy and texture of soil, climate and topography (Aaltonen 1939, 1941, Jenny 1941, Jauhiainen 1969, Petersen 1976, FitzPatrick 1980). Podzolization, the natural acidification of soil, is a slow process that started on the surficial parts of mineral soil after the Weichselian glaciation, about 10 000 - 9000 years ago, when vegetation spread to Finland (Donner 1995). Owing to the evolution of the Baltic Sea, the oldest podzols are in the supra-aquatic areas of northern and eastern Lapland. The youngest podzols are on the coast of the Gulf of Bothnia, the area with the highest uplift rate in Finland (Atlas of Finland, 1990).

In Finland, the vegetation which has developed on exposed mineral soil since the end of glaciation consists of species adapted to a harsh climate: conifers, birches and dwarf shrubs in the forested zone, and lichens, mosses, grasses and dwarf shrubs in the tundra zone. Biological activity in the soil in Arctic and sub-Arctic areas is, in general, rather low owing to the low mean soil temperature during the short summer, the small proportion of easily decomposable material in the plant litter, and the restrictions on microbiological activity posed by a high soil moisture content following the spring thaw (Boyle and Voigt 1973, Binkley and Richter 1987, Andersson 1988).

Typical podzol horizons have tended to develop in till, sand and gravel soils as a result of chemical differentiation. The high soil moisture content, high incidence of anaerobic conditions and poor decomposability of the plant litter have resulted in the gradual accumulation of an organic layer comprising acidic, partially decomposed litter and humus in the surface layer. The composition of the organic compounds varies widely, depending on the vegetation and soil properties (Evans 1980, Brady 1984). The organic acids formed in the decomposition of plants together with root and microbiological processes acidify the surficial part of the podzol and promote the leaching of nutrients and trace elements bound to mineral particles for plant uptake (Boyle and Voigt 1973, Petersen 1976, Andersson 1988).

Podzolic soils are characterized by a light-coloured eluvial horizon immediately below the organic layer, and a reddish illuvial horizon below the eluvial horizon. The eluvial horizon has been strongly leached by acidic percolation water and is low in base cations. Iron and aluminium are removed as colloids incorporated in clay minerals or as organometallic complexes. As a result of weathering and buffering processes, however, the pH of the percolation water gradually increases as it passes down through this horizon. The aluminium,

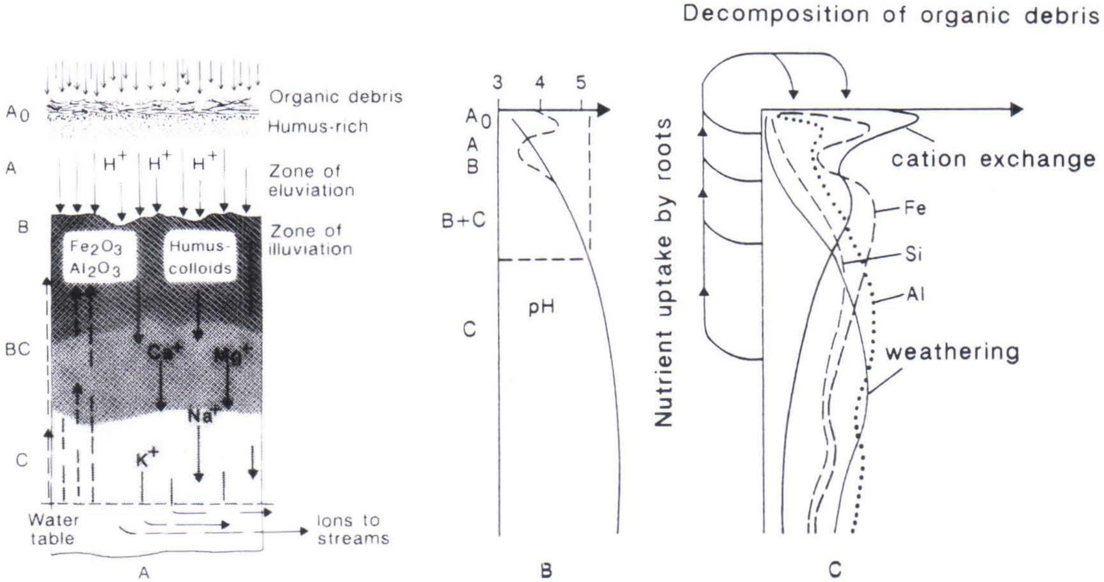


Fig. 8. Structure and horizons of a podzol profile: a) podzol profile and circulation of water,b) owing to electrolytes dissolved from the eluvial horizon, the pH of the runoff water increases in the illuvial horizon and transition zone, precipitating aluminium, iron and silicon compounds; c) cation exchange is most intense in the humus and eluvial horizons, and the chemical weathering of minerals in the transition zone and weakly altered parent material. Modified after Stahler (1970) and Jacks et al. (1984).

iron and silica compounds and organic matter dissolved in the percolation water precipitate in the eluvial horizon as aluminium-iron-silicon hydroxides (Rose et al. 1979, De Cornick 1980, Farmer et al. 1980, Anderssen et al. 1982, Rieger 1983, Farmer 1984). Soluble aluminium is bound to inorganic iron-silicon compounds, clay minerals or organic complexes. The chemically modified, surficial horizons of podzolic soils are underlain by relatively unaltered parent material. The geochemical composition of this material determines the elemental composition of the upper soil horizons to a considerable extent and also the type of vegetation that develops at the site (Boyle and Voigt 1973, Binkley et al. 1987, Andersson 1988).

Weathering

Weathering is a geological process due to which rocks and minerals are broken down mechanically, chemically or biologically. All these processes generally occur simultaneously and the intensity of each of them is controlled by the prevailing conditions. The most important factors affecting weathering are the susceptibility of minerals to weathering, grain size, climate, topography and runoff conditions (Rose et al. 1979). In mechanical weathering, rocks and minerals break into small particles without their total or mineral composition being altered. In Lapland in particular, mechanical weathering is promoted by frost wedging due to the great variations in temperature. Mechanical weathering exposes rocks and minerals to chemical weathering, because the reactive surface area increases as the grain size diminishes. The break-up of rocks and minerals is also caused by biological activity (Ollier 1969).

The chemical weathering of minerals liberates elements, ions and various chemical compounds, which, when entering into soil solution, alter the composition of the soil and runoff waters; some of these are plant nutrients, some contribute to buffering processes in the soil. Thus soil can be considered as a sink and source of elements in which elemental concentrations are much higher than in the soil solution phase. Chemical weathering usually takes place through hydrolysis (formation of OH^- and H^+ ions) but also through adsorption (hydration), oxidation and dissolution. In hydrolysis, the hydrogen ions derive from organic soil acids, carbonic acid and/or wet and dry atmospheric deposition. In the course of silicate mineral weathering, the H^+ ions replace the alkali and alkaline earth metals liberated from crystal lattices. Cations released in weathering may be adsorbed on the clay and humus particles as exchangeable cations. Chemical weathering proceeds step-wise, depending on the conditions, e.g. pressure, temperature, moisture content, pH and microbial activity.

In glaciated regions, the soil and bedrock are mainly composed of silicates, which differ markedly in their susceptibility to weathering and the solubility of elements (Goldich 1938, Ollier 1969, Rose et al. 1979). The capacity of the silicate buffer is high because the soil is usually composed of silicate minerals. The very slow weathering of silicates, however, restricts neutralization reactions. In Finland, carbonates play only a local role, and hence femic silicate minerals (amphiboles, pyroxenes, some micas) are more important in neutralizing and weathering processes. In the weathering of silicate minerals under alkaline or neutral conditions, the easily soluble salts (Ca, Mg, K and Na sulphates and chlorides) are removed first. At the same time, base cations are liberated in the hydrolysis of silicates, and alumino-silicates and clay minerals are formed. In an acidic environment, weathering releases silica and base cations but also insoluble Al_2O_3, Fe_2O_3 and MnO_2 hydroxides. The liberated base cations may be adsorbed on the surfaces of the colloidal particles thus formed, or they may remain in soil solution or be eluted by the runoff water into water courses. In chemical weathering, other minerals, and organic and inorganic compounds are also dissolved in runoff water (Rose et al. 1979).

The most common primary silicate minerals are quartz, feldspars, micas, amphiboles and pyroxenes. When they weather, secondary clay minerals such as vermiculite, kaolinite and mixed-layer minerals are formed. These secondary clay minerals have a larger reactive surface than the primary minerals and are thus more reactive in weathering processes. Moreover, they are a potential source of soluble aluminium, and the dissolution of cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) in runoff water is associated with their formation. Clay minerals can bind exchangeable cations and regulate their solution in runoff water (Wilson 1986).

Quartz (SiO_2) is a common mineral in acid and intermediate plutonic rocks and is highly resistant to weathering. In soil, the soluble silicon derives from clay minerals or metal-organic complexes (Rieger 1983). Feldspars are aluminosilicates in whose lattice aluminium substitutes for some of the silicon. Potassium feldspar ($KAlSi_3O_8$) and plagioclase ($(Ca,Na)(AlSi)AlSi_2O_8)$) are the most common feldspars. Plagioclase is mainly a sodium-predominant aluminosilicate and potassium feldspar a potassium-bearing aluminosilicate. Feldspars rich in sodium and potassium are more resistant to weathering than calcium-rich feldspars (Rose et al. 1979). In Finland, calcium-predominant feldspars are less abundant than sodium- and potassium-predominant varieties. The weathering of feldspars under acid conditions is controlled by the concentration of hydrogen ions, the concentration and type of organic acids, and their ability to form complexes, and by the properties of the clay minerals present (Holdren and Speyer 1985, Manley and Evans 1986). The resistance of feldspars to weathering varies, depending on their composition (Ollier 1969). In hydrolysis, albite is altered into kaolinite as follows:

$2NaAlSi_3O_8 + 2H_+ + H_2O$<---->
albite
$Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2Na^+$
kaolinite

Biotite, muscovite, sericite and chlorite are the most common primary micas. Biotite micas ($K(Mg,Fe)_3(Al,Fe)SiO_{10}(OH,F)_2$) are potassium-bearing magnesium-iron aluminosilicates that weather easily under acid conditions. When weathering, biotite often alters into vermiculite or smectite. Weathering of smectite into kaolinite implies an increase in acidification of the soil (Melkerud 1983, Wilson 1986). In some eluvial podzol horizons, biotite has weathered almost completely, especially when in clay fraction. In granites, biotite often weathers into chlorite, which, in turn, weathers readily due to its iron-manganese composition, particularly when in eluvial horizons. Muscovite-group micas ($KAl_2(AlSiO_3)O_{10}(OH))_2$ are potassium-bearing aluminium-predominant silicates highly resistant to weathering (Wilson 1986). Illite, a water-bearing transitional form of muscovite, may weather further into vermiculite or smectite. Chlorite and sericite may also occur as secondary minerals formed in podzol processes (Melkerud 1983, Snäll 1986). Unweatherable micas do not bind exchangeable ions or anions, whereas partly weathered, fine-grained, mixed-layer micas and clay minerals proper are capable of ion exchange and thus participate in buffer reactions in soil (Räisänen and Jylänki 1990).

$2KAl_3Si_3O_{10}(OH)_2 + 2H_+ + 2H_2O$<------>
muscovite
$3Al_2Si_2O_5(OH)_4 + 2K^+$
kaolinite

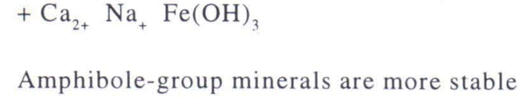
Amphiboles are usually calcium-predominant iron-magnesium aluminosilicates that weather into readily weathering aluminium-predominant chlorite. Pyroxenes and amphiboles weather stepwise and fairly rapidly through ion exchange of secondary minerals and alterations in the crystal lattice into clay minerals, thus releasing base cations into soil water (Ollier 1969, Ehlers and Blatt 1983).

$(Ca, Na)(Mg,Fe,Al)(Si,Al)_2O_6 + H_+ + H_2O$
augite
<----> Ca-montmorillonite + H_2SiO_4
$+ Ca_{2+}$ Na_+ $Fe(OH)_3$

Amphibole-group minerals are more stable under acid conditions than biotite, but they often weather more rapidly than feldspars. When weathering, calcium is leached from amphiboles and pyroxenes more readily than magnesium, which is bound to the lattice more tightly than calcium. According to Melkerud (1983), amphiboles remain unweathered in the silt fraction but alter into chlorite in the clay fraction and may further weather into vermiculite and smectite.

Cation exchange reactions

Cation exchange on the surfaces of soil particles is closely related to weathering and podzol processes in the soil. The main easily soluble exchangeable cations are Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+} and H^+ (Hesse 1971). A clay, peat or humus particle generates a negatively charged surface around itself to which positively charged cations may adhere.



In soil solution, the presence of hydrogen ions activates cation exchange reactions between clay minerals, organic matter and root nodules. Cation exchange on the surfaces of soil particles is the most important buffering

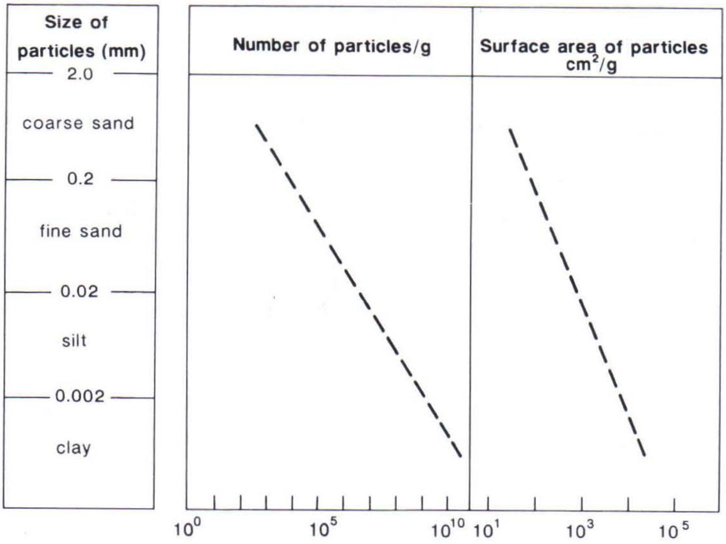


Fig. 9. The number and surface areas of particles increase as the grain size of minerals diminishes. In mineral soils, cation exchange occurs mainly on the large, negatively charged surface of the fine fraction (Birkeland 1974).

process in the humus and eluvial horizons (Boyle and Voigt 1973, Peterson 1976, Evans 1980, Brady 1984, Andersson 1988). In cation exchange reactions, H^+ ions replace the exchangeable cations adsorbed on clay minerals or the surfaces of organic matter. Cation exchange is controlled by soil pH, grain size, moisture content and organic matter content. The mobility of exchangeable cations is also affected by the abundance and type of clay minerals, the weathering degree of silicate minerals, and the concentration and adsorption properties of organic complexes and chelated compounds present in the soil (Melkerud 1983). The cation exchange capacities of humus and mineral soil differ, depending on the chemical and mineralogical composition of the soils, the decomposability of plant residues in the soils, and microbiological activity. In mineral soil, cation exchange takes place primarily in the fine fraction because of its large, negatively charged surface area (Fig. 9). Cation exchange reactions in soil and plants are closely related to each other.

In coarse-grained soils, the cation exchange rate is low due to the low clay content; this could, however, be offset to some extent by organic matter were it present in large amounts (Rose et al. 1979). In virgin podzol profiles, buffering begins with base cation exchange reactions as the hydrogen concentration increases. The uptake of base cations of plants results in natural acidification of soil, but in a virgin environment the balance is slowly restored by plant decomposition (Wiklander 1976, Rose et al. 1979, Matzner and Ulrich 1983). The concentration of base cations is highest in podzol horizons containing cation exchangeable organic complexes and/or clay minerals. In slightly acidic podzol soils, the solubility of base cations increases and their buffer capacity declines due to an increasing concentration of hydrogen ions or to increased aluminium concentrations on the exchange sites of base cations. Base cations then migrate to lower horizons and to groundwaters and surface waters. In acidic soils, the concentrations of soluble aluminium exceed those of base cations, thus initiating the buffering reactions of aluminium (Räisänen 1989).

Aluminium reactions

Aluminium occurs in the soil incorporated in the crystal structures and lattice interstices of clay minerals, as complex compounds, organic complexes, amorphous phase and secondary oxides and adsorbed on soil particles, depending on the mineralogical composition of the soil, the concentration and type of organic matter, soil pH and redox conditions (Rose et al. 1979, Page et al. 1982). For soil acidification, the relative abundances of aluminium fractions are more important than the absolute concentration of aluminium in the soil. In mineral soils, the total concentration of aluminium is about 7.5%, but the bulk of it is incorporated in silicates that dissolve in acids only with difficulty (e.g. Koljonen ed. 1992).

The aluminium in the humus layer occurs mainly as organic complexes. As these are chemically very stable, the proportion of free aluminium in the humus layer is often very low. In mineral soils, aluminium is often polymerized into insoluble hydroxides incorporated in the lattice interstices, mainly in the illuvial horizon, but in intensely podzolized soils also in the eluvial horizon. The stability and abundance of aluminium-saturated clay minerals in podzol horizons depend on the original composition of the soil and the history of podzolization along with the associated natural acidification processes. In a neutral and slightly acidic soil (pH > 4.5), aluminium is insoluble in water (Bache 1974, 1985), but when soluble, aluminium forms numerous hydrated ions and complexes whose dissolution-precipitation reactions depend on the pH (Fig. 10).

Soluble aluminium precipitates in the illuvial horizon as organic complexes and inorganic oxides (Farmer 1984) at the same time as the hydrogen ion concentration in soil water and the proportion of aluminium ions on the exchange sites of colloids increase as aluminium is hydrolyzed (Bache 1974, 1985). Should the hydrogen ion concentration in the structures of clay minerals increase sufficiently, some of the polymerized aluminium oxides

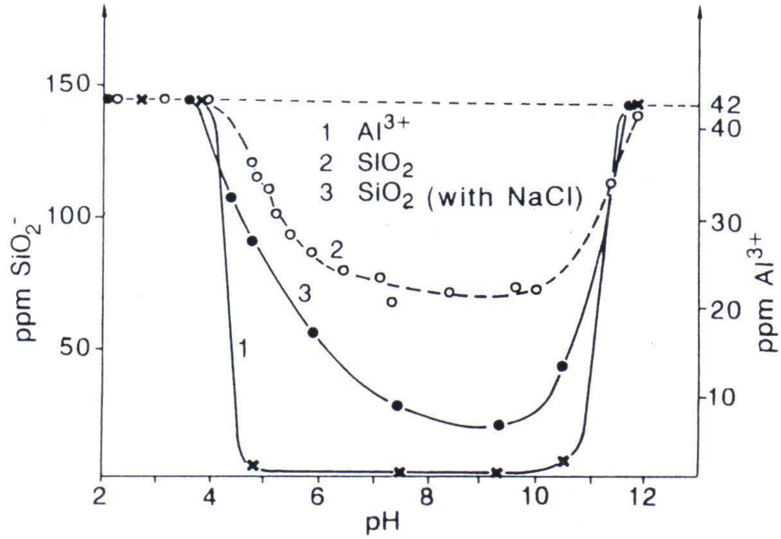


Fig. 10. In a neutral and slightly acidic environment (pH > 4.5) aluminium is insoluble in water (Wey and Siffert 1961).

will disintegrate into monomeric, exchangeable or free Al ions (Jackson 1963). The hydrolyzation of aluminium accelerates soil acidification, but at the same time the polymerization and hydrolyzation reactions of aluminium buffer acidity as they are partly associated with the weathering of minerals and the cation exchange reactions of organic complexes (Jackson 1963, Bache 1974, Jackson and Patterson 1982, Bache 1985).

$$Al_6(OH)_{12}^{6+} + 12H^+ = 2Al^{3+}X_3 + 4Al^{3}+ + 12H_2O$$

(X = incorporation in structure of host mineral) Exchangeable, monomeric Al^{3+} or $Al(OH)^{2+}$ is hydrolyzed under acid conditions according to Huang and Keller (1972) and Bache (1974) as follows:

$Al^{3+} + H_2O = Al(OH)^{2+} + H^+$ and
$Al(OH)^{2+} + H_2O = Al(OH)_2^+ + H^+$

Anion mobility

Anions that occur in soil or are incorporated in acid deposition play a significant role in the acidification of soil and watercourses because they affect the leaching and retention of elements. Sulphate, which is the dominant anion accompanying acids in the soil solution, is considered to be responsible for the accelerated leaching of cations from soils (Singh et al. 1980). Sulphuric acid may, however, be partly retained in the soil by a number of organic and inorganic mechanisms, thus delaying the response of catchment systems to inputs of acid deposition (Eriksson 1988, Warwood et al. 1986b, Courchense et al. 1989). Many studies indicate that SO_4^{2-} retention is heavily dependent on climate, soil characteristics and the rate of SO_4^{2-} input. The main processes by which sulphate is retained in soils are accumulation of organic matter, adsorption on solid surfaces, and adsorption of aluminium sulphates and sulphur in metal sulphides (Partfilt and Smart 1978, Rajan 1978, Stumm and Morgan 1981, Nordstrom 1982, Hartikainen and Yli-Halla 1985, Fuller et al. 1986a, 1986b, Schindler et al. 1986, Warwood et al. 1986b, Urban et al. 1989).

There are very many different organic sulphur compounds in soils. Sulphur is an important macronutrient, and organic sulphur constitutes a considerable proportion of the total sulphur content of most soils, especially in boreal forest-floor soils, where organic matter decomposes relatively slowly. Peat bogs are important sulphur sinks because of slow mineralization. Retained sulphur may be oxidized and leached due to drainage of these bogs, leading in turn to acidification of soils and surface waters (Stumm and Morgan 1981, Hartikainen and Yli-Halla 1985). Many studies have shown that the tendency of sulphate to be adsorbed on positively charged surfaces in soils is considerably greater than that of nitrate and chloride (Nodvin et al. 1986, Balistrieri and Chao 1987). Another possible sulphur retention mechanism, which could be of importance in soils with low pH (< 4.5),is the precipitation of basic aluminium sulphates (van Breemen et al. 1973). Traditionally, sulphate adsorption has been considered the most important sulphur retention mechanism in soils in response to increasing acidity, especially in areas with thick, well-drained B horizons with substantial accumulation of sesquioxides. Most of the evidence suggests that the concentrations of amorphous Fe and Al oxides are closely related to sulphate adsorption (Jonsson and Cole 1977, Parfitt and Smart 1978, Jonsson et al. 1986, Mc Donald 1987). Under reducing conditions, sulphate may also be lost to the system by the formation of metal sulphides.

With some exceptions, forest ecosystems are extremely effective in retaining nitrogen within the system. Despite the large amounts of nitrogen (2000 - 5000 kg ha^{-1}) in forest-floor soils in Finland, only about 1% of this is normally present in mineralized form (e.g. Nömmik 1968, Viro 1969). Nitrogen cycling in forest ecosystems is almost completely based on biological processes that are, in turn, regulated by the chemical and physical properties of the soil. Fungi, which are mainly responsible for decomposing organic matter, are important in maintaining a tightly closed nitrogen cycle. The dense mass of fungal mycelia and plant roots effectively prevent the leaching of nitrogen. The amount of nitrogen leached under natural conditions in southern Scandinavia has been estimated to be 1-2 kg $ha^{-1}a^{-1}$ (Nilsson and Grennfelt 1988). Because of the low rate of decomposition due to a cool climate and naturally acid soils, nitrogen cycling is slow in the forest-floor soils of Finnish Lapland.

Forest fires have considerable impact on the nitrogen reserves of forest-floor soils. Moreover, owing to the changed physical and chemical properties of soil, nitrogen mineralization has increased (Viro 1969). The availability of nitrogen for plants may improve for a time after burning, but the risk of nitrogen leaching increases at the same time. The proportion of organically bound nitrogen mineralized as nitrate is of decisive importance for soil acidification and nitrogen leaching. The ability of soil to nitrify depends on several factors, of which the C/N ratio of the organic matter may be the most important (Grundersen and Rasmussen 1988).

Lake-water chemistry

The buffer capacity of lake waters is closely related to the properties of the catchment soils, in particular to the reactions controlling the acid - base balance (van Breemen et al. 1984). Processes controlling the buffer capacity of water, such as primary productivity, reactions of sulphur and nitrogen compounds and the buffer effect of the sediment, take place in lakes, too (Schindler et al. 1986, Kelly 1987, Schindler 1988). The runoff water flowing from catchments to lakes is always a mixture of several acids. The natural acidity of lakes is mainly due to the organic acids and inorganic aluminium and silicon compounds leached from the catchment, the amounts of which depend on the intensity of production and decomposition of organic matter, moisture content, temperature, and the amount and quality of runoff (Kortelainen 1993). The anions of strong acids in lake waters - sulphate and nitrate - derive mainly from atmospheric deposition (Forsius et al. 1990). In many cases, however, the sulphides in the catchment soil and bedrock contribute to the locally high sulphate concentrations of lakes (Kähkönen 1993, Lahermo et al. 1995).

The buffer capacity of natural waters, which is measured as alkalinity, is usually determined as the bicarbonate (HCO_3^-) concentration of waters. In general, as well as having carbonate alkalinity, water contains compounds of organic matter and aluminium, the functional groups of whose weak acids act as buffers at low pH. Owing to the buffer carbonate system, the acidification of waters at pH < 6.0 shows up mainly as lowered alkalinity values (Fig. 11). In acid-sensitive lakes at the transitional stage, the buffer capacity of water (alkalinity) declines and the tendency to a large variation in pH increases. In weakly buffered waters in particular, pH values vary greatly and pH does not give a very reliable picture of acidification (Kämäri 1984, Forsius 1987). Once the carbonate buffer system has been exhausted (pH < 5.5), the buffer mechanism is maintained by the aluminium hydroxide system together with humic compounds. In practice, organic matter contributes to buffering once the bicarbonate capacity has been exhausted (Kortelainen 1993) As in soils, the effect of the aluminium buffer

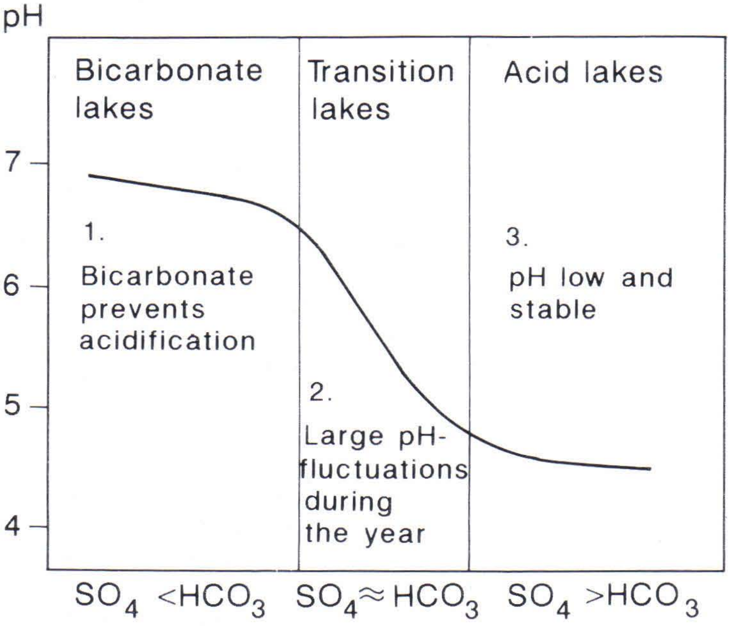


Fig. 11. Titration curve of an HCO_3^- solution showing lake acidification (Henriksen 1980, Brakke and Henriksen 1987).

in waters is based on the ionization of monomeric and polymeric aluminium hydroxides when the hydrogen ion concentration increases. Acid cations leached from catchment soils alter the colour of waters because, at low pH and in the presence of Fe^{3+} and Al^{3+}, humus coagulates and precipitates on the lake bottom, making the waters clearer (Dickson 1980).

Equilibrium reactions between soil and soil water are greatly affected by precipitation and runoff patterns in the catchment. The rate at which water percolates through the soil, eventually reaching watercourses, depends on soil depth, grain size, organic matter and moisture content, as well as on topography, vegetation cover and season. The higher the content of fine material and the deeper the soils, the higher is the water retention capacity. There is then sufficient time for slow buffering and for neutralization reactions between percolating water and soil particles to reach equilibrium. In the case of very fine-textured and compact soils, water cannot infiltrate the surface and deeper soil horizons. In coarse-grained soils with a relatively low organic matter content, the water percolates rapidly down into the surface water and groundwater, and the effect of the chemical properties of the surficial deposits on percolation water quality is minimal. Rough topography and a high proportion of exposed bedrock increase the proportion of surface runoff, which reacts only with the topsoil and outcrops. As well as by physico-chemical soil factors, the water quality of runoff, and thus that of water courses, is affected by the size of the catchment and the hydrological position of the lake. In a large catchment, the variation is slight, as the migration time of runoff is longer and the runoff water still has some retention capacity (Pätilä 1982). With an increase in the proportion of groundwater runoff, a lake receives its runoff at a more constant rate all-year round; in general, the water is also better neutralized. Lakes with a small catchment and a low proportion of groundwater runoff are, in general, the most acid-sensitive

(Eilers et al. 1983, Kähkönen 1993).

In Lapland in particular the seasons affect the water quality of lakes and rivers. The pH values of runoff waters are usually at their lowest in spring, as the acid compounds accumulated in snow in winter are liberated when the snow melts, and the effect of the neutralizing processes in the soil is at its lowest because of the frozen soil. During the autumn overturn, the runoff waters are mixed with the entire water mass. In Lapland, the water courses are more susceptible to episodic increases in acidity than elsewhere as the proportion of snow meltwaters is high and the soil is regularly frozen at depth for long periods. On the other hand, during the spring runoff, frost protects the soil nutrients from leaching.

ACID DEPOSITION

Sulphur deposition

The highest total estimated annual sulphur deposition in Lapland, 1.0 g/m^2, has been recorded in the Inari area, in northeastern Lapland, near the Finnish-Norwegian border. The figure, which is about the same as in southern Scandinavia, decreases gradually southwestwards to 0.3 g/m^2 in northern Sweden (Fig. 12) (Sandnes and Styve 1992, Tuovinen et al. 1993).

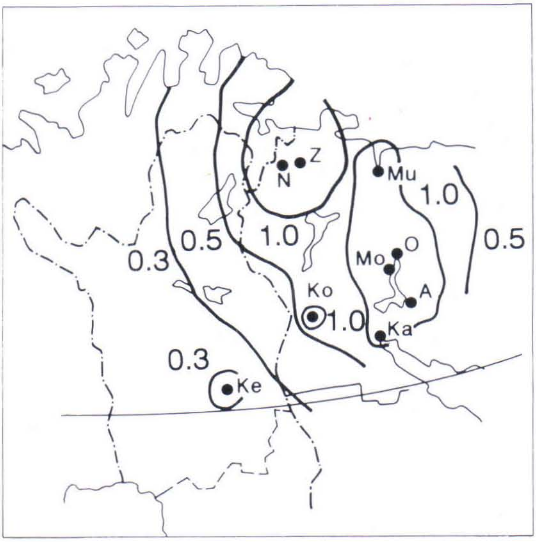


Fig. 12. Estimated sulphur deposition in northern Finland and the Kola Peninsula (g m^{-2} a^{-1}) from June 1990 to June 1991. A=Apatity, Ka=Kandalaksha, Ke=Kemijärvi, Ko=Kovdor, Mo=Monchegorsk, Mu=Murmansk, Ni=Nikel, O=Olenogorsk, Za=Zapolyarnyi (Tuovinen et al. 1992).

Sulphur deposition in northern Fennoscandia is overwhelmingly due to industry on the Kola Peninsula, specifically to emissions from the Cu-Ni smelters at Nikel-Zapolyarnyi. Sulphur emissions from each of these smelters equal Finland's total sulphur deposition (Laurila et al. 1991) (Fig. 13). Sulphur emissions from continental Europe and southern Finland arrive in Lapland in the form of episodic, long-distance deposition at times of southerly air currents. Regionally, the main local, albeit small, sources of sulphur emissions in Finnish Lapland are the pulp mills at Kemi and Kemijärvi and the Tornio steel plant (Table 1) (Lapland Provincial State Office 1990).

Table 1. Sulphur and nitrogen deposition in Lapland province in 1988 by source. The unit is one tonne per year (Iversen et al. 1990, Kangas 1990, Tuovinen et al. 1990).

Origin	**sulphur**	**nitrogen**
Provice of Lapland	1	0.3
Other Finland	3	1.9
Kola Peninsula	12	0.1
Other Russia	4	1.5
Other Europe	4	3.7
Background	19	1.4
In all	**43**	**9**

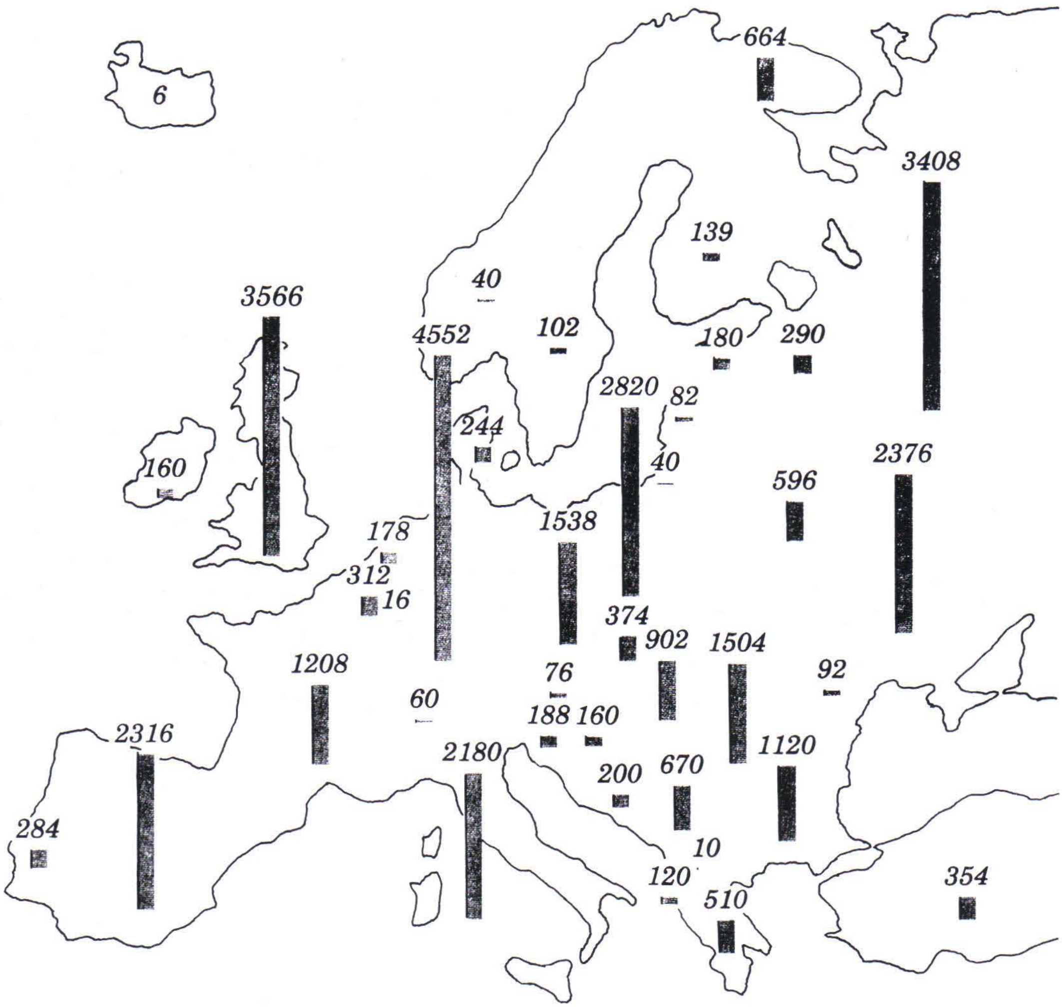
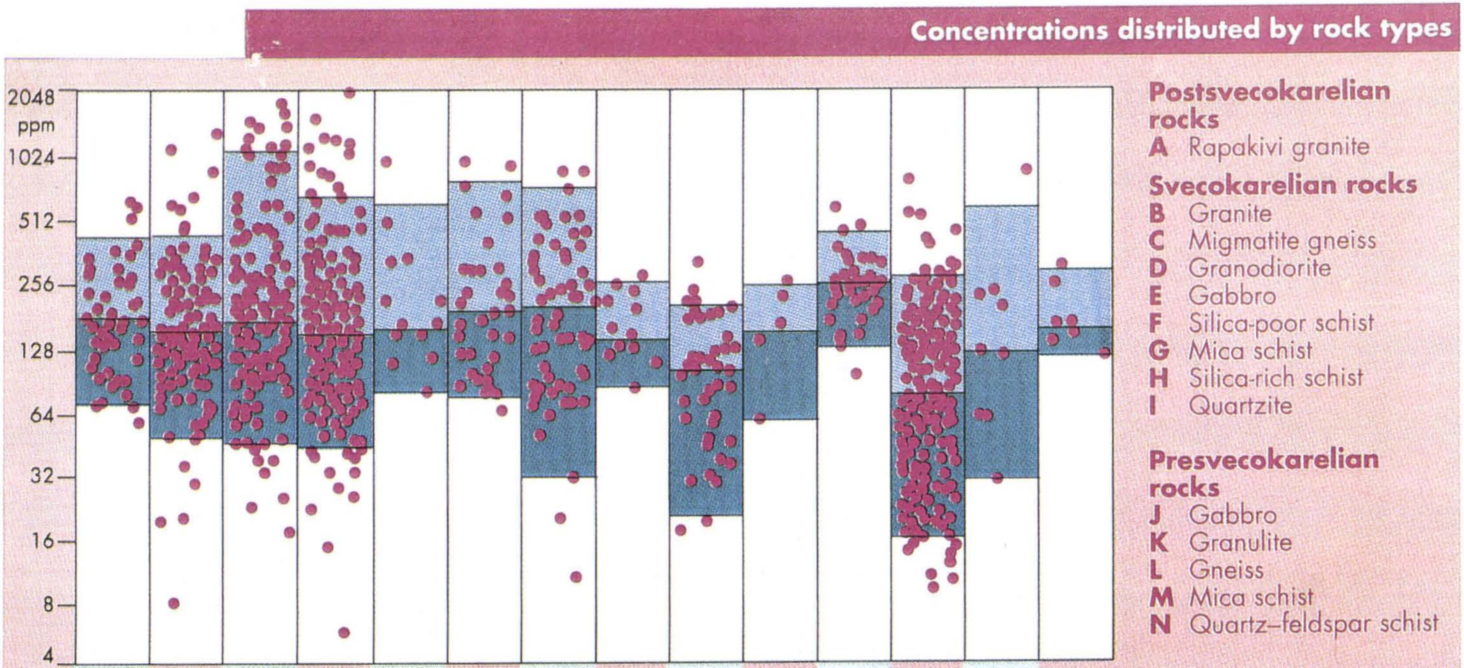


Fig. 13. Sulphur dioxide emissions in Europe in 1992 in units of 1000 tonnes of SO_2. (Source: EMEP MSC-W and the Ministry of the Environment, Tikkanen ed. 1995).

The bulk of the sulphur circulating in the atmosphere and the ground derives from natural sources, that is, volcanic activity, sea salt, wind-induced weathering of arid regions and biogenic processes (Andreae 1985). Data on the geographic distribution of sulphur emissions worldwide are very limited. Globally, biogenic sulphur emissions equal the anthropogenic flux, that is, c. 100 Tg a^{-1}, total emissions being c. 200 Tg a^{-1}. Half of the biogenic sulphur emanates from oceans. There are of course large spatial fluctuations in natural sulphur emissions, the highest rates being in coastal regions (Tuovinen et al. 1990).

The average sulphur concentrations of rocks in Finland vary substantially. According to Koljonen ed. (1992), the concentration is highest in schists, around 1100 ppm, and in gabbros and ultramafic rocks, 600 - 800 ppm. Sulphur concentrations in the fine till fraction are highest in areas where the bedrock is composed of mica schists, mafic schists and granulitic rocks,

Table 2. Sulphur concentrations by rock type (Koljonen ed. 1992).



Till, fine fraction	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Arithmetic mean	200	180	250	200	240	260	250	170	110	170	260	110	210	190
Standard deviation	120	140	240	180	210	220	200	62	67	77	98	103	260	70
Median	170	140	170	150	160	190	200	140	98	150	250	72	120	160
Number of observations	55	147	153	238	15	37	59	12	42	5	36	212	9	7

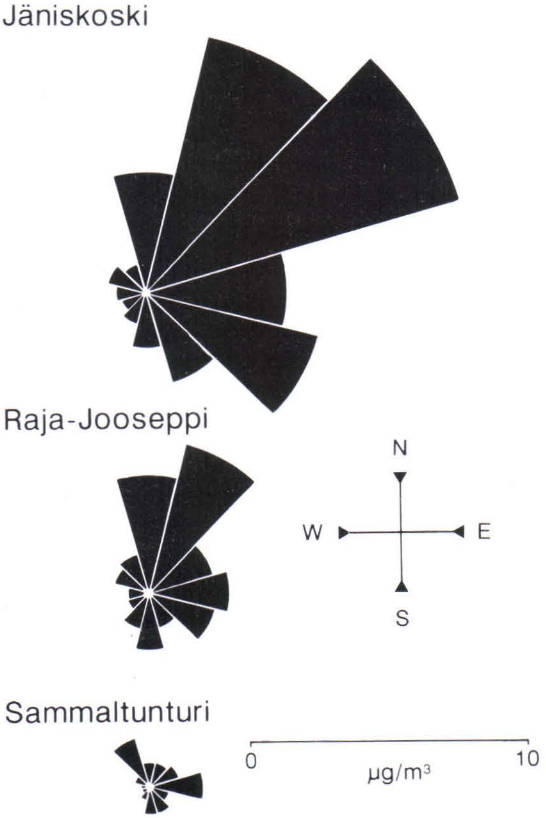


Fig. 14. Concentrations of sulphur dioxide and their averages for different wind directions at three monitoring stations in Finland (Raja-Jooseppi, Sammaltunturi) and on Kola Peninsula (Jäniskoski) in 1993. (Source: the Finnish Meteorological Institute, Tikkanen ed. 1995).

and lowest in areas of quartzites and gneissose rocks (Table 2). The concentrations fluctuate greatly, however, even within a single lithological area. Sulphides weather relatively readily and the dissolved suphur precipitates as sulphate under oxidizing conditions but as sulphides under reducing conditions. Clays containing sulphides and sulphates are fairly common in Finland, in sub-aquatic areas in particular. Most of the sulphur in the soil is incorporated in organic matter (Fuller et al. 1986a, 1986b).

Climatologically, the north is characterized by marked seasonal variations, low temperatures, low transpiration levels and atmospheric stratification, the latter reducing vertical mixing of air masses (Waddington 1988). Atmospheric sulphur dioxide concentrations in Lapland are thus high in winter and emissions distinctly cyclic; in summer, concentrations are low (Laurila and Joffre 1987, 1989, Laurila et al. 1991). They tend to increase when air arrives from the east and south, and particularly when it arrives from the Kola Peninsula. Around Nikel and Monchegorsk, however, the prevailing winds blow from the north and southwest; easterly winds are rare (Fig. 14) (Tuovinen et al. 1993). Since summer 1989 monthly averages of sulphur dioxide concentrations in winter have varied in the range of 1-15 $\mu q/m^3$ at the monitoring station in Lapland, depending on the weather and transport conditions. In winter, sulphur concentrations are highest in eastern Lapland and in southeastern parts of southern Finland. In summer, the monthly averages of sulphur concentrations are markedly lower. Yet east of the Inari area the monthly averages may be as high as 10 $\mu g/m^3$ while they are a mere 1-2 $\mu g/m^3$ in western Lapland (Laurila et al. 1991).

Sulphur deposition levels vary a great deal from day to day. Usually the air is clean in Lapland, and 60% of the time SO_2 concentrations are less than 1 $\mu g/m^3$; however, during the most polluted periods, 1% of the time, they exceed 100 $\mu g/m^3$ (Tuovinen et al. 1993). The highest hourly concentrations of sulphur dioxide, c. 400 $\mu g/m^3$, have been measured in the northeastern Kessi and Inarinjärvi area in northern Lapland. Hourly concentrations exceeding 100 $\mu g/m^3$ may, however, occur over large areas elsewhere in northern Lapland, too. Even in the least polluted areas of northern Finland, emissions from the Kola Peninsula raise the level of sulphur deposition (Laurila et al. 1991).

Nitrogen deposition

Vehicle exhaust is the principal source of emissions of the two nitrogen oxides known collectively as NO_x - nitric oxide (NO) and nitrogen dioxide (NO_2) - and nitrous oxide (N_2O). About 60% of nitrogen emissions in Lapland are due to traffic. Metallurgical processes do not produce abundant nitrogen oxides, and nitrate does not currently contribute to acid deposition in Finnish Lapland at all. Total NO_x emissions on the Kola Peninsula, however, are more than double those in the province of Lapland. The main point sources in Lapland are the pulp mills at Kemi and Kemijärvi (Laurila et al. 1991). Measurements conducted at Oulanka and Värriö, in the eastern Finland, show that, in northern Finland, NO_x emissions are low in rural areas (Pedersen et al. 1990, Leinonen and Juntto 1991), the annual average being below the detection limit of the analytical methods applied, 1 µg/m^3. In winter, however, long-distance emissions with concentrations of 10 µg/m^3 have been recorded (Laurila et al. 1991).

Average annual ammonia emissions in Finland are estimated to exceed 40 000 tonnes, of which Lapland accounts for about 2% (Iversen et al. 1990). The acidifying capability of nitrogen compounds depends on their contribution to biological activity in the soil. Although ammonia is a positive ion neutralizing acid rainwater, some acidifying protons remain in the soil when plants take up ammonia as a nutrient. The negative nitrate increases the acidity of rainwater but, as the roots of plants extract the nitrate ion, the hydroxyl ion in the soil solution tends to neutralize the soil. Thus the acidifying influence of ammonia and nitrate depends on the degree of nitrogen retention. In summer, plants use nitrate deposition very effectively, but in spring the nitrate removed with meltwaters may have an acidifying influence, because the plants are incapable of binding the nitrate.

Acid deposition

In central and eastern Europe, the regional distribution of acid deposition (H^+) does not coincide with the distribution of sulphur because the concentrations of neutralizing ions, calcium, magnesium and ammonia are usually high. As a consequence, sulphate occurs as neutral salts in calcium and magnesium compounds. On the Kola Peninsula, the proportion of neutralizing particulate emissions is fairly high; those from the mining towns of Apatity and Kovdor in particular contain considerable amounts of calcium, sodium, potassium and phosphorus (Tikkanen ed. 1995). In northern Scandinavia, concentrations of neutralising ions are distinctly lower, increasing the proportion of acid sulphate in wet deposition to such an extent that up to 70% of the sulphate and nitrate in the deposition is in acid form. Owing to the low deposition rate of base cations, wet deposition of hydrogen ions in the north is relatively high, 10 µeq/m^2, compared with that in southern Finland. In Finnish Lapland, neutralizing deposition is low, on average, and one-third of acid deposition is neutralized. On the Norwegian side of the border, wet deposition close to Nikel is 230-400 mg/m$^{2;}$ in western Lapland it is 130 mg/m^2 (Anttila et al. 1995). Because of the high contribution of dry deposition to total sulphur deposition it is, however, difficult to estimate total sulphur deposition. Along the Finnish-Norwegian-Russian borders, between 67° and 70°N, dry deposition as inferred from distribution models accounts for up to 60% - 80% of the total sulphur content (Fig. 15) (Tuovinen et al. 1993). In summer, winds often blow from the Kola Peninsula and thus it is highly probable that dry deposition contributes greatly to the total sulphur load in the Inari area (Anttila et al. 1995).

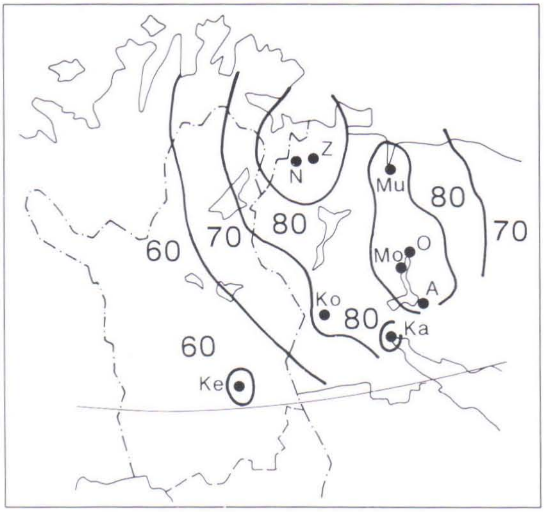


Fig. 15. Inferred proportion of dry deposition (%) in northern Finland and the Kola Peninsula from June 1990 to June 1991. A=Apatity, Ka=Kandalaksha, Ke=Kemijärvi, Ko=Kovdor, Mo=Monchegorsk, Mu=Murmansk, Ni=Nikel, O=Olenogorsk, Za=Zapolyarnyi (Tuovinen et al. 1992).

Arctic haze

The haze in Arctic polar regions consists of aerosol pollutants at higher levels of the atmosphere, transported there by the global process of atmospheric circulation in winter, i.e. strong south-north transport from Europe and Russia (Ottar et al. 1986). It has been estimated that 5% of sulphur emissions in the northern hemisphere, about 3 million tonnes, were transported to the Arctic in 1979-1980 (Barrie et al. 1989). The main pollutant sources of arctic haze are in Europe and Russia. Eastern Europe and Russia contributed 69% to the emissions, western Europe 25% and North America 6%. Arctic haze occurs in winter from December to April, when man-made emissions are less effectively removed from the air and strong south-north transport from mid-latitudes to the Arctic prevails. Background concentrations of acidic substances have increased, especially in winter; influences on acid precipitation have also been recorded. According to Ottar et al. (1986), winter arctic haze is due to human-induced pollution within the arctic air mass, which is characterized by low deposition rates and an absence of photochemical activity. Cold and stable air mass may cover large areas of northern Eurasia in winter and spring. Krasovskaya (1986) has listed the most polluted and pollutant-free areas in the Arctic. Among the most polluted are those located along the main routes of the pollutants - the Taymyr Peninsula, northern Scandinavia, and the central and northern parts of Kola Peninsula.

Critical load

The Economic Commission for Europe of the UN has surveyed the critical load of the soil and surface waters, i.e. their capability to tolerate acid deposition (Downing et al. 1993). The critical load is defined as follows: "A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment are not likely to occur according to present knowledge" (Nilsson and

Grennfelt 1988, Kämäri et al. 1992). The critical load can be considered as an internal property of the ecosystem under examination, the numerical value of which depends on the sensitivity of a certain part of physical nature to the impact of deposition. Areas and ecosystems differ in their sensitivity and thus tolerate different loads. For the most sensitive systems the numerical value of the critical load is zero, or very close to it (Kämäri et al. 1992).

A critical total load value for the most sensitive forest-floor soils is 20 kmol(H^+)/km^2/a, corresponding to a maximum of 3 kg S/ha/a (=0.3 g S/m^2/a) or 9 kg SO_4/ha/a. These values are exceeded by the sulphur load alone in the whole of Fennoscandia. In Finnish Lapland, the critical load for sulphur and nitrogen varies considerably on both a small and a large regional scale. It is estimated that in eastern Finnmark and northeastern Finnish Lapland sulphur deposition exceeds the critical load set for lakes in more than 50% of the lakes analysed (Fig. 16) (Kämäri et al. 1992, Kinnunen 1992). The critical acid load of the most sensitive forest-floor soils in northern Finland is less than 20 μeq/m^2 corresponding to annual sulphur deposition of about of 300 mg/m^2. The annual acid load on Lappish soil is 15-20 μeq/m^2 at its maximum, being thus close to the critical load. The critical load for nitrogen deposition is difficult to establish because nitrate and ammonia are among the main nutrients for vegetation, especially under the extreme conditions prevailing in Lapland (Anttila et al. 1995). As a consequence, acceptable limits for acidic deposition must be set at a lower level than in more productive environments. Areas with low productivity are the most sensitive (Nilsson and Grennfelt eds. 1988). More detailed regional research is needed on the critical loads of pollutants, acidification rates and the conditions affecting a cold-climate environment.

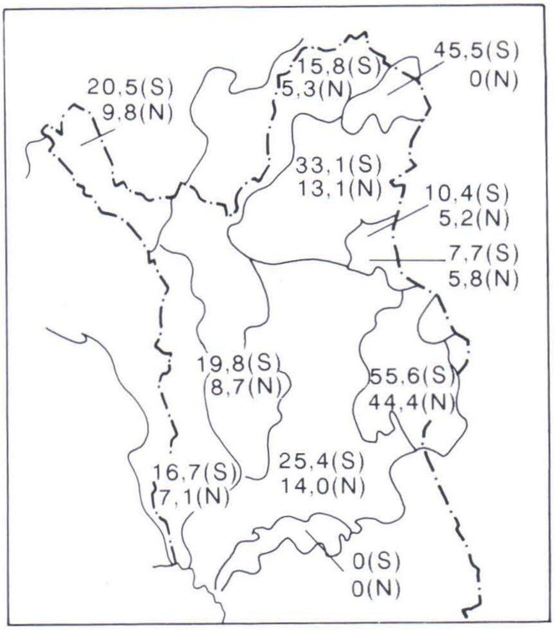


Fig. 16. The percentage of lakes in Finnish Lapland where the critical load is exceeded (ANC limit 20 μeq/l) (Kinnunen 1992). Calculation of the critical load and deposition is described by Kämäri et al. (1992).

MATERIALS AND METHODS

General

Ninety catchment areas in different parts of Lapland and their lakes were selected for the present study (Fig. 17). Most of the podzol soil and lake-water sample sites were selected on the basis of the results of the Regional Geochemical Mapping conducted by the GSF and the large-scale assessment of 1000 lakes carried out by the Water and Environment District of Lapland (Kähkönen 1993). In the selection of lakes, use was also made of the gradients applied in the Lapland Forest Damage Project (Tikkanen ed. 1995). The sulphur dep-

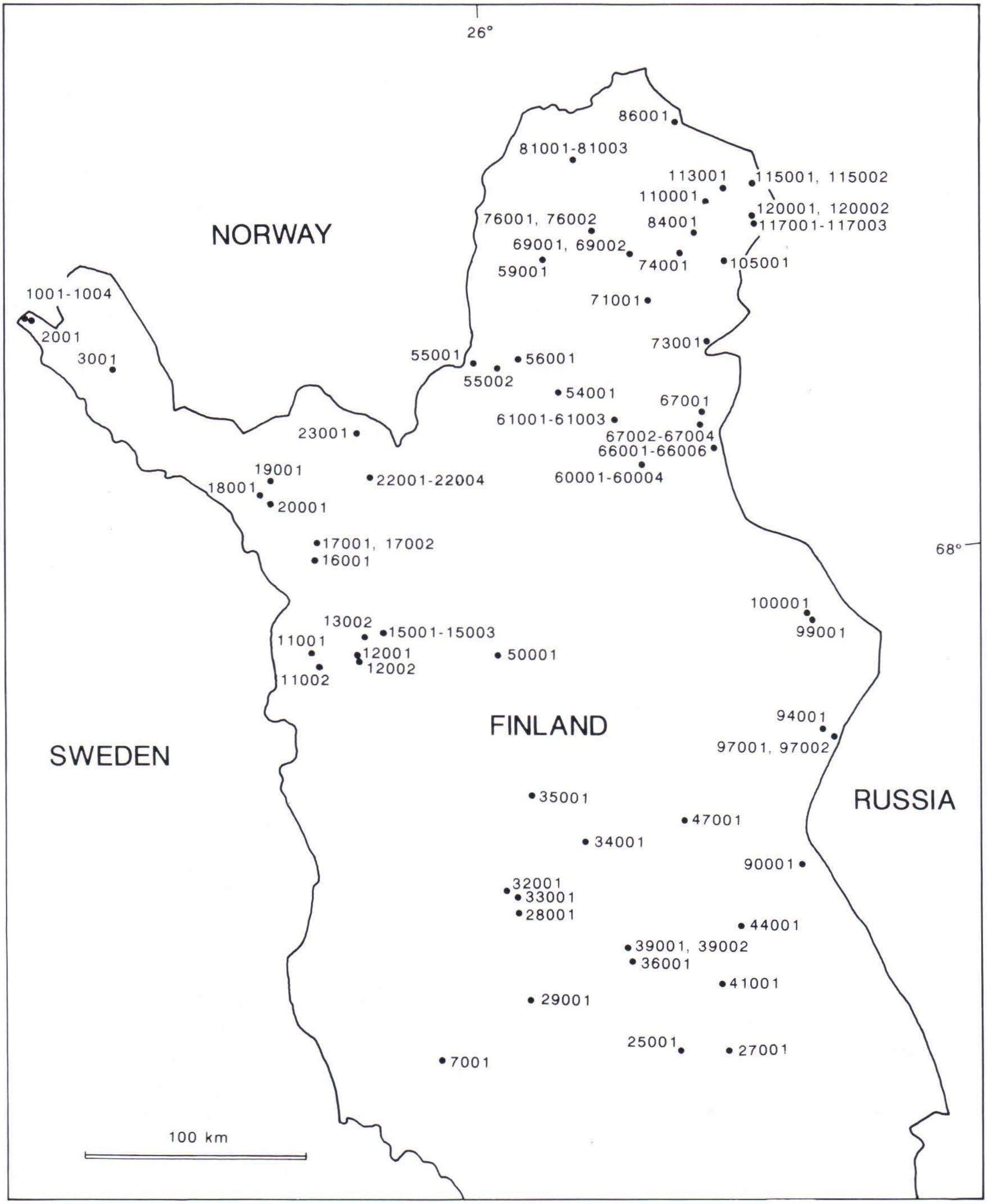


Fig. 17. Sampling sites of podzol soils and lakes.

Fig. 18. The map with the locality names referred to in the text.

osition gradient at the sampling sites varied, being highest in the northeast of Inari and lowest in western and southern Lapland. The proportion of organic acids was highest in southern and western Lapland, where the coverage of mires is greatest in the catchment areas. Extremely humic lakes were avoided.

The retention time of lake water cannot be assessed without flow measurements and volume estimation based on bathymetric mapping. The lakes were divided into three groups assumed to reflect their hydrology and mutual retention time (e.g. Kämäri 1984, Linthurst et al. 1986). The cartographic classification of closed and seepage lakes into groups was ambiguous and so these lakes were treated as a single group. Thirty-one of the lakes were classified as drainage (inflow and outflow exist), 51 as headwater (no inflow channel, outflow exists) and 8 as closed (no surficial inflow/outflow) lakes. The surface areas of the lakes and catchments were measured from 1:20 000 basic maps or 1:50 000 topographic maps. The borders of lakes and catchments were digitized into bar databases by pooling the data.

Numbers were given to the catchment areas and lakes, and the hydrological position of lakes in the chain of lakes was taken into account by numbering the headwater, closed and drainage lakes separately. The lakes uppermost in the chain - headwater and closed lakes were coded by adding the symbol 1 after the number of the lake. The number following the symbol of a drainage lake indicates the posi-

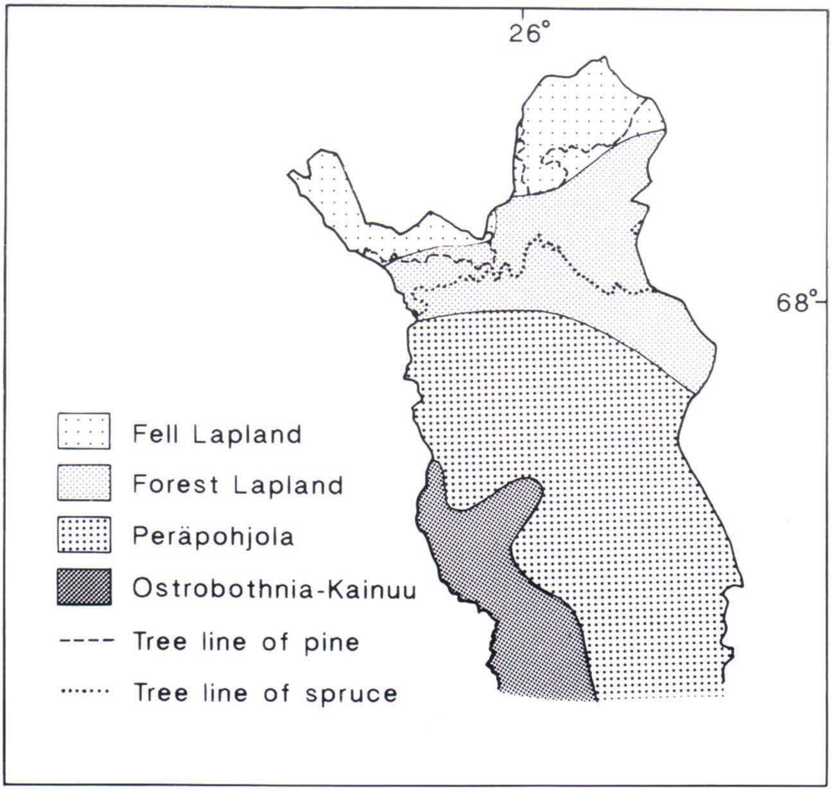


Fig. 19. Phytogeographic division of Lapland and the distribution of conifers (Atlas of Finland, 1990).

tion of the lake in the chain as counted from the headwaters.

All the podzol profile samples were taken from till at the most representative sites possible, in general on middle or lower slopes. Podzol soils of each catchment were sampled from pits with a spade sampler in summer 1991. The samples were taken from humus (A_0), eluvial (A) and illuvial (B) horizons, the transition zone (B+C) and the parent material (C). All profiles were visually podzolic. The total thickness of podzol profiles ranged from 40 to 100 cm. Humus samples were collected manually with "contamination-free" rubber gloves. Duplicate samples were taken at some sites. In inaccessible fell and wilderness terrains, a helicopter was used in both soil and water sampling. The altitude of the podzol soil sampling sites ranged from 103 to 778 m a.s.l. The median value of the altitude above sea level was 245 m, indicating that most of the sampling sites were in the supra-aquatic part of northern and eastern Lapland, where podzolization has been proceeding for a longer time than in areas which did not emerge until later in the Holocene.

Southern Lapland is part of the middle boreal zone. Most of Lapland, however, lies in the northern boreal zone, which can be subdivided into the Peräpohjola and Forest Lapland phytogeographic areas. North of the coniferous forest limit there is the subalpine-subarctic birch forest zone, which, in Finnish Lapland, mainly comprises the Enontekiö and Utsjoki areas (Fig. 19). Fell Lapland constitutes an ecotone between the boreal and arctic zones and is dominated by mountain birch; pine for-

Table 3. Forest site types (Cajander 1919, Lehto 1969).

grovelike heath forests
OMT, *Oxalis - Myrtillus*
GMT, *Geranium - Myrtillus*

moist heath forests
MT, *Myrtillus*
VMT, *Vaccinium - Myrtillus*
HMT, *Hylocomium - Myrtillus*

semidry heath forests
VT, *Vaccinium*
EVT, *Empetrum - Vaccinium*
EMT, *Empetrum - Myrtillus*
LMT, *Ledum - Myrtillus*

dry heath forests
CT, *Calluna*
ECT, *Empetrum - Calluna*

oligotrophic heath forests
ClT, *Cladina*

ests grow only in the valleys of large rivers. The largest treeless barrens occur around the Muotkatunturit and Paistunturit fells and in the Käsivarsi area of northwestern Lapland (Tikkanen ed. 1995).

The research areas were selected to represent different forest vegetation zones. The dominant tree species was Scots pine (*Pinus sylvestris*) in 70 catchments; Norwegian spruce (*Picea abies*) was dominant in only six catchments. In 24 catchments, mainly in the northernmost part of the study area or on the fells, mountain birch (*Betula pubescens* ssp. *tortuosa* and *Betula nana*) was the dominant tree species. The main forest site type in 59 catchments was oligotrophic heath forest (ClT, CT), and in 23 catchments semidry heath forest (EMT, EVT). Eight catchments comprised the moist heath forest type (HMT, VMT) (see Table 3.) (Cajander 1919, Lehto 1969).

A lake was defined as a pool larger than 0.01 km^2 and with an upper limit of 10 km^2. Water samples were taken from lakes during the autumn overturn in 1991. Field sampling was conducted from September 2 to October 17. The water samples were collected from a depth of < 2 m on lake shores using a Ruttner-type water sampler and were then placed in plastic bottles. The water samples for heavy metal analyses were collected directly into acidified plastic bottles.

Chemical analyses of soil samples

The soil samples from the humus, eluvial and illuvial horizons, the transition zone and the parent material were air-dried at < 40°C and sieved to the < 2-mm fraction (ISO/DIS 11464). The humus samples were homogenized in a Moulinex cutter before sieving. The samples were analysed at the chemical laboratory of the GSF in Rovaniemi.

Aqua regia leachable fraction

The main elements (Al, Ca, Fe, K, Na, Mg and S) of the humus and mineral soil samples were determined after 90°C aqua regia (1 HNO_3:3 HCl) digestion with ICP-AES (ISO/DIS 1146). Next, 12 ml of aqua regia and 60 ml of water were added to the dried humus and mineral soil samples (weighing 1.2 g). Most of the minerals in till are silicates that dissolve only slightly in mineral acids. Therefore, the aqua regia leach resulted in only partial dissolution for the majority of the mineral soil samples. The element concentrations in humus leached with aqua regia are total concentrations.

Aqua regia leach dissolves selectively carbonates, most of the sulphides, sulphosalts, arsenides, arsenates, phosphates, vanadates, tungstates, molybdates and sulphates, trioctahedral micas, clay minerals and precipitates on mineral grains. Primary iron and manganese oxides dissolve only partially, whereas their water-bearing secondary oxihydrates dissolve readily. The solubility of silicates declines in the order: olivine, micas (biotite), pyroxenes, amphiboles, feldspars and nesosilicates. Of plagioclases, calcium-rich anorthite dissolves in aqua regia to a considerable extent. The solubility of amphiboles and pyroxenes in aqua regia depends on their weathering degree. Biotite, phlogopite and chlorite are the most soluble micas. Muscovite is practically insoluble in aqua regia. Quartz does not contribute to the silica concentrations in till fines when submitted to partial aqua regia leach. The composition of the till fines in quartzite areas is mainly due to the interlayers containing feldspar, micas and carbonates (Dolezal et al. 1986). The material from eskers and other sorted deposits is not, therefore, geochemically comparable with the silt and clay fractions of till.

Cation exchangeable fraction

The concentrations of the main elements (Al, Ca, Fe, K, Na, Mg and S) in the cation exchangeable fraction of humus and mineral soil samples were measured with the buffered 1.0 M NH_4Ac digestion method at pH 4.5, using ICP-AES (e.g. Halonen et al. 1983, Page et al. 1982, Erviö and Palko 1984). As pH 4.5 is roughly the same as the pH in podzol profiles in Finland it can be assumed that the concentrations of exchangeable cations refer to the maximum concentrations of exchangeable cations in the soil (Räisänen 1989). For analyses, 6.0 g of dried and homogenized humus sample and 3.0 g of mineral soil sample were weighed. In the analysis, the ratio of humus to ammonium acetate solution was 1:5 and that of mineral soil samples to ammonium acetate solution 1:10. The mineral and humus samples were leached in NH_4Ac (NH_4Ac - CH_4COO) solution buffered at pH 4.5 and shaken in a pan mixer for 24 h. The total cation exchange capacity (CEC) was determined as the sum of the concentrations of base cations (Ca+Mg+K+Na) and aluminium and was expressed in meq/100 g of dried soil sample. The corresponding buffer capacity was determined as base saturation (BS), i.e. the percentage of base cations in the CEC. The concentration of sulphur determined with ammonium acetate leach refers to the soluble and adsorbed sulphur in humus and mineral soils.

Easily leachable fraction

The main elements (Al, Mg, Ca, K, Na, Fe) in the easily leachable and water-soluble fraction of mineral soil samples, from A, B, B+C and C horizons, were analysed with the unbuffered 0.025 M NH_4NO_3 digestion method by ICP-AES (Räisänen 1989). 3.0 g of dried mineral soil sample was shaken for 24 h in 0.025 M NH_4NO_3 solution, in which the sample to salt solution ratio was 1:10. The humus samples were not analysed for readily soluble ions, as the analytical method applied was not accurate enough for these samples (Niskavaara oral comm. 1995, GSF, Regional Office for Northern Finland). The analytical data refer to the concentrations of cations soluble in soil, surface waters and groundwaters, and which are partly or fully exchangeable. The pH of the mineral soil and humus samples was determined with the aid of unbuffered 0.025 M NH_4NO_3 solution leach, which characterizes the type and binding capacity of the cations better than pH measured from water solution (H_2O) (Räisänen and Lahermo 1985).

Grain-size distribution

The grain-size distribution of the fine fraction (< 0.06 mm) in < 2.0-mm fraction was available for only 17 soil sample profiles. The sampling sites were selected from geochemically different regions using the results of the Regional Geochemical Mapping programme (Kähkönen 1993, Salminen 1995). The distribution of the fine fraction was determined with the Sedigraph 5100 technique, which analyses particle size distribution with the sedimentation method. For the Sedigraph run, the till samples are usually wet-sieved, but due to their small size (< 32 g), the mineral soil samples were dry-sieved. 0.05 M sodium pyrophosphate was added to the < 0.06-mm fraction and the mixture was elutriated for 15 min. The sample was then kept in an ultrasonic bath for 2 min and in a magnetic mixer for 5 min before the Sedigraph run. The grain size distribution of the mineral soil samples was determined in the Regional Office for Mid-Finland of the GSF in Kuopio.

Chemical analyses of lake waters

Seventeen chemical variables were measured on each lake sample (Table 4). The basic analyses were made at the regional laboratory of the Water and Environment District of Lapland. The alkali and alkaline earth metals and sulphate were analysed at the regional laboratory of the Water and Environment District of Oulu (now the Regional Environment Centre of northern Ostrobothnia). All analyses were made as required by the SF standard methods of the then National Board of Waters and the Environment (now Finnish Environment Agency) (e.g. Forsius et al. 1990). The concentration of total organic carbon (TOC) was calculated from the regression equation TOC (mg/l) = 1.9 + 0.67 x COD_{Mn} (mg O_2/l), where r^2 was 0.92 (e.g. Kortelainen and Mannio 1990). The concentration of the organic anion - the dissociation product of organic acids - was calculated using the model of Oliver et al. (1983) based on the pH and organic carbonate content of water. Non-marine sulphate and base cations (denoted by asterisk SO_4*, Ca*, Mg*, K*, Na*) were calculated as the differences between total concentrations and those attributable to marine salts, the latter based on the ratios of

Table 4. Variables determined for lake waters, and the analytical methods used.

Variable	Analytical method
pH	Electropotentiometric determination with a pH meter at 25°C (SFS 3021)
electrical conductivity	In a cell with Pt electrode at 25°C (SFS 3022)
Alkalinity	Potentiometric titration with weak hydrochloric acid, the equivalent point determined by extrapolation (Gran method)
colour number	With a Hellige-Neo comparator by comparing with colour plates calibrated with Pt cobalt chloride solution (SFS 3023)
COD_{Mn}	Potassium permanganate oxidation and titration with Na tiosulphate (SFS 3036)
NH_4	By spectrometry (SFS 3032)
NO_3	Cd reduction and colorimetric determination. A method applied to Technicon automatic analyser
Ntot	Potassium peroxide oxidation, Cd reduction and colorimetric determination. A. method applied to Technicon automatic analyser
PO_4	By spectrophotometry (SFS 3025)
Ptot	By spectrophotometry, potassium peroxide oxidation (SFS 3025)
Fe	By spectrophotometry, potassium peroxide oxidation (SFS 3028)
Mn	By spectrophotometry, potassium peroxide oxidation (SFS 3033)
SiO_2	Traaks automatic analyser (application)
SO_4	Photometric titration with Thorin method applied to Technicon automatic analyser
Cl	By potentiometric titration (SFS 3002)
Na, K, Ca, Mg	By flame AAS (SFS 3017)

elements to chloride in sea water. Gran alkalinity was used as an estimate of bicarbonate, although this value also includes some organic alkalinity (Kortelainen 1993).

RESULTS

Aqua regia soluble cations

The mineralogical properties of podzol soils and the intensity of weathering related to podzolization in different podzol horizons were estimated with the aid of hot aqua regia leach. Element concentrations in the fine fraction of till soluble in aqua regia indicate the potential solubility of the elements and their availability as nutrients. The median values and the range of concentrations of the cations (Ca, Mg, K, Fe and Al) soluble in aqua regia from the humus, eluvial and illuvial horizons, the transition zone and the parent material in 90 podzol profiles are given in Table 5.

Calcium was clearly the main base cation (median 179 meq/kg), its concentration in the humus horizon being almost three times as high as that of magnesium (median 51 meq/kg). Potassium concentrations were distinctly lower (median 15 meq/kg). However, there was a large variation, especially in calcium and magnesium concentrations in the humus horizons. The range for calcium was from 72 meq/kg to 1123 meq/kg and for magnesium from 22 meq/kg to 437 meq/kg. In mineral soils, the concentrations of base cations soluble in aqua regia increased as a function of depth. Magnesium was the main base cation dissolved in aqua regia digestion, its concentrations being

Table 5. Median concentrations of aqua regia soluble base cations (Ca, Mg, K), Fe and Al (meq/kg) by sampling horizon in 90 podzol soils. Range of values in parentheses.

Horizon	Ca	Mg	K	Fe	Al
A_0	179	51	15	159	89
	(72 - 1123)	(22 - 437)	(3 - 73)	(22 - 1179)	(12 - 1166)
A	9	19	3	143	187
	(5 - 368)	(8 - 202)	(2 - 35)	(38 - 3914)	(23 - 1370)
B	33	197	11	1479	972
	(6 - 1607)	(53 - 726)	(3 - 106)	(404 - 4837)	(286 - 3760)
B + C	44	250	18	1245	795
	(7 - 1207)	(64 - 799)	(4 - 119)	(444 - 4025)	(289 - 2933)
C	62	280	25	994	693
	(10 - 778)	(53 - 995)	(4 - 217)	(258 - 3658)	(267 - 2637)

two times higher in the eluvial horizon, six times higher in the illuvial horizon and transition zone and five times higher in the parent material than those of calcium.

In the humus horizon, the aluminium concentrations were relatively low (median 89 meq/kg). In mineral soils, the concentrations of aluminium soluble in aqua regia were higher than those of base cations, especially in the illuvial horizon (median 972 meq/kg) and transition zone (median 795 meq/kg). The iron concentrations in the humus and mineral soil samples followed those of aluminium, being highest in the illuvial horizon (median 1479 meq/kg) and transition zone (median 1245 meq/kg).

Exchangeable cations, cation exchange capacity and base saturation

The median values and range of concentrations of cations soluble in buffered 1.0 M ammonium acetate (pH 4.5), CEC and BS are given in Table 6. Calcium was the dominant

Table 6. Median concentrations of base cations (Ca, Mg, K, Na) and Al, Fe (meq/kg) soluble in buffered (pH 4.5) NH_4Ac, cation exchange capacity (meq/100 g) (CEC_{tot}) and base saturation (BS%) by sampling horizon in 90 podzol soils. Range of values in parentheses.

Horizon	Ca	Mg	K	Na	Al	Fe	CEC_{tot}	BS
A_0	121	35	12	1.2	5	0.3	18.5	97
	(37 - 723)	(11 - 138)	(4 - 54)	(0.2 - 8)	(0.3 - 92)	(0 - 2)	(8.2 - 76.1)	(41 - 100)
A	2	0.8	0.3	0.2	16	3	1.9	16
	(0.2 - 9)	(0.1 - 2)	(0.2 - 1)	(0.1 - 0.6)	(5 - 188)	(0.4 - 14)	(0.6 - 19.6)	(4 - 56)
B	0.9	0.6	0.4	0.1	137	10	14	1.3
	(0.2 - 14)	(0.1 - 5)	(0.2 - 2)	(0 - 0.4)	(35 - 307)	(3 - 65)	(3.7 - 31.8)	(0.3 - 28)
B + C	0.6	0.3	0.3	0.1	77	4	7.9	1.5
	(0.1 - 10)	(0.1 - 5)	(0.2 - 1)	(0 - 0.6)	(15 - 278)	(1 - 27)	(1.6 - 27.9)	(0.5 - 21)
C	0.5	0.3	0.3	0.2	42	2	4.4	4
	(0.1 - 23)	(0.1 - 10)	(0.2 - 1)	(0.1 - 0.8)	(7 - 170)	(0.5 - 12)	(1.2 - 17.2)	(1.1 - 82)

cation (median 121 meq/kg) in the humus horizon, whereas aluminium was dominant in the mineral soil horizons - the illuvial horizon (median 137 meq/kg) and transition zone (median 77 meq/kg) in particular. The range of calcium and magnesium concentrations was high in the humus horizon. In mineral soils, calcium was the main base cation. The concentrations of calcium and magnesium decreased with depth, but those of potassium and sodium remained relatively constant down the mineral profile. The iron concentrations in the humus and mineral soil horizons followed those of aluminium, being, however, distinctly lower than the latter.

The CEC was highest in the humus horizon (median 18.5 meq/100 g). In mineral soils, it was highest in the illuvial horizon (median 14 meq/100 g) and transition zone (median 7.9 meq/100 g). The BS was highest in the humus (median 97%) and eluvial (median 16%) horizons.

Easily leachable cations

The median values and range of concentrations of cations soluble in unbuffered 0.025 M ammonium nitrate in mineral soil samples are given in Table 7. Calcium (median 1.5 meq/kg) and magnesium (median 0.8 meq/kg) concentrations were highest in the eluvial horizon, decreasing towards lower mineral horizons. Potassium and sodium concentrations were relatively uniform throughout the mineral soil horizons. The concentrations of easily soluble base cations in the mineral soils of catchments correlated with those of base cations soluble in ammonium acetate solution. Although the concentrations of easily leachable base cations were rather similar to those of exchangeable base cations, aluminium contents were clearly not. The concentration of easily leachable aluminium in mineral soil was highest in the eluvial horizon (median 3.0 meq/kg), decreasing gradually towards the parent material. On average, the concentration of easily leachable aluminium in the eluvial horizon was five times, in the illuvial horizon 98 times, in the transition zone 110 times and in the parent material 84 times lower than that of aluminium soluble in buffered ammonium acetate at pH 4.5. This is due to the difference in acidity and buffer capacity of these two extractants, as the solubility of aluminium is pH dependent. Concentrations of easily soluble iron were low in all mineral soil horizons.

Table 7. Median concentrations of base cations (Ca, Mg, K, Na), Al and Fe (meq/kg) soluble in unbuffered NH_4NO_3 and pH by sampling horizon in 90 podzol soils. Range of values in parentheses.

Horizon	pH	Ca	Mg	K	Na	Al	Fe
A_0	3.4						
	(3.0 - 5.1)	-	-	-	-	-	-
A	3.5	1.5	0.8	0.3	0.2	3	0.2
	(3.2 - 4.4)	(0 - 8)	(0 - 3)	(0.2 - 1)	(0 - 0.5)	(0.1 - 7)	(0 - 1)
B	4.2	0.6	0.3	0.3	0.1	1	0.1
	(3.5 - 4.9)	(0.1 - 6)	(0 - 5)	(0.2 - 1)	(0 - 0.5)	(0.1 - 6)	(0 - 1)
B + C	4.6	0.5	0.2	0.3	0.1	0.7	0.06
	(4.1 - 5.4)	(0 - 8)	(0 - 4)	(0.2 - 1)	(0 - 0.6)	(0. - 5)	(0 - 0.4)
C	4.5	0.5	0.2	0.3	0.1	0.5	0.03
	(4.1 - 5.7)	(0 - 16)	(0 - 9)	(0.2 - 0.9)	(0 - 0.7)	(0 - 7)	(0 - 0.2)

Acidity (pH)

The median values and range of pH in the humus and mineral soil horizons are given in Table 7. Typically of podzols, pH values increased as a function of horizon depth. In the humus horizon, the median pH value was 3.4 (range 3.0 - 5.1), in the eluvial horizon 3.5 (range 3.2 - 4.4), in the illuvial horizon 4.2 (range 3.5 - 4.9), in the transition zone 4.6 (range 4.0 - 5.4) and in the parent material 4.7 (range 4.1 - 5.7) (Table 6). The greatest deviations in soil pH were due to the variation in humus and clay contents (e.g. Räisänen 1989). The pH values of podzol soils are also affected by the organic and inorganic humic and fulvic acids produced by biological activity (Räisänen 1989, Nuotio et al. 1990).

Sulphur

The median and range of total and soluble sulphur concentrations in the humus and mineral soil horizons are given in Table 8. The sulphur concentrations in the humus and mineral soil horizons obtained with aqua regia leach are total concentrations. They are highest in the humus horizon (median 88 meq/kg, 1390 ppm). Of the mineral soil horizons, the illuvial horizon had the highest sulphur concentrations (median 7.3 meq/kg, 117 ppm). In the unaltered parent soil they were 1.8 meq/kg (30 ppm) but varied largely, from 0.6 meq/kg to 32 meq/kg (9.1 ppm - 514 ppm).

The concentrations of soluble and adsorbed sulphur in the humus and mineral soil horizons were determined with buffered (pH 4.5) ammonium acetate leach. The solubility of sulphur was higher in the humus horizon than in the mineral soil horizons. The median concentration of sulphur was 6.7 meq/kg (108 ppm) with a fairly wide range of 2.0 meq/kg to 31 meq/kg (32 ppm - 499 ppm). In the C horizon of the mineral soils the median concentration of soluble sulphur was 0.4 meq/kg (5.7 ppm) with a range of 0.06 meq/kg to 5.7 meq/kg (0.3 ppm - 10 ppm). The concentrations of soluble sulphur in mineral soils were highest in the illuvial horizon, median 2.6 meq/kg (41 ppm) and range 0.5 meq/kg to 14 meq/kg (8.1 ppm - 221 ppm).

Table 8. Median concentrations of a) aqua regia and b) buffered (pH 4.5) NH_4Ac-extractable sulphur (meq/kg, ppm) by sampling horizon in 90 podzol soils. Range of values in parentheses.

	A		B	
Horizon	**S** (ppm)	**S** (meq/kg)	**S** (ppm)	**S** (meq/kg)
A_0	1390	87	108	6.7
	(755 - 1980)	(47 - 124)	(32 - 499)	(2 - 31)
A	32	2	4.7	0.3
	(9.3 - 198)	(0.6 - 12)	(1.5 - 90)	(0.1 - 5.6)
B	118	7.3	41	2.6
	(37 - 426)	(2.3 - 27)	(8.2 - 221)	(0.5 - 14)
B+C	67	4.2	25	1.6
	(18 - 384)	(1.1 - 24)	(3.8 - 154)	(0.2 - 9.6)
C	30	2	5.7	0.4
	(9.2 - 514)	(0.6 - 32)	(0.9 - 92)	(0.06 - 5.7)

Grain size distribution

The median abundance of the fine fraction (< 0.06 mm) in the < 2-mm fraction of the eluvial horizon was 24.5%, in the illuvial horizon 13.7%, in the transition zone 13.9% and in the weakly altered parent material 19.5%. The abundance of fine fraction varied markedly in mineral soil horizons. In the eluvial horizon the range was 5.5% - 41.3%, in the illuvial horizon 6.2% - 32.7%, in the transition zone 9.4% - 59.2% and in the parent material 4.2% - 62% (Fig. 20).

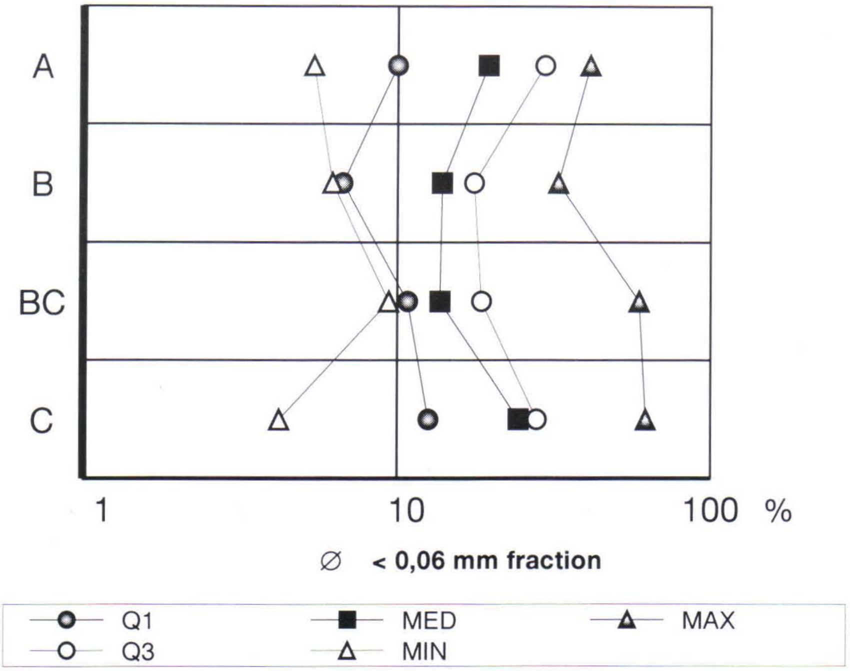


Fig. 20. Distribution of fines (fraction < 0.06 mm) in the < 2-m till fraction in different podzol horizons Median, 25% (Q1), 75% (Q3) percentiles, and minimum and maximum values.

Physical and chemical characteristics of lake waters

The physical characteristics of lake waters, their surface areas and their median and range values are listed in Table 9. The median of lake surface areas was 0.12 km^2 with a range of 0.01 to 1.4 km^2. The median catchment surface area was 1.76 km^2 with a range of 0.18 to 662 km^2. The median of the ratio of catchment to lake area was 15.2 with a range of 1.4 - 275. The ratio of the catchment area to the area of the drainage lakes was higher than that to headwater or closed lakes (Fig. 21). Elevation above sea level was slightly higher for headwater lakes (median 240 m) than for drainage (median 222 m) or closed lakes (median 205 m).

The chemical characteristics (median and range) of lake waters are given in Table 10. Calcium was the main cation (median 77 µeq/l) in all lakes studied. The median of the magnesium concentration was 31 µeq/l but the medians of potassium and sodium were distinctly

Table 9. Physical characteristics of lakes and catchments. Median and range values.

All lakes	**Median**	**Range**
Lake area km^2	0.12	0.01 - 1.4
Catchment area km^2	1.76	0.18 - 62
Catchment / lake ratio	45.4	6.7 - 275
Lake elevation above sea level (m)	235	96 - 776
Drainage lakes		
Lake area km^2	0.17	0.02 - 1.15
Catchment area km^2	10.4	0.33 - 62
Catchment / lake ratio	45	6.7 - 275
Lake elevation above sea level (m)	222	99 - 776
Headwater lakes		
Lake area km^2	0.11	0.01 - 1.4
Catchment area km^2	1.46	0.18 - 12.3
Catchment / lake ratio	11.1	1.36 - 94
Lake elevation above sea level (m)	240	97 - 640
Closed lakes		
Lake area km^2	0.07	0.03 - 0.25
Catchment area km^2	0.73	0.53 - 1.78
Catchment / lake area	10.4	1.48 - 29
Lake elevation above sea level (m)	205	96 - 300

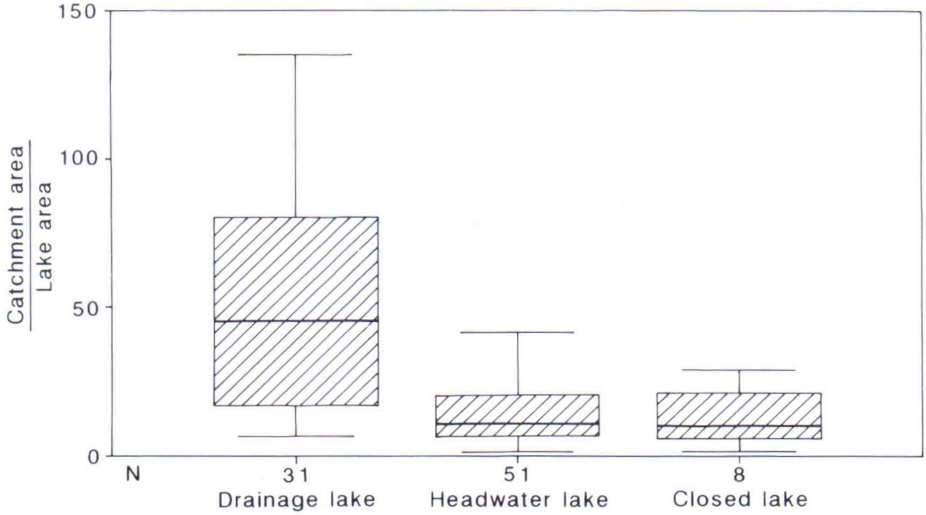


Fig. 21. The ratio of catchment to lake surface area was distinctly higher for drainage than for headwater or closed lakes.

Table 10. Chemical characteristics of lake waters. Median and range of values in parentheses.

Variable	Dimension	All lakes	Drainage lakes (n =31)	Headwater lakes (n = 51)	Closed lakes (n = 8)
pH		6.8	7	6.8	6.6
		(4.8 - 7.9)	(6.2 - 7.5)	(5.8 - 7.9)	(4.8 - 7.4)
ANC	µeq/l	93	138	75	40
		(-16 - 1711)	(4 - 818)	(-2 - 1711)	(-16 - 225)
Conductance	mS/m	2.3	2.5	2.2	1.4
		(0.7 - 20)	(0.8 - 9.6)	(0.7 - 20)	(0.9 - 4.6)
NO_3	µeq/l	0.4	0.4	0.4	0.5
		(0.01 - 4.6)	(0.4 - 4.6)	(0.01 - 1.5)	(0.4 - 1.1)
NH_4	µeq/l	0.4	0.4	0.4	0.6
		(0.07 - 27)	(0.07 - 27)	(0.1 - 5.8)	(0.1 - 1.1)
TOC[1)]	mg/l	4.4	4.4	4.1	5.8
		(2.2 - 11)	(2.2 - 9 0)	(2.4 - 11)	(2.8 - 8.6)
COD_{Mn}	mg O_2 /l	3.7	3.8	3.2	5.8
		(0.4 - 13)	(0.4 - 11)	(0.8 - 13)	(1.4 - 10)
Colour	mg Pt/l	20	20	20	35
		(5.0 - 70)	(5.0 - 70)	(5.0 - 60)	(5.0 - 60)
Fe	µeq/l	50	51	41	71
		(4.0 - 506)	(9.0 - 204)	(7.5 - 506)	(4.0 - 229)
Mn	µeq/l	0.4	0.4	0.4	0.5
		(0.07 - 7.3)	(0.2 - 0.9)	(0.07 - 7.3)	(0.2 - 3.3)
Ca*	µeq/l	76	78	76	52
		(10 - 802)	(20 - 533)	(10 - 802)	(20 - 180)
Mg*	µeq/l	32	33	31	23
		(0.6 - 376)	(5.8 - 376)	(0.6 - 334)	(15 - 342)
Na*	µeq/l	28	29	29	25
		(-53 - 74)	(8 - 61)	(-53 - 74)	(9 - 39)
K*	µeq/l	7.3	7.3	7.2	7.3
		(0.9 - 25)	(1.8 - 25)	(0.9 - 23)	(2.4 - 16)
CaMgKNa*	µeq/l	139	181	131	104
		(33 - 1171)	(61 - 961)	(33 - 1171)	(53 - 475)
SO_4*	µeq/l	36	24	35	37
		(13 - 198)	(14 - 82)	(14 - 198)	(16 - 73)
Cl	µeq/l	19	44	19	13
		(6.5 - 124)	(13 - 107)	(7.1 - 124)	(6.5 - 82)
Organic anion[2)]	µeq/l	33	33	31	42
		(16 - 78)	(16 - 68)	(18 - 78)	(21 - 48)

* values corrected for marine concentration

[1)] TOC calculated by the regression equation TOC = 1.9 x COD_{Mn} (mg O_2/l)

[2)] Organic anion estimated by the method of Oliver et al. (1983)

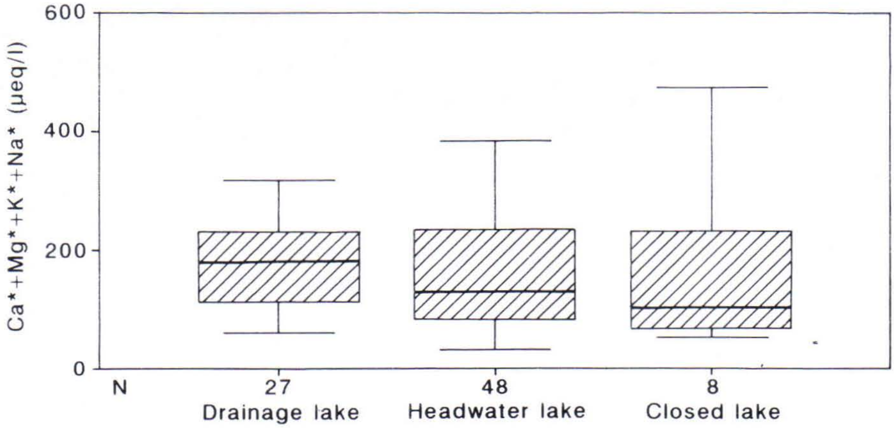


Fig. 22. The sea-salt-corrected base cation concentrations (Ca+Mg+K+Na) were clearly higher in drainage than in headwater lakes and markedly higher than in closed lakes.

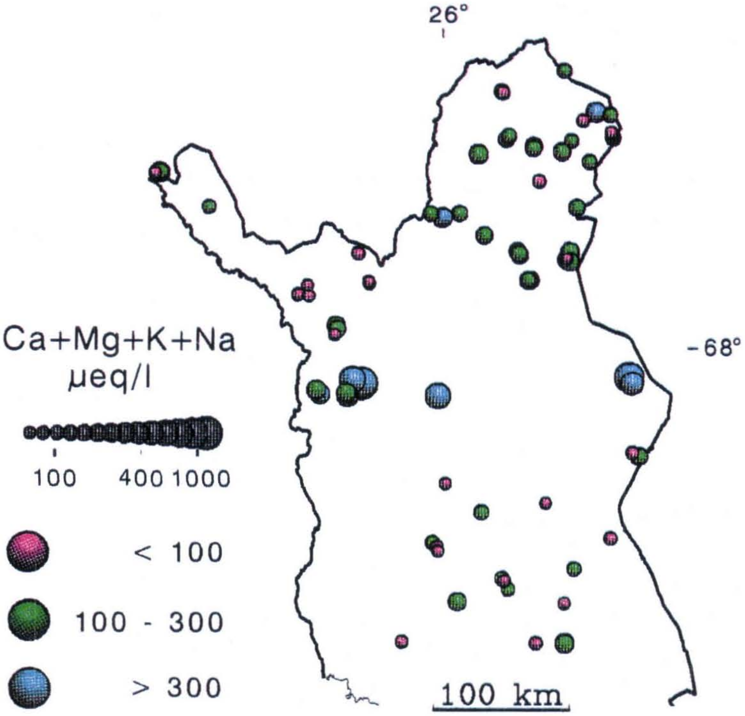


Fig. 23. Regional distribution of sea-salt-corrected base cation concentrations in lake waters.

lower. In general, the base cation concentration (Ca* + Mg* + K* + Na*) was markedly higher (median 181 μeq/l) in drainage than in headwater (median 131 μeq/l) or closed (median 104 μeq/l) lakes (Fig. 22). The highest base cation values (> 300 μeq/l) were recorded in lakes in northwestern Lapland; the lowest (< 100 μeq/l) were encountered throughout northern Finland, most frequently, however, in northeastern, southern and northwesternmost Lapland (Fig. 23).

The median of the alkalinity of the lakes was 93 μeq/l, which comprises over half of the anion sum. Alkalinity was clearly higher in drainage (median 138 μeq/l) than in headwater (median 75 μeq/l) lakes and markedly higher than in closed (median 40 μeq/l) lakes (Fig. 24). In 33 lakes, alkalinity had completely disappeared (Gran alkalinity < 0.0 μeq/l) or was critically low (Gran alkalinity < 0-50 μeq/l). In 26 lakes, buffer capacity was moderate (Gran alkalinity 50 - 150 μeq/l) and in 31 lakes good (Gran alkalinity > 150 μeq/l). Acidic lakes and those with low buffer capacity occurred throughout Lapland, but their frequency was highest in the northeastern Inari area, the Enontekiö area in northwestern Lapland and over a fairly large part of southern Lapland in the Rovaniemi-Ranua-Posio area. In these areas, too, the buffer capacity varied greatly between adjacent lakes (Fig. 25).

Chemical oxygen demand (COD_{Mn}), total organic carbon (TOC) and colour correlated with each other. The median of COD_{Mn} was 3.7 mg/l, that of TOC 4.4 mg/l and that of colour 20 mg Pt/l. These values were higher in closed than in drainage or headwater lakes. Thirty-eight per cent of the lakes studied could be considered humic, because their TOC was over 5 mg/l (see Kortelainen and Mannio 1990). The humic lakes were located in the catchments of southern and western Lapland (Fig. 26). The

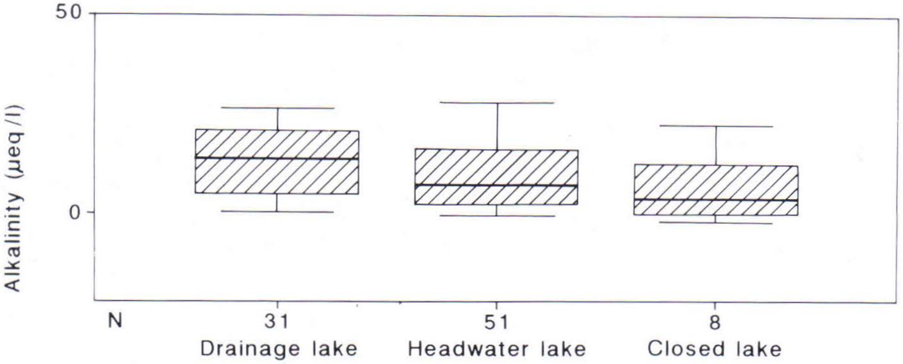


Fig. 24. Alkalinity was higher in drainage than in headwater lakes and markedly higher than in closed lakes.

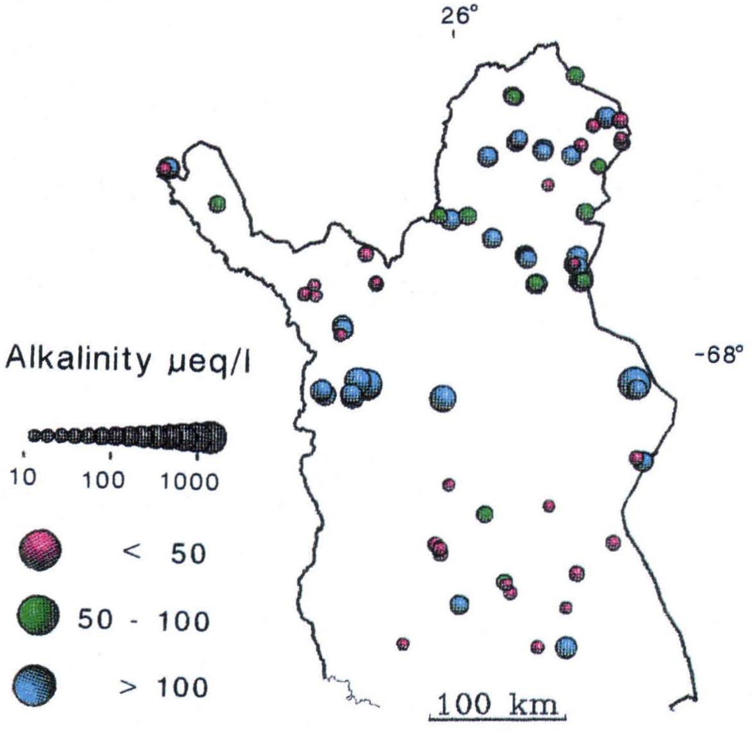


Fig. 25. Regional distribution of lake-water alkalinity.

median of the organic anion concentration (A^-) was 33 µeq/l.

The median of sulphate concentrations (36 µeq/l) in the lakes studied was almost the same as that of the organic anion. In drainage lakes the sulphate concentrations were slightly higher (median 44 µeq/l) than in headwater (median 35 µeq/l) or closed (median 37 µeq/l) lakes. Sulphate concentrations in clear waters are usually 10 - 15 µeq/l in areas without atmospheric sulphur deposition (Bråkke et al. 1989). Most of the 22 lakes with sulphate concentrations of < 20 µeq/l in this study were located in northwestern Lapland. The highest sulphate

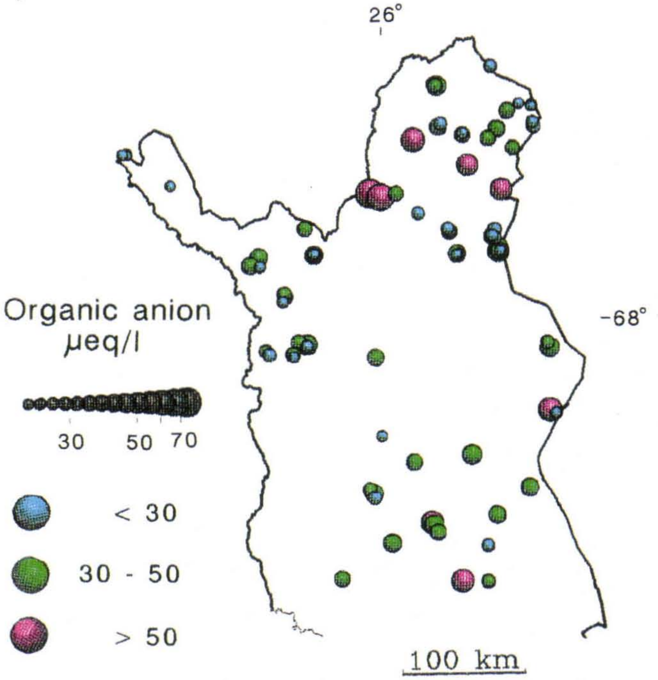


Fig. 26. Regional distribution of organic anion concentrations in lake waters.

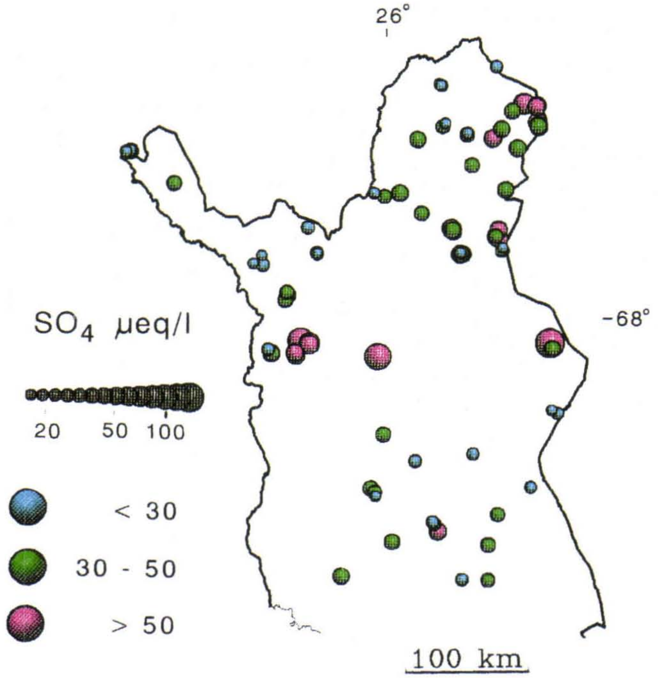


Fig. 27. Regional distribution of sulphate concentrations in lake waters.

concentrations (> 50 µeq/l) were recorded in 20 lakes in northeastern and western Lapland (Fig. 27). The nitrate concentrations of the lakes were low (median < 0.4 µeq/l). The median value of lake-water iron concentrations was 50 mg/l and that of manganese 0.4 µeq/l.

DISCUSSION

Solubility of elements in soil of catchments

Base cation concentrations

Although aqua regia digestion implies a strong partial leach, no more than 42% of the total magnesium, 9% of the calcium and 8% of the potassium concentrations in Finnish till are soluble in aqua regia (Koljonen 1992). Magnesium occurs mainly in silicate minerals, particularly in olivine, serpentine and chlorite minerals of mafic and ultramafic rocks. The relative low solubility of calcium indicates that Finnish soils are poor in carbonates and that calcium is mainly incorporated in soluble Ca-plagioclases and amphiboles and in the interlayers of rocks containing these minerals. The bulk of potassium is leached from micas, especially from biotite, and only slightly from feldspars (Koljonen ed. 1992, Kähkönen 1993).

The highest concentrations of base cations soluble in aqua regia (> 800 meq/kg) in the parent material were found in catchments in the Central Lapland Greenstone Belt, the Peräpohja schist belt and the Sokli carbonatite and Angeli anorthosite massifs. The Central Lapland Greenstone Belt is rich in mafic and volcanic rocks; hence the high magnesium concentrations. Carbonate-rich rocks are common at Sokli and in the Peräpohja schist belt, a fact which is reflected in the high calcium concentrations in podzol soils. In the Angeli area, high calcium concentrations are due to the Ca-rich plagioclase of anorthosite (Fig. 28). Some catchments in northern and western Lapland also had high concentrations of base cations in the parent material. This is mainly due to the mosaic-patterned occurrence of mafic and volcanogenic rocks in areas regionally characterized by acid plutonic rocks and schists. Occasionally carbonates of mafic and ultramafic rocks have caused high calcium concentrations in soils. The base cation concentrations (< 250 meq/kg) in mineral soils were lowest in the granulite area of southern Lapland and in the granite gneiss areas of eastern and northern Lapland.

Concentrations of base cations in the parent material correlated with those in the humus and upper mineral soil horizons, implying that the chemical composition of the parent material controls the element composition of the podzol soil to a considerable extent. The highest calcium and magnesium concentrations (> 600 meq/kg) in humus horizons were found in catchments of the Central Lapland Greenstone Belt and the Peräpohja schist belt, and also in some catchments in northern Lapland. The lowest base cation concentrations (< 200 meq/kg) in humus horizons were in catchments in northern, southern and western Lapland (Fig. 29a).

The concentration patterns of the base cations analysed with weak leach correlated with those of the base cations soluble in aqua regia, although, due to the difference in strength of the leach, the concentration levels varied (Fig. 30). The concentration of exchangeable base cations increases logarithmetically when the concentrations of base cations soluble in aqua regia in catchments were > 800 mg/kg (Fig. 31), which implies that the till in these areas contains abundant material from easily soluble mafic, ultramafic and carbonate-bearing rocks. The greatest difference between leaches was due to dissimilar solubilities of calcium and magnesium. Calcium was the base cation with the highest solubility in soil, surface waters

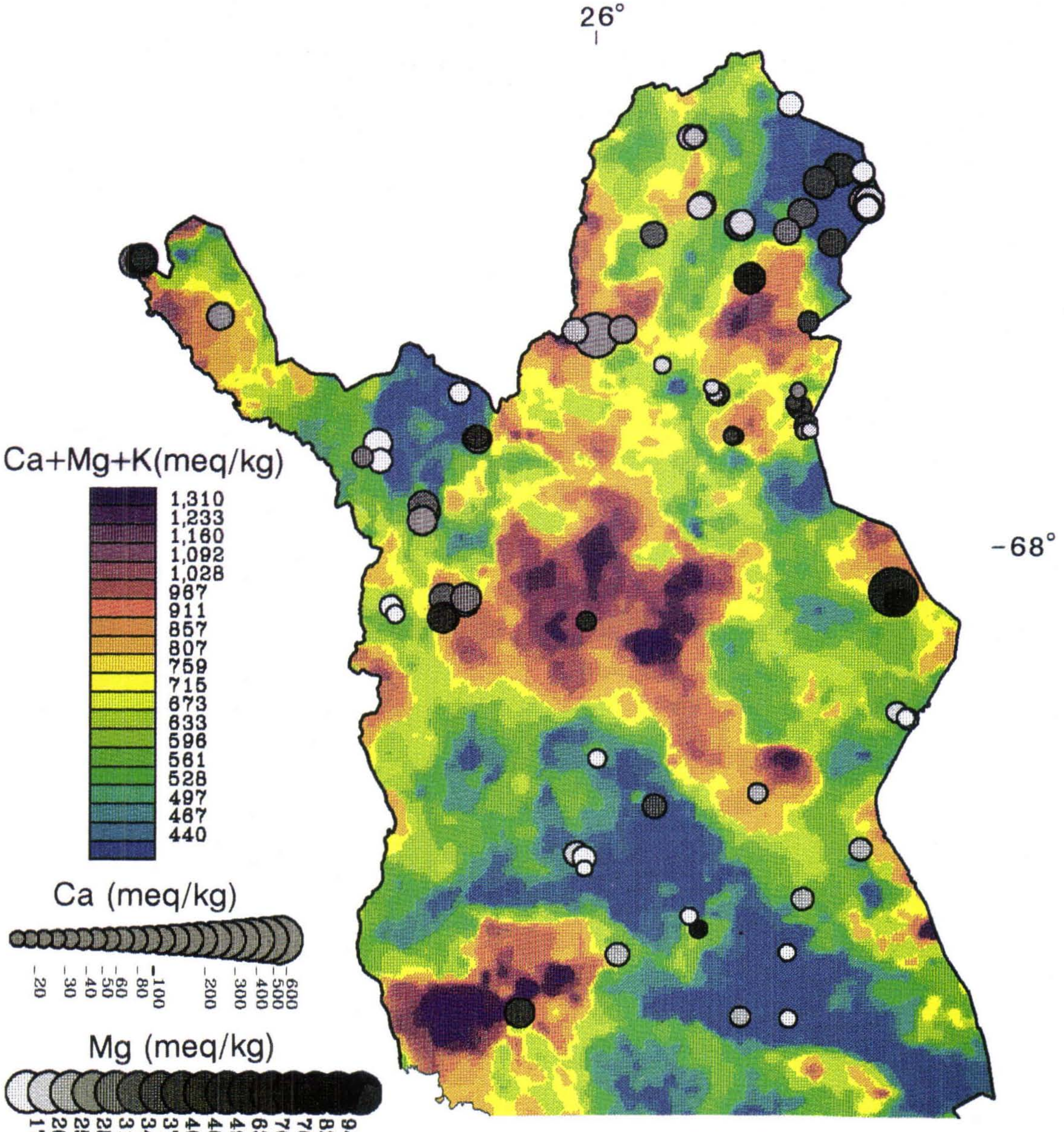


Fig. 28. Concentrations of aqua regia leachable calcium and magnesium in the parent material of catchments. In the background, the base cation concentrations in the parent material from the Regional Geochemical Mapping programme (Salminen 1995).

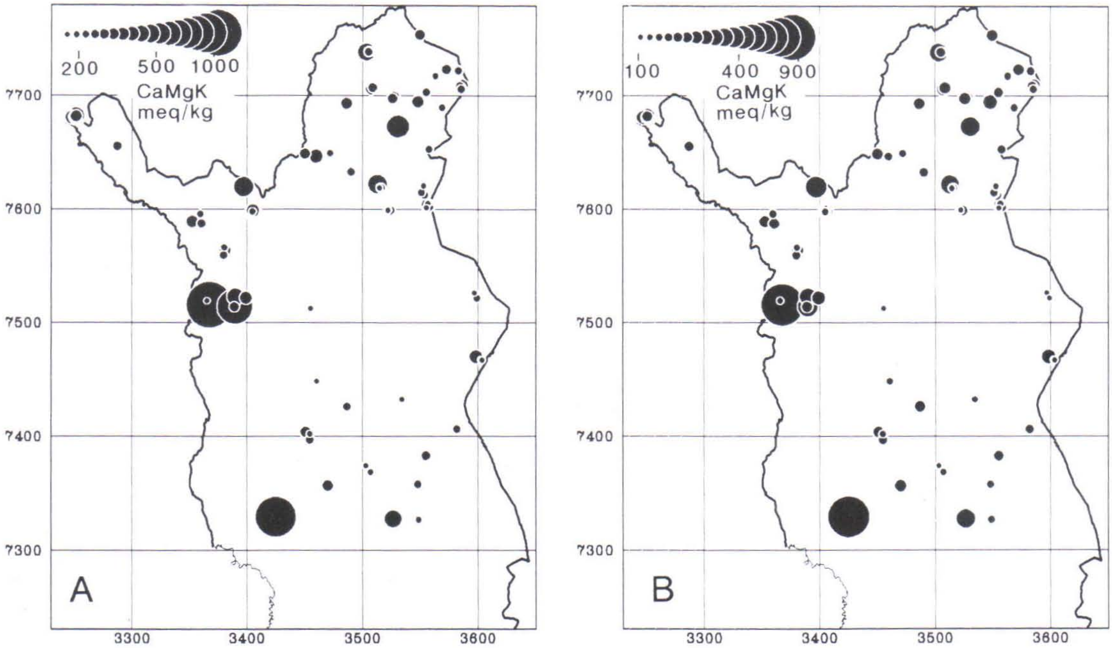


Fig. 29. Concentrations of base cations soluble in a) aqua regia and b) buffered (pH 4.5) NH_4Ac in the humus horizons.

and groundwaters and the highest CEC, whereas magnesium had the highest solubility in strong aqua regia. This was also reflected in lake waters, as calcium is the main base cation in Finnish lakes.

The concentrations of base cations participating in the cation exchange reaction in the humus horizon were high, and, on average, 67% of magnesium and 69% of calcium were in the exchangeable fraction. Concentrations of exchangeable base cations were highest (> 400 meq/kg) in the humus horizons of the catchments, where the soil is composed of easily weathering mafic, volcanic and carbonate-bearing rocks (Fig. 28b). In mineral soils, concentrations of both exchangeable and easily soluble base cations decreased as a function of depth. In the eluvial horizon, the average concentration of calcium participating in cation exchange reactions was 22% and that of magnesium 4% of the concentrations of these elements soluble in aqua regia. The relatively high solubilities indicate the presence of organic matter in the illuvial horizon and the high abundance of micas and clay minerals. In the C horizon, the concentration of the exchangeable fraction of calcium was < 1% and that of magnesium only about 0.1% of the concentrations of these elements soluble in aqua regia (Fig. 32a). Concentrations of easily leachable base cations in the mineral soil were almost the same as those of the exchangeable base cations. In northern Lapland, elevated base cation concentrations (> 4 meq/kg) were found in some catchments, but there the base cations were not in such an easily soluble form as they were in the catchments composed of mafic, volcanogenic and carbonatite rocks (Fig. 30b).

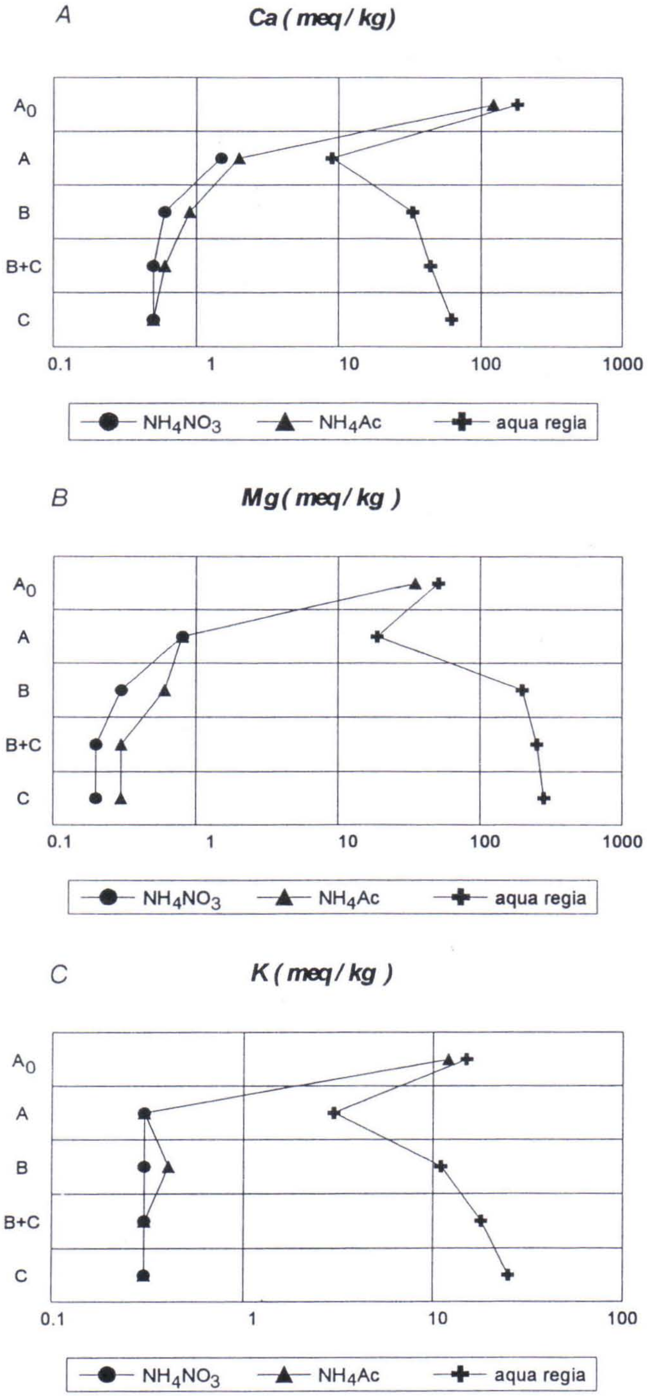


Fig. 30. Median concentratios of a) calcium, b) magnesium and c) potassium soluble in aqua regia, buffered (pH 4.5) NH_4Ac and unbuffered NH_4NO_3 in different podzol horizons.

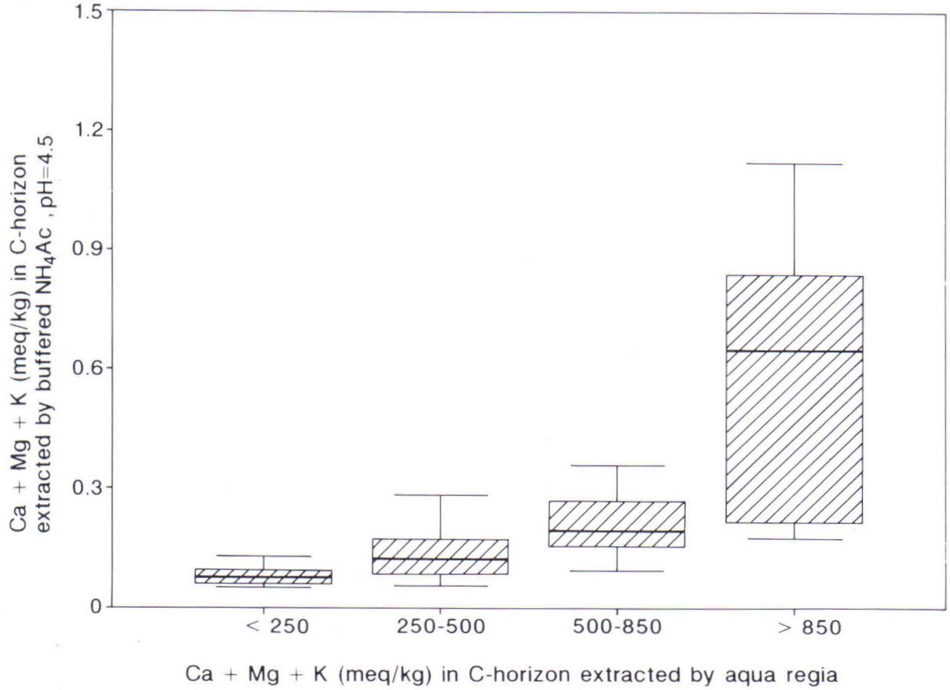


Fig. 31. Concentrations of base cations soluble in aqua regia in C podzol horizons in the catchments correlate well with concentrations of base cations soluble in buffered (pH 4.5) NH_4Ac solution.

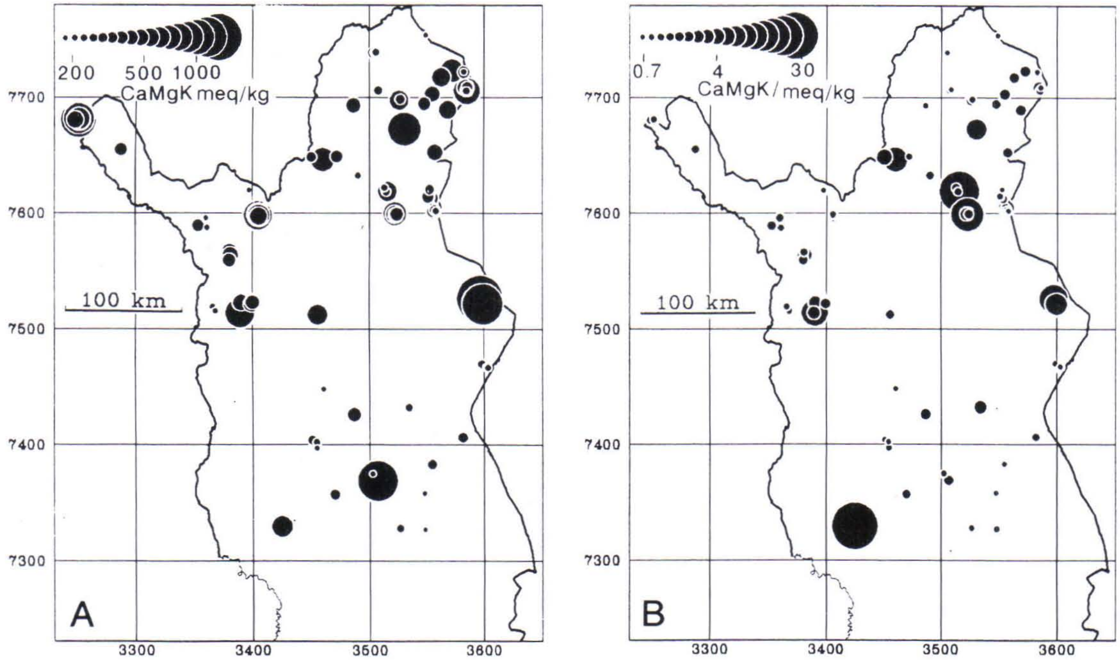


Fig. 32. Concentrations of base cations soluble in a) aqua regia, b) buffered (pH 4.5) NH_4Ac and c) unbuffered NH_4NO_3 in the parent material in 90 catchments.

Aluminium and iron concentrations

The proportion of aluminium soluble in aqua regia in till averages 18% of the total aluminium concentration (Koljonen 1992). Aluminium goes into solution most easily when in clay minerals, chlorite, biotite and, depending on the degree of weathering, in amphiboles and pyroxenes. The largest continuous areas with high aluminium concentrations in mineral soils (> 2500 meq/kg) are in northern and eastern Lapland. Typical of granulites in Lapland are the aluminium-rich minerals, garnet and sillimanite. They are highly resistant to weathering, although in places garnet has altered into biotite. High concentrations of aluminium soluble in aqua regia are thus mainly due to the biotitization of garnet. In eastern and central Lapland, the high aluminium concentrations are caused by Al-Fe-rich clay minerals in the preglacial weathering crust.

A potential risk for soil and lake water acidification exists in catchments with a high ratio of aluminium to base cations, i.e. in the Lapland granulite area, central Lapland and northeastern Inarinjärvi (Fig. 33). The aluminium concentrations in the humus horizons were highest (> 600 meq/kg) in the Lapland granulite area and in a few catchments in western and northeastern Lapland (Fig. 34a).

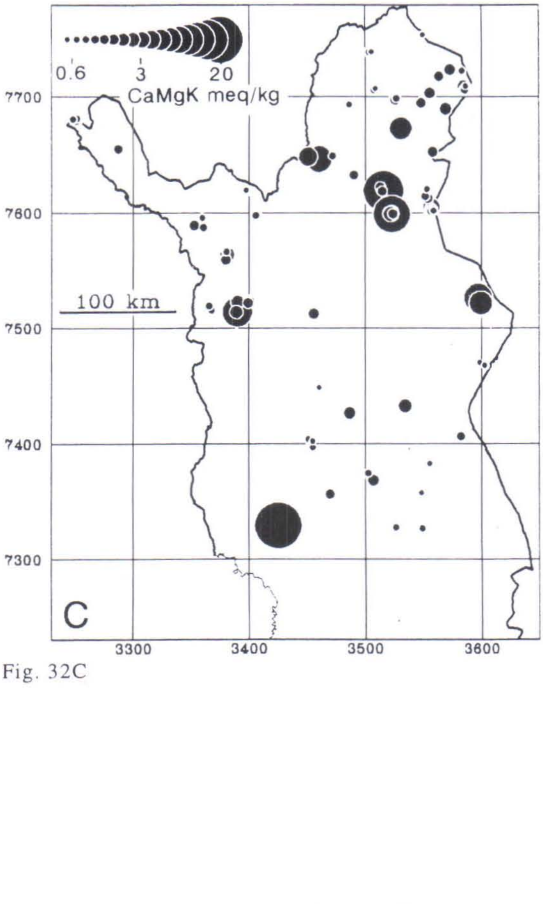


Fig. 32C

In till, iron soluble in aqua regia accounts for 52% of total iron, on average (Koljonen ed. 1992). The concentration of iron was highest in the central Lapland schist belt and in catchments in the area of preglacial weathering crust.

In the humus horizon, the concentration of exchangeable aluminium was, on average, only 6% of that of aqua regia extractable aluminium (Fig. 34b). This implies that aluminium is tightly bound to the organic compounds and complexes in the humus horizon. In the mineral soil horizons, the concentrations of exchangeable aluminium were clearly higher than those of base cations (Fig. 35b). The concentrations of aluminium in podzol soils soluble in aqua regia correlate well with those soluble in NH_4-acetate solution (Fig. 36 and 37). The concentrations of exchangeable aluminium ranged from 6% to 14%, on average, of the aqua regia soluble aluminium, being highest in the illuvial horizon (Fig. 35a). The variation in the concentrations of iron and aluminium in different podzol horizons illustrated the variation in the intensity of eluviation (A horizon) and illuviation (B horizon). As most of the aluminium and iron liberated in the weathering of mineral soil have migrated downwards with the gravitational water, towards lower acidity, the dissolved elements have precipitated. The aluminium dissolved from the upper part of the illuvial horizon had frequently reprecipitated in the transition zone. Concentrations of easily leachable aluminium in the mineral soil horizons were low, on average only 1% of the aluminium soluble in aqua regia (Fig. 35b). Thus only a small portion of the aluminium incorporated in silicate minerals in podzol soils is soluble in soil water.

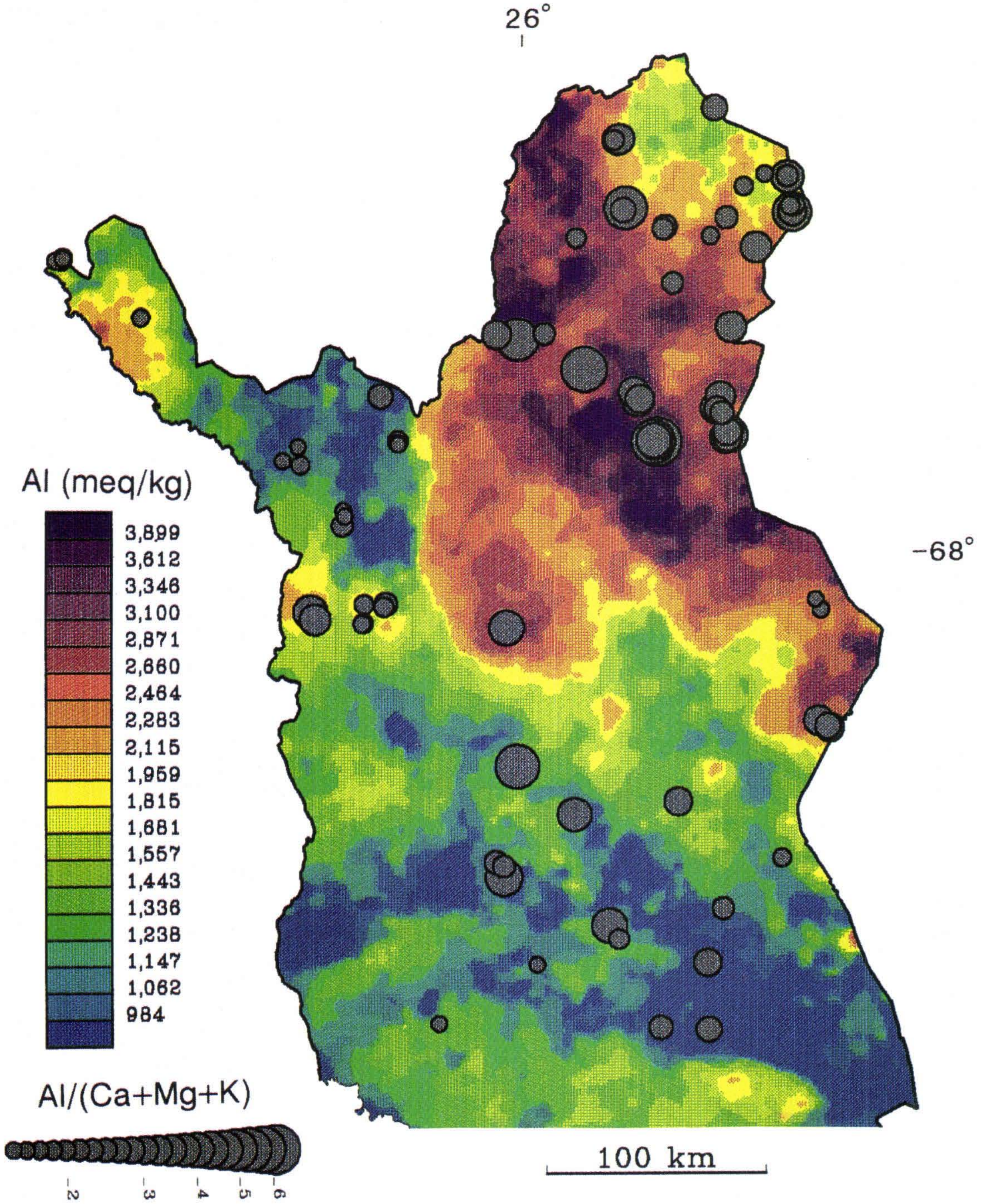


Fig. 33. The ratio of aluminium concentrations to those of base cations soluble in aqua regia in the parent material of catchments. In the background, aluminium concentrations from the Regional Geochemical Mapping programme (Salminen 1995).

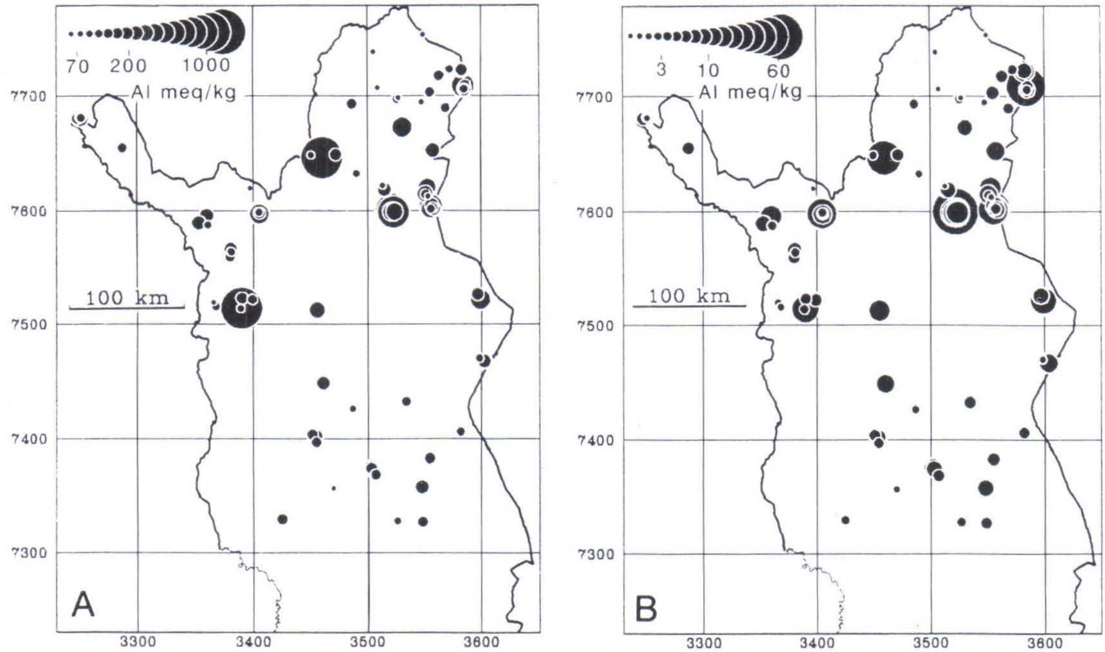


Fig. 34. Concentrations of aluminium soluble in a) aqua regia and b) buffered (pH 4.5) NH_4Ac in the humus horizons of 90 catchments

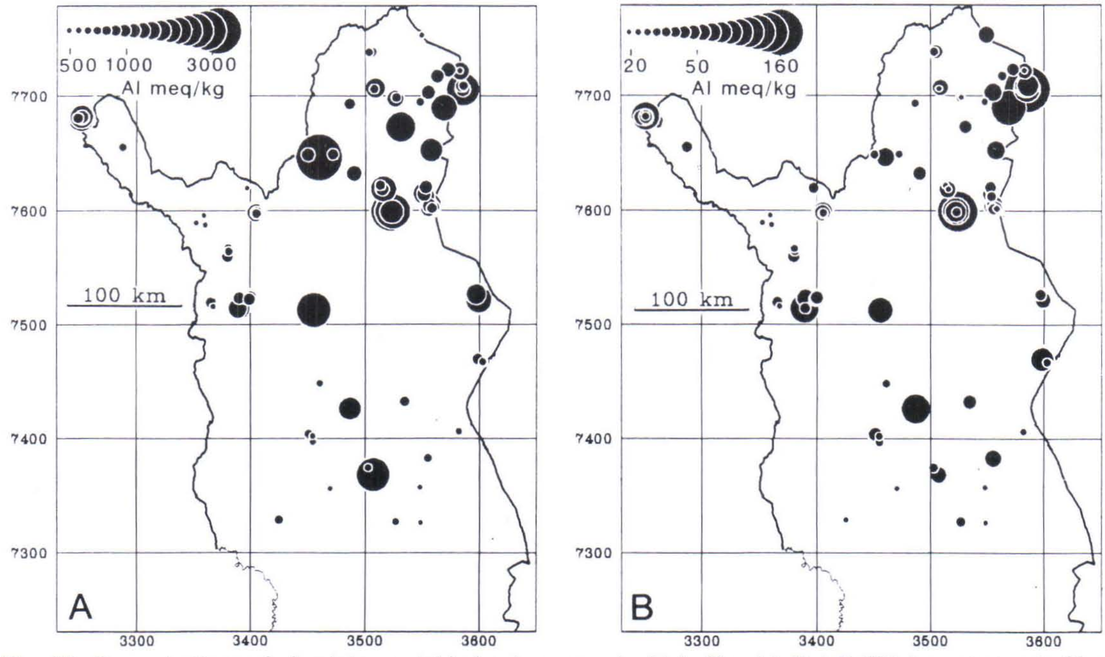


Fig. 35. Concentrations of aluminium soluble in a) aqua regia, b) buffered (pH 4.5) NH_4Ac and c) unbuffered NH_4NO_3 in the parent material of 90 catchments.

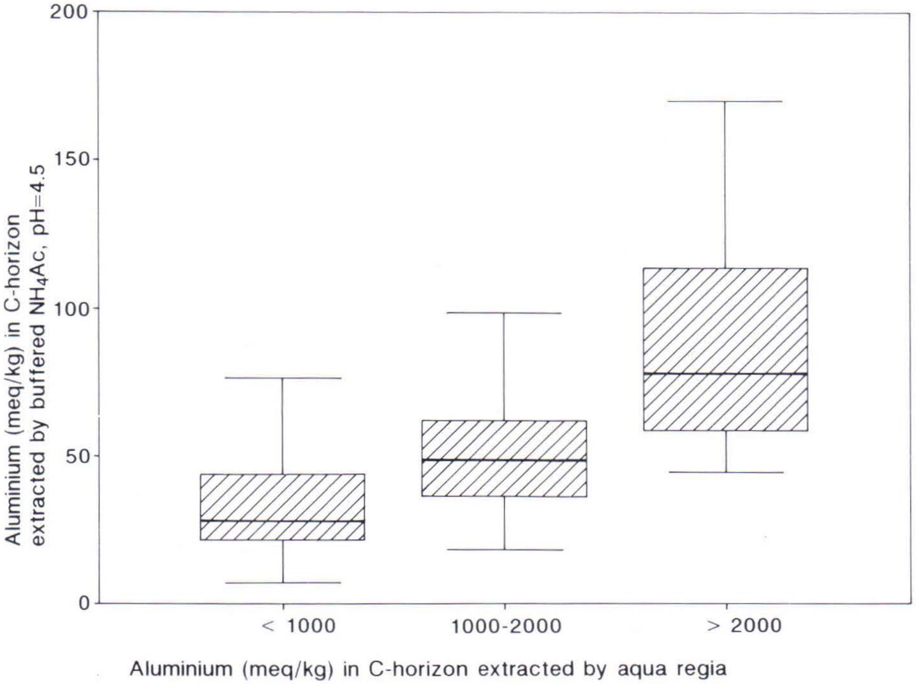


Fig. 36. Concentrations of aluminium soluble in aqua regia and those soluble in buffered (pH 4.5) NH_4-acetate solution correlate well with each other in the C horizons of podzol soils.

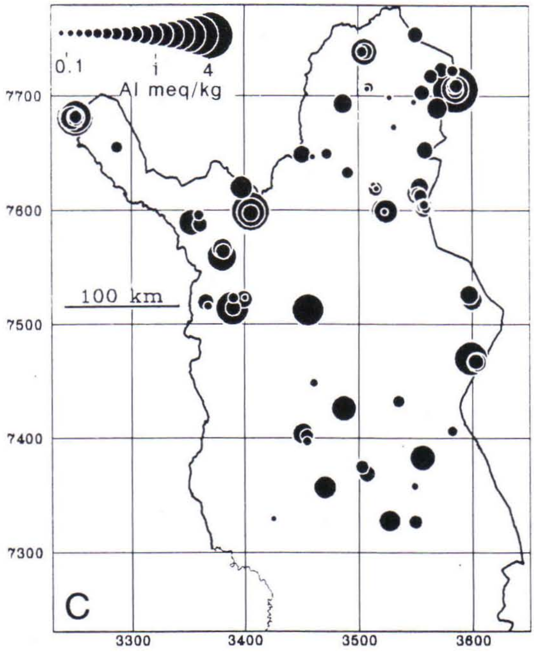


Fig. 35C

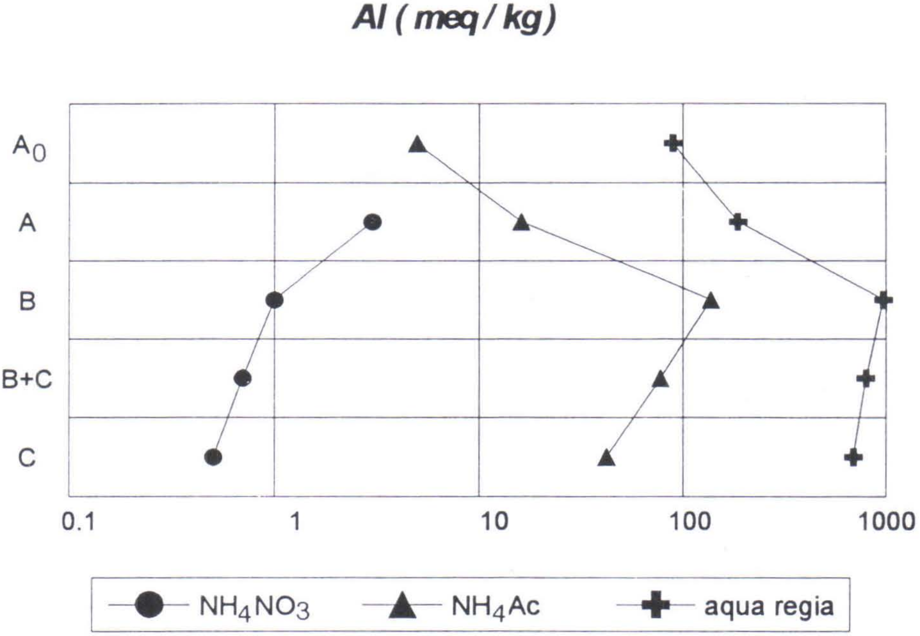


Fig. 37. Median concentrations of aluminium soluble in aqua regia, buffered (pH 4.5) NH_4Ac and unbuffered NH_4NO_3 solutions in different podzol profiles.

Sulphur concentrations

The high total (> 100 meq/kg, > 1600 ppm) and soluble sulphur (> 20 meq/kg, > 320 ppm) concentrations in the humus horizon indicate that sulphur is an essential component and macronutrient (Fig. 38a). On average, soluble sulphur in the humus horizons was only 7-8% of total organic sulphur. Regionally, the high sulphur contents in humus were restricted to the catchments of the Central Lapland Greenstone Belt, the Peräpohja schist belt and the Käsivarsi Caledonian area, where they are naturally high in till due to sulphide mineralization.

Data on sulphur and heavy metal concentrations in Finnish forest podzol soils are scarce, and sulphur deposition and the specification of sulphur processes in forest-floor soils have not been studied adequately. The average concentrations of soluble sulphur in the humus horizon determined by the Lapland Forest Damage project varied in the range 120 ppm - 150 ppm, the gradient increasing southwards (Tikkanen 1995). In the 90 catchments studied, the natural variation in concentrations of soluble sulphur (32 ppm - 499 ppm) and total sulphur (755 ppm - 1980 ppm) was substantially higher, irrespective of the level of sulphur deposition. However, in eastern Inarinjärvi the relatively high total sulphur (1500 ppm - 1900 ppm), nickel (> 15 ppm) and copper (> 10 ppm) concentrations in the humus horizons imply that heavy-metal and sulphur deposition from the Kola Peninsula contributes to the load of this area. On the Kola Peninsula, close to the Monchegorsk Cu-Ni smelters, soluble sulphur concentrations in humus horizons were markedly higher, varying in the range 180 ppm - 730 ppm (Derome et al. 1995). It has been established that the sulphur load recorded in humus covers larger areas than the sulphur load indicated by the moss (Kohonen and Salminen 1993). In sparsely populated eastern Lapland

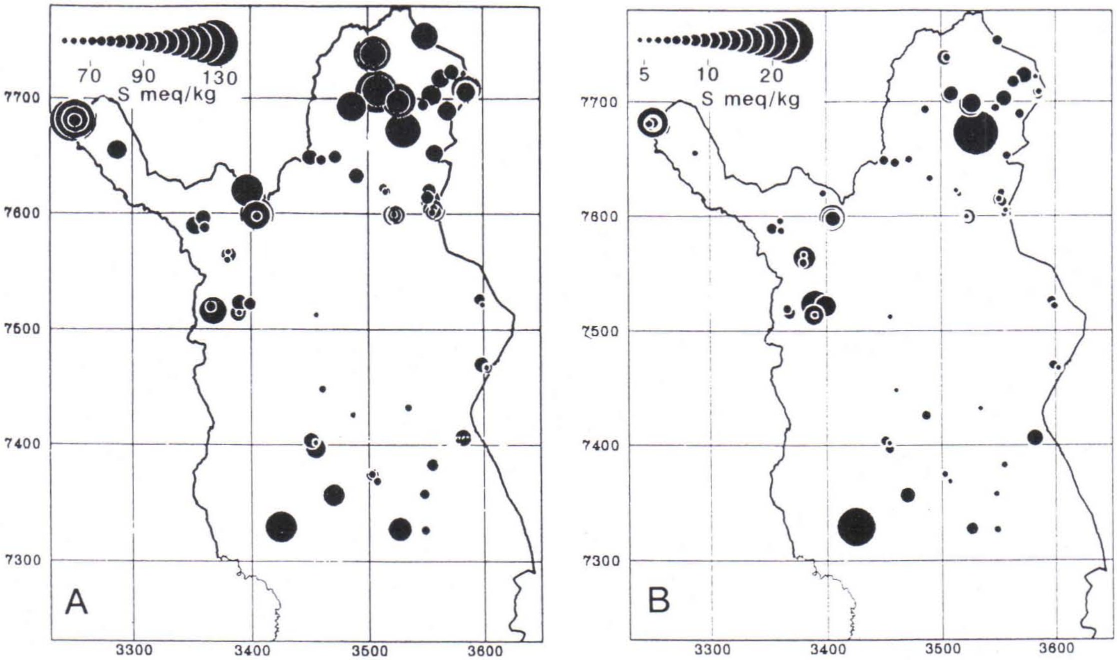


Fig. 38. Concentrations of sulphur soluble in a) aqua regia and b) buffered (pH 4.5) NH_4Ac in humus horizons in 90 catchments.

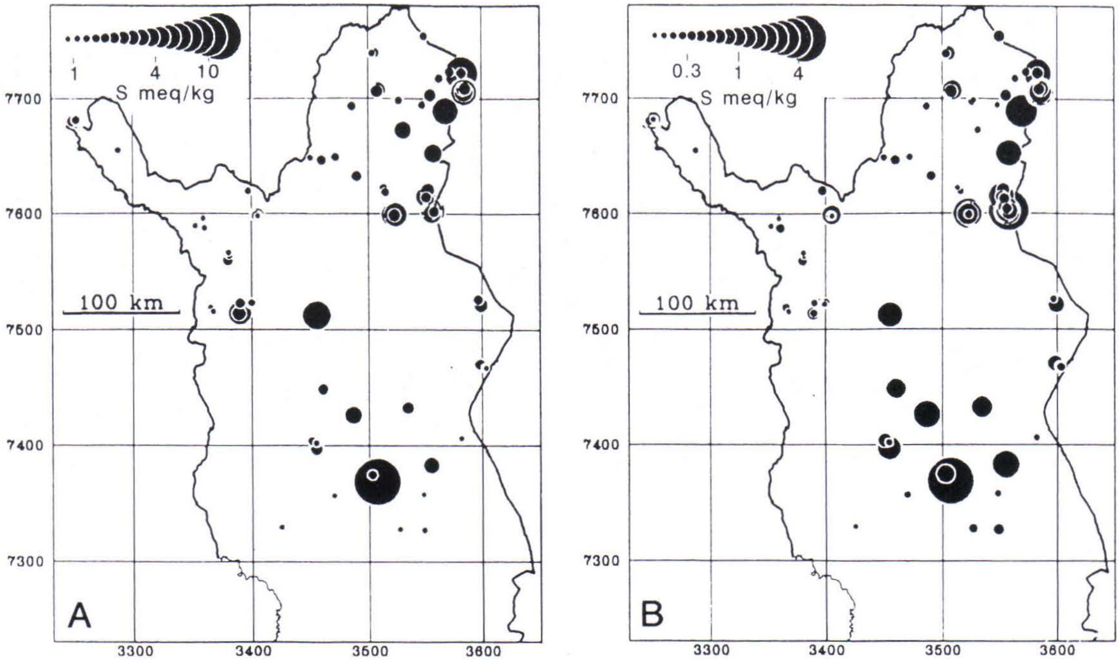


Fig. 39. Concentrations of sulphur soluble in a) aqua regia and b) buffered (pH 4.5) NH_4Ac in the parent material in 90 catchments.

the sulphur contents in moss (*Hylocomium splendens*) were about 1200 - 1700 ppm, which can be attributed to natural variation (Niskavaara and Lehmuspelto 1990).

In mineral soils, the high sulphur concentrations were due not to sulphur deposition but to the primary sulphide minerals in schists (especially black schists) and some mafic and volcanic rocks, which are common in the Central Lapland Greenstone Belt and also in northern Lapland (Fig. 39a). In the bedrock of northern Lapland primary sulphides do not contribute markedly to sulphur concentrations; the elevated sulphur concentrations in the soil indicate, however, the presence of small but locally important sulphide mineralizations (Kesola 1991). In mineral soil horizons, the soluble sulphur concentrations were distinctly low, being on average < 10 meq/kg, < 160 ppm, compared with the concentrations in the humus horizons (Fig. 39b). Soluble sulphur accounted for about 10% - 20% of the total sulphur concentration. In the assessment of soil pollution, a recommended permissible level of 200 ppm and a maximum limit of 2000 ppm have been set for sulphur concentrations (e.g. Manninen and Willamo 1993). Thus, in places natural sulphur concentrations in soil in Lapland exceed the recommended level owing to the presence of sulphide mineralizations.

Susceptibility of catchment soils to acidification

To assess the role of geochemical properties and processes in the podzol soils of catchments and their relations to the acidification of soils and lakes, we must know which elements are mobile or could be mobilized in catchment soils. In Finland, the most important neutralizing process is mineral weathering, but it is the only long-term buffer in forest-floor podzol soils. As soils in Finland are young, they have enough weatherable minerals; the problem is that silicate mineral weathering is too slow. The two main factors controlling weathering rate are the mineral assemblage present and the specific surface area of the soil. The weathering rate depends on the acidity of the soil solution, but it is highly improbable that increasing acidity of soil profiles would provoke a weathering rate high enough to maintain bicarbonate buffering in the soil, lake waters and groundwaters. In Lapland, the cold climate retards both the weathering of minerals, and the decay of organic matter and its mixing with mineral soils.

Cation exchange and the aluminium buffer are the main buffering mechanisms in the podzol soils of the boreal coniferous forest zone. Cation exchange is the most important buffer in the humus and underlying eluvial horizons. Buffer capacity is dominated by the properties of the organic matter in the surface horizons, but is controlled by the abundance and type of clay minerals in deeper horizons. According to Nuotio et al. (1990), the CEC and BS are higher in southern Finland than in eastern and northern Finland due to differences in podzolization. Large parts of eastern and northern Finland were supra-aquatic immediately after deglaciation, with the consequence that podzolization has been proceeding there for longer than elsewhere. Acidification and the acid-sensitivity of the soil in catchments were assessed with the concentrations of soluble, exchangeable and easily weatherable base cations in relation to aluminium concentrations and with the CEC and BS. It has been established that BS indicates the chemical state of the soil better than does pH, which is very sensitive to interference (e.g. Nuotio et al. 1990).

Naturally acidic soils

Buffer capacity was good in 22 catchments (Fig. 40). In their podzol soils the concentrations of soluble base cations in the eluvial horizons (median 3.7 meq/kg) was distinctly higher than that of soluble aluminium (1.4 meq/kg) (Fig 41a). The chemical properties of till varied as shown by the marked fluctuation in the concentrations of base cations, 0.3 meq/kg to 10.6 meq/kg (Table 11a). The BS in the eluvial horizons ranged from 16% to 48% of the total CEC (Table 12a). Excess acidity is buffered by base cation exchange reactions in these podzol soils. According to Ulrich et al. (Ulrich and Matzner 1981, Ulrich 1983a, Ulrich and Pankrath 1983b), the exchange reactions of base cations in the soil are capable of buffering excess acidity, provided that soil BS is > 10%. The buffer capacity of base cations is most effective in slightly acid soils (pH > 4.5) (Schwertmann et al. 1964, Bache 1986). The median value of BS was 29%. Well-buffered catchments are mainly located in the Central Lapland Greenstone Belt and in northern Lapland. The concentrations of base cations in catchment soils sensitive to weathering (Fig. 42a) were clearly higher and the ratio of aluminium to base cations was clearly lower (Fig. 42b) than in slightly acidic and acidic soils.

Slightly acidic soils

The natural acidity of the soil had been disturbed in a total of 27 catchments. They were located all over Lapland, but mainly in the south, west and north of the province (Fig. 40). Regionally, the concentration of base cations from weatherable minerals was lower (Fig. 42a) and the ratio of aluminium to base cations was higher (Fig. 42b) in parent material than in naturally acidic soils. In slightly acidic catchments, aluminium solubility (median 2.1 meq/kg) was elevated in the eluvial horizons, being higher than in the illuvial horizons (Fig. 41b). The concentration of soluble base cations (median 3.7 meq/kg) in the eluvial horizon was higher than that of aluminium (Table 11b). However, due to the solubility of aluminium, the concentrations of soluble base cations in the buffering reactions in the soil had declined, because in all podzol soils the pH in the eluvial horizons was < 4.5. In some podzol soils, the concentrations of base cations were clearly higher in the parent soil than in the surface horizons, implying that excess acidity was due to the leaching of base cations. The BS was somewhat lower in these soils than in well-buffered soils. The range was from 4.2% to 56% of the total CEC in the eluvial horizon (Table 12b). The median value of the BS was 22%. The more cation exchange sites are filled with aluminium as the acidity of the soil increases, the more base cations are eluted to the lower soil horizons, surface waters and groundwaters, and buffer reactions are gradually replaced by the hydrolysis reactions of aluminium as the pH and redox conditions of the soil change (Bache 1986, Goh et al. 1987).

Acidic soils

Soil acidity had increased in 39 catchments (Fig. 40). All were located in the granite and granite gneiss areas of southern and northern Lapland, where the concentrations of weatherable base cations in parent soils were lower (Fig. 42a) and the concentrations of weatherable aluminium distinctly higher (Fig. 42b) than in naturally and slightly acidic catch-

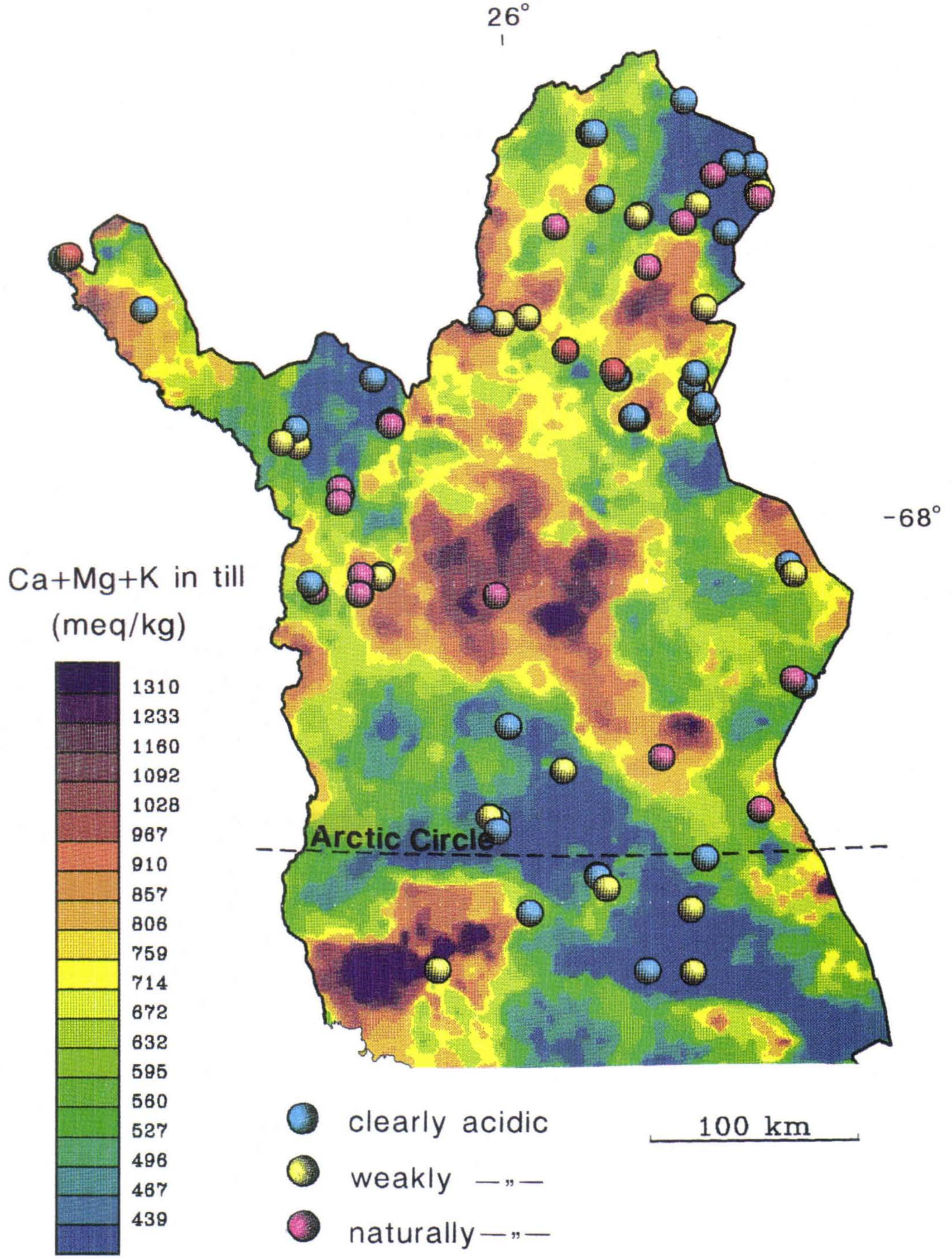


Fig. 40. Locations of naturally acidic, slightly acidic and acidic podzol soils shown with balls. Background: concentrations of base cations soluble in aqua regia in parent material from the Regional Geochemical Mapping programme (Salminen 1995).

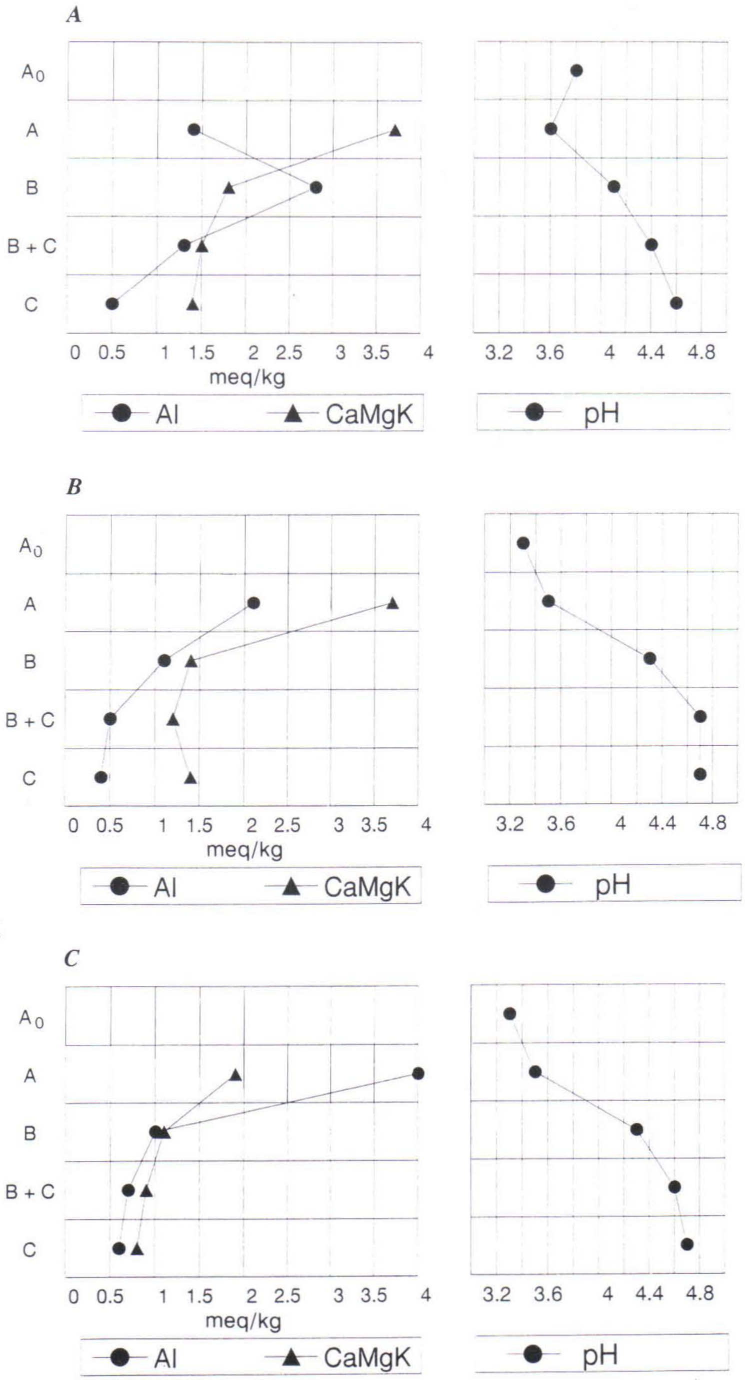


Fig. 41. Acidification degree of catchments: a) naturally acidic podzol soils, b) slightly acidic podzol soils and c) acidic podzol soils. Median concentrations of aluminium and base cations soluble in unbuffered NH_4NO_3 (meq/kg) and pH by podzol soil profile.

Table 11. Median values of concentrations of base cations, aluminium (meq/kg) and pH soluble in unbuffered NH_4NO_3 by podzol horizon in 90 catchments in a) naturally acidic podzol soils, b) slightly acidic podzol soils and c) acidic podzol soils. Range of values in parentheses.

A

Horizon	pH	Al	Ca + Mg + K
A_0	3.8 (3.0 - 5.1)		
A	3.6 (3.0 - 3.9)	1.4 (0.06 - 5.2)	3.7 (0.3 - 10.6)
B	4.1 (3.5 - 4.4)	2.8 (1.0 - 5.9)	1.8 (0.5 - 12.0)
B + C	4.4 (4.1 - 5.1)	1.3 (0.1- 4.2)	1.5 (0.5 - 10.4)
C	4.6 (4.3 - 5.2)	0.5 (0.06 - 2.6)	1.4 (0.5 - 9.1)

B

Horizon	pH	Al	Ca+Mg+K+Na
A_0	3.3 (3.0 - 4.3)		
A	3.5 (3.3 - 4.4)	2.1 (1.0 - 4.2)	3.7 (1.1 - 6.6)
B	4.3 (3.8 - 4.8)	1.1 (0.2 - 3.8)	1.4 (0.5 - 6.5)
B + C	4.7 (4.2 - 5.1)	0.5 (0.06 - 3.0)	1.2 (0.6 - 4.3)
C	4.7 (4.3 - 5.7)	0.4 (0.06 - 2.0)	1.4 (0.4 - 26)

C

Horizon	pH	Al	Ca+Mg+K+Na
A_0	3.3 (3.0 - 3.9)		
A	3.5 (3.3 - 4.0)	4 (1.5 - 7.2)	1.9 (0.7 - 5.0)
B	4.3 (3.9 - 4.9)	1 (0.1 - 4.6)	1.1 (0.5 - 9.4)
B + C	4.6 (4.2 - 5.4)	0.7 (0.06 - 4.6)	0.9 (0.4 - 9.2)
C	4.7 (4.1 - 5.0)	0.6 (0.06 - 7.0)	0.8 (0.4 - 14.8)

Table 12. Median values of concentrations of aluminium and base cations (meq/kg) soluble in buffered (pH 4.5) NH_4Ac, cation exchange capacity (meq/100 g) (CEC) and base saturation (BS%) by podzol profile in a) naturally acidic podzol soils, b) slightly acidic podzol soils and c) acidic podzol soils. Range of values in parentheses.

A

Horizon	Al	Ca + Mg + K	CEC	BS %
A	1.4	3.7	0.5	73
	(0.06 - 5.2)	(0.3 - 10.6)	(0.4 - 1.3)	(56 - 87)
B	2.8	1.8	0.6	38
	(1.0 - 5.9)	(0.5 - 12.0)	(0.2 - 1.2)	(18 - 83)
B + C	1.3	1.5	0.3	53
	(0.1- 4.2)	(0.5 - 10.4)	(0.1 - 1.1)	(25 - 99)
C	0.5	1.4	0.6	73
	(0.06 - 2.6)	(0.5 - 9.1)	(0.1 - 1.0)	(20 - 98)

B

Horizon	Al	Ca+Mg+K+Na	CEC	BS %
A	2.1	3.7	0.6	60
	(1.0 - 4.2)	(1.1 - 6.6)	(0.2 - 0.9)	(27 - 87)
B	1.1	1.4	0.3	66
	(0.2 - 3.8)	(0.5 - 6.5)	(0.08 - 0.8)	(20 - 92)
B + C	0.5	1.2	0.2	73
	(0.06 - 3.0)	(0.6 - 4.3)	(0.08 - 0.5)	(31 - 99)
C	0.4	1.4	0.2	76
	(0.06 - 2.0)	(0.4 - 26)	(0.6 - 2.6)	(38 - 100)

C

Horizon	Al	Ca+Mg+K+Na	CEC	BS %
A	4	1.9	0.6	35
	(1.5 - 7.2)	(0.7 - 5.0)	(0.3 - 1.1)	(17 - 52)
B	1	1.1	0.2	60
	(0.1 - 4.6)	(0.5 - 9.4)	(0.08 - 1.0)	(17 - 95)
B + C	0.7	0.9	0.1	62
	(0.06 - 4.6)	(0.4 - 9.2)	(0.08 - 1.0)	(15 - 96)
C	0.6	0.8	0.1	68
	(0.06 - 7.0)	(0.4 - 14.8)	(0.08 - 1.5)	(20 - 100)

ments. In acidic podzol soils, the concentration of soluble aluminium (median 4.0 meq/kg) was distinctly higher than that of soluble base cations (median 1.9 meq/kg) in the eluvial horizon (Fig. 41c). On average, the concentration of easily soluble base cations was only half that in well-buffered catchment soils (Table 11b). In all these soils, pH was < 4.0 in the eluvial horizon, maintaining the high solubility of aluminium. An increase in aluminium

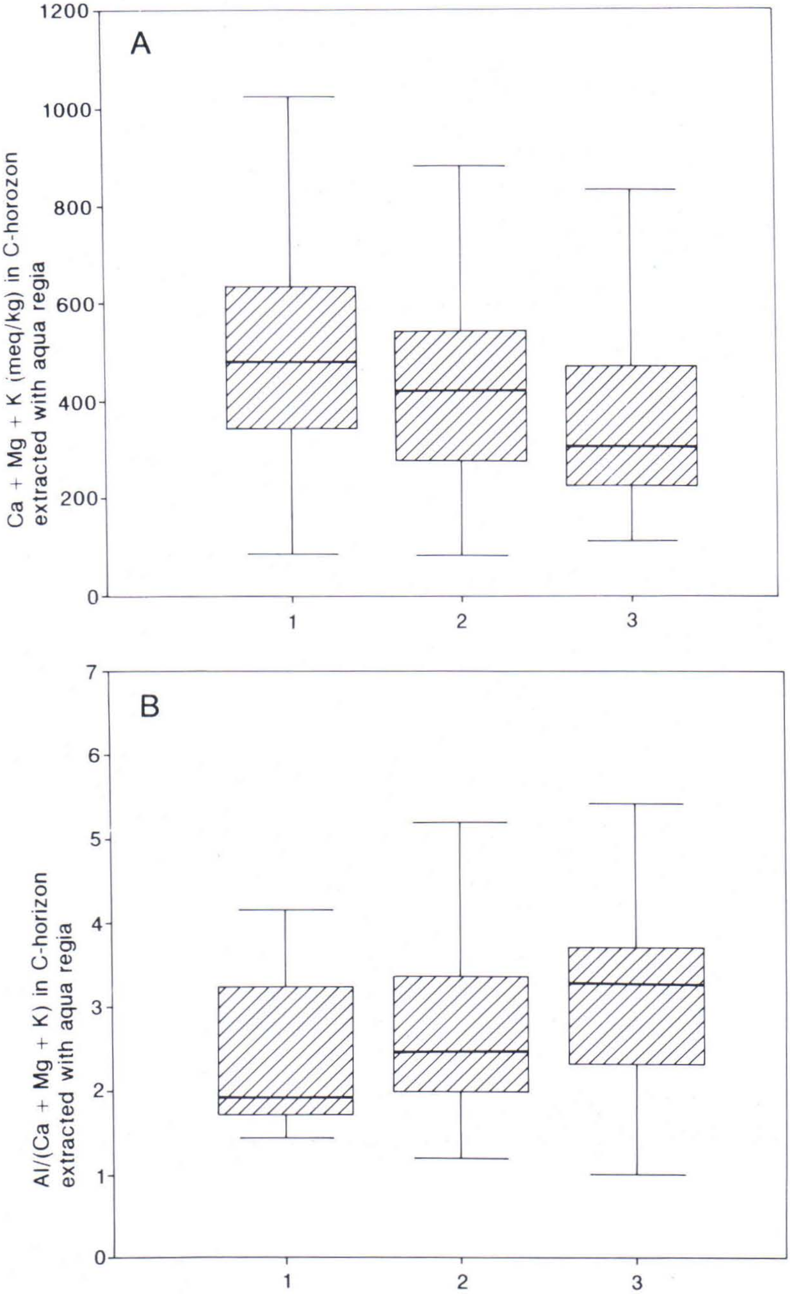


Fig. 42a) Concentrations of weatherable base cations and b) ratio of the concentrations of weatherable aluminium to those of weatherable base cations in the parent material of 1) naturally and 2) slightly acidic and 3) acidic podzol soils.

solubility in the eluvial horizon implies an increase in the concentration of organic and inorganic acids in surficial podzol horizons. The BS of the total CEC was conspicuously low (range 3.5% -18%) (Table 12c). The median value of the BS was 11%. The aluminium buffer is operational in the soil when the BS is less than 5% - 10% on average (Ulrich et al. Ulrich and Matzner 1981, Ulrich 1983a, Ulrich and Pankrath 1983b). Although aluminium hydrolysis promotes soil acidification, simultaneous polymerization and hydrolysis reactions may have buffered soil acidity in association with the mineral weathering and cation exchange reactions of organic complexes.

The reason for excess soil acidity was difficult to establish, as the intensification of acidity does not depend only on the chemical and mineralogical compositions of the mineral soil but also on the contributions of natural processes and agents to acidification, that is, podzolization, nutrient uptake by plants, organic humic and fulvic acids, acid deposition and other anthropogenic factors. The high proportion of mires in some catchments compounded the difficulty of determining acidity. Organic soils neutralize strong acids but they also produce organic, mainly humic and fulvic, acids. Moreover, owing to its acidic character and ability to form complexes, eluted organic matter plays a role in dissolving and transporting inorganic substances, such as Fe, Al, P, S and heavy metals, in the soil. The long-term regional contribution of peatlands to soil acidification is not known adequately. In the boreal coniferous zone, undiversified vegetation enhances the natural acidification caused by podzolization because soil acidification is largely controlled by microbial activity (Brady 1984, Binkley et al. 1987).

Susceptibility of lakes to acidification

Till geochemistry

The abundance of rocks containing alkaline earths (Ca, Mg) and their solubility were the main factors controlling the alkalinity (HCO_3^-) and the concentrations of base cations, or buffer capacity, of lake waters. The sodium and potassium concentrations of lake waters are affected by the weathering degree of parent minerals rather than by their abundance in the soil and bedrock. The buffer capacity of lake waters, which is distinctly higher than that in the environment, correlates with the acidification stage of catchments. The base cations, especially calcium concentrations, of waters were distinctly higher in lakes on naturally acidic catchment soils than in those on slightly acidic or acidic podzol soils, where concentrations of soluble base cations exceeded those of aluminium in surface horizons (Fig. 43).

The bicarbonate dissolved by runoff waters directly from the carbonates in the catchments has a substantial, albeit only local, influence on the buffer capacity of lakes in Lapland. The most extensive continuous area is in the Kemi-Tornio-Tervola region, where carbonate-bearing rocks and interlayers are typical of the Peräpohja schist belt. The waters in the lakes of the Sokli carbonatite massif in eastern Lapland are also well buffered. Soluble calcium most frequently derives from calcium-rich silicates, e.g. from anorthite in the Angeli area and from apatite in the western part of the Central Lapland granite area and the Utsjoki area, and also from amphiboles if they are sufficiently weathered. The magnesium concentrations of lake waters depend on the abundance of silicates, biotite, chlorite, amphiboles, pyroxenes and olivines, their degree of weathering and their solubility in catchments. The Central Lapland Greenstone Belt is largely composed of mafic and ultramafic plutonic and volcanic rocks, as demonstrated by the high concentrations of magnesium in the catchment soils. In the Central Lapland granite area with its acid plutonic rocks and schists, in

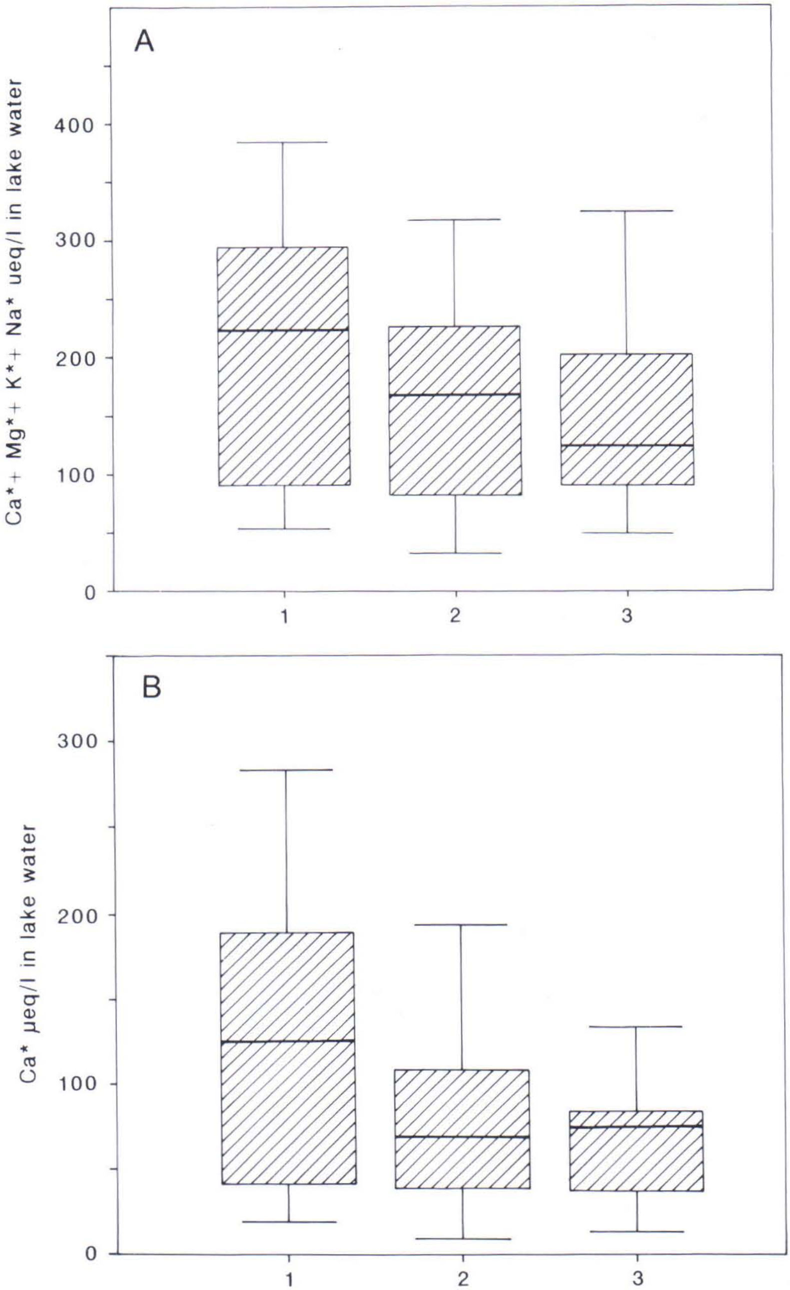


Fig. 43. a) The sea-salt-corrected base cation and b) especially the calcium concentrations of lake waters were distinctly higher in 1) naturally acidic than in 2) slightly acidic or 3) acidic catchment soils.

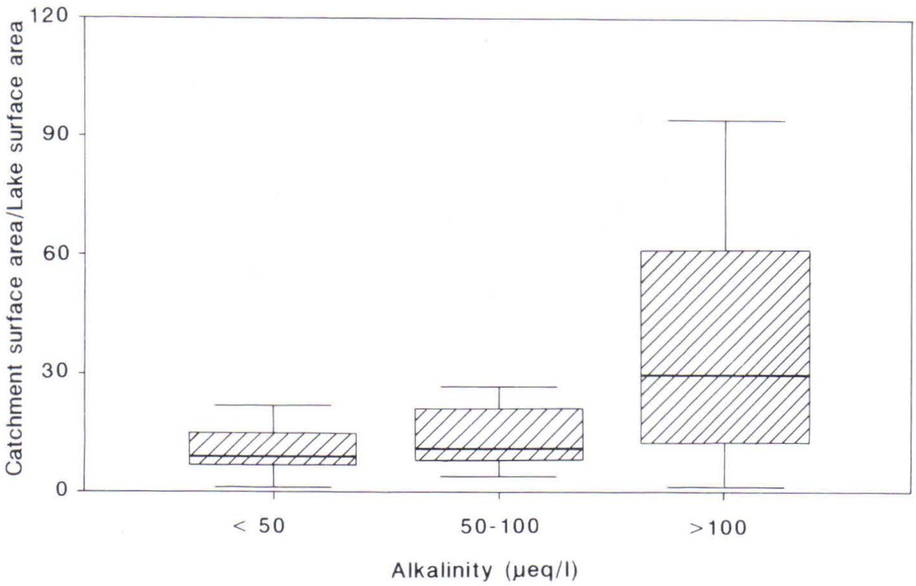


Fig. 44. The ratio of catchment to lake area was distinctly lower for acidic and poorly buffered lakes (ANC < 50 μeq/l) than for well buffered lakes (ANC > 100 μeq/l).

the small granite areas of northern and eastern Lapland and in other small granite-gneiss areas, the buffer capacity of catchment lake waters was usually lower than in other parts of Lapland. In these areas, the catchment soils mainly consist of weathering-resistant, coarse-grained minerals such as quartz, K-feldspar and Na-rich plagioclase. The variation in chemical composition of the catchment soils was mainly due to layers containing micas and carbonates and to metavolcanites.

The buffer capacity of lake waters correlates strongly not only with the chemical properties of the till in the catchments but also with the size of the catchment. The ratio of catchment to lake area was distinctly lower for acidic and poorly buffered (ANC < 50 μeq/l) than for well-buffered (ANC > 150 μeq/l) lakes. Thus, the long retention time of the runoff water has homogenized the quality of lake waters because the slow neutralizing and buffering reactions have had enough time to reach equilibrium (Fig. 44). The lakes with low catchment to lake surface ratios were more likely to be headwater and closed lakes. The combined effect of the chemical and mineralogical properties of the soil and catchment size was the main factors controlling the buffer capacity of lake waters (Fig. 45). The ratio of catchment to lake area in acidic and poorly buffered lakes on naturally acidic catchment soils was more than four times lower (median 7) than that of well buffered lakes (median 32). In general, the ratio of catchment to lake area, especially in well buffered lakes (median 52), was clearly higher in the lakes on acidic catchment soils.

Acidification stage of catchment soils in relation to lake acidity

In lake waters, as in soils, it was difficult to distinguish for sure between the influence on lake acidity of acids from anthropogenic sources and that of natural weak organic and inorganic acids derived from the catchments. Although the estimated proportions of naturally and anthropogenically acidic lakes are uncertain, determination of the concentrations of the dominant anion gave an indication of the origin of lake-water acidity.

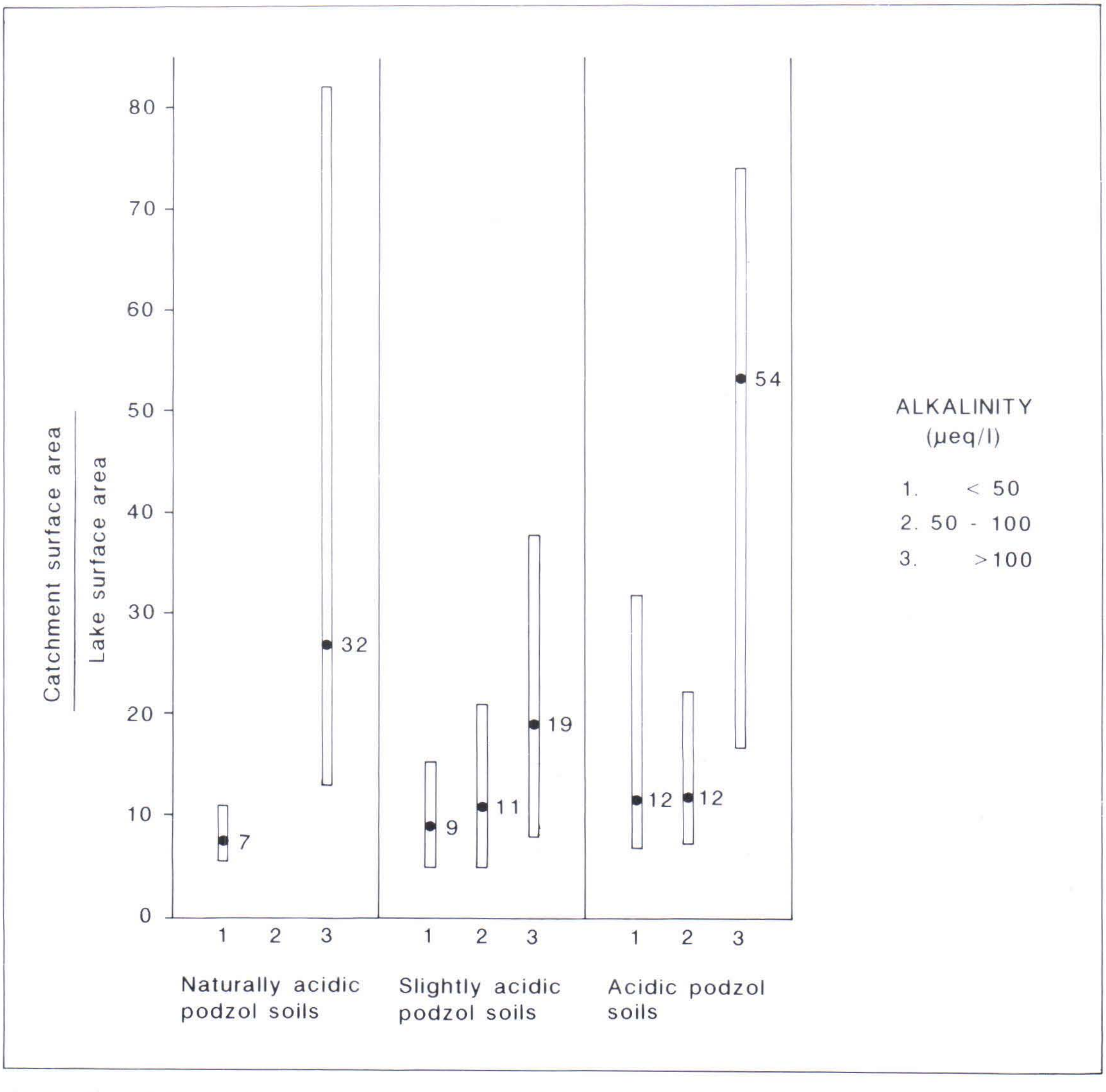


Fig. 45. The combined effect of the geochemical properties of the soil and catchment size was the most important factor controlling the buffer capacity of lake waters.

Organic anion

Compared with the results of lake acidification surveys conducted in Scandinavia and North America (Linthurst et al. 1986, Brakke et al. 1987, Henriksen et al. 1988a, Landers et al. 1988), studies of Finnish lakes indicate that their generally high concentrations of organic matter make a significant contribution to acidity, even in acidic lakes (e.g. Kortelainen 1993). The natural acidity of lake waters in this country is due to the presence of various organic humic and fulvic acids, inorganic aluminium and silica compounds leached from humus and mineral soil horizons. The high organic acid concentration has lowered the alkalinity of Finnish lake waters, and many lakes have been acidic for hundreds of years (Simola et al. 1985, Tolonen et al. 1986). According to Brakke et al. (1987), the effect of strong mineral acids is superimposed on organic acid contributions to acidity in humic lakes in regions receiving acidic deposition. Organic acids make humic lakes more sensitive to atmospheric acid deposition than clearwater lakes even when they have the same concentrations of base cations.

In the 90 lakes studied, the TOC and organic anion concentrations were usually lower than in lakes in southern and central Finland (e.g. Forsius et al. 1990, Kortelainen and Mannio 1990), but, except in northernmost and eastern Lapland, peatland accounts for a higher proportion of the total land area than anywhere else in Finland. One of the main reasons might be the lower production rate of organic matter in Finnish Lapland due to the colder climate and shorter summers. Despite the high percentage of peatland, the amount of organic matter leached from the coniferous forest zone north of the Arctic circle is only about half of that in Finland on average (Sallantaus 1986). The occurrence of thinner soils at higher elevations in northern Finland probably also contributes to the lower organic matter concentrations. Henriksen et al. (1988a) demonstrated that lake water TOC decreased markedly with elevation. In closed lakes, in general, organic anion concentrations were higher than in drainage or headwater lakes (Fig. 47). The closed lakes were usually small and had a relatively small catchment area.

The organic anion was the dominant anion in 14 of the lakes studied (Fig. 43). Most of these lakes were in parts of southern and western Lapland with the highest proportion of peatland in catchments. Various forms of peatland use, e.g. ditching and drainage, which change the catchment vegetation and the cycle of elements and compounds in runoff, could have had a marked impact on the natural acidity of lake waters, especially in southern Lapland. Twelve of the lakes were acidic and poorly buffered (ANC < 50 µeq/l), but also the other two had a relatively low buffer capacity (ANC < 75 µeq/l). Hence, all can be considered recipients of organic humic and fulvic acids. Sulphate concentrations were low in all these lakes. The median values of the chemical characteristics of the lakes and podzol soils are given in Table 13.

The humic acidic and poorly buffered lakes were situated on naturally acidic (22001, 47001, 71001, 90001 and 94001), slightly acidic (18001, 22003) and acidic catchment soils (19001, 22002, 25001, 33001 and 39001). In the lakes on naturally acidic soils, the concentrations of easily soluble base cation were generally twice as high as the concentrations of easily soluble aluminium (median Al/CaMgK=0.5) in the eluvial horizon, but the ratio of catchment to lake area was extremely low (median 2.8) and the concentrations of the organic anion were relatively high (median 40 µeq/l). The lakes on slightly acidic and acidic catchment soils had somewhat lower organic anion concentrations, but the ratio of catchment to lake area was clearly higher. In these catchment soils, aluminium solubility had increased in the eluvial horizon due to the presence of organic and inorganic acids. Two of the humic, moderately buffered (ANC 50 - 150 µeq/l) lakes (39002 and 55001) were situated on acidic catchment soils and the concentrations of the organic anion were high (median 50 μeq/l). The acidic and poorly buffered lakes were distinctly smaller than the moderately buffered lakes

Sulphate

The sulphate concentrations in Finnish lake waters are due to anthropogenic airborne sulphur deposition, sulphide minerals and compounds in the soil and bedrock, and sulphur compounds in organic matter (e.g. Lahermo et al. 1995). In sub-aquatic areas, near the Gulf of Bothnia in particular, the sulphides in postglacial clays dating back to later Baltic Sea marine phases may also contribute to the high sulphate concentrations in the soil and lake waters. In much of the country, however, these factors overlap.

Sulphur occurs in soils mainly as sulphate accumulated in organic matter and as aluminium sulphates adsorbed on solid surfaces but also as sulphur in metal sulphides. Oxidized sulphur can be leached from the soil and, under reducing conditions, sulphate may be transformed into metal sulphides. Organic sulphur constituted a considerable proportion of the total sulphur content in the podzol soils studied, especially in forest-floor soils with relatively slow decomposition of organic matter. Hence, sulphur is an essential non-toxic nutrient. It was difficult to distinguish between natural and anthropogenic sources of lake-water sulphate concentrations, because not enough is yet known about either sulphur deposition in forested catchments or the quantitative importance of sulphur retention and leaching processes.

Nitrate compounds in Finnish soils usually derive from decomposing organic matter, atmospheric deposition and other anthropogenic pollutants, depending on their composition and whether the impact of fertilizers is acidifying or neutralizing. The contribution of nitrate to the acidity of the lake waters studied was very small (median < 0.4 μeq/l). The high concentrations found in a few lakes in Finnish Lapland have been due to decomposing organic matter or anthropogenic pollution (Kähkönen 1993). The effect of nitrate is strongest during the thaw, when the soil is still frozen and nitrate uptake by plants is minimal. At present, nitrate does not contribute significantly to the acidity of Finnish lakes. The importance of nitrate to the acidity of surface waters, especially in southern Finland, is likely to increase, because no major reduction in emissions of nitrogen compounds is expected (e.g. Forsius et al. 1990, Kämäri et al. 1992).

Sulphur concentrations in acidic lake waters were clearly higher in southern and central Finland (e.g. Forsius et al. 1990) than in Finnish Lapland (Kähkönen 1993). In southern Finland, the sulphate concentrations of lakes are frequently > 100 μeq/l (Forsius et al. 1990). Lakes with high concentrations of sulphate are generally better buffered in southern Finland than in Finnish Lapland, mainly due to the higher neutralizing base cation deposition and thicker soils in southern Finland (e.g. Forsius et al. 1990, Järvinen and Vänni 1990).

Sulphate was the dominant anion in 17 of the lakes studied (Fig. 40); all had a low buffer capacity (ANC < 57 μeq/l). The median values of chemical properties of the lakes and podzol soils are given in Table 13. Most of the lakes were situated on slightly acidic (7001, 20001, 36001, 41001, 84001, 117003, 120001 and 120002) and acidic (22004, 35001, 67002, 115001, 115002 and 117002) catchment soils. Only three lakes were in naturally acidic catchments (16001, 110001 and 117001). The ratio of catchment to lake area was relatively low for all these lakes. In acidic catchments, aluminium solubility was high, being more than three times that of the base cations in the eluvial horizon (Al/CaMgK=3.5). The sulphate concentrations of the lakes were distinctly higher than the concentrations of organic anions; hence the contribution of organic compounds to acidity was minimal.

The origin of the sulphate of these lakes was ambiguous. The sulphate concentrations of acidic and poorly buffered and well-buffered lakes throughout Lapland were higher than would be expected from sulphur deposition. Almost half of the lakes are in western and southern Lapland, where the level of anthropogenic sulphur deposition is about the same as the background values. The sulphate concentrations of these lakes were mainly due to sulphide minerals in soil and bedrock. The high solubility of aluminium could then have enhanced the leaching of sulphate. In the Central Lapland Greenstone Belt, there were some very well buffered lakes with anomalously high sulphate concentrations (> 100 μeq/l). The mafic and volcanogenic rocks in the Central Lapland Greenstone Belt are locally carbonated, containing copper-bearing sulphide mineralizations (Keinänen et al. 1988).

The other lakes are situated in northern and northeastern Lapland, in the area with the highest sulphur deposition in Finnish Lapland. The pattern of sulphate concentrations in lake water is known to be similar to that of sulphur deposition, i.e. the highest concentrations are in southern Finland and northeastern Lapland, the two areas with the highest sulphur deposition (Forsius et al. 1990, Kinnunen 1990, Kähkönen 1993). Both the relatively high sulphate concentrations in the acidic lakes and the high concentrations of soluble sulphur in the humus horizons indicate that sulphur deposition from the Cu-Ni smelters on the Kola Peninsula has contributed to the lake sulphate and soil sulphur values, at least in the easternmost Inari area.

Bicarbonate

Bicarbonate was the dominant anion in most of the lakes studied (N=59) (Fig. 43). The median values of the chemical properties of the lakes and podzol soils are given in Table 15. Five of the lakes (2001, 23001, 28001, 32001 and 44001) were acidic or poorly buffered and the concentrations of sulphate and the organic anion were almost the same. Four of the lakes were on acidic catchment soils (Al/CaMgK=1.7) and one lake (32001) was in a slightly acidic catchment (Al/CaMgK=0.9). The ratio of catchment to lake area was generally low. The acidity of the lakes was controlled by the combined effect of the naturally weak buffer capacity of the catchments, the amount of leached organic matter, and contents of aluminium and silica compounds. The concentrations of weatherable base cations in the parent material of the catchment soils was low. Lakes 2001 and 23001 are in mountainous areas and their catchment areas are at > 450 m a.s.l.

Twenty-three of the lakes were moderately buffered, with alkalinity ranging from 50 μeq/l to 150 μeq/l. These lakes were situated on slightly acidic (1001, 34001, 56001, 60002, 67003, 69001, 73001 and 76002) or acidic (3001, 29001, 60001, 60003, 61002, 61003, 66003, 76001, 81001, 81002, 86001 and 105001) catchment soils. Only three of them (60004, 74001 and 81003) were in naturally acidic catchments. The ratio of catchment to lake area for these moderately buffered lakes was twice as high as that for acidic and poorly buffered lakes. The buffer capacity (alkalinity) of these lakes decreased as a function of catchment soil acidity, that is, the lakes in acidic catchments had the lowest alkalinity (median 80 μeq/l). The sulphate concentrations of these moderately buffered lakes were clearly higher than the concentrations of the organic anion.

The remaining 31 lakes were all well-buffered (ANC > 150 μeq/l); their alkalinity was generally > 200 μeq/l and they were situated on naturally acidic (median Al/CaMgK=0.3) (1002, 1003, 1004, 11002, 12001, 12002, 13002, 17001, 17002, 50001, 59001 and 69002), slightly acidic (15001, 15003, 27001, 54001, 55002, 61001, 66002 and 99001) or acidic (11001, 66001, 66004, 66005, 66006, 67001, 67004, 97001, 97002, 100001 and 113001) catchment soils. Most of the naturally and slightly acidic catchment areas were in the Central Lapland greenstone belt and on the Angeli anorthosite and Sokli carbonatite massifs, which are rich in volcanic, mafic and carbonate rock components. On acidic catchment soils the solubility of aluminium (median Al/CaMgK = 1.2) was clearly lower in the well-buffered lakes than in acidic and poorly buffered lakes. The ratio of catchment to lake area was three to five times higher than that for acidic and poorly buffered lakes. The ratio was particularly high (median 55) for lakes in acidic catchments. The sulphate and organic anion concentrations in these well-buffered lakes were about the same as or even higher than in acidic and poorly buffered lakes. The large size of the catchment area had ensured a good buffer capacity for these lakes, even in catchments where the solubility of aluminium was higher than that of base cations.

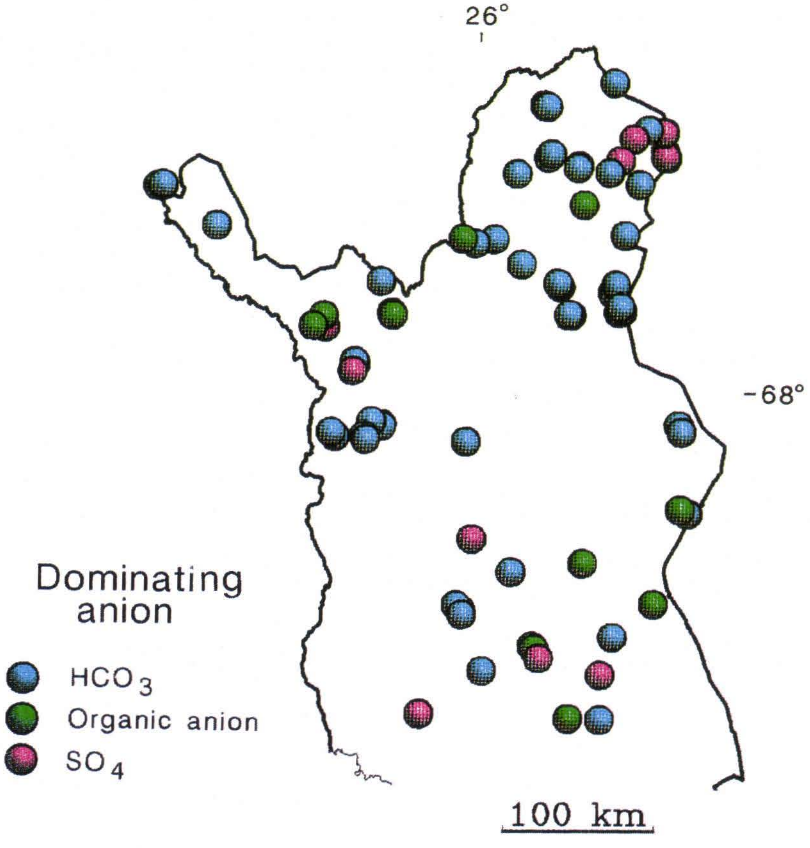


Fig. 46. The dominant anion of lake waters: bicarbonate was the main anion. Sulphate was the dominant anion in 17 lakes and the organic anion in 14.

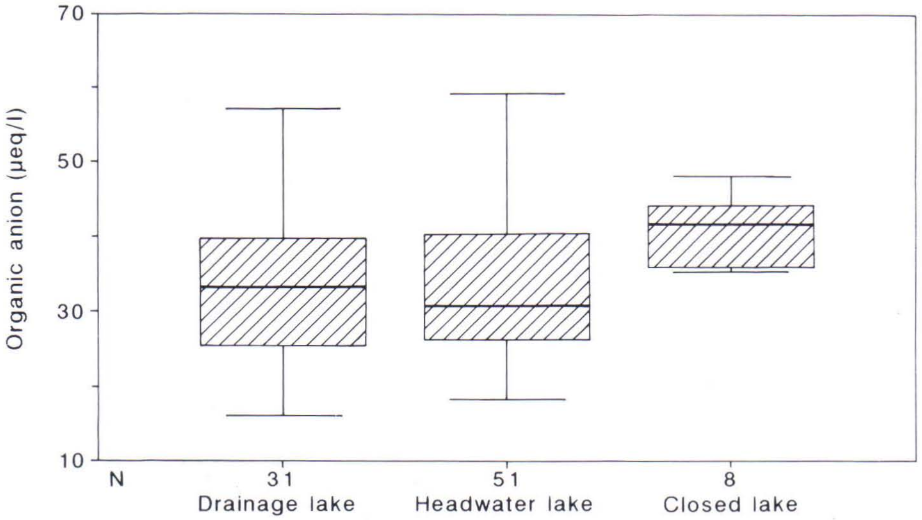


Fig. 47. Organic anion concentrations were usually higher in closed lakes than in drainage or headwater lakes. Closed lakes are generally small with a relatively small catchment area.

Table 13. Median values of chemical and physical properties of lakes and podzol soils with the organic anion as the dominant anion. Ranges are in parentheses.

	Alkalinity			
	< 50 µeq/l			50 - 150 µeq/l
Variable	Naturally acidic soils (N=5)	Slightly acidic soils (N=2)	Acidic soils (N=5)	Acidic soils (N=2)
Al/CaMgK (meq/kg) NH_4NO_3, eluvial horizon	0.5 (0.3 - 0.6)	0.7 (0.5 - 1.0)	1.5 (1.2 - 3.2)	2.1 (2.0 - 2.2)
Al/CaMgK (meq/kg) NH_4AC, eluvial horizon	7 (4.9 - 11.3)	4 (3.0 - 5.1)	8.6 (7.6 - 26)	9.2 (8.7 - 9.6)
Ca+Mg+K (meq/kg) aqua regia, parent material	322 (253 - 967)	501 (367 - 634)	240 (180 - 832)	224 (143 - 306)
$\frac{\text{catchment surface area}}{\text{lake surface area}}$	2.8 (2.0 - 5.3)	11.5 (7.4 - 15.7)	13.3 (7.1 - 179)	10.2 (8.7 - 11.6)
lake surface area (km^2)	0.09 (0.07 - 0.12)	0.055 (0.05 - 0.06)	0.07 (0.02 - 0.35)	0.34 (0.11 - 0.57)
HCO_3 (µeq/l)	31 (-16 - 350)	15 (3 - 27)	21 (12 - 38)	64 (53 - 75)
organic anion (µeq/l)	40 (29 - 62)	26 (11.6 - 39.4)	32.3 (28 - 47.4)	49.8 (42.5 - 57.2)
SO_4 (µeq/l)	22 (14 - 34)	18 (17 - 20)	24 (12.7 - 30.2)	21.6 (19.3 - 23.8)

Table 14. Median values of chemical and physical properties of lakes and podzol soils with sulphate as the dominant anion. Ranges are in parentheses.

	Alkalinity			
	< 50 µeq/l			50 - 150 µeq/l
Variable	Naturally acidic soils (N=3)	Slightly acidic soils (N=8)	Acidic soils (N=5)	Acidic soils (N=1)
Al/CaMgK (meq/kg) NH_4NO_3, eluvial horizon	0.33 (0.208 - 0.6)	0.55 (0.25 - 0.8)	3.5 (1.9 - 5.8)	2.1
Al/CaMgK (meq/kg) NH_4AC, eluvial horizon	1.8 (1.7 - 2.9)	3.5 (1.3 - 6.6)	13.4 (8.4 - 34)	15.5
Ca+Mg+K (meq/kg) aqua regia, parent material	405 (344 - 564)	398 (83 - 1162)	441 (112 - 782)	358
$\frac{\text{catchment surface area}}{\text{lake surface area}}$	8 (6.6 - 15.1)	9.6 (1.4 - 63)	8.6 (6.7 - 81)	4.1
lake surface area (km^2)	0.33 (0.05 - 0.38)	0.09 (0.02 - 0.35)	0.22 (0.11 - 0.26)	0.15
HCO_3 (µeq/l)	25 (19 - 45)	11 (-5 - 41)	13 (-20 - 48)	57
organic anion (µeq/l)	16.5 (9.7 - 16.8)	31 (16 - 43)	14.6 (9.9 - 48)	2.7
SO_4 (µeq/l)	42 (36 - 50)	47 (28 - 57.3)	36.3 (26 - 56)	53.8

Table 15. Median values of chemical and physical properties of lakes and podzol soils with bicarbonate as the dominant anion. Ranges are in parentheses.

	Alkalinity							
	< 50 μeq/l		50 - 150 μeq/l			> 150 μeq/l		
Variable	Slightly acidic soils (N=1)	Acidic soils (N=4)	Naturally acidic soils (N=3)	Slightly acidic soils (N=8)	Acidic soils (N=12)	Naturally acidic soils (N=12)	Slightly acidic soils (N=8)	Acidic soils (N=11)
Al/CaMgK (meq/kg) NH_4NO_3, eluvial horizon	0.9	1.7 (1.2 - 3.3)	0.65 (0.5 - 0.8)	0.68 (0.16 - 3.1)	2.2 (1.1 - 5.1)	0.3 (0.16 - 0.6)	0.8 (0.2 - 1.1)	1.2 (1.0 - 2.9)
Al/CaMgK (meq/kg) NH_4AC, eluvial horizon	5	8.6 (7.9 - 17.2)	3.3 (3.1 - 3.9)	4.2 (0.82 - 17.4)	9.9 (6.9 - 18.2)	2.4 (1.1 - 4.8)	4.7 (2.3 - 24.0)	7 (4.9 - 11)
Ca+Mg+K (meq/kg) aqua regia, parent material	289	242 (132 - 499)	403 (328 - 406)	487 (266 - 882)	300 (162 - 687)	595 (86 - 1025)	381 (145 - 1164)	334 (209 - 1508)
$\frac{\text{catchment surface area}}{\text{lake surface area}}$	9.3	14.3 (7.1 - 62.4)	20.5 (4.8 - 58)	11.3 (5.1 - 41.8)	18.3 (4.4 - 201)	42 (4.2 - 275)	30 (5.5 - 49.6)	55 (1.5 - 235)
lake surface area (km^2)	0.17	0.105 (0.03 - 0.22)	0.17 (0.04 - 0.41)	0.105 (0.03 - 0.52)	0.205 (0.01 - 0.97)	0.09 (0.01 - 1.4)	0.14 (0.05 - 1.1)	0.1 (0.01 - 0.25)
HCO_3 (μeq/l)	39	42 (33 - 45)	138 (88 - 142)	109 (70 - 149)	80 (53 - 145)	218 (157 - 550)	210 (152 - 1020)	219 (175 - 1711)
organic anion (μeq/l)	28.9	27.5 (17.0 - 41.5)	32.1 (22.9 - 33.1)	29.1 (21.2 - 44.3)	19.4 (8.2 - 56.8)	26 (-35 - 63)	70 (12 - 274)	16 (-968 - 47)
SO_4 (μeq/l)	37	23 (16 - 32)	47.5 (19.1 - 51.9)	40 (21.2 - 54.3)	36.3 (16.1 - 47.6)	43 (32 - 113)	42 (30 - 74)	52 (20 - 198)

SUMMARY

The chemical and mineralogical composition, acidification stage and role of the catchment surface area in lake-water acidification were studied in 90 forest-floor podzol soil catchments in Finnish Lapland. The catchments and lakes were selected from geochemically diverse provinces and subprovinces on the basis of the results of Regional Geochemical Mapping programme carried out by the GSF. Total sulphur deposition was highest (1.0 g $Sm^{-2} a^{-1}$) in the northeastern Inari area, being about the same as in southern Scandinavia, and decreasing gradually westwards to 0.3 g $Sm^{-2} a^{-1}$. The contribution of organic humic and fulvic acids to acidity is highest in southern and western Lapland, where not only do catchments have the highest proportion of peatland but many of the mires have been ditched and drained for forestry.

Three different selective leaches were used to determine the concentration and solubility of the main elements (Al, Ca, Fe, K, Na, Mg, S) in the humus, eluvial and illuvial horizons, the transition zone and the parent material. All mineral soil samples were taken from till (< 2.0-mm fraction). The element concentrations indicating weatherability, the potential availability of elements and the acid sensitivity of podzol soils were analysed with hot aqua regia leach. The concentrations of exchangeable cations were analysed with buffered (pH 4.5) 1.0 M NH_4-acetate leach; pH 4.5 corresponds roughly to the acidity of Finnish forest-floor soils. Hence the CEC and the corresponding BS refer to the maximum concentrations of exchangeable cations. The concentrations of easily leachable cations and pH values were established using unbuffered 0.025 M NH_4NO_3 leach. The total sulphur concentration was determined with hot aqua regia leach and the soluble/adsorbed sulphur concentration with buffered (pH 4.5) NH_4-acetate leach. All analyses were made with ICP-AES.

The lake-water samples from corresponding catchments were taken during the autumn overturn. The main chemical characteristics - pH, Gran alkalinity, conductivity, COD_{Mn}, colour, NH_4, NO_3, Cl, Fe, Mn, SO_4 and base cations (Ca, K, Na, Mg) - were determined as required by SF standards. Sulphate and base-cation concentrations were sea-salt corrected. Gran alkalinity was used as an estimate for bicarbonate. The organic anion was determined with the method of Oliver. The lakes were divided into drainage, headwater and closed types, depending on their hydrological position in the drainage system. The surface areas of lakes and catchments were determined from their borders, and were then digitized and stored in databases.

Regionally, the geochemical properties of till correlated with the lithology of the underlying bedrock, and the chemical and mineralogical compositions of the parent material controlled the element composition of the humus and the upper mineral podzol soil horizons to a considerable extent. In catchments composed of mafic, volcanic and carbonate-bearing rocks in the schist areas of Central Lapland and in the Peräpohja, Sokli, Angeli and Kilpisjärvi areas as well as in some parts of northern Lapland, calcium, magnesium and potassium concentrations in till were substantially higher than in catchments composed of weathering-resistant felsic rocks in the Central Lapland granite area and in the gneiss granite areas of northeastern, eastern and western Lapland. Aluminium concentrations were highest in the Lapland granulite area and in tills rich in Al-Fe preglacial regolith in eastern and central Lapland. Aluminium concentrations were lowest in the catchments of the Central Lapland granite area and in the granite gneiss area of westernmost Lapland.

The concentration patterns of elements soluble in aqua regia correlated with those of

elements soluble in NH_4 acetate and NH_4NO_3, but owing to differences in the strength of the leach the concentration levels varied markedly. The humus layers contained large amounts of exchangeable base cations and BS was 80% or more. The concentration of exchangeable calcium in the eluvial horizon was, on average, 22% and that of magnesium 4% of the concentrations of these elements soluble in aqua regia. The fairly high concentrations of exchangeable base cations imply that some organic material is present in the eluvial horizons but also that the abundances of micas and clay minerals are high in areas with weathering crust. In the C horizon the concentrations of exchangeable and easily leachable calcium were, on average only 1%, and those of magnesium < 0.5% of the concentrations of these elements soluble in aqua regia. For the acidification of soil and water courses, the abundances of different aluminium fractions in the podzol soils of catchments are more important than the absolute concentration of aluminium. In the humus horizon, the concentrations of exchangeable aluminium were only 6% of the total concentrations, which means that aluminium is tightly bound to organic complexes and compounds. In mineral soil horizons, the concentrations of exchangeable aluminium ranged from 6% to 14% of that of aluminium soluble in aqua regia, being highest in the illuvial horizons. Only about 1% of the aluminium incorporated in the most common silicate minerals was in soluble form.

The acidification stage was determined from the ratio of the concentration of easily leachable aluminium to that of base cations, pH values, CEC and BS. In the naturally acidic podzol soil (Al/CaMgK < 1), base cation exchange reactions provided the main buffer capacity as the excess of acidity increased. In slightly acidic podzol soils, the low pH values (< 4.5) in the eluvial horizons maintain aluminium solubility, and buffer capacity declined as the concentrations of hydrogen and aluminium on the exchange sites increased. Acidification of the mineral soil had increased in a third of the catchments studied. In all acidic podzol soils, the pH values were < 4.0 in the eluvial horizon. The concentration of monomeric aluminium had exceeded that of the polymeric form and the concentrations of base cations (Al/CaMgK > 1). The podzol soils have become more acidic and in most podzols aluminium acts as a buffer. As well as the mineralogical and chemical properties of till, the increase in the solubility of aluminium also indicated the increasing concentrations of organic and inorganic acids in the surficial podzol horizons. Regionally, acidification stage correlated with the concentration and ratio of aluminium to base cations soluble in aqua regia. Locally, however, there was a larger spatial variation in the geochemistry and mineralogy of the soils, and the buffering properties varied, even in adjacent catchments, indicating a mosaic-like pattern in soil geochemistry in Finnish Lapland.

There was a large natural variation in the sulphur concentrations of the humus and mineral soil horizons. Both total and soluble sulphur concentrations were highest in organic matter in the podzol soils studied, indicating that sulphur is an essential component of and nutrient in plants and organic matter. Regionally, total concentrations of sulphur (> 1500 ppm) and concentrations of soluble sulphur (> 150 ppm) in humus were high in catchments of the Central Lapland Greenstone Belt and Peräpohja schist belt, and in the Kilpisjärvi Caledonian area, where the sulphur concentrations in till parent material are naturally high due to sulphide mineralizations. In northern and southern Lapland the high sulphur concentrations in humus layers were of a more complex origin. They could be due to the combined effect of sulphide minerals and sulphur deposition. However, the high total sulphur (1500 - 1900 ppm), nickel (> 15 ppm) and copper (> 10 ppm) concentrations in humus imply that heavy-metal and sulphur deposition from Kola Peninsula Cu-Ni smelters has contributed, and still is contributing, to concentrations of these elements, at least in the easternmost catchments of the Inarinjärvi area. Clearly, more work needs to be done to estimate sulphur deposition on forest-floor soils, and evaluate and specify the quantitative importance of sulphur retention and leaching processes.

Acidic and poorly buffered (ANC < 50 µeq/l) lakes were found throughout Lapland, although mainly in the south, northwest and northeast of the province. The good buffer capacity of lake waters in the Central Lapland Greenstone Belt, Peräpohja schist belt and the Sokli carbonatite and Angeli anorthosite massifs is overwhelmingly due to the mafic, volcanic and carbonate rock components in the catchments. Elsewhere in Lapland, the till geochemistry is more varied, and the acid-sensitivity of lake waters is controlled by a complex combination of catchment surface area and the hydrological pathway and retention time of runoff as well as by the chemical and mineral compositions of the catchment. The ratio of catchment to lake area was three to five times higher for well-buffered lakes than for acidic and poorly buffered lakes, especially on acidic catchment soils. In lakes with a small catchment, mainly closed and headwater lakes, the chemical and mineralogical properties of the catchment soil are the main factors controlling acidification. Lakes with a small catchment abound, especially in northern and northeastern Lapland. Owing to local climatic and geological features and point emission sources on the Kola Peninsula, the lakes are highly sensitive to acidification.

The natural acidity of lake waters was due to organic humic and fulvic acids, inorganic aluminium and silica compounds eluted from humus and mineral soil horizons. Except in the far north, peatland accounts for the highest proportion of the total land area in Finnish Lapland, but the values indicating organic matter in lake waters, such as TOC, colour and organic anion, were clearly lower than those for lakes in southern Finland. This can be attributed to the lower production and leaching rate of organic matter in the coniferous forest zone north of the Arctic circle in Finnish Lapland. Bicarbonate was the main anion in more than half of the lakes studied. The organic anion was the dominant anion in the 14 acidic and poorly buffered lakes in peat-rich catchment areas in southern and western Lapland. Closed lakes, which are usually small and have a relatively small catchment area, had the highest organic anion concentrations. The humic acidic and poorly buffered lakes were situated on naturally and slightly acidic or acidic catchment soils.

Seventeen acidic and poorly buffered lakes had sulphate as the dominant anion. The majority were situated on slightly acidic and acidic catchment soils; almost half were in western and southern Lapland, where anthropogenic sulphur deposition is often of the same magnitude as the background values. The sulphate concentrations of these lakes mainly derived from the primary sulphide minerals in soils and bedrock typical of these mineralized areas. The high solubility of aluminium in acidic catchment soils could have enhanced the leaching of sulphate. In the Central Lapland Greenstone belt there were some very well-buffered lakes with anomalously high sulphate concentrations (> 100 µeq/l). Thus in some places the mafic and volcanogenic rock belts are carbonated and contain copper-bearing mineralizations. The rest of the acidic and poorly buffered lakes with high sulphate concentrations (> 50 µeq/l) were situated on acid-sensitive catchment soils in northern and northeastern Lapland, demonstrating that the source of sulphur deposition was in the Kola area. Nitrate does not contribute to lake acidity in Finnish Lapland.

The proportion of acidic and poorly buffered lakes receiving similar amounts of organic, inorganic and anthropogenic acidity varied, depending on catchment factors, mainly the combination of base cation and aluminium concentrations and the size of the catchment area. Thus, the present findings on the catchment factors affecting the acid-sensitivity of lakes are compatible with those from other glaciated terrains. Arctic ecosystems with only a few species are extremely vulnerable to anthropogenic risk factors. Relatively large areas, such as the Central Lapland Greenstone Belt and the Peräpohja schist belt, are eutrophic in geological structure and thus have good buffer capacity. Areas with a high risk of soil and lake acidification are those with Al-Fe-rich preglacial weathering products intermixed with till in central and eastern Lapland and the extensive oligotrophic granite and granite gneiss areas in eastern and northeastern Lapland. Moreover, the humus layer so important for buffer processes is often shallow in these northern areas. The acid-sensitivity of forest-floor soils and lakes is highest adjacent to the point emission sources on the Kola Peninsula, in the northeast of Inarinjärvi, where the frequency of small lakes is highest, and extreme climatological conditions (a harsh climate with wide temperature fluctuations), geological conditions and the vicinity of large Cu-Ni smelters on the Kola Peninsula intensify both lake-water and soil acidification more than in other parts of Finnish Lapland.

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