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AHTI LEPISTÖ

Hydrological processes contributing to nitrogen leaching from forested catchments in Nordic conditions

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Ahti Lepistö

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I Lepistö, A. & Seuna, P. 1990. Hydrological characteristics affecting the runoff water acidity. In: Kauppi, P., Kenttämies, K. & Anttila, P. (eds.) Acidification in Finland. Springer-Verlag, Berlin. P. 825–847.

II Bengtsson, L., Lepistö, A., Saxena, R.K. & Seuna, P. 1991. Mixing of meltwater and groundwater in a forested basin. Aqua Fennica 21: 3–12.

III Lepistö, A. 1995. Increased leaching of nitrate at two forested catchments in Finland over a period of 25 years. Journal of Hydrology 171: 103–123.

IV Arheimer, B., Andersson, L. & Lepistö, A. 1996. Variation of nitrogen concentration in forest streams – influences of flow, seasonality and catchment characteristics. Journal of Hydrology (in press).

V Lepistö, A., Andersson, L., Arheimer, B. & Sundblad, K. 1995. Influence of catchment characteristics, forestry activities and deposition on nitrogen export from small forested catchments. Water, Air, and Soil Pollution 84: 81–102.

VI Lepistö, A., Seuna, P. & Bengtsson, L. 1994. The environmental tracer approach in storm runoff studies in forested catchments. In: Seuna, P., Gustard, A., Arnell, N.W. & Cole, G.A. (eds.) FRIEND: Flow Regimes from Experimental and Network Data. Proceedings of the Braunschweig Conference, October 1993. IAHS Press, Wallingford. IAHS Publication No. 221: 369–379.

VII Lepistö, A. 1994. Areas contributing to generation of runoff and nitrate leaching as estimated by empirical isotope methods and TOPMODEL. Aqua Fennica 24: 103–120.

VIII Lepistö, A. 1995. Runoff generation processes in peaty forest catchments – possibilities for regionalization. In: Leibundgut, Ch. (ed.) Tracer technologies for hydrological systems. Proceedings of the Boulder Symposium, July 1995. IAHS Press, Wallingford. IAHS Publication No. 229: 285–294.

Hydrological processes contributing to nitrogen leaching from forested catchments in Nordic conditions

Ahti Lepistö

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The major objective of this study was to improve the understanding of the factors affecting temporal and spatial variation of nitrogen leaching from forested soils in Nordic conditions, by analysing the impact of hydrology, N deposition and forestry activities. A 'new' event water fraction of runoff provides atmospheric pollutants with a rapid pathway to channels and watercourses, with minor transformations in surface soils. Variation of the event water fraction was studied in mineral and peat soil catchments during snowmelt periods, using oxygen-18 as a tracer. In the mineral soil catchment, snowmelt runoff consisted to a minor degree of 'new' event water (15–25%), whereas in the peatland catchment, the average fraction of event water in the stream was clearly higher, 55–65%. Results of these isotope hydrograph separations were compared with results from Swedish catchments. Peatland fraction and maximum streamflow during the melt period explained 42% and 60% of the variation of the fraction, respectively.Temporal variation of leaching of N over a period of 25 years was studied in two catchments in southern Finland. In one catchment, the total nitrogen output increased almost threefold, from 1.1 kg N $ha^{-1}a^{-1}$ in 1969–79 to 2.9 kg N $ha^{-1}a^{-1}$ in 1980–90. The increase in nitrate leaching particularly during the summer months provides evidence of the onset of nitrogen saturation and the inability of biomass to utilize the N available. The increase during snowmelt and the autumn period, when the fraction of event water in runoff is higher, indicates the impact of N deposition. In the adjacent catchment the nitrate levels were lower but the increasing trend in nitrate leaching was comparable. In the study of 20 forested catchments (0.3–42 km^2) in Finland and Sweden, links between concentrations, flow dynamics and seasonal variation were detected. Further, multivariate regression models were developed in order to explain spatial variation in nitrogen export fluxes and to predict the average export of different nitrogen fractions. A combination of high inorganic N deposition or air temperature and a low extent of organic soils was related to (R^2=0.64) high losses of NO_3-N. A combination of extent of drainage and temperature was related to losses of NH_4-N, whereas the most important factors explaining spatial variability of organic N losses were forestry activities. A high percentage of organic soils contributes to high amounts of recent, event water, but low amounts of released NO_3-N from a catchment. It seems probable that increase of the contributing area fraction increases possibilities for leaching, but only to a certain limit, above which retention processes start to dominate the N cycling. In Finland, losses of nitrate to watercourses are expected to increase mainly from the most fertile forest ecosystems in southern and central parts of the country, where N deposition is also highest.

1 Introduction

1.1 General overview

Nitrogen leaching may considerably affect ground and surface water quality and contribute to the eutrophication of watercourses and marine areas. Eutrophication has been one of the main water problems in Europe for decades. Appearing first mainly in lakes receiving domestic or industrial effluents, it is now affecting many coastal areas and lakes in rural areas without identified point sources of pollution (e.g. Kauppi et al. 1990). In Finnish coastal waters as a whole, the total input of N increased from the 1970s to the 1980s, despite decreased total industrial loading especially in the early 1970s, due to increased inputs from agriculture, municipalities, fish farms and via the atmosphere, as well as increased river flows (Pitkänen 1994). The 'background' load (which consists of forestry, atmospheric inputs and natural leaching) was 56–63% of the total N inputs to the Bothnian Sea and Bothnian Bay in the period 1986–90 (Pitkänen 1994). Since the contribution from forests to the total nitrogen load to the watercourses and the sea is significant, it is important to quantify the load of different fractions of nitrogen and to analyze the magnitude of spatial variation and the reasons behind this variation. Spatial variability may be explained by natural catchment characteristics, but may also be a response to climatic and anthropogenic factors such as deposition and forestry activities. Effects of such factors have been indicated by upward trends in nitrogen loads and concentrations (e.g. Kauppi 1984, Pitkänen 1986, Grimvall et al. 1991).

The atmospheric N input to forests in Europe and North America has increased dramatically during recent decades due to the emission of NO_x from combustion processes and of NH_3 from agricultural activities (Pacyna 1989). Forest ecosystems may accumulate considerable amounts of N in biomass and soil organic matter, but there is increasing concern that forest ecosystems may be overloaded or saturated with N from atmospheric deposition, leading to increased nitrate leaching.

The effect of increased N deposition to freshwater depends not only on the capacity of soils and vegetation to utilise extra N but also on the net effect of uptake processes. When catchment acidification is considered, certain forms of N may acidify soils while other forms are essential for freshwater acidification. Enhanced inputs of N can have a fertilizer effect leading to increased growth, which results in an increased demand for other essential plant nutrients, and may cause nutrient imbalances (Pitcairn 1994).

Nitrate leaching may also be a response of the N cycle to other factors such as management changes, forest decline and climatic change, which may alter N cycling by decreased plant uptake or enhanced mineralization and cause accumulation of inorganic N in the soil, nitrate leaching and/or increased denitrification (Gundersen and Bashkin 1994).

Some of the complex interactions and feedback of causes and effects in the N cycle may be addressed by studying small catchments in different environmental conditions. However, the interpretation of N leaching from forested catchments is rather complex, since the output fluxes are small compared to the possible natural variation and very small compared to the N pools in the forested ecosystem. The links between hydrology of the catchment and processes contributing to N cycling are important. Which contributes more to the increased leaching of nitrate, older pre-event water or recent event water? What are the most important areas within the catchments from the point of view of N leaching? In the following, possible factors affecting leaching of nitrate – hydrology, N deposition and management activities – are discussed.

1.2 Catchment hydrological processes

1.2.1 Small catchment approach

In humid regions chemical flux and cycling are intimately linked to the hydrological cycle. Small catchments provide a natural framework for various types of research, e.g. studies concerning nutrient leaching and cycling, mass balances, effects of landuse change and hydrological processes. The requirements are that the ecosystem must be a watershed underlain by tight bedrock (Likens et al. 1977) and that surface and subsurface water divides coincide.

Catchment investigations have evolved significantly over the past century; they have become more sophisticated than comparisons of paired catchment outputs, incorporating multiple basins and catchment manipulation, as well as within-basin process studies. In addition, there is now considerably more emphasis on the environmental aspects of local and global environmental change.The complex interactions between hydrology, chemistry and ecology have ensured that process studies remain a vital element of catchment studies, with catchment outputs providing an integration of within-site processes (Whitehead and Robinson 1993). A fundamental premise of many hydrochemical studies is that hydrological processes – the source, pathway and residence time of water – in a catchment exert a strong control on the water chemistry (e.g. Hooper and Shoemaker 1986, Whitehead et al. 1986). One of the key areas in any attempt to understand variability in catchment outputs is runoff generation. How is water routed through the catchment and how is runoff generated?

1.2.2 Theories of runoff generation in a forested catchment

Hewlett and Hibbert (1967) put forward the variable source area concept of runoff generation as a basis for understanding the catchment response to storm events. This dynamic framework for storm runoff generation was based on the notions that infiltration is seldom a limiting factor in forested environments and that *subsurface stormflow* (see the glossary of terms, app. 1) (Kirkby 1978) rather than overland flow per se is capable of making a significant contribution to the flood hydrograph (Bonell 1993). The view of Burt (1989) that 'subsurface stormflow is now viewed as the major runoff-generating mechanism both because of its influence on *saturation excess* (saturation overland) *flow* (Dunne and Black 1970) and as an important contributor to stormflow in its own right (Anderson and Burt 1978)' is probably appropriate for many relatively undisturbed humid environments (Bonell 1993).

Bishop (1991) reviewed a variety of different mechanisms of runoff generation during several decades of hydrological research (Fig. 1). These include a) infiltration excess overland flow (Horton 1933), b) overland flow from partial contributing areas (Betson 1964), c) saturation excess overland flow (Dunne and Black 1970), d) macropore flow (Jones 1979), e) subsurface stormflow (Hewlett and Hibbert 1967), f) saturated wedge interflow (Weyman 1973), g) groundwater ridging (Sklash and Farvolden 1979) and h) 'transmissivity feedback' (Lundin 1982). All of these mechanisms can coexist in a catchment in a continually varying spatial pattern (Bishop 1991).

When the runoff mechanisms are viewed in terms of the balance between new water and pre-event water in the hydrograph, Bishop (1991) made a distinction between the processes in a) – d) where pre-event water is a small component of the storm runoff, and the processes in e) – h) where pre-event water is a large component, i.e. pre-event water plays an active role in runoff generation. Saturation excess overland flow (c) may, however, have highly varying fractions of event water precipitated to or melting on saturated areas, and pre-event water discharged from the soils as return flow. This means that pre-event water may in some cases have a major contribution to the total amount of runoff from saturated areas.

Modeling (Smith and Hebbert 1983) and field experiments from hydrometric and environmental tracer studies (e.g. Wheater et al. 1991) support to the idea of a continuum in both spatial and temporal occurrence of infiltration-excess overland flow, saturation overland flow and subsurface stormflow within individual catchments under different conditions of rainfall, antecedent soil moisture and intensity of land use impacts (Bonell 1993).

In forested catchments in Finland and Sweden, a large proportion of the overall runoff is generated by water recharge from rather shallow soils. These soils vary in terms of conductivity, soil depth and preferential pathways. However, the most important factor for wetness distribution and runoff generation is topography. The surface topography is often a good descriptor of the subsurface flow directions and velocities (Sivapalan et al. 1987). Soil depths must also be considered, since many areas consist of shallow soils or bare rock. The distribution of vegetation must be assessed in order to be able to understand the spa-

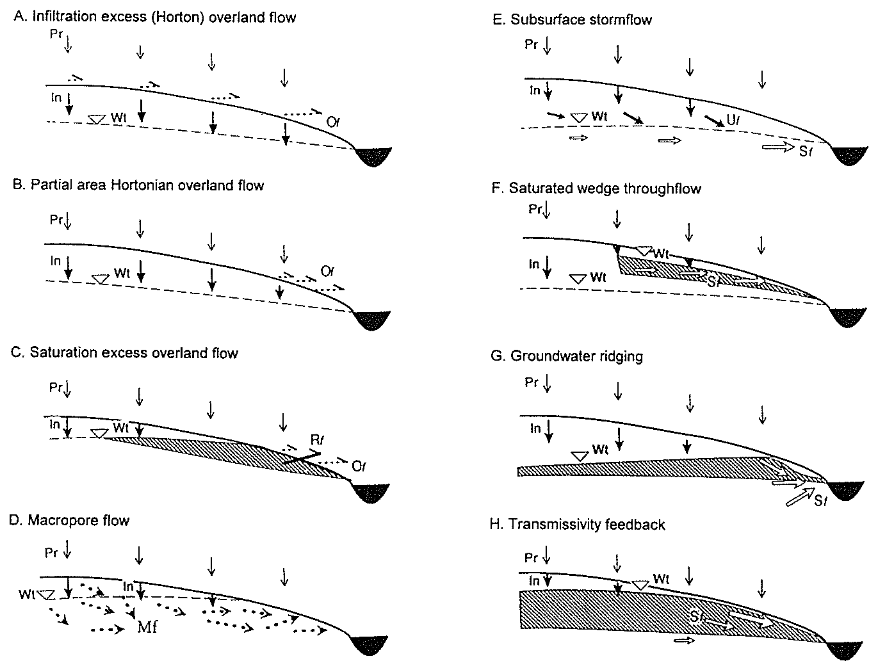

Fig. 1. Schematic representation of different runoff generation mechanisms. Pr is precipitation, In infiltration, Wt groundwater table, Of overland flow, Rf return flow, Mf macropore flow, Sf saturated lateral flow through the soil matrix, and Uf unsaturated lateral flow (from Wood et al. 1990 and Bishop 1991, with minor modifications).

tial and temporal distribution of flow and evapotranspiration. The importance of various runoff generation mechanisms is assumed to depend highly on the physiographic and climatic conditions of the catchment. A catchment can be seen as a mosaic of elements, with different wetnesses and different transit times for the incoming precipitation. It can be hypothesised that elements with similar hydrological responses have similar combinations of physiographic factors, such as soils, bedrock, vegetation and topography (Andersson and Sivertun 1991).

Typical for forested areas in Nordic conditions is the dominance of till soils which constitute more than 90% of the surface sediments (Haldorsen 1990). In till soils, saturated hydraulic conductivity is often high at the soil surface and decreases rapidly with depth (Lundin 1990). The hydraulic conductivity of a given layer of soil decreases rapidly as the larger pores drain, leading to a strong co-variation between the degree of saturation and the transmissivity (lateral flow through the saturated profile) of a soil profile. During conditions of low flow, water drains slowly from the catchment because the most conductive superficial soil layers are unsaturated. Fresh inputs of rainfall to the soil increase the saturated depth in the soil profile and reduce the proportion of air-filled pores in the unsaturated zone. The resulting increase in transmissivity leads to an increase in runoff from the catchment (Bishop 1991).

Contributing areas in generation of runoff

Betson (1964) defined *contributing area* as an area of a catchment contributing to storm runoff. This means that the contributing sub-area in some way causes an increase of streamflow. Dunne and Black (1970) pointed to the ability of the source (contributing) area to generate saturation overland flow plus return flow, whereas the remainder of the catchment acts mainly as a reservoir during storms to provide baseflow after the storm and to maintain the wet areas. Hewlett and Nutter (1970) visualized the growth of the contributing areas as 'an expansion of the perennial channel system into zones of low storage capacity, and thus rapid subsurface seepage into small draws, swampy spots and intermittent channels'. Efforts to acquire information on the runoff generating processes, contributing areas and flow paths have been assisted by the use of environmental isotopes as tracers of water movement and by physically based modeling, discussed in sections 1.2.4 and 1.2.5.

1.2.3 Runoff generation in peatland systems

Peatlands are poorly drained areas in a transitional state between terrestrial and aquatic systems, where the water table is periodically at or near the surface or the land is covered by water. Peatlands occupy a substantial part of the land area in many temperate and cold regions of the world. Originally, peatlands covered about one third of the area of Finland. However, comprehensive drainage has changed over half of the peatland areas to forested-like areas (Seuna 1988).

Peatlands are classified according to the origin and chemistry of their water supplies. Bogs (ombrotrophic mires) are peatlands which receive water solely from precipitation, whereas fens receive precipitation, interflow and groundwater that has percolated through mineral soil. Fens develop in topographic basins and valleys, whereas bogs develop in flat areas with limited surface and subsurface flow (e.g.Turner et al. 1990). Flow within peatlands is difficult to constrain because of the highly variable properties of the peatland sediments. Organic layers near the surface (the acrotelm layer) can be highly porous, with a hydraulic conductivity as high as three orders of magnitude greater than that in the deeper peatland horizons; most water flow occurs primarily through the acrotelm. As a consequence of the limited storage capacity of the surface layers, surface discharge from peatlands responds rapidly to changes in inputs, with little or no detention or regulation of streamflow (Verry and Boelter 1978). In flat, peaty areas the 'new' near-surface runoff may have a significant role in runoff generation.

1.2.4 Empirical isotope studies vs. physically based modeling

Two main paths have been followed in the assessment of flow generation processes. The first is based on analyses of the isotopic composition of streamwater during runoff events, which reflects the integrated result of the various processes contributing to streamflow generation. In these *tracer studies* (e.g. Herrmann and Stichler 1980, 1982, Bottomley et al. 1984, Rodhe 1987, Bengtsson et al. 1989, I,II) a separation to two runoff components, *event* and *pre-event water*, is usually made. A clear definition of the streamflow generation processes behind these terms is often lacking, i.e. the relative age of the runoff can be calculated, but less is known about the flow paths. Although the simple two-component mixing-model approach to stream hydrograph separation does not directly identify the actual runoff-generation mechanisms, the model does allow the hydrologist to evaluate the importance of given conversion processes in a catchment, e.g. 'rapid' saturation overland flow vs. 'slow' Darcian subsurface flow (Sklash 1990).

The second path is based on applications of *distributed hydrological models*, which calculate runoff generated by different processes, and which can be separated into different fractions (e.g. direct flow or quick flow, delayed flow or baseflow). Several problems have been associated with distributed 'physically based' catchment models (e.g. Philip 1980, Klemês 1986, Beck 1987, Beven 1989). There is a lack of measurement techniques to obtain grid scale properties of the catchment soil. Instead, single "effective" physical parameters are used to represent heterogeneous catchment properties. These models are often only calibrated against runoff, i.e. the spatial distribution and the division of flow with different transit times are not tested against field data. In contrast to tracer techniques, the models may contain a more detailed description of flow paths. The terms used for describing flow paths are, however, defined from the structure of the model, not by observed physical processes in catchments were they are applied. The calculated flow dynamics depend considerably on the chosen values of the model parameters, and due to interdependence, several sets of parameters can yield similar calculated hydrographs.

1.2.5 Hydrograph separation using environmental isotope methods

Excellent reviews of the nature of environmental isotopes and their use in hydrograph separations have been provided by e.g. Rodhe (1987), Sklash (1990), Herrmann (1993) and Buttle (1994). Analyses of the chemical or isotopic composition of streamwater during runoff events provide information on the integrated result of the various processes contributing to streamflow generation. Hydrograph separation using isotopes has been performed since the early 1970s, first in mountainous areas in central Europe and in Canada. During the past two decades it has been pointed out in many isotope studies that pre-event water is the dominating component (> 50%) of runoff even during the high flow period (e.g. Dincer et al. 1970, Fritz et al. 1976, Herrmann and Stichler 1980, 1982, Bottomley et al. 1984, Bottomley et al. 1986, Rodhe 1987, Lepistö et al. 1988, Bengtsson et al. 1989, Buttle 1994). In most cases, however, it has not been explained where event and pre-event water within a basin mix and which pathways are used by the runoff water.

Most of the isotope hydrograph separations performed worldwide (n=92), reviewed by Buttle (1994), have been conducted in small, upland forested basins in mid- and high-latitude regions (e.g. Scandinavia, eastern North America, Australasia), and the method has rarely been applied in urban, agricultural and permafrost environments. In arid and semi-arid areas in low-latitude regions, however, the amplitude of the sinusoidal curve of the isotope input may be too small for the use of stable isotopes.

The main advantages of stable isotopes as tracers are the following (Buttle 1994):

1) They are applied naturally over entire drainage basins. This avoids the problems of realistic application rates and the extent of application associated with the use of artificial tracers (Sklash 1990).

2) They are not subject to chemical reactions during contact with mineral matter at the temperatures encountered at or near the earth's surface (Drever 1982).

3) They undergo fractionation during evaporation and condensation. The saturation vapour pressure of water molecules containing the light isotopes (^{1}H and ^{16}O) exceeds that of water molecules containing the heavy isotopes (D and ^{18}O). The result is that during evaporation, water vapour is relatively depleted in the heavy isotopes while the remaining liquid water becomes progressively enriched in D and ^{18}O (Drever 1982).

There are seasonal as well as spatial changes in the levels of stable isotopes in precipitation. δ ^{18}O values of precipitation decrease with surface air temperature, increasing latitude, increasing altitude, increasing distance of vapour transport and increasing amounts of precipitation (Dansgaard 1964, Rodhe 1987).

4) These variations in isotopic content of precipitation appear to be dampened as water passes through the vadose zone to the water table, with the result that the δ-values of groundwater may approach uniformity in time and space, and are changed only by mixing with waters having different isotopic contents (Sklash 1990). This greater temporal variability in the isotopic content of precipitation relative to that of soil and groundwater means that there is frequently a difference between the δ of water input and the δ of water stored in the catchment prior to the event.

It is clear from the streamflow isotopic signatures that substantial proportions of storm hydrographs consist of pre-event water, at least within the framework of antecedent catchment moisture conditions and prevailing low rain intensities experienced in humid temperate latitudes. The fundamental challenge is still how to explain the discharge of such large volumes of pre-event water. Another problem is how to interprete the hydrograph separation results spatially? Which areas inside the catchment are the most important sources of 'new', recent meltwater or precipitation?

1.2.6 Spatial interpretation of the hydrograph separation results

Environmental isotope data can be useful in estimating the areal extent of overland flow (surface-saturated) contributing areas (Sklash 1990), but spatial interpretations in the literature are very sparse. Rodhe (1987), assuming that overland flow is generated entirely as saturated overland flow, estimated the overland flow contributing area by dividing V_n (total volume of 'new' water which leaves the catchment) by V_{tn} (total volume of 'new' water which falls on the catchment). He estimated discharge areas of 0.2–17%, with a median value of 3%, for 14 snowmelt events in forested catchments in Sweden.

Eshleman et al. (1993) found that estimates of new water-contributing areas determined from chemical hydrograph separations were consistent with estimates of areas of likely surface saturation (e.g. perennial channels, open water and riparian wetland areas) based on field observations and topographic maps. However, they compared the sizes of new water-contributing areas, which ranged from 0.1 to 2.9% of the watershed area. The computed contributing areas were much larger than the sum of total channel and pond areas, but smaller than the total channel, pond, and wetland areas. This comparison indicated that the storm flow response could not be explained by an expansion of the stream channel network alone; the areas of nearly saturated to saturated land that lie within the riparian zone had also to be considered. The dynamics of these contributing areas can be calculated using TOPMODEL (e.g. Beven and Wood 1983).

The recognition that spatial variations in soil moisture, and therefore runoff producing areas, are driven by topographic gradients has led to the recent rapid developments in topographically and physically based hydrological models, based on digital terrain models (Moore et al. 1991). These spatial process models, e.g. TOPMODEL (Beven and Wood 1983, Beven et al. 1995), have the ability to indicate contributing areas that are hydrologically vulnerable to disturbance because of preferential waterlogging and the associated runoff generation and erosion (Bonell 1993).

1.3 Factors contributing to nitrogen leaching

1.3.1 Atmospheric N input, nitrogen saturation

Recent measurements of elevated nitrate leaching from certain high-elevation forests suggest that these forests have reached saturation; cumulative nitrogen deposition inputs have exceeded the capacity of these systems to accumulate nitrogen (e.g. Aber et al. 1989). Geographical differences in nitrogen export from forested catchments may reflect atmospheric deposition patterns, but they also reflect an effect of geographical variability of physiographic factors, forestry activities and natural dynamics (Vitousek et al. 1979, Dillon and Molot 1990, V). In order to estimate the present nitrogen export and potential changes in export from forests, there is a need to evaluate factors controlling nitrate mobility in these ecosystems (Cooper and Thomsen 1988, Malanchuk and Nilsson 1989, Dillon and Molot 1990), and to assess the combined effect of factors influencing short- and long-term dynamics.

Inputs of nitrogen to a forested catchment (Fig. 2) may occur through: 1) wet deposition of NO_3^- and NH_4^+ and organic nitrogen; 2) dry deposition; 3) N_2 fixation; or, 4) as a result of forest management, through fertilizing. The atmospheric nitrogen load to terrestrial ecosystems in Europe and North America has increased dramatically during recent decades (Grennfelt and Hultberg 1986, Galloway and Likens 1981). The main sources are emission of NO_x from combustion processes and emission of NH_3 from agricultural activities, which together now account for 90 % of the oxidized and reduced nitrogen in the atmosphere over Europe (Pacyna 1989). The deposition of N compounds (wet+dry) approaches 30 to 40 kg $ha^{-1}a^{-1}$ in many areas in Central Europe, even reaches 100 kg $ha^{-1}a^{-1}$ in some areas (Hauhs et al. 1989), and is greater than 20 kg $ha^{-1}a^{-1}$ in southern parts of Scandinavia (e.g. Grennfelt and Hultberg 1986). Löfgren (1991) estimated the range of wet deposition to be 2–19 kg N $ha^{-1}a^{-1}$ in Scandinavia, and dry deposition to be up to 6 kg N $ha^{-1}a^{-1}$ in background areas. In southern Finland the bulk deposition of nitrogen (mostly wet deposition) exceeds 10 kg $ha^{-1}a^{-1}$ at many observation stations. The deposition of nitrate N increased in 85% of the 37 stations monitored in Finland during 1971–87, and deposition of ammonium N increased in 60% of the stations (Anttila 1991).

There is growing evidence that otherwise undisturbed catchments may show effects of increased N deposition (e.g. Smith et al. 1987, Driscoll et al. 1989a, Dise and Wright 1995). Increased nitrogen deposition can have two types

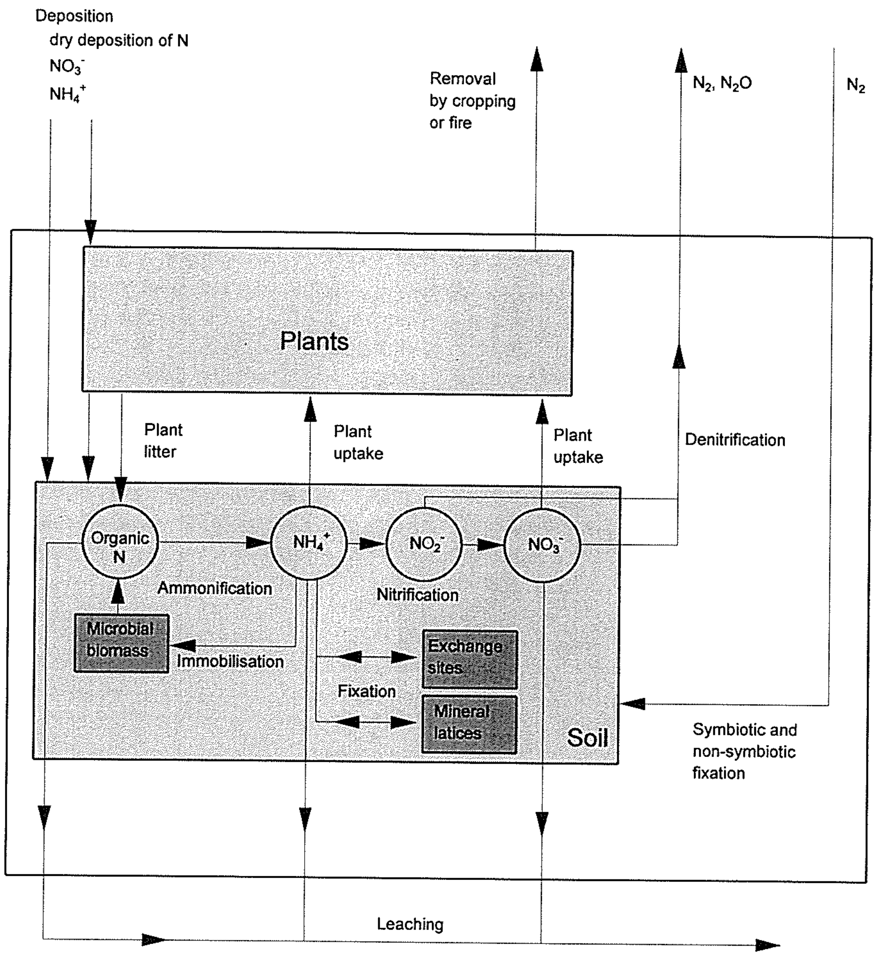

Fig. 2. N cycle and N transformations and transfers in soil (modified from Pitcairn (1994)).

of indirect effects at the ecosystem level. With increased nitrogen availability, biomass accumulation will increase. The second type of effect will prevail where nitrogen is no longer buffered by biomass uptake. These ecosystems show nitrogen saturation indicated by nitrate leaching (e.g. Hauhs et al. 1989). The range in fluxes can span from complete retention to nitrogen saturated sites. A recent analysis of the input-output database covering 65 forest ecosystem studies (plots and catchments) across Europe showed that nitrate leaching was close to zero below throughfall inputs of 10 kg N $ha^{-1}a^{-1}$, highly variable at intermediate levels of 10–25 kg $ha^{-1}a^{-1}$, whereas a considerable part of the input (10–35 kg N $ha^{-1}a^{-1}$) was leached in all systems with inputs above 25 kg N $ha^{-1}a^{-1}$ (Dise and Wright 1995).

Deposition of nitrogen compounds currently plays only a rather minor role in the long-term acidification of lakes (Forsius 1992). In a regional 1000-lake survey conducted in the autumn of 1987 in Finland, Kämäri et al. (1991) found that even in southernmost Finland, 73% of the lakes had nitrate concentrations <5 µeq l^{-1} (70 µg l^{-1}). However, the anthropogenic influence was evident in forested basins, with clearly higher median nitrate concentration in the southernmost part of the country (1.8 µeq l^{-1}) than in northern Finland (0.1 µeq l^{-1}) (Kämäri et al. 1990). The relative importance of nitrogen compounds to the acidity of surface waters in Finland is probably increasing, because the sulphate/nitrate -ratio in precipitation is decreasing and the future reduction in NO_x emissions will be smaller than for SO_2 (Forsius 1992).

1.3.2 Forest management

Forest management practices may upset the nitrogen cycle by decreasing uptake by plants or enhancing mineralization, and may cause accumulation of nitrogen in the soil and increased leaching (Hornung et al. 1988, Wiklander et al. 1991, Gundersen 1992). The outflow of water and nutrients increases for a number of years after forestry drainage. Drainage is a prerequisite for the utilization of peatlands and wet mineral soils in forestry. Forest draining is one of the largest scale human impacts to have taken place in Finland this century. By the end of 1984, slightly under 6 of 11 million ha of swamp and peatland forest had been ditched for forestry (Seuna 1989). In Sweden during the present century over 1 million ha of peatland and mineral soil have been drained. The rate during the 1980s has been more than 50000 ha per year, and during the next 20–40 years about 1.5 million ha are planned to be drained (Ahl and Andersson 1988).

Transpiration, interception and hence evapotranspiration are generally reduced by forest harvesting, which produces more soil water available for the remaining plants and/or increased water movement to streams or groundwater (Swank and Johnson 1994). Increased nitrification in the forest floor after cutting may significantly increase amounts of nitrate N available for leaching. Of all forest management activities, logging is perhaps the most disruptive to element cycles. The paired small catchment method has proved to be a useful tool for studying the effects of logging and other forest management activities on element dynamics in forests (see reviews by Mann et al. 1988, Swank and Crossley 1988).

1.3.3 Nutrient cycling and retention of N

Quantitative assessment of the nitrogen cycle in forested ecosystems is difficult because of the many gaseous, aqueous and particulate forms of nitrogen, and the large number of complex pathways involved. Nitrogen exists in inorganic and organic forms in both the solution and the solid phases of soils. Inorganic N in soil solution includes nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+), in addition to the dissolved gaseous forms (ammonia NH_3, nitrous oxide N_2O, other N oxides).

The nitrogen transformations which operate in soils are shown in Fig. 2. More than 90% of the N in soils is present in organic forms not available to plants. For this N to become available, it must first be transformed (*ammonification*) by micro-organisms to NH_4^+, which is available for plant uptake and/or for oxidation to NO_3^- (*nitrification*) by nitrifying micro-organisms (Fig. 2). The process of *denitrification* (anaerobic NO_3^- reduction to N_2 or N_2O) in forest soils has received increasing attention in recent years (Ineson et al. 1991), since this process might balance some of the N inputs. Most observations still indicate very low denitrification rates in soils of undisturbed forests (< 1 kg N $ha^{-1}a^{-1}$) (Gundersen and Bashkin 1994).

Forests constitute large and highly heterogenous pools of nitrogen. Forest soils in Finland usually contain large amounts of nitrogen (2 000–5 000 kg N ha^{-1}), of which only about 1% is present in mineralized form (Viro 1969). Fungi, which are mainly responsible for decomposing organic matter, are important in maintaining a tightly closed nitrogen cycle (e.g. Mälkönen et al. 1990).

Retention of nitrogen is usually high in forest ecosystems. The forest floor often acts as a major site of nutrient retention (Vogt et al. 1986). Stand age can be a critical factor regulating leaching losses of nitrogen. During early regrowth, the large accumulation of biomass facilitates nitrogen retention and minimizes drainage losses. With time, the rate of nitrogen accumulation peaks and older stands require less net nitrogen inputs and show greater leaching losses (e.g. Driscoll and Schaefer 1989). In 25 catchments in northern and central Wales, Emmett et al. (1993) found that tree uptake was the most important control for inorganic-N leaching losses until stands reach maturity. Thereafter, nitrogen deposition appeared to determine leaching losses.

In peatlands, NO_3^- inputs are efficiently retained and the concentrations of NO_3^- in peatland waters are low (Hemond 1983, Gorham et al. 1984). Export of aqueous N from peatlands as organic N or NH_4^+ has been observed but is usually only a small part of the overall N budget for the peatland and also a minor component of the total solute concentration of the waters draining peatlands (Hemond 1983).

1.3.4 Hydrological processes contributing to nitrogen leaching

Flow pathways form a key concept for the transport of substances through surface and subsurface compartments of a catchment. Combining analyses of the spatial variability and the dynamics of streamflow generation with analyses of spatial and temporal variability of surface and subsurface concentrations of various substances, it should be possible to identify key processes of material fluxes in different parts of a catchment (Sundblad and Andersson 1993). It seems obvious that only by using integrating distributed models together with experimental studies, including tracers and hydrochemical variables, and internal variables such as groundwater levels and extensions of saturated areas, can hypotheses of physical processes behind streamflow generation be validated. Since the main objective for increasing knowledge about flow processes and incorporating this information into hydrological models is to obtain a better understanding of hydrochemical processes, it is a great advantage if hydrological and chemical variables can be measured simultaneously.

Relationships between runoff and nitrogen concentrations, seasonal variation

Part of the variance in streamwater concentration is usually a function of stream flow. This comes about as a result of two different kinds of physical phenomena (e.g. Helsel and Hirsch 1992). One is *dilution*: a solute may be delivered to the stream at a reasonably constant rate, whereas the flow changes over time. The result of this situation is a decrease in concentration with increasing flow. The other process is *wash-off*: a solute, sediment, or a constituent attached to sediment can be delivered to the stream primarily from (surface-saturation) overland flow, or from streambank erosion. In these cases, concentrations as well as fluxes tend to increase with increasing flow (Helsel and Hirsch 1992).

Relations found in regression analyses are often non-linear and the patterns may be very different for different substances as well as for different catchments (Sundblad and Andersson 1993). When nitrogen export from a catchment is estimated, calculations are often based on weekly or monthly measurements and linear interpolation of concentrations. However, the estimated load may be very different from the 'true' load, since concentrations rarely change linearly over time. There is considerable short-term variation in nitrogen concentrations in forest streams, which is influenced by e.g. water flow paths and transit times, and by seasonal variability of biological processes (e.g. Roberts et al. 1984, Burt et al. 1988, Turner and Macpherson 1990). Incorporation of knowledge about such links into load estimates would significantly improve the accuracy and precision of these estimates in small forested catchments.

Rapid changes in runoff acidity and nitrate concentrations during snowmelt

The proportion of direct surface runoff, or near-surface runoff with short transit times, may be especially high in the initial phase of the increasing flow, when the total discharge volume is still low (Turner and Macpherson 1990). Increased concentrations in the increasing phase of a high flow situation might be explained by the near-surface flow paths and 'flushing' of accumulated nitrates.

In Finland and Sweden, winter precipitation is often in the form of snow, resulting in low winter flows and a pronounced spring flow during snowmelt periods. In Finland, a considerable proportion of the annual precipitation falls as snow, 15–25% of the annual precipitation in the south and 25–35% in the north (Kuusisto 1984). The snowpack is able to store, and after melting, suddenly release large amounts of different substances. In a large variety of studies, both in the laboratory and in the natural scale, it has been found that the first fractions of the meltwater contain the highest ionic concentrations (e.g. Overrein et al. 1981, Johannessen et al. 1980, Jenkins et al. 1987). Laboratory and field experiments carried out by Johannessen and Henriksen (1978) indicated that 50–80% of the pollutants, e.g. NO_3^- and SO_4^{2-}, are released when the first 30% of the snow melts.

The dominant runoff generating mechanism in small forested catchments during the snowmelt period might be replacement of 'old' pre-event water from the soil (Rodhe 1987, I,II,VII). This pre-event water may have rather high NO_3-N concentrations due to long periods with limited wash-out, low biological uptake, and mineralization/nitrification during winter (Denning et al. 1991, Stottlemyer and Troendle 1992). Another fraction of streamflow is 'new' meltwater, which has had limited contact with the soil layers but may have highly elevated inorganic-N concentrations derived from atmospheric sources.

The riparian areas as sources or sinks of nitrate

The riparian zone is a chemically and hydrologically complex environment which, together with the streambed, can profoundly influence some aspects of stream chemistry. Because of wet soils adjacent to the streams, riparian buffers may occur between agricultural or urban activities in the uplands of the catchments and small streams. These riparian areas have been shown to be very valuable for the removal of nonpoint-source pollution from drainage water. Several investigators have measured >90% reductions in sediment and nitrate concentrations in water flowing through the riparian areas (Gilliam 1994).

Much less information is available concerning totally forested catchments. Contributing areas (riparian zones) may, however, have a high potential to regulate nutrient fluxes between upland areas and the stream. Groundwater is frequently present at a shallow depth beneath the riparian area, and vegetation and soil processes may therefore modify the chemistry of groundwater before it enters the stream (Swanson et al. 1982, Lowrance et al. 1985). One might assume that atmospheric N deposition on saturated contributing areas will contribute more or less instantly to the N leaching during flow events (Löfgren 1991). This could be an important link between the effects of high stream density and high N deposition on increased nitrate leaching from the forested soils.

These contributing areas probably play an important role in the reduction of nutrient export, having a potential to capture nitrate leached from upper parts of the catchment, either by nutrient uptake or denitrification. Wetlands have been found to remove NO_3^- transported from upland areas, preventing its movement into surface water bodies (e.g. Nixon and Lee 1986).

1.4 Objectives of this study

The major objective of this thesis was to improve the understanding of the factors affecting nitrogen leaching from forested soils in Nordic conditions, particularly in Finland and Sweden. This was achieved by analysing the impact of catchment hydrology, deposition and forestry activities. Detailed studies of temporal and spatial variation of streamflow generation and transit times of water were conducted, together with an attempt to identify areas contributing to N leaching inside the catchment. To fulfil this objective, the following studies were performed:

* the variation of the event water fraction in runoff, on an event (I,II,VI,VIII) and annual scale (VI,VII), was studied by isotope methods, relating variation during snowmelt or rainfall events to catchment characteristics and to meteorological and hydrological variability

* an attempt to regionalize the 'rapid', event water fraction of runoff was conducted, relating it to the volume of the melt peak and the percentage of organic soils in the catchments (VIII)

* a combination of information obtained from tracer studies and measurement of internal variables was used:

– to estimate spatial variability of saturated contributing areas using isotope methods and distributed modeling (VII)

– to study variation in the groundwater table and runoff in the catchment (II,VII)

– to study residence times of water within a catchment (VII)

– to identify catchment areas contributing to nitrate-N leaching (VII)

* the influence of atmospheric deposition, hydrology and internal factors affecting temporal variation (20–25 years) in nitrate and total N leaching from two southern catchments was investigated (III)

* links between concentrations of N, flow dynamics and seasonal variation of N were detected and related to catchment characteristics using statistical methods (IV)

* relevant factors (hydrological, meteorological, physiographic, N deposition, forest management) affecting spatial variation of nitrogen export from forested soils were identified, with an attempt to quantify the role of separate factors using multiregression analyses (V)

2 Materials and methods

2.1 Characteristics of the catchments

The locations of the studied forested catchments are shown in Fig. 3 and the major catchment characteristics in Table 1.

The Teeressuonoja catchment (0.69 km^2) in southern Finland (I,II,III) (Fig. 4) is covered with forests dominated by Norway spruce. Only some minor household loggings occurred in the catchment during the study period 1966–90. The soil consists of 75% coarse and fine sand moraines, 12% sorted soils and 13% peat soils. The soils are relatively deep, varying from a few meters at the brook valley up to 20–25 m. Yli-Knuutila catchment (0.07 km^2) (I,III) (Fig. 4) adjacent to Teeressuonoja is also dominated by Norway spruce, and was almost undisturbed during the study period 1969–90. The soils are more fertile; 67% are sand and fine sand moraines, the remainder are silt and clay moraines (Mustonen 1963). The time series used cover the period until the end of 1990 because after that, on August 1991, an intensive clear-cutting (about 80% of the catchment area) was made in the catchment. These catchments, as well as the Rudbäck catchments 6,7 and 8 (VI,VII) (Fig. 5) in southern Finland, and the Liuhapuro peatland catchment (VIII) (Fig. 6) in eastern Finland are described in greater detail in the original articles.

For the studies concerning spatial variation of nitrogen leaching (V), and the influences of flow, seasonality and catchment characteristics on N concentrations (IV), a data base including physiographical, meteorological, hydrological, deposition and forest management factors was constructed for eight Finnish and twelve Swedish catchments (Table 2). Geomorphological variables were defined from 1:20 000 maps of the Finnish and Swedish Land Surveys. Mean slope calculations (IV,V) for the Finnish catchments were based on point line surveys, with 100 to 200 points in each catchment (Mustonen 1965). For the Swedish catchments, slope was measured on a map basis and converted to a comparable value on the basis of the equation presented by Mustonen (1971). Stream density was defined and measured from maps as the total length of natural streams divided by the catchment area. In drained catchments, the total length of the main ditches was summated to arrive at the total stream density.

Concerning soil types, the percentages of fine soils (clay and silt), organic soils and bare rock were used (IV,V) (Table 2). In the percentage of fine soils, only graded silt soils were included, since the division of fractions in the till soils was not available for all the catchments. Arable land percentages, at the most up to 3%, are also given. The figures used for the Finnish catchments are taken from Mustonen (1965) and Ahtiainen et al. (1988). For the Swedish catchments, the division is based on maps of the Swedish Soil Survey, descriptions of catchments included in the IHD-period (Falkenmark 1972) and information obtained from publications by Rosén (1982), Brink (1979) and Lundin (1982).

The forest management data (IV,V) includes information about percentages of the catchments that were fertilized, clear-cut or drained during the monitoring period (1979–1988). The data were

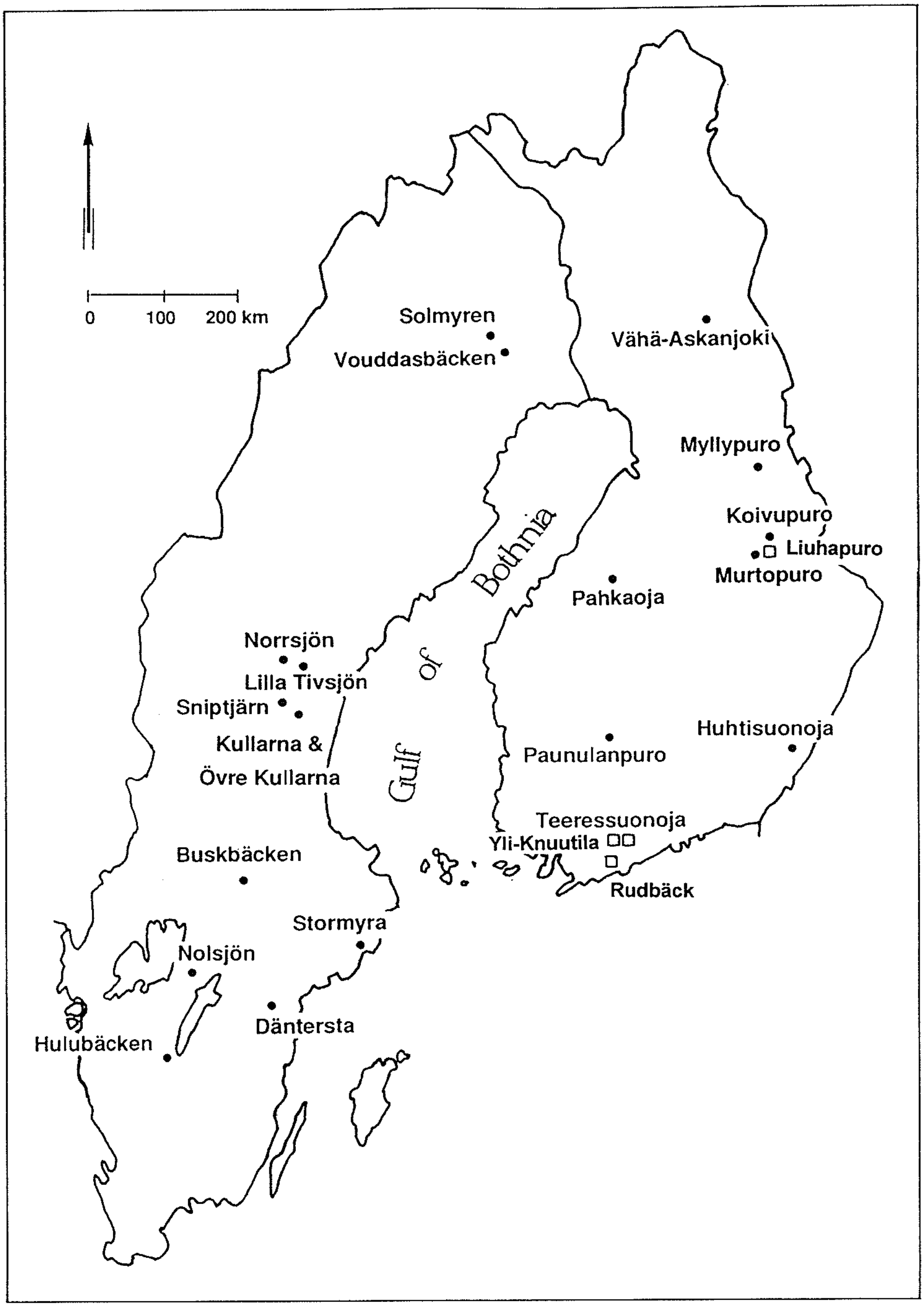

Fig. 3. Location of the study catchments in Finland and Sweden. The catchments used in the more detailed process studies: Yli-Knuutila (I,III), 6, 7 and 8 Rudbäck (VI,VII) and Liuhapuro (VIII) are marked with (□), while the catchments included in spatial studies (IV,V) are marked with dots (●). Teeressuonoja is included in both groups (I,II,III,IV,V).

Table 1. Some characteristics of the catchments studied in Finland and Sweden.

	Area km^2	Altitude m	Organic soils %	Fine soils %	Open bedrock %	Arable land %
6 Rudbäck	4.2	5	3	11	32	7
7 Rudbäck	1.4	18	7	8	29	0
8 Rudbäck	0.18	34	6	2	41	0
13 Yli-Knuutila	0.07	42	0	20	4	0
14 Teeressuonoja	0.69	42	13	7	2	0
31 Paunulanpuro	1.5	117	18	8	2	1
44 Huhtisuonoja	5.0	98	45	0	0	0
54 Murtopuro	4.9	176	50	0	0	0
55 Liuhapuro	1.7	184	48	0	0	0
59 Koivupuro	1.2	209	57	0	0	0
93 Pahkaoja	23.3	150	67	0	0	2
103 Myllypuro	9.9	178	27	0	0	2
114 Vähä-Askanjoki	16.4	168	17	0	0	0
2305 Hulubäcken	3.7	322	94	0	0	0
Däntersta	0.3	35	2	37	6	0
1912 Nolsjön	18.0	124	28	0	1	3
1835 Stormyra	3.9	10	8	20	58	0
2227 Buskbäcken	1.8	280	7	9	3	0
Kullarna	2.0	259	13	0	14	0
Kullarna övre	0.4	315	11	0	28	0
Sniptjärn	0.4	325	22	0	17	0
1920 Lilla Tivsjön	12.8	246	2	0	0	0
2053 Norrsjön	15.3	391	10	0	2	0
1963 Vuoddasbäck	42.0	185	27	0	0	0
2002 Solmyren	27.5	326	34	0	0	0

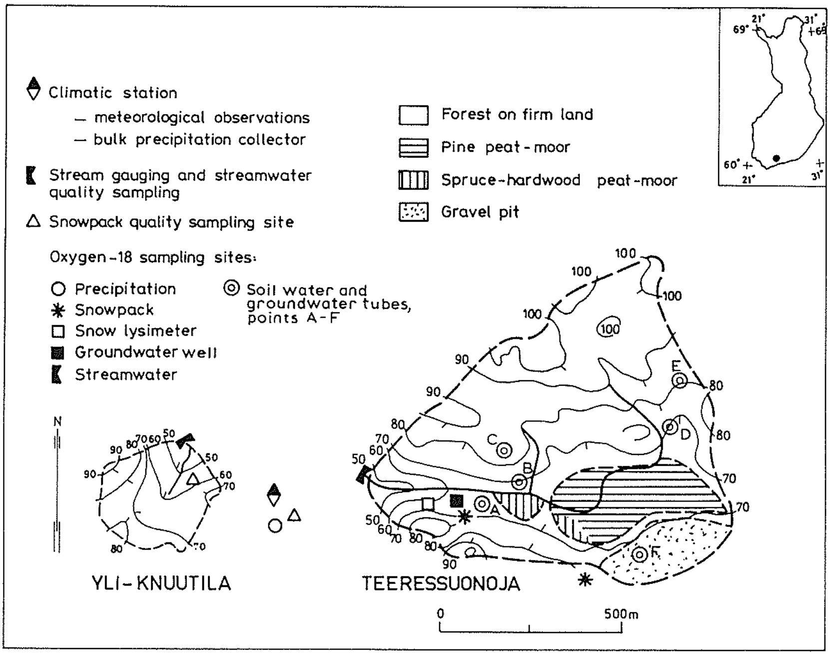

Fig. 4. Location, sampling and monitoring sites, and topography of the catchments Yli-Knuutila (I,III) and Teeressuonoja (I,II,III,IV,V).

obtained from the National Board of Waters and Environment and from the Water and Environmental Districts in Finland, and from local forestry authorities in Sweden. No data bank with continuous information of forest management was available either for Finland or for Sweden. In some cases, the catchments were divided between tens of land-owners, making exact estimates extremely tedious. This means that in some catchments, e.g. Vähä-Askanjoki, the extent of forestry activities may have been underestimated.

2.2 Observations, sampling and analysis methods

2.2.1 Meteorological and hydrological observations

The meteorological variables used in the papers IV and V were average (1979–88) annual air temperature and uncorrected precipitation. These were normally obtained from local climatological stations, run by the Finnish Meteorological Institute or the National Board of Waters and the Environment in Finland and the Swedish Meteorological and Hydrological Institute in Sweden. In the Liuhapuro (VIII), Rudbäck (VI) and Teeressuonoja catchments (I,II), daily precipitation and temperature values from local climatological stations were used. In detailed process studies (VI), the amount of rainfall was also registered every 10 minutes during the summer season with a tipping-bucket rain gauge.

In each of the catchments, runoff was measured continuously by weirs fitted with recording gauges. In Finland, runoff monitoring was run by the National Board of Waters (Seuna 1983), and in Sweden by the Meteorological and Hydrological Institute and the Swedish University of Agricultural Sciences. In the Rudbäck catchments 7 and 8, runoff monitoring began in early June 1991.

The runoff index values were calculated from continuous monitoring data from measuring weirs (V). To indicate variability in the runoff dynamics, three index values were calculated for the 10-year period 1979–88: 1) average maximum monthly runoffs, 2) average minimum monthly runoffs and

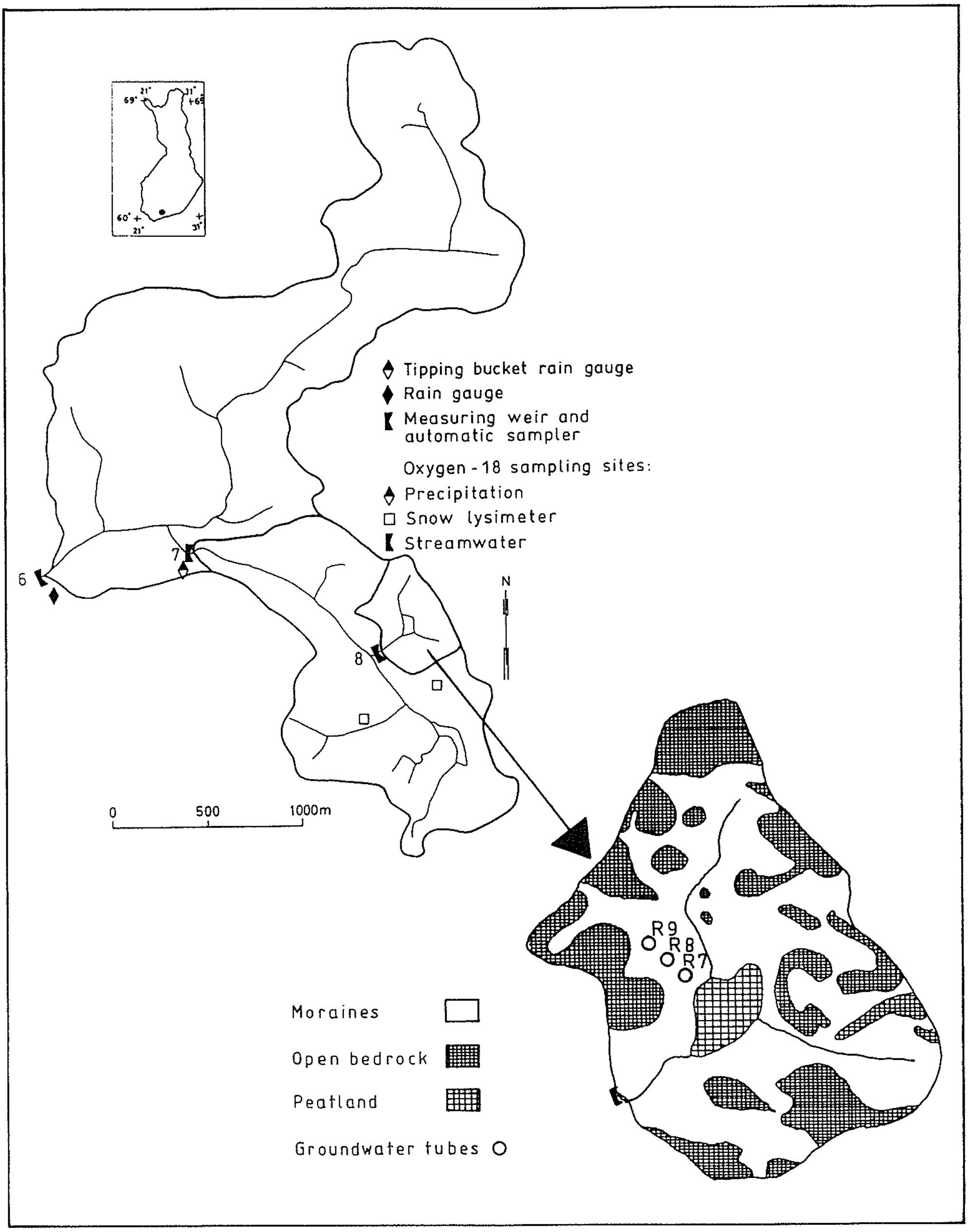

Fig. 5. Locations, and sampling and monitoring sites of the Rudbäck catchments 6, 7 and 8 in Siuntio, southern Finland (VI,VII).

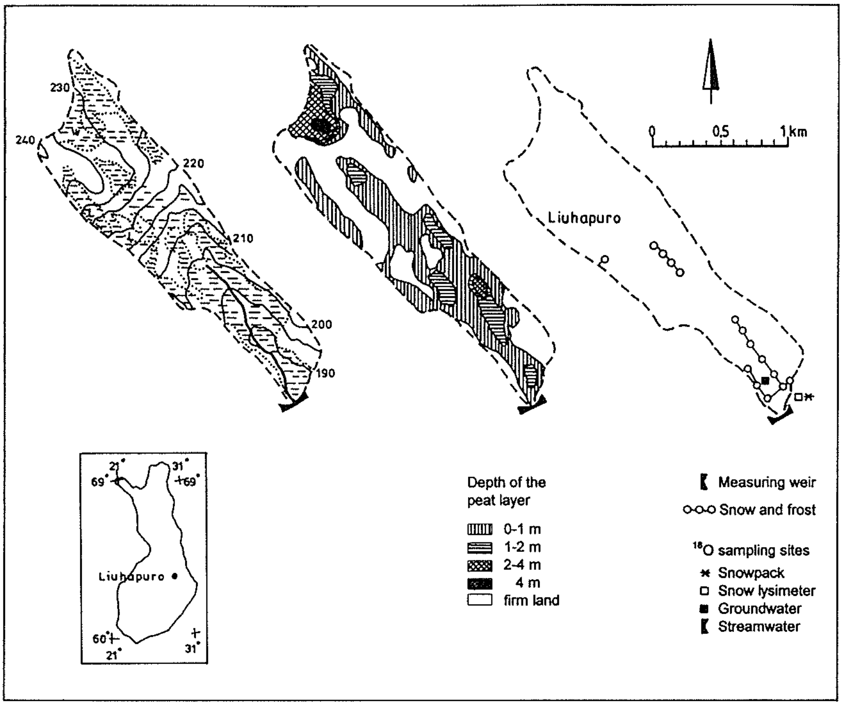

Fig. 6. Location, topography, depths of the peat layer and sampling sites of the Liuhapuro catchment in eastern Finland (VIII).

3) ratio between maximum and minimum monthly runoffs, describing the dynamics of the runoff.

Groundwater levels were registered from six groundwater tubes at Teeressuonoja in spring 1988 (II), and from three tubes along a hillslope transect at Rudbäck in 1991–93 (VII). In Rudbäck, spatial distribution of soil moisture at the surface layer of 0.2 m was measured by time domain reflectometry (TDR) on 12 October, 1994, at 56 measuring points (Tattari, unpublished data) (VII), located in the mineral soil parts of the catchment, with a distance of 30 m between the survey lines and 30 m between the points along the lines.

In the process studies in the catchments Teeressuonoja (I), Rudbäck (VII) and Liuhapuro (VIII), snow water equivalent (SWE) and soil frost were measured from survey lines including measuring points in the forested areas and peaty areas of the catchments.

2.2.2 Streamwater sampling and chemical analyses

Streamwater samples were normally taken from the measuring weir of the catchment studied. In Finland, streamwater sampling was run by the National Board of Waters, later National Board of Waters and the Environment; and the Water and Environment Districts. In Sweden, sampling was run by the Swedish Meteorological and Hydrological Institute, SMHI, and the Swedish Agricultural University.

In most cases manual sampling was used. In process studies, however, automatic sampling devices were used in the catchments 6,7 and 8 Rudbäck (VI,VII), Teeressuonoja, and Yli-Knuutila, when possible. The sampling system (Fig. 7) comprises a flow meter, battery- or 220 V AC-powered automatic sampler, a tipping bucket rain gauge, all interconnected, and a laptop computer or a modem (Lepistö 1991). A detailed descrip-

Table 2. Geomorphological characteristics, soil types, average meteorological and hydrological conditions, average bulk deposition of inorganic N and forestry activities in the study catchments. In most cases, except [a,b,c], the period 1979–88 is used for averages.

Catchment	Geomorphology					Soil types					Meteorology			Hydrology				Forest management			
	Area	Altit	Relief	Slope	Str_D	Fine soil	Org soil	Rock	Arabi	Lake	Temp	Precip	N_Dep	Flow	Max_Q	Min_Q	Q_Dyn	Drain_old	Drain 79–88	Fertil	Clearc
	km^2	m	m	%	km^{-1}	%	%	%	%	%	°C	mm	$kg\ km^{-2}\ year^{-1}$	mm	$mm\ month^{-1}$	$mm\ month^{-1}$		%	%	%	%
1 Hulubäcken	3.7	322	26	3.0	1.5	0	94	0	0	0	5.0	892	850	650	192.0	3.3	58.6	–	0.0	0.0	0.0
2 Däntersta	0.3	35	20	6.1	1.6	37	2	6	0	0	5.5	582	710	274	89.0	1.0	90.9	2.2	0.0	0.0	9.5
3 Nolsjön	18.0	124	51	6.6	1.9	0	28	1	3	2	5.1	749	740	343	80.2	1.3	60.1	–	0.0	0.0	5.6
4 Stormyra	3.9	10	67	14.9	2.3	20	8	58	0	0	5.4	664	770	336	106.2	0.9	113.2	–	0.0	0.0	0.0
5 Buskbäcken	1.8	280	70	7.7	3.1	9	7	3	0	0	3.8	880	700	452	107.7	1.3	84.4	–	25.8	0.0	13.7
6 Kullarna[a]	2.0	259	149	15.4	1.6	0	13	14	0	0	3.5	671	430	506	199.3	3.8	52.4	0.0	0.0	0.0	54.0
7 Övre Kullarna	0.4	315	129	12.3	2.5	0	11	28	0	0	3.4	658	430	324	115.0	1.2	99.9	0.0	0.0	0.0	0.0
8 Sniptjärn[a]	0.4	325	70	11.3	4.4	0	22	17	0	0	3.5	671	430	554	200.9	5.7	35.0	0.0	15.0	0.0	90.0
9 Lilla Tivsjön	12.8	246	224	9.2	1.6	0	2	0	0	3	1.4	708	420	295	104.0	1.4	74.2	–	3.1	7.1	27.3
10 Norrsjön	15.3	391	139	11.8	1.4	0	10	2	0	2	1.4	708	380	403	148.8	3.6	41.2	–	3.9	0.0	30.1
11 Vuoddasbäcken	42.0	185	113	8.7	0.9	0	27	0	0	1	0.0	662	340	461	209.8	5.4	38.7	–	0.0	0.0	19.7
12 Solmyren	27.5	326	140	6.6	0.5	0	34	0	0	1	0.0	662	280	410	171.5	4.9	35.2	–	0.0	0.0	1.7
13 Teeressuonoja	0.7	42	59	10.2	2.6	7	13	2	0	0	3.7	661	840	303	64.5	8.2	7.9	0.0	0.0	0.0	0.0
14 Huhtisuonoja	5.0	98	34	5.0	3.4	0	45	0	0	0	3.4	657	580	258	87.9	2.9	30.0	39.3	0.0	33.2	2.4
15 Paunulanpuro	1.5	117	30	6.8	3.7	8	18	2	1	0	3.5	743	410	347	94.1	1.1	89.1	8.0	0.0	2.9	0.0
16 Pahkaoja	23.3	150	52	2.1	0.8	0	67	0	2	1	2.5	621	680	359	124.5	1.7	71.4	10.8	5.4	0.0	0.0
17 Murtopuro[b]	4.9	176	74	3.8	1.0	0	50	0	0	0	1.4	621	480	455	213.5	2.4	89.0	0.0	0.0	0.0	0.0
18 Murtopuro[c]	4.9	176	74	3.8	4.0	0	50	0	0	0	1.3	677	510	458	176.1	2.5	71.6	0.0	40.0	0.0	57.9
19 Koivupuro[b]	1.2	209	28	3.6	0.5	0	57	0	0	0	1.4	608	480	342	153.2	2.4	62.8	0.0	0.0	0.0	0.0
20 Koivupuro[c]	1.2	209	28	3.6	2.7	0	57	0	0	0	1.3	634	510	387	131.6	4.1	31.8	0.0	30.5	0.0	5.0
21 Myllypuro	9.9	178	81	7.4	1.8	0	27	0	2	1	0.3	612	500	379	162.3	2.1	78.1	32.9	2.5	12.1	9.7
22 Vähä-Askanjoki	16.4	168	215	10.9	1.1	0	17	0	0	0	–1.2	527	240	454	142.8	7.2	19.9	6.0	3.5	0.0	0.0

[a] post-treatment period 1981–88.
[b] pre-treatment period 1979–82.
[c] post-treatment period 1983–88.

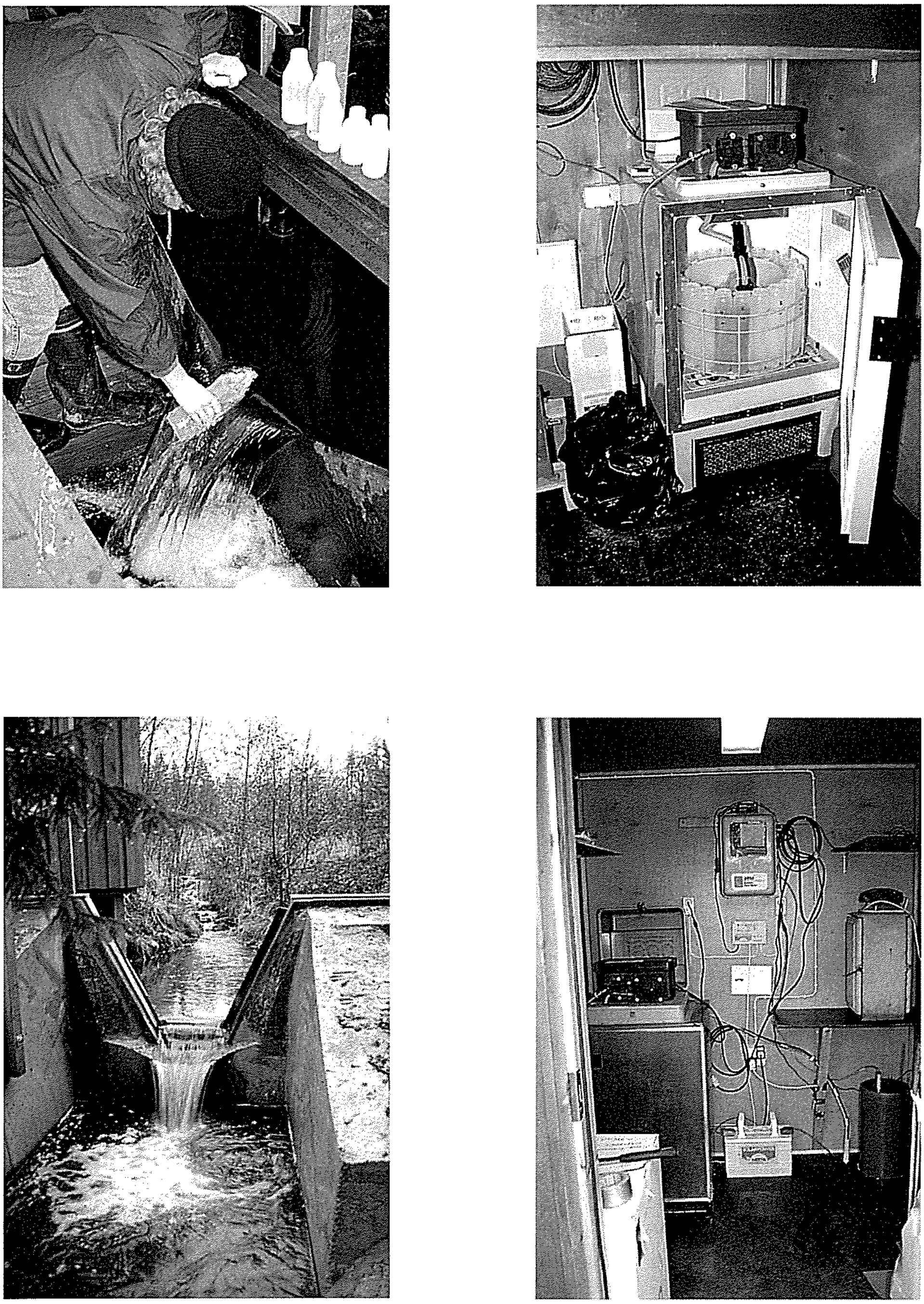

photo Yrjö Kivinen

Fig. 7. Manual and automatic sampling at the measuring weirs of the catchments Rudbäck and Huhtisuonoja.

tion of hydrochemical monitoring of the Rudbäck catchment (throughfall, melt-, ground- and streamwater chemistry) is given by Kämäri et al. (1992b).

All the chemical analyses of streamwaters were made in the laboratory using the standard methods of the water administration. Base cations (I) were measured with a flame-AAS. pH was determined with a Radiometer pH meter, SO_4^{2-} by a turbidimetric method and Cl^- by titration with mercury nitrate. Alkalinity was determined by potentiometric titration to the pH values of 4.5 and 4.2 with HCl (I) (National Board of Waters 1981).

In both Finland and Sweden, during the study period 1979–88 (IV, V), NH_4-N was analysed by a spectrophotometric method with hypochlorite and phenol, and the sum of NO_2-N and NO_3-N by the cadmium amalgam method (Erkomaa et al. 1977). Total N was analysed as NO_3-N after oxidation with $K_2S_2O_8$ (National Board of Waters 1981, Rosén 1982). Total nitrogen and NH_4-N were only available for four of the Swedish catchments. The results from the different laboratories in Finland and Sweden are assumed to be comparable. Organic N fractions were calculated for each sampling occasion as the difference between total and inorganic nitrogen. In the early phases of the monitoring period (1966–73), nitrate-nitrogen (I, III) was analyzed by the sodium salicylate method and later by the manual cadmium amalgam method (Erkomaa et al. 1977). Comparable results were obtained by the old and new methods, the difference in concentrations being less than 10% (National Board of Waters 1979).

2.2.3 Atmospheric deposition of nitrogen

The monitoring of N deposition (I,III,IV,V) was based on monthly bulk collections within the national monitoring program in Finland (Järvinen and Vänni 1990). For the Finnish catchments, averages of measurements from nearby stations were used, whereas for the Swedish catchments interpolations were made from a general deposition pattern (Granat 1990). Deposition of inorganic N, obtained from monitoring of bulk deposition of nitrate and ammonium, was used as an index of total deposition. This is justifiable, since the areas are situated far from emission sources and it is unlikely that there would be major differences in the dry deposition fraction of the total deposition. Different estimates of deposition were compared, using data from snowpack in an open forested site and spruce stand site, snowfall and liquid precipitation (I).

2.2.4 Isotopic sampling and analysis

Samples for ^{18}O analysis were taken from different stages of the hydrological cycle, i.e. from streamwater, meltwater, snowpack, shallow groundwater, soil water and precipitation. Sampling was concentrated on snowmelt periods and rainfall events.

In Teeressuonoja (Fig. 4), streamwater was collected 3–6 times a week at the basin outlet during the melt periods, and on two 24 h occasions in 1985 every 2 h for oxygen-18 analysis (I). Groundwater samples were taken from a well near the outlet. Precipitation water samples were taken from every storm event in the spring of 1987. In 1987, daily samples of meltwater were taken from a 1 m^2 snow lysimeter. In 1985, samples were taken from the snowpack, assuming these samples to be representative of the meltwater. In 1988 (II), samples of precipitation, streamwater and lysimeter meltwater were taken daily, and samples of soil- and groundwater weekly from different depths at the six sites, using tension soil water samplers and groundwater tubes.

In Rudbäck (Fig. 5), the oxygen-18 content of streamwater was intensively monitored in 1991 and 1992 (VI,VII) with up to 240 samples a year (7 Rudbäck). Daily precipitation samples were taken at the meteorological station of Vihti, 25 km from the catchments, from most events. Monthly accumulated samples were also collected. Meltwater samples were taken from the outflow of a 1 m^2 snow lysimeter in open and forested areas inside the catchment 7.

In the peaty Liuhapuro catchment (Fig. 6) (VIII), during the melt periods of 1989 and 1992, streamwater samples for oxygen-18 analysis were collected daily from a measuring weir. Meltwater samples were taken daily from the outflow of a 1 m^2 snow lysimeter. At the same time, the daily amounts of meltwater were measured. Weekly samples were taken from the snowpack and from a groundwater tube close to the measuring weir.

The O-18-contents of water samples were determined by ratio mass spectrometry at the University of Uppsala, Sweden, until 1989 (I,II), and thereafter at the University of Copenhagen, Denmark (VI,VII,VIII). The O-18-content was expressed as the relative deviation of the isotopic ratio of the sample from that of a reference water, Vienna SMOW (Standard Mean Ocean Water) (Appendix 1). The accuracy of the measurements was about 0.1 δ-units.

2.3 Computational methods

2.3.1 Isotopic hydrograph separation on an event and monthly basis

Event basis

The basic assumption of the tracer method for stream hydrograph separation is that two components contribute to stream flow, i.e. precipitation (as rain or snowmelt) and groundwater (e.g. Fritz et al. 1976) (I,II,VI,VIII). From the mass and tracer balance in steady state, the fraction of event water contribution in the stream is:

$$f_{event} = 1 - [(\delta_s - \delta_p)/(\delta_g - \delta_p)] \qquad (1)$$

where δ_s, δ_p and δ_g are the tracer compositions of streamwater, precipitation and groundwater, respectively.

In humid regions the isotopic composition of groundwater is about the same as the annual weighted mean content of the precipitation. During low flows the oxygen-18 content of the streamwater is the same as that of groundwater. The meltwater is isotopically much lighter than the groundwater, which in combination with the large runoff volumes of meltwater, enables rather accurate stream hydrograph separation computations.

Monthly basis

The isotope hydrograph separation has mostly been used on an event basis, making a common assumption that groundwater $\delta^{18}O$ will be stable during an event. Concerning annual patterns, this assumption may not be valid. Rather, at least in small catchments with shallow soil layers, a sinusoidal change of groundwater $\delta^{18}O$ is more probable (VII).

The monthly fraction of event water contribution (which has an average residence time of less than one month) in the stream (VI,VII) is expressed as:

$$f_{month} = 1 - [(\delta_s - \delta_p)/(\delta_g - \delta_p)] \qquad (2)$$

where δ_s, δ_p and δ_g are the monthly isotopic compositions of streamwater, precipitation and groundwater, respectively.

Monthly volume-weighted average precipitation contents of oxygen-18 as input and monthly volume-weighted average contents of streamwater oxygen-18 as output were used in Eq. 2. There is no direct method to estimate the groundwater (pre-event) value during the whole month. The monthly value for groundwater (here groundwater and soil water are treated as one component, groundwater) was estimated by assuming that the streamwater oxygen-18 content, measured during low flow (0.1–1 mm d^{-1}), represents groundwater during the same month. These estimated monthly values for groundwater were used for sinusoidal fitting (see Herrmann and Stichler 1982, Burgman et al. 1983) (VII), according to equation 3:

$$\delta^{18}O = a*\sin(2\pi(t-b)) + c \qquad (3)$$

where a = the amplitude of variation (o/oo), b = phase shift of the curve (years), c = mean $\delta^{18}O$ (o/oo), and t = time (years).

These sinusoidal curve estimates were used during those months when no measurements were available.

2.3.2 Estimation of contributing areas of the event water and annual variation of nitrate N

Event water contributing areas (discharge areas) were estimated by dividing the specific discharge (mm d^{-1}) by the rate of precipitation (mm d^{-1}) and multiplying by the event water fraction, f_{event} (II,VI,VII). In other words, event water amount (mm) was divided by precipitation input (mm).

All precipitation on recharge areas was assumed to infiltrate, whereas all such water on discharge areas was assumed to generate saturated overland flow. Monthly average fractions of the contributing area of event water were estimated by dividing the specific discharge (mm month^{-1}) by the rate of precipitation (mm month^{-1}) and multiplying this figure by the monthly event water fraction, f_{month}.

Furthermore, a simple two-component model (Eq. 4) (VII) was established for estimating annual variation of nitrate-N (monthly concentration) in streamwater, using monthly observed NO_3-N concentrations in precipitation and a stable NO_3-N concentration level in groundwater:

$$NO_3\text{-}N_s = f_{n\text{-}cont} * NO_3\text{-}N_g + f_{cont} * NO_3\text{-}N_p \qquad (4)$$

where NO_3-$N_{s,g,p}$ = nitrate concentration in streamwater, groundwater and precipitation, respectively, and $f_{n\text{-}cont}$ and f_{cont}= fractions of 'non-contributing' and contributing areas of the catchment.

It was assumed (Eq. 4) that all the nitrate N deposited on saturated, contributing areas was flushed relatively quickly (as quickflow) to the streams, whereas nitrate N deposited on 'non-contributing' areas was infiltrated to the soil layers or retained by the biomass.

2.3.3 Export estimates of nitrogen fractions

Export of the different fractions of nitrogen (III, V) were calculated by the interpolation method (Eq. 5), i.e. observed concentrations were interpolated linearly to estimate daily concentrations and then multiplied by daily flow.

Variation of the estimated export may be significant when using different calculation methods. To study the variation of annual nitrate export estimates, a comparison was made between the three following methods, using data from one of the catchments (III):

Method 1: Interpolation method; observed concentrations were interpolated linearly to estimate daily concentrations $c_{int}(t_i)$, which were multiplied by daily flow q (t_i) and summated to arrive at the annual export

$$E = \sum_{i=1}^{n} c_{int}(t_i)\, q(t_i) \qquad (5)$$

Method 2: Volume-weighting method; the sampled concentrations were weighted with the flow measured on the day of sampling q(t_i) to calculate annual volume-weighted concentrations, which were multiplied by annual flow

$$E = \frac{\sum_{i=1}^{n} c(t_i)\, q(t_i)}{\sum_{i=1}^{n} q(t_i)} \, q_{mean} \qquad (6)$$

Method 3: The flow-concentration relationship (statistically significant) was used to estimate daily concentrations, which were multiplied by daily flow and summated to arrive at the annual export

$$E = \sum_{i=1}^{n} c_{reg}(t_i)\, q(t_i) \qquad (7)$$

Method 3 (Eq. 7) was considered to be the most accurate one, because it takes into account both daily flow and daily concentration values and, for example, high runoff events during summer and autumn with no or few samples. However, it can be used only if a sufficiently significant relationship exists. During the 25-year period, when calculating the sums of the nitrate outputs, the differences were not high. The total output was 7% higher by method 1 than by method 3, and 3% higher by method 2 than by method 3 (III). Based on this comparison, the method chosen for calculating e.g. 10-year average export for nitrogen fractions is not very critical.

2.3.4 Statistical analysis used to detect links between concentrations of N, flow and seasonality

Regression analyses were performed to assess whether there were significant correlations between concentrations and flow, for whole time series and for various seasons (IV). The analyses were performed with and without logarithmic transformation of nitrogen concentration and/or flow. When restricting the regressions to samples taken during certain flow conditions or seasons, only log-log transformed data were used. Datasets used in a regression analysis were defined to contain at least 30 samples for the results to be trustworthy (Helsel and Hirsch 1992), datasets with fewer samples being excluded.

Because the concentrations showed very skewed distributions, a non-parametric Wilcoxon test (Helsel and Hirsch 1992) was used to examine whether the concentrations were significantly different during certain flow conditions (IV). A difference between two datasets was considered significant if P was less than 0.05. Since the test is non-parametric, and thus not dependent on normal distribution of the data, it was decided to exclude only datasets with less than 10 samples.

To estimate the influence of different flow situations on concentrations, the dataset was analysed to determine whether a significant difference occurred in concentrations measured during: 1) high flow vs low flow, 2) increasing flow vs stable or decreasing flow, and 3) high flow vs low flow during September-May. The limit for low flow was set so that 50% of the days with lowest flows, and the limit for high flow so that 25% of the days with highest flows were included. These limits were chosen since they generally provided sufficient samples in each group to enable the statistical analyses. If the average flow of the sampling day and the preceding two days was higher than the average of the days 3–5 before the sampling day, the flow was considered as increasing.

To estimate the influence of seasonality, the dataset was analyzed to determine whether significant differences were found in concentrations measured during:

1) Low flow during summer (June–August) vs low flow during the dormant season (September–May)

2) High flow during the first part of the year (January–June) vs high flow during the second half (July–December)

3) Increasing flow vs decreasing flow during the first part of the year (January–June)

4) Increasing flow vs decreasing flow during the second part of the year (July–December)

The first test 1) was made to assess the influence of biological activity on concentrations. Samples taken only during the low flow period were used to avoid a bias caused by under-representation of sampling during high flow events in summer. The second test 2) was mainly a comparison of concentration levels during corresponding spring and autumn flows. The third and fourth tests should provide an assessment of the effect of flow increase during the spring and autumn half-year periods.

2.3.5 Multivariate regression methods

Multiple regression techniques were used to identify correlations between site-specific variables and nitrogen export (V). The analyses were based on a limited number of catchments which, when compared, showed rather skewed distributions of export. In the case of nitrate-N, the model was tested by the use of half the data to generate the model and the other half to validate it (Snee 1977). Interrelations between explanatory variables and residuals were also examined. The multivariate regression models were selected using the following criteria: 1) High R^2, high adjusted R^2 and a Mallow's C_p value close to p (Eq. 8). 2) All parameters should be significant at an error level below 5%. 3) The number of explanatory variables should be low compared with the number of included catchments.

Mallow's C_p (Mallow 1973) is a measure of total squared error defined as:

$$C_p = RSS_p/s^2 - (n-2p) \qquad (8)$$

where RSS_p = residual sum of squares, p = number of parameters including the constant and s^2 = residual mean square from the largest equation postulated containing all functions of one or more variables.

A plot of C_p versus p will show statistically adequate models as points rather close to the C_p = p line.

2.3.6 Trend analysis

Time series of water quality are often characterized by seasonality, serial dependence and skewed distributions, and the non-parametric tests have been shown to be suitable for the analysis of such data (Grimvall et al. 1991). A multivariate extension of the non-parametric Mann-Kendall rank test (Hirsch and Slack 1984) was used for detecting trends (III). Because of the seasonal variation in water quality time series, trend tests were first performed separately for each month and then combined to form an overall trend test for all observed data. A flow-adjustment of observed concentration was performed using rank correlations between mean monthly concentration values and mean monthly flows (Grimvall et al. 1991).

2.3.7 Hydrological modeling

TOPMODEL is a semi-distributed, topography-based hydrological model (e.g. Beven and Wood 1983) derived from the variable contributing area theory (e.g. Dunne and Black 1970). Topographic input data is based on the digital elevation model of a catchment. A short description of the main assumptions of the groundwater-based version of TOPMODEL (VII) is given here. Details of the rationale of the model can be found elsewhere (e.g. Beven and Kirkby 1979, Beven and Wood 1983, Robson et al. 1992). Beven et al. (1995) recently reviewed the model, its theoretical framework and recent implementations.

The inputs of the model are rainfall, temperature, potential evaporation and the distribution of the topographical index. Temperature is not used in the general form of the model, but was used in the snow subroutine, which was added to the model in Linköping University, Sweden, and made possible the use of the model in Nordic conditions. The outputs are runoff separated into two components (surface runoff on the saturated area, and subsurface runoff), average water content in soil moisture storage, average groundwater table and the fraction of saturated areas within the catchment. The flow is separated into a surface runoff generated by precipitation or meltwater on the saturated contributing areas and a subsurface downhill flow. The local groundwater level is linked to the mean level via the topographic index (ln(a/tanB)), all the points with the same index value being modelled as having identical groundwater levels at each time step. Hydraulic conductivity is assumed to have an exponential decreasing profile with depth. Flow generation due to saturation excess is assumed to occur from those squares where the groundwater level is at the soil surface (e.g. Durand et al. 1992).

A digital elevation model (DEM), to be used as an input to TOPMODEL, was produced (VII) for assessment of the distribution of a topographic index ln(a/tanB), where a is the area draining through a grid square and tanB is the average outflow gradient from the square. A high ln(a/tanB) index value indicates a wet part of the catchment; this can arise either from a large contributing drainage area (e.g. valley bottoms) or from very flat slopes. Areas with low index values are usually drier, which results from either steep slopes or a small contributing drainage area. Grid squares with the same index value are assumed to behave in a hydrologically similar manner (e.g. Robson et al. 1992).

This DEM was generated at a scale of 5 m x 5 m by interpolation with the IDRISI GIS program, from the contours of a 1:10 000 map, and converted to a scale of 30 m x 30 m in order to be comparable to the scale used for TDR-measurements. The DEM must have a fine enough resolution to properly reflect the effect of topography on surface and subsurface flow pathways. Coarse resolution data may, for example, fail to represent some convergent slope features. However, too fine a resolution may introduce perturbations to flow directions and slope angles that may not be reflected in the smoother water table surface. The appropriate resolution will depend on the scale of the hillslope features, but 50 m or better data is normally suggested (Beven et al. 1995).

3 Streamflow generation processes

In this section streamflow generation processes are discussed, including the dynamics of contributing areas of the event water. Event waters generated from these areas are proposed to contribute to leaching of N. Results of isotopic hydrograph separations performed during snowmelt (I,II,VIII) and rainfall events (II,VI) are discussed. The results of the snowmelt separation studies are discussed in section 3.1.3 (VIII), and compared with other results obtained in Scandinavian conditions (Rodhe 1987). Furthermore, estimations of annual patterns of event water fractions are presented (VI,VII). Contributing areas of event water are estimated on event (II,VI) and monthly (VI,VII) scales, using isotope methods. The dynamics of contributing areas as simulated by TOPMODEL are presented, and compared to estimations based on isotope methods (VII).

3.1 Event water fraction of runoff on an event scale

Melting of snow is the most important physical process in the formation of spring floods in Finland. The water equivalent at the beginning of melting is usually 6–10 times greater than the total precipitation during the snowmelt period. Only occasionally does precipitation provide an essential contribution to the 'potential' of the spring flood (Kuusisto 1984).

Isotopic hydrograph separation (Eq. 1) is based on analyses of the isotopic composition of streamwater during runoff events, which reflects the integrated result of the various processes contributing to streamflow generation. The main assumptions behind the use of stable isotopes as tracers were discussed in section 1.2.5.

3.1.1 Snowmelt events

Teeressuonoja

During the snowmelt of 1985 (I), the total runoff during the first phase of the melt period (14–29 April) was 23 mm. The average computed fraction of pre-event groundwater in the stream, using Eq. 1, was 85% (19 mm) and event water run-

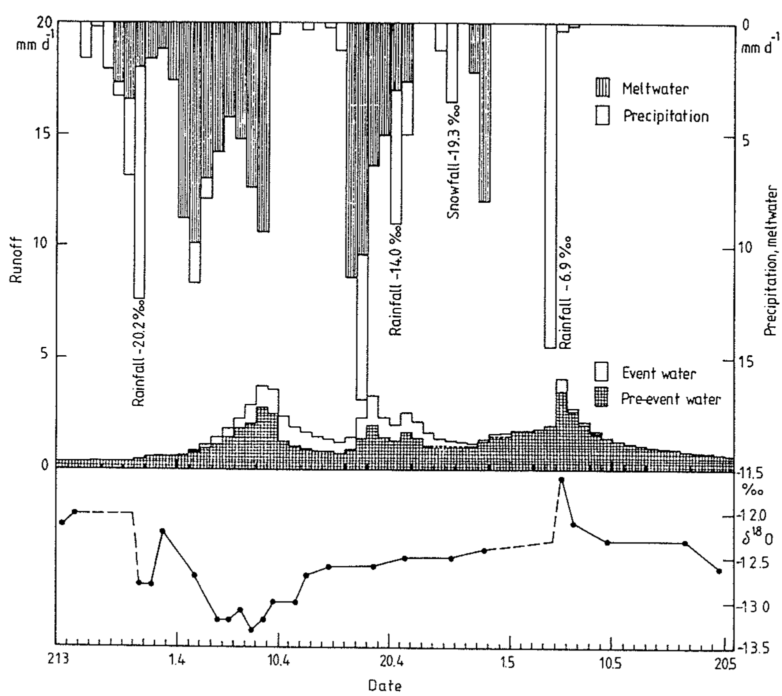

Fig. 8. Meltwater and precipitation (mm d^{-1}), total runoff and calculated event and pre-event fractions of runoff (mm d^{-1}), and oxygen-18 content (o/oo) in streamwater in Teeressuonoja, spring 1988.

off 15% (4 mm). During the snowmelt in 1987 (I), the event water contribution in the discharging water was about 17% (3 mm) of the total runoff of 18 mm. In 1988 (II), the event water contribution was about 22% (14 mm) of the total runoff of 64 mm during the melt period (Fig. 8).

Based on the papers (I) and (II), it seems that only about 5–10% of the total meltwater and rainfall input produced within the Teeressuonoja catchment immediately runs off during the snowmelt season. Ponded water, soil water and shallow groundwater are mixed in areas contributing to rapid runoff before surface flow and shallow groundwater reach the streams. During snowmelt, meltwater reaches the groundwater in poorly drained areas where the shallow groundwater constitutes part of the ponded water, and also in some low-permeability areas where meltwater reaches the shallow groundwater through macropores. In surface-saturated areas nearby the channels infiltration capacity is zero, so that all meltwater discharges quickly to the stream. The dominant mechanism in Teeressuonoja is the displacement of old soil water and groundwater by infiltrating meltwater. A rapid discharge of the 'old' water into the stream channels and the increase in the groundwater table also require an effective infiltration of the meltwater into the frozen soil, as found clearly in spring 1985 when there was still soil frost of about 30 cm left at the time of the flow peak (I). Correspondingly, Espeby (1990) showed that macropores in till soil can drain water from the ground surface when almost the entire soil matrix is frozen. The estimated pre-event water fractions (I,II) agree with the results of studies made in comparable conditions in forested catchments in Sweden (Rodhe 1987).

During the snowmelt season of 1988, a totally agricultural and small, flat catchment with clay soils (Hovi, 0.12 km^2) was also studied (Bengtsson et al. 1992). Hovi is located close (1.7 km) to the totally forested Teeressuonoja, which is covered with deep (up to 20–25 m) coarse and sand moraine layers (II). The first objective was to obtain information about the movement of melt water in a subdrained agricultural catchment and the hydrological processes involved. The second objective was to test the validity of the isotopic hydrograph separation approach to contrasting, adjacent catchments during the same melt period. In Hovi, the pre-event water contribution was minor, less than 10% of the total runoff of 85 mm, during the melt period 28 March–11 April, 1988 (Bengtsson et al. 1992). In Teeressuonoja, however, the situation was very different, with a pre-event water contribution of almost 80% (II). This provides evidence of the validity of the method in significantly different environments.

Liuhapuro

In peaty catchments, it might be assumed that event water fractions would be higher because of higher percentages of surface-saturated areas. The totally forested Liuhapuro in eastern Finland, with 48% of organic peaty soils, was studied to test this hypothesis.

In Liuhapuro, the total runoff during the melt period in 1989 was relatively high, 210 mm (VIII). The average computed fraction of event water in the stream was high, 63% (131 mm), during the melt period (Fig. 9). In 1992, the total runoff during the melt period was 201 mm, with a somewhat lower event water fraction of 53% (101 mm).

The melt periods of 1989 and 1992 were somewhat different. The water equivalent of snowpack (SWE) in 1992 was lower (196 mm) compared with that in 1989 (234 mm). Event water runoff (mm) was divided by input (SWE mm) to obtain contributing area of the event water during the melt period. It was about the same, 52% and 56% during 1992 and 1989, respectively. This points out the importance of the amount of snow in explaining the variation between different years. During 1992, the isotopic input of meltwater was clearly lower (about 1.5 o/oo) than during 1989, reflecting low contents (highly negative) of oxygen-18 during the winter snowfalls. This is another factor explaining the lower fractions of event water.

The contributing area of event water during the melt periods of 1989 and 1992, 52–56%, was very close to the peatland percentage of 48. This provides evidence that new event water (meltwater) was mostly discharged from these peat areas, which also acted as 'reservoirs' for mixing pre-event water and event water.

Buttle and Sami (1992) studied a small forested wetland basin on the Canadian Shield, and noted that although pronounced changes in storm-

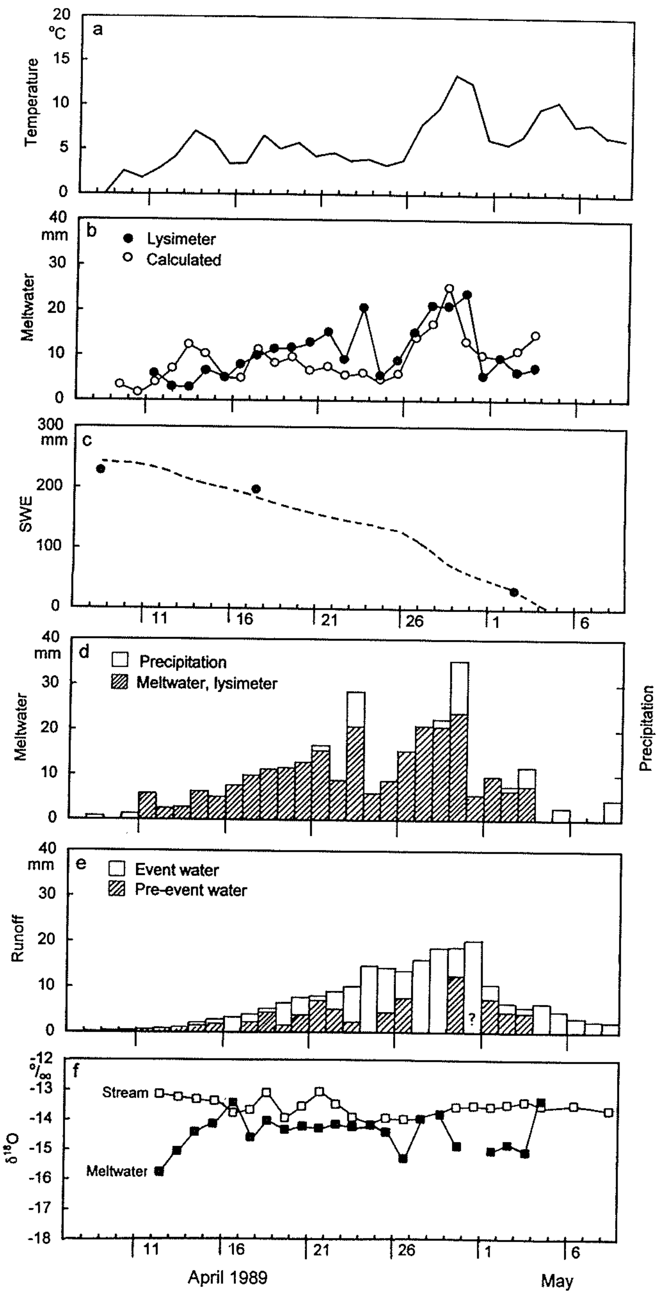

Fig. 9. a) Daily mean temperature (°C), **b)** measured and calculated amounts of meltwater (mm), **c)** SWE of the snowpack (calculated /observed points) (mm), **d)** daily precipitation and meltwater (lysimeter) amounts (mm), **e)** daily event and pre-event fractions of runoff (mm), and **f)** the $\delta^{18}O$ of streamwater and meltwater during the melt period of 8 April–8 May, 1989, in the Liuhapuro catchment.

flow were observed over the course of the melt, there was relatively little change in the isotopic content of streamflow. The observed isotopic response could be explained by displacement of standing water from the wetland. It appears from studies of Bay (1969) and Seuna (1988) that considerable quickflow can be generated from wetlands when the water level is high. Jacks et al. (1986) found that in a 33.5 km^2 bogland-dominated (50%) catchment in north central Sweden, the streamflow during the melt peak consisted almost entirely of melt water, but they did not make a detailed hydrograph separation during the whole melt period. In the Svartberget catchments, with peat percentages of 20–40%, Rodhe (1987) found that the fraction of event water varied between 41 and 59% during snowmelt events in 1981–82.The fractions in Liuhapuro during the melt periods of 1989 and 1992, 53–63% (VIII), were somewhat higher, which is reasonable taking into account the higher percentage of peaty area in Liuhapuro. Relationships between peat percentage and the fraction of event water are discussed further in section 3.1.3.

3.1.2 Rainfall events

It is reasonable to assume that high-intensity, high-volume rainfall events are more efficient at producing 'new' event water in a stream than are low-intensity events, because they cause saturation to occur over greater areas of the catchment.

At the Rudbäck catchments in Siuntio, total volume fraction of event water was compared to rainfall volume and max. hourly runoff (mm h^{-1}) during three studied rainfall events (VI). The percentage of event water amounted to 50–70% of the runoff during the largest event, which occurred in August 1991 (80 mm d^{-1}) and which has a return period of about 100 years. According to this data, streams were dominated by 'new' rainwater only in response to a very intense storm. During the second largest rainfall event in August this fraction remained lower than 25% in all the catchments. In November, in the case of smaller rainfall (max.intensity 2.2 mm h^{-1}), the fraction was unexpectedly low, 2–8%, and was not fully representative of the rainy November. The event water fraction increased with increasing rainfall volume and maximum runoff (VI). However, limited data (8 cases) provides no evidence of the type of relationship between those variables. Correspondingly, Eshleman et al. (1993) found a positive correlation between the event water fraction of runoff and the volume of rainfall.

3.1.3 Possibilities for regionalization of the event water fraction of runoff

Buttle (1994) recently published a review of isotope hydrograph separation studies. One of his conclusions was that the method has rarely been applied in urban, agricultural and permafrost environments. These are areas where one might anticipate surface runoff mechanisms such as Horton overland flow to be relatively important in streamflow generation, leading to the enhanced contribution of event water to stormflow. This hypothesis was partly supported by Buttle's (1994) observation that some of the highest fractions of event water have been recorded in such basins. The Hovi agricultural catchment in southern Finland (Bengtsson et al. 1992), with over 90% of event water during the snowmelt period, belongs to this group.

Generalizations of the large number of available case studies from the early 1970s concerning isotopic hydrograph separation are very rare. How is the event water fraction related to major catchment characteristics, such as percentage of peatlands?

Fig. 10a (VIII) presents the fractions of event water during the snowmelt periods for forested catchments with varying percentages of peatlands in Scandinavia (Rodhe 1987, I,II,VIII). Included are twelve catchments and 21 snowmelt events (total melt events), separated using oxygen-18. It is obvious that the peatland types varied considerably, e.g. the Svartberget catchments (upper and lower) had considerable percentages (33–40) of open bog areas whereas e.g. Liuhapuro had 29% of spruce mires and 18% of open bogs. Percentage of peatland explained 42% of the variation of the event water fraction of the runoff ($f(x)=0.025x^2 - 0.65x + 35.6$, $r=0.64$, $p<0.01$) (Fig. 10a). A Swedish catchment with no peatlands at all (Aspåsen) also had a high event water fraction of 58%. In this case, a relatively high slope of 16% might

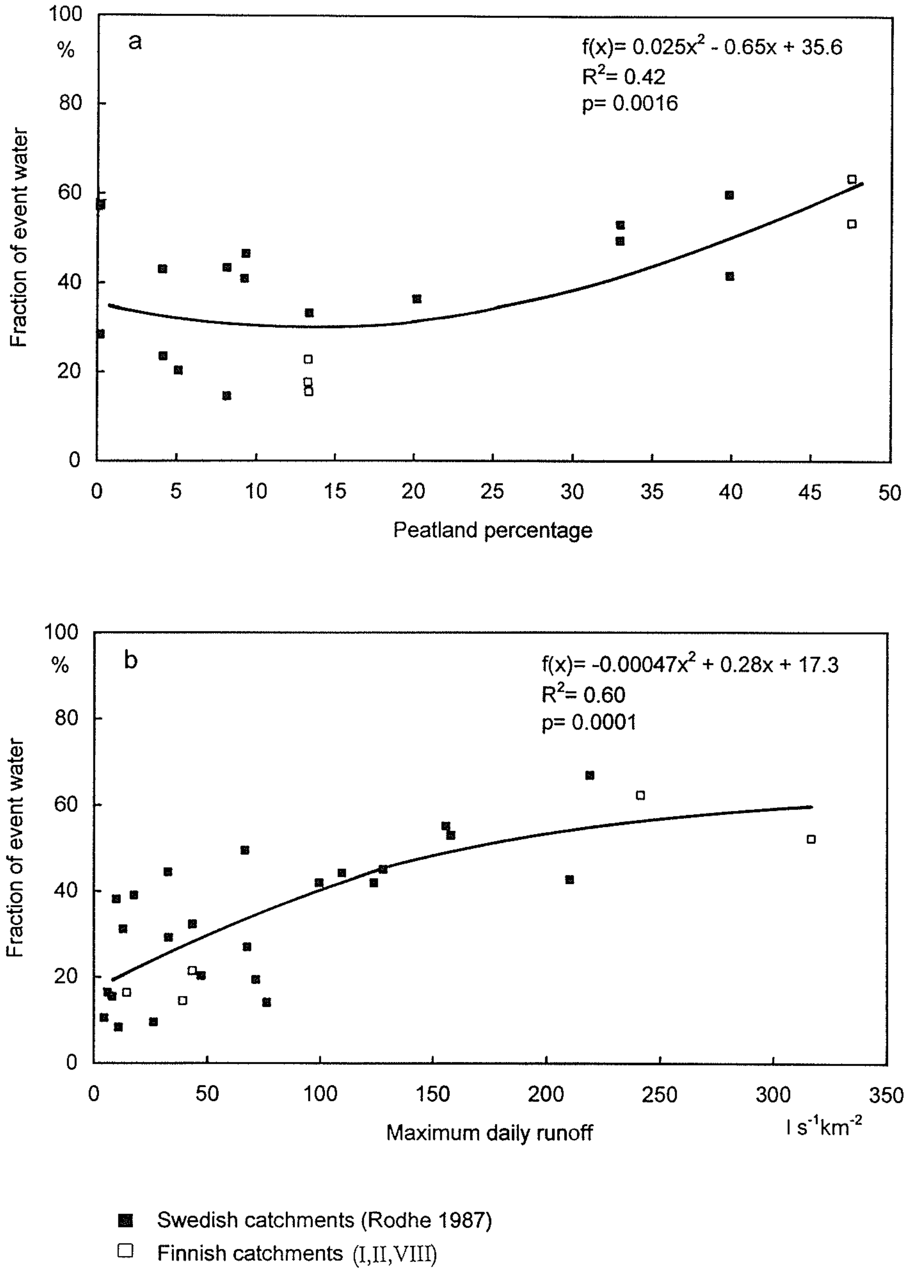

Fig. 10. The fractions of runoff consisting of event water during snowmelt periods, as a function of **a)** peatland percentage and **b)** maximum daily runoff (l $s^{-1}km^{-2}$) in peaty forest catchments in Scandinavia (Rodhe 1987; I; II; VIII).

have affected the rapid flow paths of the runoff and high event water fractions correspondingly. In theory, a parabolic distribution is probable, with the highest event water fractions (quickflow) on the one hand in mineral, shallow soil catchments with steep topography, and on the other hand in flat, surface flow-dominated bogs. The Liuhapuro study (VIII) provided further information about the snowmelt periods with high runoff volumes in a catchment where organic soils dominate.

Fig. 10b presents the fractions of event water during the snowmelt period as a function of maximum streamflow during the period, for the same forested catchments. Some of the spring floods were composed of two or more distinct melting periods (Rodhe 1987), each of which was included. Maximum streamflow during the melt period explained 60% of the variation of the event water fraction ($f(x) = -0.00047x^2 + 0.28x + 17.3$, $r=0.77$, $p<0.001$). The snowmelt periods of Liuhapuro had the two highest values, providing further information about the relationship during high runoff intensities. The equation cannot be used for extrapolating event water fractions during higher runoff intensities. The relationship curve is assumed to increase slightly when the runoff intensities are high, but event water fractions of over 80% are probable only in urban, agricultural or permafrost catchments (Buttle 1994).

3.2 Event water fraction on a monthly scale

The annual pattern (years 1991–92) of the event water fraction was estimated for the 8 Rudbäck catchment (VII), using Eq. 2. In 1991, monthly fractions of event water varied between 0 and 66% (Fig. 11), with a mean value of 20%, and were highest in August (180 mm of rainfall). During those months when no measurements were available, the estimates of event water percentage were based on the sinusoidal curves (Eq. 3) for precip-

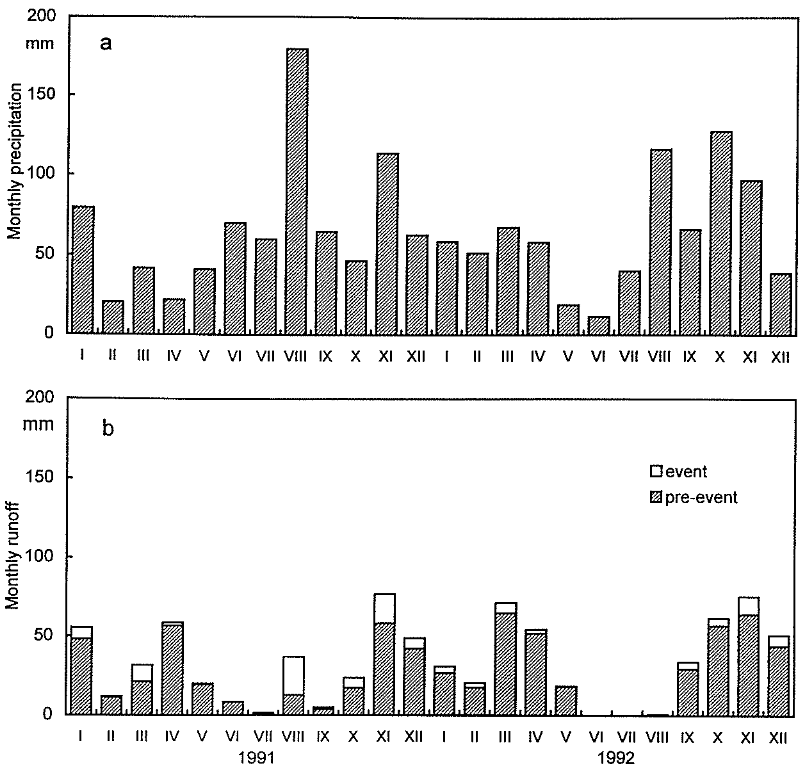

Fig. 11. Monthly precipitation (mm), monthly runoff (mm) and monthly fractions of pre-event and event water during 1991-92 in the catchment 8 Rudbäck.

itation, groundwater and streamwater (VII). In the case of precipitation, this causes uncertainty, because of the large variation in input between different years. Annual 'new' water runoff (quickflow) was 78 mm (21% of annual runoff).

In 1992, the event water fractions were lower, one of the main reasons being the less extreme rainfall pattern. For example in August 1991, 180 mm of rainfall contributed to 37 mm of runoff, whereas in August 1992, 117 mm of rainfall contributed only to 0.6 mm of runoff. In 1992, annual 'new' water runoff (quickflow) was 43 mm (10% of annual runoff). The total amount of precipitation in 1992 was 50 mm lower than in 1991, which resulted in lower percentages of event water. It should be borne in mind that event water in this case means water which is 'new' in that it has a residence time of less than one month. When discussing 'new' event water e.g. in a rainfall event scale (section 3.1.2), the scale is considerably shorter, consisting of the length of the event which is from hours to days.

3.3 Contributing areas to the event water

Betson (1964) defined *contributing area* as an area of a catchment contributing to storm runoff. This means that the contributing sub-area in some way causes an increase of streamflow. It is assumed that event water in the stream mostly originates from these surface-saturated, contributing areas. A *contributing area of the event water* is here defined as an area from which event water – a 'new' meltwater or rainwater – flows to the stream with a short transit time.

3.3.1 Event scale

The accumulated runoff from the Teeressuonoja catchment from the beginning of snowmelt in late March 1988 to when a major storm of 15 mm occurred on 5 May, was 64 mm (II). The volume of event water that left the basin before this storm was determined as 13–15 mm. Since the total melt and rainfall input to the basin was 157 mm, the area (section 2.3.2) contributing to meltwater runoff was about 8%. During a 15 mm rainfall event in May, 1988, the area that contributed to the rapid release of event water particles was about 4% in Teeressuonoja (II). The increase of the runoff as a consequence of the 15 mm rain storm was 3.8 mm, of which 0.6 mm was event water.

In Rudbäck, contributing area percentages during rainfall events (section 2.3.2) ranged between 1 and 11 of the catchment areas, with higher values in the smallest catchment (average 6.5% at 8 Rudbäck) compared to the mid-catchment (average 3.3% at 7 Rudbäck) (VI). For catchment 6, arable land areas near the catchment outlet and main stream have an increasing effect on the contributing area percentage (average 8.1%). Fractions during the event III (16.4 mm) in November were of the same order as that calculated for the forested Teeressuonoja catchment (4%) during 15 mm of rain (II). However, the autumn rainfall event was rather small, and cannot fully represent the conditions of a rainy November.

This method of estimating contributing areas attempts to spatially interpret the results of hydrograph separation. The estimates provide a means for a field check of the hydrograph separation results. These estimates may also be used when studying the relationships between the dynamics of saturated areas and nutrient loading (Andersson et al. 1993).

3.3.2 Monthly scale

Monthly average fractions of event water contributing area were estimated by dividing specific discharge (mm month^{-1}) by the rate of precipitation (mm month^{-1}) and multiplying by the event water fraction. In the 8 Rudbäck catchment, the fraction varied between 0 and 16%, with the highest fraction occurring during the rainy November of 1991 (VII). The results are compared with those based on modeling in section 3.3.4.

3.3.3 Dynamics of contributing areas on the basis of modeling

A TOPMODEL application was made for the period 1991–92 with a daily time step, using a model version with a snow subroutine (VII; Lepistö and Kivinen 1994). The main criteria in the model calibration were to fit simulated and observed runoff, to have an adequate water balance and to simulate adequately the annual dynamics of groundwater level. Description of TOPMODEL and the generation of the digital elevation model DEM used were discussed in section 2.3.7.

The measured range of saturated hydraulic conductivity K_s in the surface layer was 5–454 * 10^{-7} m s^{-1} and in the lower depths (80–250 cm) 0.001–346 * 10^{-7} m s^{-1} (Ahonen and Roos, in prep.), i.e. the maximum range was five orders of magnitude. A range of 2.8–2800 * 10^{-7} m s^{-1} was used in the 'trial and error' and optimisation runs, and a value of 2.8 * 10^{-5} m s^{-1} was used as an average. High heterogeneity of the forest soil and the presence of varying types of macropores and cracks complicates the modeling attempt. In the ordinary forested tills of Fennoscandia, hydraulic conductivity in different types of till has been found to vary between 10^{-3} and 10^{-9} m s^{-1} (Lundin 1990). There are morainic formations with large heterogeneities both within short distances and disorderly organized with depth. In fine-grained till, e.g. silty till, the conductivity is generally low but may be locally high in the upper soil layers due e.g. to cracks (Lundin 1990). On the basis of the measured pF curves (Ahonen and Roos, in prep.), maximum soil moisture storage was estimated to be 315 mm in the 0-80 cm layer (72% * 100 mm peat layer + 35% * 700 mm moraine layer). This 80 cm is about the same as the estimated average depth for the whole catchment (section 3.4). In the model runs, a somewhat smaller storage of 250 mm was obtained, of which 150 mm was assumed to be between the wilting point and the field capacity. In the snow subroutine, the estimated parameters were the degree-day factor, 3.0 mm $°C^{-1}d^{-1}$, the correction factor for snowfalls of 1.25 and the limit temperature for melting, which was estimated to be 1.0 °C. These para meter values appeared to be physically realistic.

The water balance was adequate, with a simulated accumulated runoff of 779 mm during the 2-year period, compared to the measured runoff of 792 mm, but the value of R^2 between measured and simulated daily runoffs was not higher than 0.57 (VII). Particularly during summer, simulated runoff had somewhat higher peaks than the observed runoff. The effect of the water retaining capacity of the peatland in the middle of the catchment could not be modelled adequately in the summer of 1992; after a very dry period, simulated runoff started too early. In the following section, monthly fractions of saturated contributing areas within the catchment will be compared to the results based on isotope methods.

3.3.4 Comparison of isotope methods and modeling

The percentages of saturated contributing areas based on 1) measured, 2) estimated (sinusoidal curves) monthly $\delta^{18}O$ values for precipitation, groundwater and streamwater, and 3) the percentages estimated by TOPMODEL are compared in Fig. 12 (VII). Concerning isotope methods, these areas by definition produce 'new' event water to the stream. TOPMODEL estimates fractions of saturated contributing areas. These areas are assumed to covariate, but there is no clear evidence for this. However, the fractions can be compared.

There was no marked difference between the average percentages, 3.9–5.0%, based on those 12 months (VII) from which values by all the three methods were available. Normally, TOPMODEL gave somewhat lower values than the isotope methods. However, during certain months, e.g. March, April, August and October 1991, the methods differed considerably. The isotope methods have higher uncertainty in April and in September-October, when all the three components – precipitation, groundwater and streamwater – have $\delta^{18}O$ values close to each other and close to the analysis accuracy, 0.1 o/oo. In August 1991, no representative value for $\delta^{18}O$ of groundwater was found due to intensive rainfall just after a long dry period. Therefore, an isotope method (measured values) gave an overestimate. The annual range of contributing areas is discussed in the following.

Those areas having a late autumn soil water content of greater than 40%, measured on 12 October 1994 by TDR (VII), were assumed to be at or close to saturation state. On the basis of TDR measurements, 21 measuring points of 63 had water contents of higher than 40%. These points, if assumed to represent a 30x30m grid each, covered 1.8 ha of the catchment area. Computed event water contributing areas were compared to

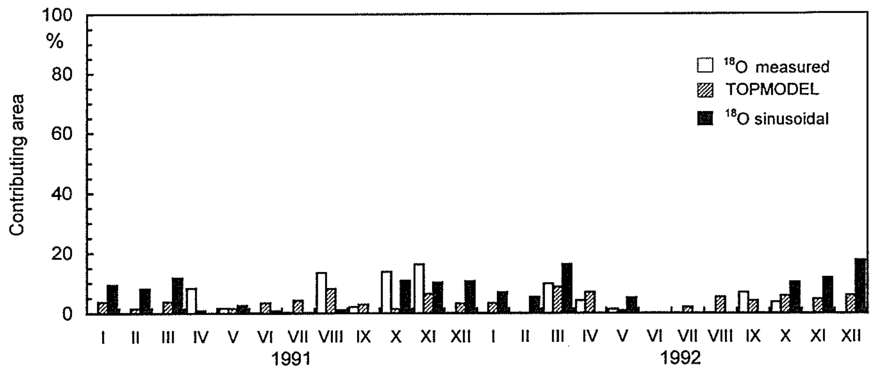

Fig. 12. The percentages of saturated, contributing areas based on 1) measured monthly δ ^{18}O values of precipitation, groundwater and streamwater, 2) the percentages estimated by TOPMODEL, and 3) estimated δ ^{18}O values (sinusoidal curves) during 1991–92 in the catchment 8 Rudbäck.

areas of probable surface saturation in the Rudbäck catchment, i.e. a peatland area (1.1 ha), a channel area (0.03 ha) and areas close to saturation (1.8 ha), totalling 2.9 ha. The estimated monthly range of contributing areas was from 0.0% (July 1992, no outflow) to 17.6% (December 1992, 3.2 ha). This means that the computed range of event water contributing areas was realistic. The average percentage of contributing areas of 3.9–5.0% (0.7–0.9 ha), estimated by the above three methods, was also close to the peatland percentage of 6% (1.1 ha) of Rudbäck.

The results coincide with those of Eshleman et al. (1993), who reported that estimates of new water-contributing areas determined from the chemical separations were found to vary as a function of antecedent conditions and were also found to be consistent with estimates of areas of probable surface saturation. Rodhe (1987) compared the areal extent of discharge areas (contributing areas) estimated by isotopic methods to the field surveys and found reasonably good agreement.

At present there are still clear differences and inaccuracies with the methods and it cannot be stated which method is the most accurate. Seasonal comparisons of different methods; isotope based, modeling based or field survey based estimates of saturated contributing areas, will become possible when more catchment scale field survey data of the extent of those areas, measured by e.g. TDR, become available.

3.4 Residence times of water in the Rudbäck catchment

Residence times of water in the catchment provide hydrologically relevant information, as well as information about the capability of the forest ecosystem to recover from e.g. a certain decreased atmospheric load.

The time series of δ ^{18}O input and output, covering a 2-year period, provide an insight into the turnover mechanism of the Rudbäck catchment (VII). A sinusoidal curve (Eq. 3) was fitted to the monthly time-series of precipitation, streamwater and groundwater (see Herrmann and Stichler 1982, Burgman et al. 1983). The amplitude attenuation (damping) for the Rudbäck catchment during 1991–92 was 0.22, and a mean residence time of about 8.3 months was obtained (VII). The observation period of only two years causes uncertainty in the calculation. An inaccuracy of ±1 o/oo of the amplitude a_p for precipitation gives an uncertainty of ± 1.5 months in a mean residence time. With a residence time of 8.3 months (0.69 years) and 400 mm runoff during the study years 1991–92, an average, total water storage estimate of 275 mm was obtained (VII). However, during 1991–92, runoff was higher than the long-term average. If long-term runoff is assumed to be 300 mm and residence time is assumed to remain about the same, this would correspond to a water storage estimate of

210 mm. Assuming the mean volumetric water content of the soil to be 25...30%, water storage of 200–275 mm corresponds to a mean soil thickness of 0.7–1.1 m, which seems reasonable. Taking into account that 41% of the catchment is covered by open bedrock and only a 5 cm humus layer, the rest of the catchment has a mean soil thickness of about 1.5 m ± 0.3 m.

The residence time obtained is a mean residence time for the whole catchment and for the contribution of different types of runoff. Theoretically, a long mean residence time can arise from retention in either surface or sub-surface water storages. At Rudbäck, there are no surface reservoirs but the retaining capacity of the peat areas in the middle of the catchment contributes to the relatively long residence time of 8 months, considering the small size of the catchment and the high percentage of open bedrock areas within it. In the surface layers, however, residence times e.g. for shallow groundwater flow are shorter. The time lag between the isotopic inputs and outputs was approximately 2.5 months, which is the mean residence time for water in the upper layers, and which can be considered to be the most important, e.g. from the point of view of the material fluxes. By contrast, deeper groundwater below the clay layers and the peaty area may have very long residence times, remaining outside the 'quick', effective turnover of water. Rodhe (1987) used a mixing model with an input of daily values for the amount of precipitation and $\delta^{18}O$, air temperature and PET, and estimated water storages (reservoir volumes) of 200–300 mm and residence times of 0.5–1.5 years in seven forested catchments in Sweden.

4 Temporal and spatial variation of nitrogen leaching

In addition to the hydrology of a catchment, factors such as natural catchment characteristics, climatic factors and anthropogenic factors including N deposition and forestry activities may affect the temporal and spatial variability of nitrogen leaching from forest soils. In the following, firstly temporal variation, secondly spatial variation and finally the role played by contributing areas of the catchment to N leaching will be discussed.

4.1 Temporal variation of nitrogen leaching

4.1.1 Seasonal variation of streamwater N concentration

Nitrogen uptake by the biomass of the forested ecosystem, accumulation of deposited N in the snowpack and of mineralized nitrogen in the catchment soils followed by a leaching period during the snowmelt, and flow dynamics are the most important factors affecting seasonal variation of nitrate N. Twenty forested catchments, eight from Finland and twelve from Sweden, were selected in order to detect links between concentrations of fractions of N, flow dynamics and seasonality (IV, Arheimer et al. 1993) and to investigate the factors affecting spatial leaching of nitrogen (V). First, these links concerning NO_3-N will be discussed.

Influence of flow, seasonality and catchment characteristics on N concentration

Significant correlation between NO_3-N concentration and flow of the sampling day was detected in 13 of the 22 catchments studied (Table 3, IV). When comparing the correlations at different flow conditions, most correlations were found when only samples taken during stable or decreasing flow were considered. Even if seasonality to some extent explains the low R^2-values in the regression analyses and the scattered distribution of concentration values, the explained variance was generally low (Table 3). On average, only 22% of the variation in NO_3-N concentration could be explained by variation in flow volume. At best, flow explained 62–73% of the variation of nitrate concentration (negative correlation) in two undisturbed catchments in Eastern Finland, Murtopuro and Koivupuro. After intensive drainage and clear-cutting which took place in these catchments in 1983, the R^2-values decreased close to zero. This figure was affected by a significant increase in concentrations and by their scattered variation during high flows. Of the 13 catchments with significant correlation between nitrate concentration and flow, the correlation was negative at ten of

Table 3. Number of catchments with significant correlation ($p < 0.05$) between NO_3-N concentration and flow measured on the day of sampling, according to regression analyses in which logarithmic values of both variables were used (IV).

Flow and/or seasonal conditions	Average n	No. of catchments with sign. correlation (total no. of catchments)	Min. and max. R^2	Average R^2
All data	130	13 (22)	0.02 - 0.73	0.22
Stable or decreasing flow	96	14 (22)	0.05 - 0.71	0.26
Increasing flow	51	7 (17)	0.06 - 0.32	0.16
Autumn/winter (September-Dec.)	72	9 (20)	0.09 - 0.45	0.24
Winter/spring (January-May)	65	11 (19)	0.05 - 0.51	0.22
Summer (June-August)	45	2 (11)	0.14 - 0.52	0.34

Correlations were calculated using all data and using data from specified flow conditions and/or seasons. Data sets with less than 30 samples were excluded. R^2 values refer to catchments in which significant correlation was found.

Table 4. Number of catchments with significant difference ($p < 0.05$) when comparing NO_3-N concentrations sampled during various flow conditions and/or seasons, using the Wilcoxon test. Datasets with less than ten samples were excluded (IV).

Compared flow/seasonal conditions	No. of catchments with:		No. of catchments without significant difference
	Higher conc.	Lower conc.	
High flow vs low flow	4	12	5
High flow (dormant season) vs low flow (dormant season)	3	13	5
Increasing flow vs stable/decreasing flow	7	0	14
Increasing flow - spring vs stable/decreasing flow - spring	8	1	11
Increasing flow - autumn vs stable/decreasing flow - autumn	1	0	18
Spring high flow vs autumn high flow	7	2	10
Summer low flow vs dormant season low flow	0	10	4

the catchments and positive at three. All the northern catchments, but also Teeressuonoja which has an extraordinarily high base flow, showed clear dilution, i.e. negative correlations between flow and concentration.

Most of the investigated catchments had very low annual mean NO_3-N concentrations (IV). For the catchments with lowest annual mean concentrations, up to 14 times lower concentrations were observed during high flow compared with low flow. Catchments with positive correlation were shown to have relatively high annual median concentrations. Similar results of links between average concentration levels and flow in forest streams have been reported from North American surveys (Driscoll et al. 1989b). Catchments with higher concentrations during high flow were situated in the south and at low altitudes. Consequently, they had significantly higher mean annual temperatures and mean annual NO_3-N concentrations. In boreal forests, temperature is crucial for the regulation of rates of mineralization and nitrification, and thereby regulates the availability of plant nutrients in the soil. Since nitrogen conservation in a boreal ecosystem is reduced at increased nutrient availability (Vitousek et al. 1979, Plymale et al. 1987), the southern catchments are more disposed to leakage.

Increasing flow vs. stable or decreasing flow. One third of the catchments (7 of 21) had significantly higher concentrations during periods of increasing flow compared with stable or decreasing flow (Table 4, IV). This group of catchments also had significantly higher annual mean NO_3-N concentration levels, indicating that more nitrogen was available for leaching. Roberts et al. (1984) noted that in an upland area of Britain, high NO_3-N concentrations were only accompanied by flow increases when preceded by a warm dry period. During wet winter months no or only minor reactions to flow increase were observed. Rather different results were obtained in this study, in which significantly higher concentrations during increasing flow were recorded in 40% of the catchments during the first half of the year, with most of the events occurring in connection with the spring flood. In the second half of the year, only one catchment revealed significantly higher concentrations in connection with increasing flow (Table 4). The high flow concentrations were also significantly higher during spring in several of the catchments (Table 4), which could not be explained by differences in discharge volumes at the times of sampling.

Spring vs. autumn high flows. In Finland and Sweden, winter precipitation is often in the form of snow, resulting in low winter flows and a pronounced spring flow during snowmelt periods. The dominant runoff generating mechanism in small forested catchments during the snowmelt period might be replacement of 'old' pre-event water from the soil (Rodhe 1987,I,II). This pre-event water may have rather high NO_3-N concentrations due to long periods with limited washout, low biological uptake and winter mineralization/ nitrification (Denning et al. 1991, Stottlemyer and Troendle 1992). Another fraction of streamflow is 'new' meltwater, which has had limited contact with the soil layers but may have highly elevated inorganic-N concentrations compared with rainfall. The snowpack is able to store, and after melting, suddenly release large amounts of different substances. Laboratory and field experiments carried out by Johannessen and Henriksen (1978) indicated that 50–80% of pollutants are released when the first 30% of the snow melts.

Those catchments not having significant differences between spring and autumn high flow concentrations were the northern ones with significantly lower annual mean air temperatures and consequently having lower mineralisation rates, less accumulation of NO_3-N in soil and low N deposition. The main reasons for increased NO_3-N concentrations during spring flow are release of nitrates accumulated in the soil and more importantly in the south, release of concentrated, nitrate- (and sulphate-) rich meltwater, in which N is derived from dry and wet atmospheric deposition.

Summer vs. dormant season low flows. 10 of the 14 catchments studied had significantly lower NO_3-N concentrations during the summer low flows (Table 4, IV), with biological uptake being the most obvious explanation. Important sources of mobile NO_3-N to surface waters during the dormant season are mineralisation of soil organic-N followed by nitrification and atmospheric deposition (Vitousek et al. 1979). Furthermore, uptake of inorganic-N deposition by the canopy apparently does not occur during the dormant season (Grennfelt and Hultberg 1986).

Three of the four catchments (Teeressuonoja, Hulubäcken, Stormyra and Murtopuro) with no significant differences between concentrations during the growing and dormant season low flows (Table 4) were southern ones and exposed to higher inorganic-N deposition. Driscoll et al. (1989a) reported that at some sites in Germany, the seasonal patterns of NO_3-N concentrations in drainage water from forests had diminished, with chronically high concentrations resulting from high inorganic-N deposition. Although the inorganic-N deposition in Germany is several times higher than in the region of this study, the link between high inorganic-N deposition and a lack of seasonal pattern might be one of the first signs of nitrogen excess due to increased inorganic-N deposition.

Nitrate concentrations vs. daily flow and seasonality, Yli-Knuutila and Teeressuonoja

Nitrate concentration and runoff of the sampling day in the Teeressuonoja catchment were compared by dividing the observation period into two periods; the years 1966–76 and 1977–88 (I). A statistically significant negative correlation ($r = -0.48$, $p<0.001$, $n=259$) was found between runoff and nitrate during the second period (Fig. 13). Correlation during the first period was also negative but relatively weak, although significant at the 0.05 probability level ($r= -0.18$, $p<0.05$, $n=128$). Fig. 13 shows that concentrations increased particularly during the periods of low flow. For Yli-Knuutila during the period 1969-90, the correlation was also significant, but positive ($r= 0.23$, $p<0.001$, $n=235$), indicating higher quantities of nitrate available for leaching during the highest flows. The r values were very low, however, because of the highly scattered variation and seasonality. In Yli-Knuutila, seasonal variation of nitrate was more extensive than in Teeressuonoja, contributing to the large differences between annual median and volume-weighted average concentrations.

The seasonal variation of nitrate in the Yli-Knuutila stream is presented separately for the 1970s and 1980s in Fig. 14 (III). When comparing the two time periods, the average increase in concentrations was highest (700–1000 $\mu g\ l^{-1}$) during dormant seasons, but was also clearly evident

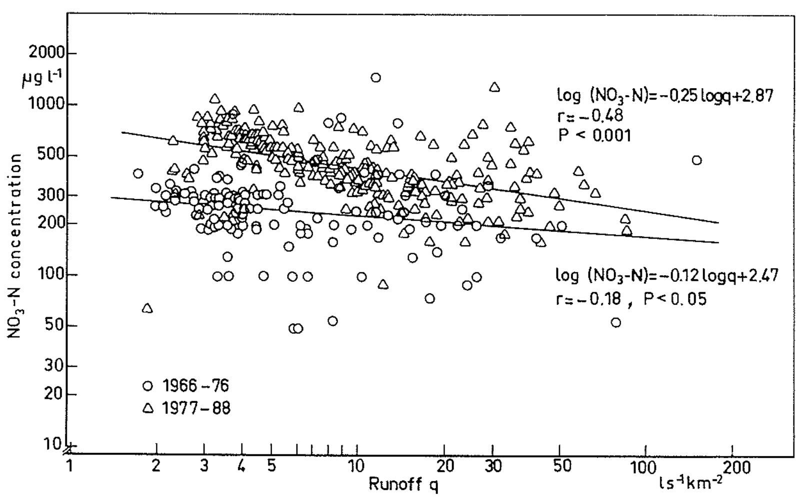

Fig. 13. Nitrate-N concentration vs. runoff in Teeressuonoja during the years 1966–76 (o) and 1977–88 (Δ).

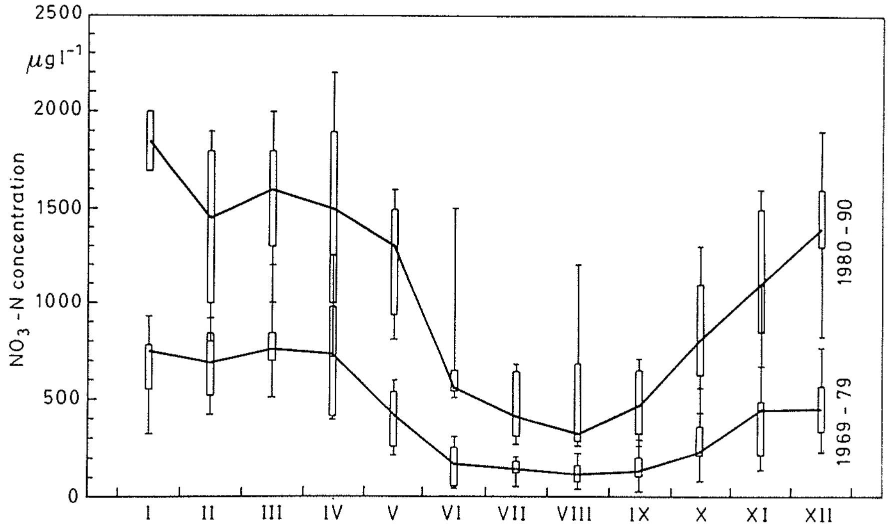

Fig. 14. Seasonal variation of NO_3-N concentration in Yli-Knuutila as Box-whisker plots (the medians are joined, the 'box' defines the interquartile range and the 'whiskers' define 10 and 90 per cent limits of the distribution) associated with samples collected during individual months. The study periods of 1969–79 and 1980–90 are shown separately.

during the growing seasons, June–August, being 200–400 μg l^{-1}. The 'normal', undisturbed seasonal NO_3^- pattern (Stage 0) in a stream draining a catchment would be one of very low, or unmeasurable, concentrations during most of the year, and of measurable concentrations only during snowmelt or rain storms (Stoddard 1994). At Stage 1 in Stoddard's classification, the seasonal pattern is amplified and it has been suggested that this amplification of the seasonal NO_3^- signal may be the first sign that catchments are proceeding towards the chronic stages of N saturation (Driscoll and Schaefer 1989, Stoddard and Murdoch 1991). In Stage 2 of catchment N loss (Stoddard 1994), biological demand exerts no control over winter and spring N concentrations and the period of N limitation during the growing season is much reduced. At Yli-Knuutila increased variation of nitrate in June and August (Fig. 14), and the general increase during the entire growing season despite nutrient uptake suggest that the catchment is in a transitional stage between stages 1 and 2 with regard to N saturation. The high increase in nitrate concentrations during the snowmelt period of (February)–March–April indicates the importance of N deposition impacting on nitrate N losses. When comparing the 1970s and 1980s at Yli-Knuutila, however, there was no clear change in seasonality pattern towards stage 3, lack of coherent seasonal pattern in NO_3-N concentrations (Stoddard 1994).

4.1.2 Increasing trends in nitrogen leaching during the past 20–25 years in two catchments

Increasing trends in concentrations

The average level of nitrate in streamwater in the study catchments in southern Finland, Yli-Knuutila and Teeressuonoja, is high considering the fact that the catchments are forested and were in almost a natural state during the study period 1966–90. A long-term increase in nitrate nitrogen concentration was observed in both the catchments (III). Figures 15b and 16b show Box-whisker plots of nitrate in the catchments for the period 1966 to 1990 (starting in 1969, Yli-Knuutila). The volume-weighted annual average concentration in Yli-Knuutila increased over twofold, from 580 μg l^{-1} in 1969–79 to 1350 μg l^{-1} in 1980–90 (Fig. 15b).

Table 5. Test statistics (t-values) for trends in NO_3-N concentrations in Yli-Knuutila and Teeressuonoja streamwater, for the separate months during 1969–1990 and for the whole period (III). HS = Hirsch & Slack non-parametric test; F_{adj} = flow-adjustment.

	Yli-Knuutila		Teeressuonoja	
Month	HS	HS, F_{adj}	HS	HS, F_{adj}
1	0.943	0.834	2.102*	2.413*
2	2.085*	1.460	3.172**	3.050**
3	3.291***	2.743**	2.983**	2.920**
4	3.394***	3.394***	2.934**	3.074**
5	0.940	1.336	4.366***	4.037***
6	2.196*	2.440*	2.332*	2.227*
7	1.791	1.791	3.661***	3.728***
8	1.830	1.098	2.992**	2.462*
9	3.460***	3.460***	2.881**	2.341*
10	3.603***	3.569***	1.934	1.933
11	2.841**	3.068**	3.118**	3.114**
12	2.961**	3.011**	2.581**	2.521*
Combined, whole year	3.488***	3.531***	4.269***	4.105***

Significance level		Critical values
5 %	*	> 1.96
1 %	**	> 2.56
0.1 %	***	> 3.28

In Teeressuonoja, concentrations of NO_3-N were somewhat lower, but the increasing trend was obvious. The volume-weighted annual average concentration in Teeressuonoja increased 1.5-fold, from 280 $\mu g\ l^{-1}$ in 1966–79 to 420 $\mu g\ l^{-1}$ in 1980–90 (Fig 16b). The main increase in both catchments occurred between the mid-1970s and the mid-1980s.

A highly statistically significant ($p<0.001$) upward trend was detected for both nitrate (Table 5) and total nitrogen concentration ($t=3.421$, $p<0.001$) of the Yli-Knuutila stream during 1969–90, using the non-parametric Mann-Kendall rank test (Hirsch and Slack 1984). Highly significant ($p<0.001$) upward trends were also observed for nitrate (Table 5) and total N ($t=3.732$, $p<0.001$) concentrations in Teeressuonoja during the same period. The monthly values of runoff, used as covariate, were used to adjust the values of nitrate concentrations. This adjustment did not have significant effects on the observed trends.

The above Mann-Kendall rank test was also used for detecting trends during separate months of the monitoring period of 1969–90. It was found that the highest increasing trends in Yli-Knuutila were found during the snowmelt period in March–April and during September–October (Table 5) (III). For Teeressuonoja, clearly increasing trends were also found during snowmelt, but the trend continued further, with the most significant increase occurring in May. Increasing trends in Teeressuonoja, compared to Yli-Knuutila, were also more profound during baseflow periods, in January–February, and during the growing season in July–August (III). Deeper soil layers of coarse sands and moraines, the higher percentage of baseflow and the longer transit times of Teeressuonoja probably explain the differences. Isotope studies have shown that the snowmelt runoff in Teeressuonoja consists to a considerable degree (75–85%) of pre-event water, which was present in the soil before melting (I,II). Yli-

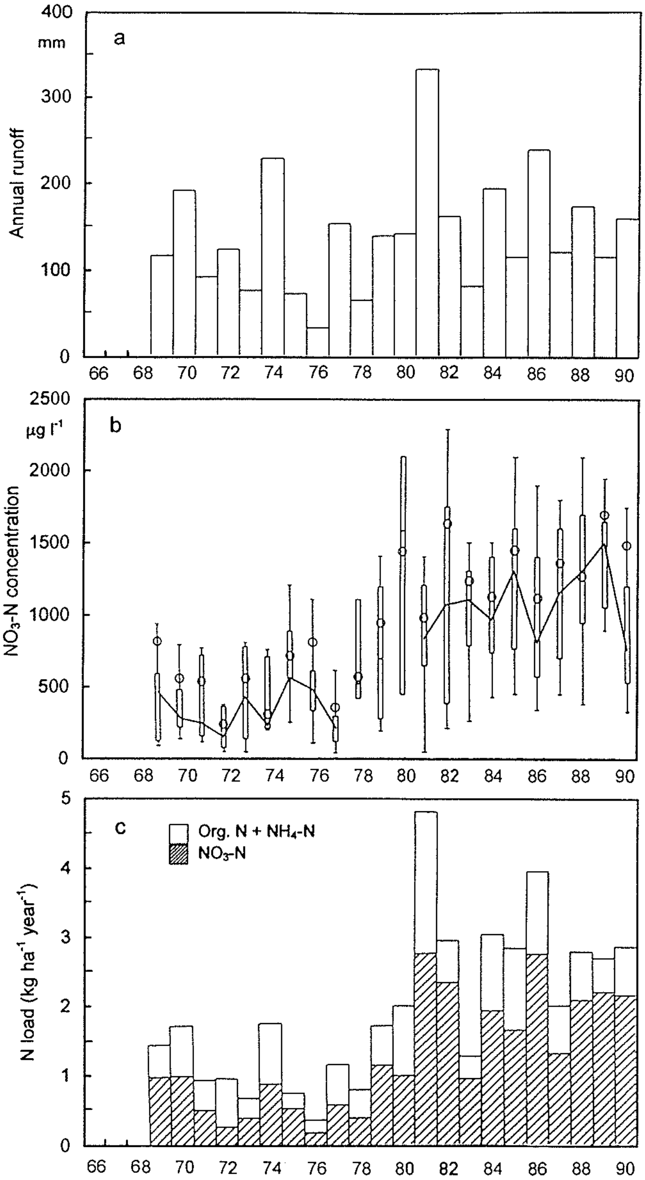

Fig. 15 a) Annual runoff (mm) in the Yli-Knuutila catchment during 1969–90, **b)** Box-whisker plots of NO_3-N concentrations in Yli-Knuutila streamwater during 1969–90. The medians are joined, the 'box' defines the interquartile range, the 'whiskers' define 10 and 90 per cent limits of the distribution, and o denotes volume-weighted annual averages. Note incomplete sampling during the years 1978–80, **c)** Annual stream-water output of total N and NO_3-N (kg $ha^{-1}a^{-1}$) in the Yli-Knuutila catchment during the period 1969–90.

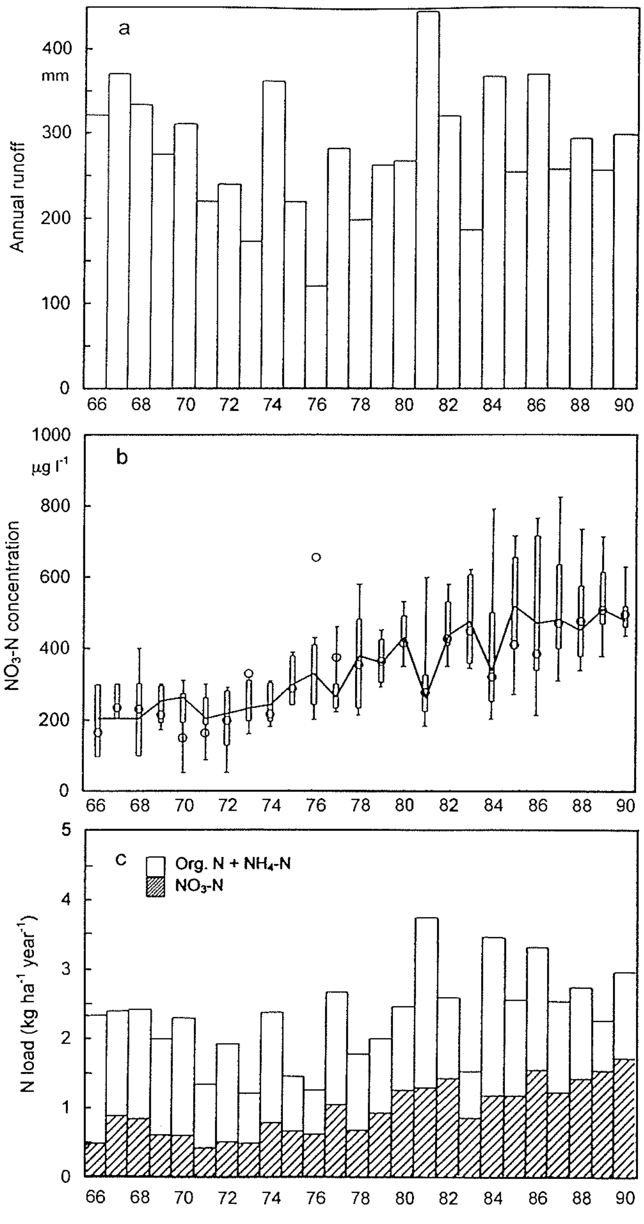

Fig. 16 a) Annual runoff (mm) in the Teeressuonoja catchment during 1966–90, **b)** Box-whisker plots of NO_3-N concentrations in Teeressuonoja streamwater during 1966–90. The medians are joined, the 'box' defines the interquartile range, the 'whiskers' define 10 and 90 per cent limits of the distribution, and o denotes volume-weighted annual averages, **c)** Annual stream-water output of total N and NO_3-N (kg ha^{-1}a^{-1}) in the Teeressuonoja catchment during the period 1966–90.

Knuutila, with a positive relationship between flow and nitrate, seems more to resemble a quickflow-dominated catchment. Furthermore, Yli-Knuutila has clay and silt moraines close to the brook and outlet, comprising one third of the area and making quick, near-surface flow possible in these areas.

It is probable that an increase in the atmospheric deposition of nitrogen has been a contributing factor to the increase of nitrate concentrations in the forest streams of Yli-Knuutila and Teeressuonoja. Apart from deposition, the only anthropogenic impacts in Teeressuonoja have been some excavation of sand and gravel, and minor household leggings. These might have had local effects on groundwater nitrate concentration but, on a catchment scale, the effect can be considered negligible. Nitrate increase in the undisturbed (during the study period 1969–90) catchment, Yli-Knuutila, was even higher. The input-output budget of N and the effect of N uptake by trees are discussed below (p. 49).

Kauppi (1984) reported increasing nitrate levels in four forested catchments in southern and central Finland. Increasing nitrate concentrations have been observed e.g. in Norwegian surface waters (Henriksen and Brakke 1988) and in runoff from forested catchments in Germany (Hauhs et al. 1989). In southern Sweden, the nitrate concentration in deep oligotrophic lakes not affected by agriculture or forest fertilizers increased by 50–100% during the last 10–20 years (Dickson 1986). In a study of 20 forested catchments in Sweden and Finland (Andersson et al. 1994, V), atmospheric inorganic N deposition proved to be one significant explaining variable for the spatial variation of nitrate export. In southernmost Finland, where nitrogen deposition is highest, 73% of the lakes still have low nitrate concentrations <5 μeq l^{-1} (70 μg l^{-1}) (Kämäri et al. 1991), indicating that the deposition of nitrogen compounds currently plays a rather minor role in the acidification of the lakes. However, the anthropogenic influence was evident in forested catchments, with clearly higher concentrations in southernmost Finland compared with the north.

Atmospheric deposition of inorganic nitrogen

Dry deposition data are more scarce than wet deposition data, because of the lack of practical routine methods for taking direct measurements of dry deposition (e.g. Lövblad and Erisman 1992). Dry deposition flux can be estimated from measured air concentration multiplied by the dry deposition velocity. Most estimates of regional or local dry deposition fluxes are based on models. It is evident that dry deposition is higher in forests than in open areas (e.g. Hultberg 1985, Ferm and Grennfelt 1986).

Estimates of deposition to forest ecosystems from throughfall measurements have been reported in many publications. In previous throughfall studies in Finland it has been observed that nitrogen is taken up by the canopy during the growing season in spruce, pine and birch stands (Helmisaari and Mälkönen 1989, Hyvärinen 1990). Kallio and Kauppi (1990b) studied the Yli-Knuutila catchment and observed that both ammonium and nitrate N deposition was lower than to open fields, indicating the significance of nitrogen uptake by the foliage. In the United States in 12 integrated forest study areas, Lovett (1992) reported that on average about 60% of the inorganic N deposition passes through as throughfall, while the other 40% is taken up by biological surfaces. For nitrogen species, Lövblad and Erisman (1992) concluded that throughfall measurements of inorganic N generally underestimate the total atmospheric deposition at least in nitrogen-deficient ecosystems.

Löfgren (1991) estimated the range of wet deposition to be 2–19 kg N $ha^{-1}a^{-1}$ in Scandinavia, and dry deposition to be up to 6 kg N $ha^{-1}a^{-1}$ in background areas. Integrated over the whole of Finland, 65% of both oxidized (NO_y) and reduced (NH_z) nitrogen is deposited with precipitation (Tuovinen et al. 1990), the total deposition of N being on average 1.5-fold the wet deposition. Dry deposition of N in Yli-Knuutila could be of the order of 4–6 kg N $ha^{-1}a^{-1}$.

Because of the lack of direct measurements of dry deposition, and because throughfall measurements may underestimate the total deposition, inorganic N deposition was used as an index of the total deposition (III). There was a gradual increase in inorganic deposition of N during 1971–90, with major changes from the mid-1970s to the mid-1980s and high variation between years. The annual average inorganic deposition of nitrogen at the station in an open area, close to the catchments, increased from 6.2 kg $ha^{-1}a^{-1}$ (bulk 7.8) in 1971–79 to 8.5 kg $ha^{-1}a^{-1}$ (bulk 11.2) in 1980–90. The range for the whole period was 4.2–13.9 kg $ha^{-1}a^{-1}$. Precipitation during the latter period was 1.2 times higher than during 1971–79. NO_3-N deposition comprised on average 45% and NH_4-N 55% of the total inorganic deposition. There is also a fraction of organic N deposition (about 20% of the total bulk), which was not considered in this study. Possible sources include particulate material originating from soils and vegetation (e.g. pollen, soil dust, spores).

Total and nitrate nitrogen outputs from the 1960s to 1990

The total stream-water nitrogen output at Yli-Knuutila increased almost threefold, from 1.1 kg N $ha^{-1}a^{-1}$ in 1969–79 to 2.9 kg N $ha^{-1}a^{-1}$ in 1980–90 (Fig. 15c, III). The nitrate output during the same period increased over threefold, from 0.6 to 2.0 kg NO_3-N $ha^{-1}a^{-1}$. The annual runoff was 1.4 times higher, 170 mm in 1980–90 compared to 121 mm in 1969–1979 (Fig. 15a), and therefore runoff accounts for only a minor part of the increase in the nitrogen outputs. During 1978–81, there was a major increase in annual outputs, 1978 being one of the driest and 1981 the wettest year of the whole period. The concentrations also increased during the same period but during 1978–80 very few samples, only 3–5 a year, were taken, and these years therefore cannot be compared fully with the other years of the time series. The average proportion of the NO_3-N output of the total nitrogen output increased from 56% in the 1970s to 68% in the 1980s.

For Teeressuonoja, the stream-water output of total nitrogen increased from 2.0 kg $ha^{-1}a^{-1}$ in 1966–79 to 2.8 kg $ha^{-1}a^{-1}$ in 1980–90 (Fig. 16c, III). The NO_3-N output increased almost twofold during the same period, from 0.7 to 1.3 kg $ha^{-1}a^{-1}$. Changes in amounts of runoff do not account for these changes; in 1980–90 the runoff was only 1.1 times higher than in 1966–79 (Fig. 16a).

Ammonium losses from mineral soil forests are generally low. In both catchments in this study, the output was also minor, comprising on average about 5% of the total N output. Organic N losses comprised on average 30% and 50% of the total N output at Yli-Knuutila and Teeressuonoja, respectively.

Elevated nitrate leaching needs to be considered in comparison with background levels from unaffected areas. The nitrate N output in the 1980s, particularly in Yli-Knuutila (2.0 kg N $ha^{-1}a^{-1}$), was clearly higher than the amount of nitrate N, (0–1 kg N $ha^{-1}a^{-1}$), estimated to leach from natural coniferous forests in Europe (Nilsson and Grennfelt 1988, Rekolainen 1989, Hauhs et al. 1989). However, significantly higher leached amounts have been reported in Central Europe. Annual nitrate leaching in the range of 13–30 kg N $ha^{-1}a^{-1}$ has been found in coniferous forests in The Netherlands (Mulder et al. 1989, van Dijk et al. 1992) and in Germany (Matzner 1988, Nilsson and Grennfelt 1988, Wiedey and Raben 1989). All these sites received 30 to 70 kg N $ha^{-1}a^{-1}$ in throughfall and are examples of nitrogen saturation of forests caused by atmospheric deposition (Gundersen and Bashkin 1994).

Input-output nitrogen budget at Yli-Knuutila

The input-output budget of inorganic N at Yli-Knuutila confirms the decreasing nitrogen retention during the past twenty years; output/input increased from 12% during 1971–79 to 24% during 1980–90. The output/input of the Teeressuonoja catchment increased from 13% during 1971–1979 to 17% during 1980–90 (III). The cycling of nitrogen between forest soil and biomass was not investigated, but an attempt was made to estimate the temporal pattern of aboveground net N accumulation by trees during 1960–90 at Yli-Knuutila. In the beginning of the 1960s, the mature stand was about 70–80 years old, and in the beginning of 1990s, 100–110 years. The volume of growing stock amounted to 162 m^3 ha^{-1} in the early 1960s (Mustonen 1965) and 275 m^3 ha^{-1} in 1991. The forest is of Oxalis–Myrtillus (OMT) type according to Cajander's (1949) classification.

Table 6. Average growth of OMT spruce stand in southern Finland (Päivinen 1991) and estimated stemwood growth of Yli-Knuutila, biomass stemwood increment, and estimated aboveground net N accumulation by stand (stemwood and bark) during 1960–90.

			Yli-Knuutila		
Year	Age of stand at Yli-Knuutila (years)	Average growth of OMT spruce stand ($m^3\ ha^{-1}a^{-1}$)	Estimated stemwood growth ($m^3\ ha^{-1}a^{-1}$)	Biomass stemwood increment (kg $ha^{-1}a^{-1}$)	Net N accumulation by stand (kg N $ha^{-1}a^{-1}$)
1960	70	9.7	4.3	1630	1.7
1970	80	8.7	3.9	1480	1.5
1980	90	8.0	3.6	1360	1.4
1990	100	7.7	3.4	1300	1.4

The annual net stand volume increment in stemwood, 3.8 $m^3\ ha^{-1}a^{-1}$ ((275–162) / 30 $m^3\ ha^{-1}a^{-1}$) was assumed to vary according to the growth table of OMT spruce stand in southern Finland (Päivinen 1991) during the 30-year period (Table 6). Stand volume increment in stemwood was converted to dry mass by multiplying by a wood density of 0.379 t m^3 (Kellomäki 1992). The net aboveground N accumulation was calculated by multiplying the biomass increment by a nitrogen concentration of 0.104% (bark and stemwood) (Kellomäki 1992), based on the material by Kubin (1983) and Finer (1989). Stemwood and bark are included in the biomass estimations of Table 6, but not needles or branches. Net accumulation to needles or branches was assumed to be zero in spruce stand of this age.

Growth at Yli-Knuutila during 1960–90 was less than half the average growth of thinned OMT spruce stands in southern Finland. Part of the stands in the catchment consist of pine (about 15%), which grows in the water divide areas where the soils are less fertile and include some open bedrock areas. Furthermore, in the Yli-Knuutila catchment no thinning was carried out during the study period. These points explain only part of the difference. Factors behind the low growth should be studied further.

Finér (1989) found that the annual net N accumulation by above-ground tree biomass (aboveground parts minus leaf and other above ground litter) in spruce stands in eastern Finland was 3.2 kg N $ha^{-1}a^{-1}$, but N accumulation to stemwood and bark was only 0.8 kg N $ha^{-1}a^{-1}$, half of that at Yli-Knuutila.

As a part of the International Biological Programme forest studies, Kazimirov and Morozova (1973, ref. Cole and Rapp 1981) followed the patterns of cycling in spruce in a southern Karelian fertile site, through a series of age classes ranging from 22 to 138 years. According to their data, net N uptake decreased by about 1 kg $ha^{-1}a^{-1}$, when stand age increased from 80 to 100 years, but understory vegetation uptake increased by about the same amount, which means there was no change in the total net N uptake (tree+vegetation biomass).

Fig. 17 shows the annual nitrogen budget at Yli-Knuutila in 1970, 1980 and 1990, each column representing the average of five year periods (1969–73, 1978–82 and 1986–90). According to the data available and estimates, net aboveground N accumulation and uptake by trees in a 20-year period, from the early 1970s to the late 1980s was relatively stable, which means that it cannot explain increased leaching of nitrate. Increasing N deposition from the mid-1970s to the mid-1980s contributed to increasing leaching of nitrate. As was discussed before (p. 45), the increase was most profound during the dormant season, spring and autumn, when uptake by biomass had no effect.

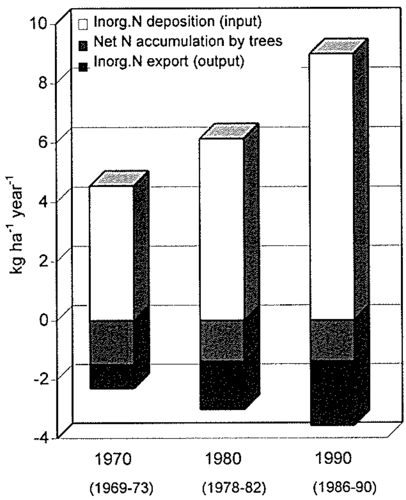

Fig. 17. Input-output budget of inorganic N (kg ha^{-1}a^{-1}) at Yli-Knuutila in 1970, 1980 and 1990. Each column represents the average of five years (1969–73, 1978–82 and 1986–90).

Driscoll et al. (1989b) and Stoddard (1994) summarized the relationship between N export and N deposition indicated by input/output budget data from a large number of catchments in the United States and Canada, indicating that the amount of N leached is higher in areas where N deposition is highest, but that the relationship is highly variable between the catchments. If the output/input fraction of nitrogen in the catchments in central Ontario was 25%, this was still regarded as low (Dillon et al. 1991). In Scandinavia, however, the same situation (20–25% leaching and 75–80% retention), as found in this study (III), implies that N leaching has increased considerably above that of the original forest ecosystem (Rosen et al. 1992, Fleischer et al. 1993).

Representativeness of the catchments

In southern Finland, the concentrations of nitrate N in streamwater increased significantly in two forest catchments, in the more fertile Yli-Knuutila and in Teeressuonoja. However, only in 5 of the 15 forested catchments studied in Finland and Sweden did the trend analysis show upward trends of nitrate N concentration during the period 1971 to 1988 (Lepistö et al. 1991). Teeressuonoja was one of those five catchments, but Yli-Knuutila was not included because of some uncertainty about how representative it is for Nordic conditions. In a 20 catchment study (V), it was found that Teeressuonoja had significantly higher average nitrate N export (1.3 kg ha^{-1}a^{-1}) when compared to other relatively undisturbed (no forest management) catchments (0.05–0.70 kg ha^{-1}a^{-1}). It should be kept in mind that in the study concerned (V), there were no catchments from southern/southwestern Sweden receiving higher amounts of nitrogen deposition, and highest excesses of critical load of nitrogen (Rosen et al. 1992). Both Yli-Knuutila and Teeressuonoja, however, are situated in an area where excess of the critical load of N is high (5–7 keq ha^{-1}a^{-1}).

The average 30-day summer minimum runoff divided by annual runoff at Teeressuonoja was 0.36, over threefold compared to that of Yli-Knuutila, 0.10 (Seuna 1982). Teeressuonoja has a very high baseflow fraction for its size. Yli-Knuutila behaves more like a surface-flow dominated catchment with significantly lower storages of water in the saturated zone. The dominance of baseflows seems to increase nitrate N concentrations during the growing low-flow season at Teeressuonoja. This could be due to the fact that in a catchment with deep soils consisting of sand and gravel, the significant part of nitrificated N is not reached by nutrient uptake by the biomass and is also available for leaching during the summer period. About one third of the soils of Yli-Knuutila are silt/clay moraines, making quickflow and also rapid leaching of nitrate N possible during the snowmelt period and autumn storms.

The forest of Yli-Knuutila is of Oxalis-Myrtillus (OMT) type, according to Cajander's (1949) classification. OMT type is the second most fertile type in Finland and accounts for 16.3% of the forest soils of southern Finland (Urvas and Erviö 1974). Correspondingly, the forest of Myrtillus (MT) type dominates at Teeressuonoja. This forest type is the third most fertile and accounts for 49.1% of southern Finland (Urvas and Erviö 1974). The figures show that these forest types are not very exceptional in Southern Finland. Based on these figures, the catchments can be assessed to represent these relatively fertile forest ecosystems in southern Finland. It has to be remembered, however, that Teeressuonoja has a very high base flow fraction (deep soils); catchments with shallow soils and MT type forest probably behave in a different way, e.g. reacting more rapidly to the changes in atmospheric deposition.

Nitrogen is generally the growth-limiting nutrient in forest ecosystems in Finland and Sweden. The deposited nitrogen is in most cases still efficiently retained within the catchment areas, the better the more nutrient-poor is the forest ecosystem. In Yli-Knuutila and Teeressuonoja, the nitrogen inputs have been assimilated by the biomass over a long period of time, but retention particularly in Yli-Knuutila has clearly reduced during the study period. In Finland, losses of nitrate to watercourses are expected to increase mainly from the most fertile forest ecosystems (MT and OMT site type) in southern and central parts of the country where N deposition is also highest.

4.2 Spatial variation of nitrogen leaching

It was hypothesised that the spatial variability of nitrogen leaching from forested catchments can only be explained by the combined effect of hydrological, meteorological, physiographical, forest-management and deposition factors. Multiple regression methods were used to analyse and explain which factors are associated with release of nitrate, ammonium and organic nitrogen from the catchment soils. Average losses (1979–88) of different nitrogen fractions from twenty small forested catchments in Finland and Sweden were used (V, Table 7). A data base including the explaining factors for the catchments is presented as Table 2 (p. 24).

4.2.1 Factors associated with release of nitrate-N

NO_3-N export varied between 2.1 and 133 kg km^{-2}a^{-1}, with a median of 25.3 kg km^{-2}a^{-1} (Fig. 18, Table 7, V). Positive correlations were found with inorganic N deposition (Fig. 19a), temperature (Fig. 19b), stream density, percentage of fine soils and clearcut percentage, whereas negative correlations were found with the percentage of organic soils. Taking into account the low number of included catchments, a model with two or three explaining variables was considered acceptable. The model explaining NO_3-N export could be based on either air temperature (R^2=0.63) or N deposition (R^2=0.64), giving similar results in both cases. The following equation, explaining 64% of the variation, was selected:

$$NO_3\text{-N export (kg km}^{-2}\text{a}^{-1}) = -1.7 + 0.09\ \text{N\_DEP} - 0.53\ \text{ORGSOIL} \quad (9)$$

where N_DEP = inorganic N deposition (kg km^{-2}a^{-1}), and ORGSOIL = percentage of organic soils in a catchment.

Table 7. Average export fluxes of different nitrogen fractions in the studied catchments (V). In most cases, except [1,2,3], the period 1979–88 is used.

	NO_3-N export kg km^{-2}a^{-1}	NH_4-N export kg km^{-2}a^{-1}	Org.N export kg km^{-2}a^{-1}
1 Hulubäcken	40.1	-	-
2 Däntersta	75.6	22.2	355
3 Nolsjön	35.0	-	-
4 Stormyra	69.9	-	-
5 Buskbäcken	63.1	-	-
6 Kullarna[1]	47.3	25.5	219
7 Övre Kullarna	5.8	11.1	134
8 Sniptjärn[1]	133.0	55.9	273
9 Lilla Tivsjön	37.3	-	-
10 Norrsjön	16.0	-	-
11 Vuoddasbäcken	23.2	-	-
12 Solmyren	16.6	-	-
13 Teeressuonoja	124.6	7.9	137
14 Huhtisuonoja	30.2	25.9	110
15 Paunulanpuro	46.7	7.5	167
16 Pahkaoja	23.3	27.0	194
17 Murtopuro[2]	3.2	4.3	201
18 Murtopuro[3]	27.3	25.9	441
19 Koivupuro[2]	2.1	2.6	112
20 Koivupuro[3]	12.9	32.5	210
21 Myllypuro	7.8	2.7	165
22 Vähä-Askanjoki	18.6	8.3	126

[1] post-treatment period 1981-88
[2] pre-treatment period 1979-82
[3] post-treatment period 1983-88

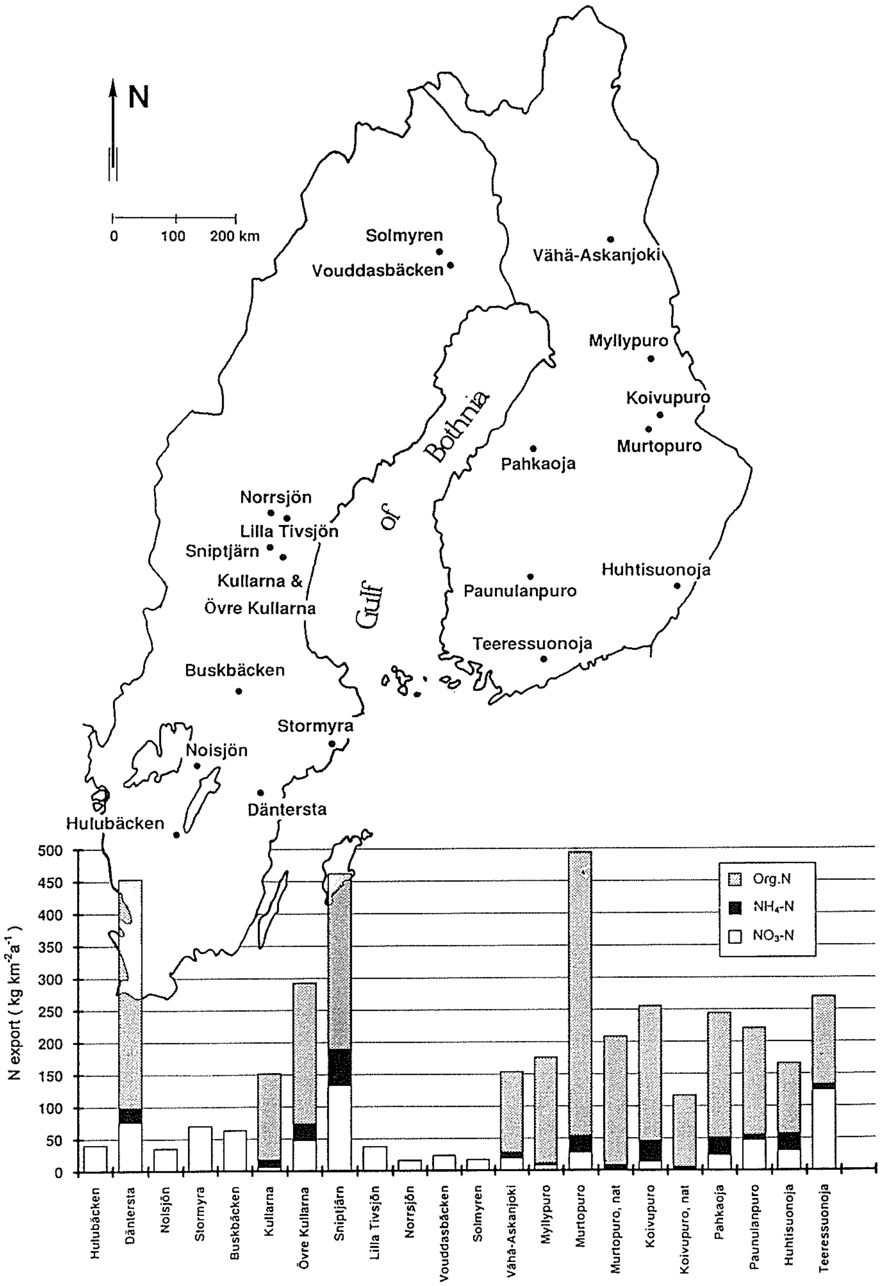

Fig. 18. Calculated average export of different nitrogen fractions (1979–1988) in the study catchments in Finland and Sweden. For eight of the Swedish catchments, only NO_3-N was available. For Murtopuro and Koivupuro, pre- (1979–1982) and post- (1983-1988) treatment export are shown. For Kullarna and Sniptjärn the mean export for the post-treatment period (1981–1988) is presented.

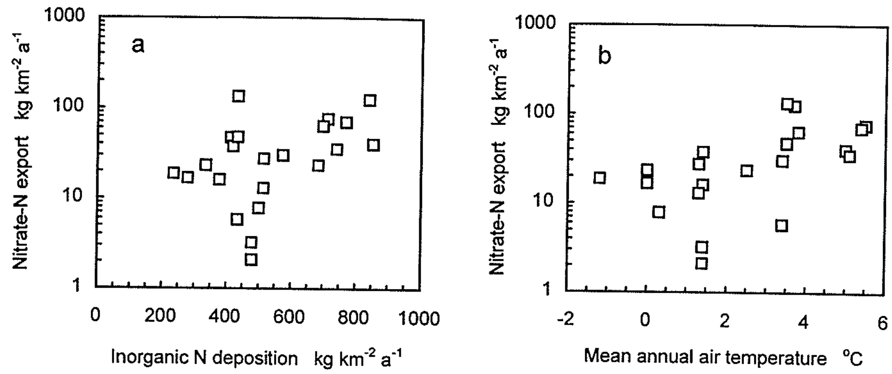

Fig. 19. NO_3-N export as a function of **a)** inorganic N deposition and **b)** mean annual temperature. All catchments (n=20+2) were included.

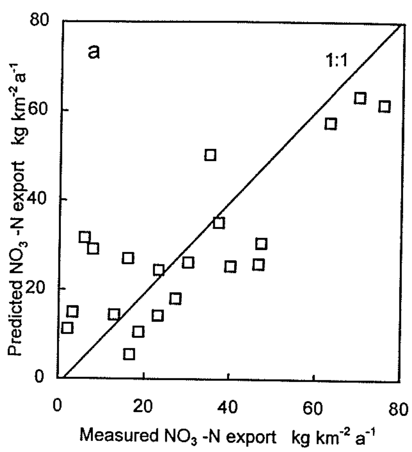

Fig. 20a) Comparison of measured and predicted NO_3-N export as a function of N-deposition and organic soils (Eq.9; NO_3-N export= −1.7 + 0.09 N_DEP − 0.53 ORGSOIL). All catchments except Sniptjärn and Teeressuonoja are included.

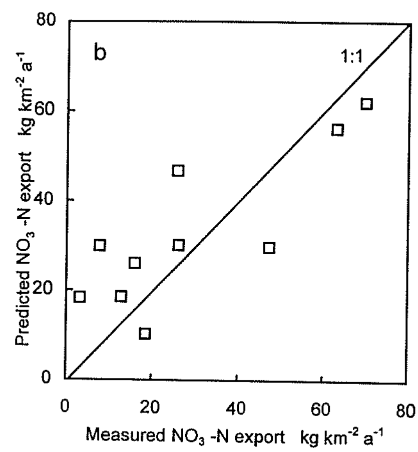

Fig. 20b) Comparison of measured and predicted NO_3-N export as a function of N-deposition and organic soils. The model was generated using one half of the data (NO_3-N export= −3.8 + 0.09 N_DEP − 0.42 ORGSOIL) and predictions were made with the other half.

Fig. 20a shows the comparison between measured and predicted (Eq. 9) loss. Furthermore, the model was tested by the use of half the data to generate the model and the other half to validate it and the results were adequate (V) (Fig. 20b).

Inorganic N deposition and temperature. Atmospheric N-deposition was of significant importance for the nitrate leaching losses. However, the strong correlation with air temperature made it difficult to distinguish the effect of one variable from the other. Higher temperatures in the south correlate with more productive stands and a higher deposition of N, and thus the turnover of nitrogen should generally be more rapid in the southern catchments. The detailed studies (I,III) showed that the NO_3-N concentration in Teeressuonoja and Yli-Knuutila has undergone a significant increase during 20–25 years, increased N-deposition being the major affecting factor. Neither Teeressuonoja nor Yli-Knuutila were included in the above equation, however, because of their potential to have an overriding influence on parameter estimates.

Retention of the inorganic N deposition (calculated as [(input-output) / input] of NO_3-N and NH_4-N) (Kämäri et al. 1992a) in the 12 catchments for which data of all fractions of nitrogen were available, varied between 0.56 (Sniptjärn) and 0.99 (Koivupuro, pre-treatment), with a median of 0.93. For all 20 catchments, the median of nitrate retention was 0.93, with a minimum of 0.69 and a maximum of 1.00. Of the catchments without forest management, the lowest retention was at Teeressuonoja, where inorganic N export was 16% of inorganic N deposition. In southern catchments variation is large, in Hulubäcken in southern Sweden with 94% organic soils, retention of N deposition was almost total. At Teeressuonoja in southern Finland, with only 13% of organic soils and receiving about the same N deposition, the average NO_3-N export flux was over threefold. Retention was generally high, and most of the studied catchments can still accumulate incoming deposition into the biomass or soil.

Physiographic factors. A high extent of organic soils was correlated to lower losses of NO_3-N. Mass balances of catchments with high percentages of organic soils suggest high retention of NH_4-N and NO_3-N (Kallio and Kauppi 1990a). According Gundersen (1992), at high C/N ratios in soil organic matter there may be more C readily available for microbes. Available C increases the potential for immobilization of N by the microflora, and thus C availability may be a very important factor for the capacity of soils to retain N. Retention of N might also be due to the fact that in organic soils, denitrification is promoted since the soils are often saturated and there is a plentiful supply of organic matter available as an energy source for the bacteria. Nitrification may be inhibited due to acidic soil (e.g. Alexander 1980) or certain organic compounds (e.g. Martikainen 1986), also restricting the possibility for nitrate loss.

High losses were also related to high stream density. A high stream density promotes short transit times. With a higher stream density, it might be assumed that a greater part of the atmospheric nitrogen deposition reaches the stream water without transformations, affecting the stream nitrate concentrations.

Forestry activities. The effect of clear-cutting was mainly due to increased runoff volumes, as evidenced by the lack of correlation between concentrations and clear-cutting, while correlation existed between exports and clear-cutting percentage (V). It has been stated that considerable nitrification in coniferous forests is possible after clear-cutting (Tamm et al. 1974), when plant nutrient uptake is decreased and pH is increased. However, clear-cutting was only significant if Sniptjärn was included. This indicates that in a regional comparison of catchments with different climatic and physiographic characteristics, only very extensive clear-cutting will be a significant explaining factor of regional differences.

The magnitude of the nitrate output increase following clear-cutting varies e.g. with site fertility and the status of the ground flora. According Stevens and Hornung (1990), the duration of the enhanced nitrate ouput seems to be controlled mainly by the rate of groundflora development. Studies in North America (e.g. Vitousek et al. 1982) have linked the magnitude and duration of losses following felling to the age of the forest and site fertility. Generally, NO_3-N export increases immediately after clearcutting; the results of this study also indicate that because of the short-term effect, only very high percentages of clear-cutting affect 10-year means on a regional scale.

4.2.2 Factors associated with release of ammonium-N

The export of NH_4-N was generally lower than that of NO_3-N. There were however some exceptions, including catchments both with and without intensive forestry activities. The export varied between 2.6 and 56 kg $km^{-2}a^{-1}$ (Table 7, V) with a median of 16.7 kg $km^{-2}a^{-1}$. Regression runs were made without the most intensively (90%) clear-cut catchment, Sniptjärn, which had the highest NH_4-loss and the potential to have an overriding influence on parameter estimates. For the remaining catchments the 'best' equation (R^2 =0.53) was:

$$NH_4\text{-N export (kg km}^{-2}\text{a}^{-1}) = 4.7 + 0.6\ \text{DRAIN} + 3.2\ \text{TEMP} \quad (10)$$

where DRAIN = drainage percentage of a catchment, and TEMP = average annual temperature (°C).

Forestry activities. High ammonium-N losses had the strongest correlation with forestry activities and variables related to such activities. The effects of drainage were clearly seen in Murtopuro and Koivupuro in eastern Finland, where losses were 5-10 times higher during the post-treatment period and considerably higher than in a reference area (Ahtiainen 1992). This supports the observation that drainage of organic soils causes increased mineralisation in the aerated soil profiles, but since the environmental conditions (pH) conducive to nitrification are not present, this ammonium nitrogen will remain in an available form, leading to increased outflow of ammonium (Sikora and Keeney 1983). If the extremely clear-cut catchment Sniptjärn was included, the model included clear-cutting percentage instead of drainage. Both activities often took place in the same catchments, making it hard to separate the two effects. However, clear-cutting increases the water flow significantly, which explains why this factor is important for the export. Increased mineralization following clear-cutting was described e.g. by Grip (1982), who reported that the leaching of ammonia increased about 10 times during the three years studied.

Temperature was an explanatory variable for concentrations of ammonium-N. This indicates that in otherwise similar catchments, a higher productivity and more rapid nitrogen turnover leads to a higher amount of nitrogen available for leaching from the soil.

4.2.3 Factors associated with release of organic N

The major part of the total N transported from the catchments consisted of organic-N. This fraction was 1–20 times higher than the others. Export of organic-N varied between 110 and 441 kg km^{-2}a^{-1}, with a median of 181 kg km^{-2}a^{-1} (Table 7, V). There were significant correlations between average organic-N export and forestry activities in the form of clear-cutting and drainage. The regression runs for organic N losses resulted in an equation with two variables included and an R^2 of 0.81:

$$\text{Org.N export (kg km}^{-2}\text{a}^{-1}) = 140 + 4.2\ \text{DRAIN} + 1.3\ \text{CLEARC} \quad (11)$$

where DRAIN = drainage percentage of a catchment, and CLEARC = clear-cut percentage of a catchment.

The most important factors explaining spatial variability of organic-N leaching were found to be forestry activities in the form of drainage and clear-cutting. In addition, extreme runoff dynamics and a high air temperature promoted high leaching losses.

Forestry activities. The effect of drainage on organic-N export is supported by Eq. 11. Drainage percentage alone explained 67% of the skewed variation. There was no significant correlation between export values and either stream density or previous drainage (r=-0.34). This indicates that the increased losses were to a large extent direct effects of increased erosion due to the drainage activities. In spite of the cuttings which took place in the intensively drained catchments Murtopuro and Koivupuro, and a somewhat higher precipitation during the post-treatment period, no significant increase in runoff was observed and the increase of the export was comparable with that of concentrations.

Clear-cutting showed a significant correlation with organic N losses, but not with concentrations. This indicates that the effect of clear-cutting is mainly caused by increased runoff. The sudden removal of the forest cover results in a number of changes in, for example, canopy-atmosphere interactions, plant uptake, decomposition rates and evapotranspiration (Hornung et al. 1988). Compared with drainage, the effects of clear-cutting on organic-N losses are probably not as important in the long term, because of less impact on erodibility. In the Hubbard Brook Forest in the United States (Bormann and Likens 1979), large increases of particulate matter were observed during 4–5 years after clear-cutting, after which the system began to recover. In the Nurmes study including the Murtopuro and Koivupuro catchments in eastern Finland, it was shown that the concentrations and losses of organic-N increased considerably after clear-cutting and drainage (Ahtiainen 1992), but the duration of the effect still remains to be seen.

5 Hydrology of a catchment affecting N dynamics and leaching

5.1 The role of contributing areas as sources/sinks of nitrate-N

Contributing, saturated areas may have a high potential to regulate nutrient fluxes between upland areas and the stream. Groundwater is frequently present at a shallow depth beneath the contributing (riparian) area and vegetation and soil processes may therefore modify the chemistry of groundwater before it enters the stream (Swanson et al. 1982, Lowrance et al. 1985). One might assume that atmospheric nitrogen deposition on saturated contributing areas will contribute more or less instantly to the nitrogen leaching during flow events (Löfgren 1991). This might be an important link between high stream density and increased nitrate N leaching from the forested soils.

As a hypothesis, it was assumed that contributing areas might play an important role in nitrate leaching from a forested catchment. The hypothesis was tested in the catchment 8 Rudbäck (VII). It was assumed that all the nitrate N deposited on saturated, contributing areas was flushed relatively quickly (as quickflow) to the streams, while nitrate N deposited on 'non-contributing' areas was infiltrated to the soil layers or retained by the biomass. The annual dynamics of contributing areas were estimated on the basis of the isotopic method (VII).

A simple two-component model (Eq. 4) was established for estimating annual variation of nitrate nitrogen (monthly concentration) in streamwater, using monthly observed NO_3-N concentrations in precipitation and a stable NO_3-N concentration level in groundwater: In 1991–92, monthly NO_3-N concentration in precipitation varied between 170 and 1330 $\mu g\ l^{-1}$ with an average of 560 $\mu g\ l^{-1}$. Runoff from the non-contributing areas was assumed to have a stable concentration of 24 $\mu g\ l^{-1}$, based on the two-year 1991–92 average of groundwater measured from the tube R7 inside the catchment. Fig. 21 shows the comparison between observed and modelled monthly values. The two-component model roughly explained the annual dynamics of nitrate concentration in streamwater. However, the model only takes into account the hydrological separation of the catchment into 'active' and 'non-active' parts. Nutrient uptake, biochemical processes and retention/fractionation in the snowpack are not in-

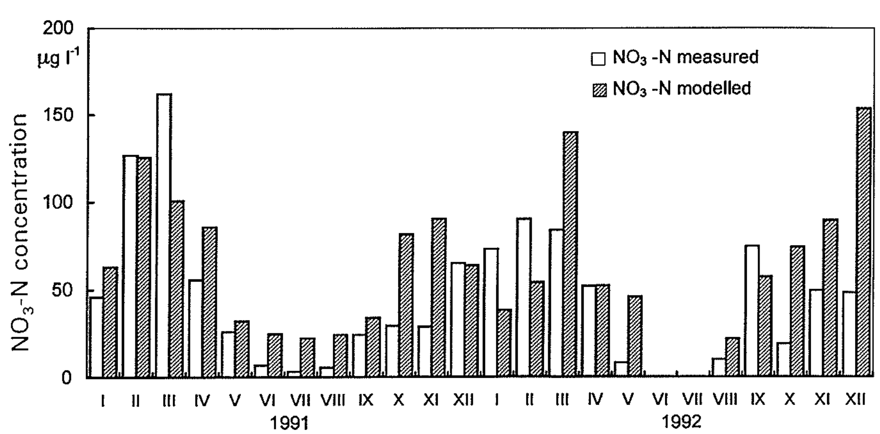

Fig. 21. Measured and modelled monthly mean NO_3-N concentration during the years 1991–92 in the catchment 8 Rudbäck.

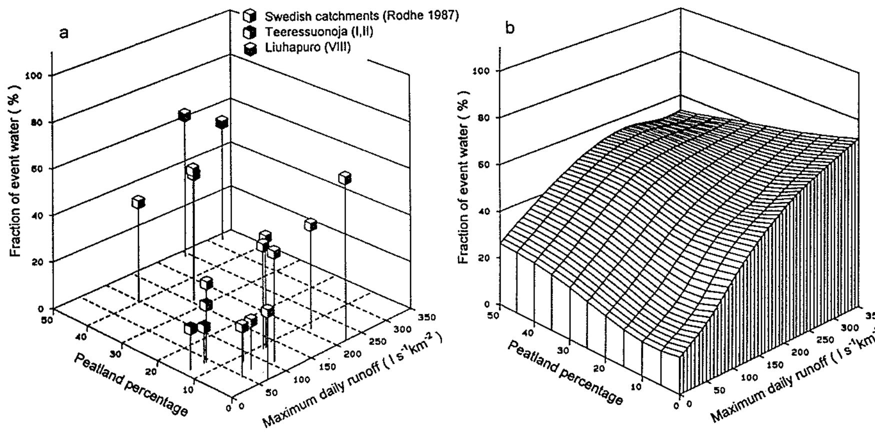

Fig. 22. The fractions of runoff consisting of event water during snowmelt periods, as a function of peatland percentage and maximum daily runoff (l $s^{-1}km^{-2}$) in peaty forest catchments in Scandinavia (Rodhe 1987; I; II; VIII). **a)** shows the observed points and **b)** shows the interpolated surface of the distribution.

cluded. In the mild winters of these years there was no marked retention in the snowpack. During the summer of 1991 modelled values were clearly higher than the measured ones, biological factors and nutrient uptake by the biomass being the most obvious explaining factors.

It is probable that atmospheric nitrogen deposition on saturated, contributing areas will contribute more or less instantly to the nitrogen loading during flow events, at least in shallow mineral soil catchments where open bedrock exists, because of the fact that a simple two-component model was able to describe the major part of the annual dynamics of nitrate nitrogen. These contributing areas are hypothesized to potentially contribute to increased leaching of nutrients in changed climatic conditions.

5.2 Assessment of the role of organic soils affecting hydrology and the leaching of nitrate-N

A high percentage of organic soils seemed to be a factor which contributes to high amounts of recent event water (VIII), but low amounts of released nitrate from a catchment (V).

One might assume that the higher is the fraction of saturated, contributing areas within the catchment, the higher will be leaching of easily mobilized nitrate from the catchment. In a study of 20 catchments, there was a significant positive correlation ($r=0.51$, $P<0.01$) (V) between nitrate-N export and the stream density of a catchment, which is related to the fraction of contributing areas. With a higher stream density, it is probable that during the dormant season a greater part of atmospheric N deposition reaches the streamwater with minor transformations.

It is probable that increase of the above contributing area fraction increases possibilities for leaching, but only to a certain limit, above which retention processes start to dominate the N cycling.

Fig. 22a shows a 3-d plot of event water fraction as a function of organic soils percentage and maximum daily runoff during snowmelt, based on isotope hydrograph separations reported in the papers I, II and VIII and by Rodhe (1987). Regionalization of the results was also discussed in section 3.1.3. Fig. 22b shows an interpolated surface based on the observations. Maximum runoff during snowmelt is the most important affecting factor, but high percentages of organic soils are also related to high fractions of event water. It is suggested that surface storages and surface-

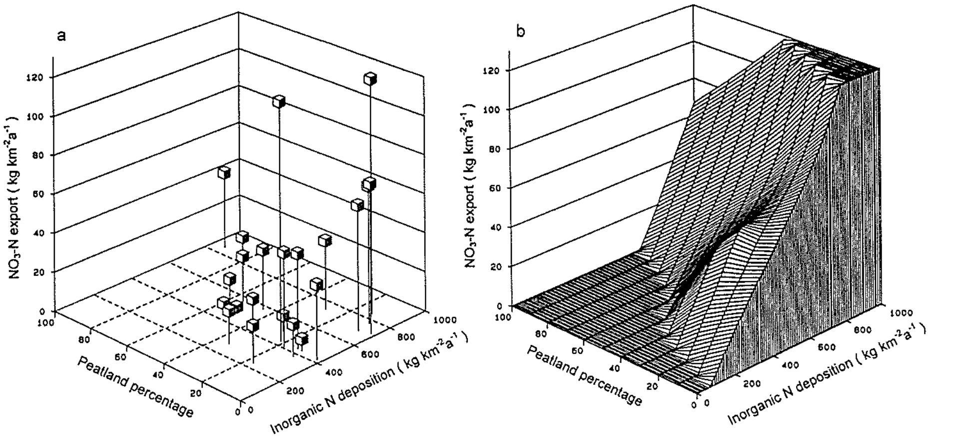

Fig. 23. NO_3-N export (kg km^{-2}a^{-1}) as a function of inorganic N deposition (kg km^{-2}a^{-1}) and percentage of organic soils. **a)** shows the observed points and **b)** shows the interpolated surface of the distribution.

saturated areas play a major role in explaining quickflow and high event water contributions to the stream.

In the case of nitrate leaching, however, higher percentages of organic soils lead to higher retention processes of N, making less N available for leaching (Figs. 23ab, Eq. 9,V). In peatlands, NO_3^- is used by plants during growth, by NO_3^- reduction, and by denitrification. Because of this biogeochemical reactivity, nitrate-N inputs are efficiently retained by peatlands, and the concentrations of NO_3^- and dissolved organic N in peatland waters are low (Hemond 1983, Gorham et al. 1984, Urban and Eisenreich 1988). In central Finland, Sallantaus (1992) found that the Lakkasuo catchments retained total N provided by deposition or groundwater very efficiently (65–80%). In natural mires, leaching of organic nitrogen is practically the only mechanism of nitrogen loss from the ecosystem in addition to fire (Sallantaus 1994), because of the almost total lack of N_2O emissions suggests very low denitrification rates (Martikainen et al. 1993). Urban and Eisenreich (1988) found that the N cycle of a forested bog in northern Minnesota was dominated by internal regeneration and plant uptake. In this bog, approximately 65% of the N inputs were efficiently retained.

6 Summary

A fundamental premise of many hydrochemical studies is that hydrological processes – the source, pathway and residence time of water – in a catchment exert a strong control on the water chemistry and nutrient export. The higher the fraction of recent, event water in the runoff, the higher is the theoretical response of a catchment to a change in the amount of atmospheric deposition. Streamflow generation processes and contributing areas of the event water were hypothesized to be important both hydrologically and in connection with leaching of nitrogen from the forest soils to watercourses. In order to obtain information about hydrological processes which might be relevant in this context, isotopic hydrograph separations on an event and annual basis were made, as well as estimates of the contributing areas in the catchment. Seasonal patterns of N concentrations as well as factors affecting temporal and spatial variability of N leaching were investigated. In the following, the major findings are summarized.

1. In the mineral soil forested catchment (Teeressuonoja), the isotope studies using oxygen-18 showed that snowmelt runoff consisted to

a considerable degree of *pre-event water* (75–85%) being expelled from the catchment by infiltrating 'new' meltwater. In the study years the total snowmelt runoff and peakflows were smaller than the long term averages. It can be expected that in the case of higher runoff the fraction of the *event water* (15–25% in this study) would be somewhat greater.

2. In the peatland catchment (Liuhapuro), the average computed fraction of event water in the stream during snowmelt was clearly higher, 55–65%. Except for urban, agricultural or permafrost catchments, the event water fractions of Liuhapuro were among the highest recorded in natural forested catchments. The amount of snow was the most important factor explaining variation between the years. As a consequence of the limited storage capacity of the surface layers, surface runoff responded rapidly to high melt intensities and surface-saturated peat areas also acted as 'reservoirs' for mixing of 'old' water and new meltwater.

3. In an attempt to regionalize factors affecting runoff generation, results of the above isotope hydrograph separations during snowmelt were compared with results from Swedish catchments (Rodhe 1987). Results from 21 snowmelt periods and 12 catchments were included in the comparison. The event water fraction of the runoff, having a range of 10–65%, appeared to increase together with high percentages of peatland. Percentages of peatland and maximum streamflow during the melt period explained 42% and 60% of the variation of the event water fraction, respectively.

4. Storm events were studied using the isotope methods in the Rudbäck catchments in Siuntio. Only in response to a very intense storm were streams dominated by 'new' rainwater. Event water fraction increased together with increasing rainfall volume and runoff intensity. The annual event water fraction corresponded to 10–20% of the total runoff in the sub-catchment 8 Rudbäck, with low soil depths and relatively high percentages of open bedrock.

5. The increase in the size of the discharge area (contributing area) seemed to be essential for producing both large pre-event and event water contributions to the stream. Saturation-excess 'overland' flow and sub-surface storm flow (mostly pre-event water) probably, in many cases, dominate runoff generation in boreal, undisturbed forested catchments where till soils dominate.

6. Modelled monthly fractions of saturated contributing areas were compared to the estimates obtained by isotopic methods (Rudbäck, Siuntio). During some months differences were detected, but in general the annual dynamics of saturated contributing areas was acceptable. When comparing the range of computed new water-contributing areas (0–17%) to areas of likely surface saturation, i.e. peatland area, channel area and areas close to saturation, it was found that the computed range was quantitatively consistent with expected saturated areas. The average percentage of estimated new water-contributing areas of 4–5% (0.7–0.9 ha) was also close to the peatland percentage of 6% (1.1 ha).

7. A simple two-component model was established for estimating annual variation of NO_3-N in streamwater, using monthly observed NO_3-N concentrations in precipitation and a stable NO_3-N concentration level in groundwater: The model was based on the assumption that all the nitrate N deposited on saturated, contributing areas was flushed relatively quickly (as quickflow) to the streams, whereas nitrate N deposited on 'non-contributing' areas was infiltrated to the soil layers or retained by the biomass. The two-component model roughly explained the annual dynamics of streamwater nitrate concentration of the Rudbäck catchment.

8. Ten years of monthly concentration and daily flow measurements from 20 forested catchments (0.3–42 km^2) in Finland and Sweden were used to study the influence of flow and seasonality on N concentrations. One third of the catchments had significantly higher nitrate N concentrations during periods of increasing flow compared with stable or decreasing flow. The main reasons for increased NO_3-N concentrations during spring flow are release of NO_3-N accumulated in the soil

and release of concentrated, nitrate-rich meltwater, in which N is derived from the dry and wet atmospheric deposition.

Two thirds of the catchments studied had significantly lower NO_3-N concentrations during the summer low flows, with biological uptake being the most obvious explanation. Important sources of mobile NO_3-N to surface waters during the dormant season are mineralisation of soil organic-N followed by nitrification, and atmospheric deposition. Those catchments with no significant differences between concentrations during the growing and dormant seasons were exposed to higher inorganic-N deposition.

9. In 5 of the 15 forested catchments studied in Finland and Sweden, the trend analysis showed upward trends of nitrate N concentration during the period 1971 to 1988 (Lepistö et al. 1991). Temporal variation of leaching of N was studied more in detail in two catchments in southern Finland. In Yli-Knuutila, the volume-weighted average concentration of NO_3-N increased over twofold, from 580 $\mu g\ l^{-1}$ in 1969–79 to 1 350 $\mu g\ l^{-1}$ in 1980–90. In Teeressuonoja, the nitrate levels were lower but the increasing trend was comparable to that of Yli-Knuutila. The largest increase of concentrations of NO_3-N occurred from the mid-1970s to the mid-1980s. The total nitrogen streamwater output of Yli-Knuutila increased almost threefold, from 1.1 kg N $ha^{-1}a^{-1}$ in 1969–79 to 2.9 kg N $ha^{-1}a^{-1}$ in 1980–90. The average proportion of the NO_3-N output of the total nitrogen output increased during the same period from 56% to 68%.

10. Decreasing retention was reflected in the input-output budget of inorganic N at Yli-Knuutila; output divided by input increased from 12% during the 1970s to 24% during the 1980s. Net accumulation of N by the stand was estimated to be relatively stable during the 1970s and 1980s. Increased leaching in the Yli-Knuutila and Teeressuonoja catchment streams indicates the effects of increased nitrogen deposition. The increase in nitrate leaching in Yli-Knuutila, particularly during the summer months, provides evidence of nitrogen saturation and the inability of the biomass to utilize the N available, whereas increase during snowmelt and the autumn period indicates the impact of N deposition. The forest of Yli-Knuutila is of Oxalis-Myrtillus (OMT) type, which is the second most fertile type in Finland and accounts for 16.3% of the forest soils of southern Finland, and can be assessed to represent the relatively fertile forest ecosystems in southern Finland.

11. Data from the 20 forested catchments (0.3–42 km^2) in Finland and Sweden were used, in order to develop multivariate regression models capable of explaining spatial variation in nitrogen export fluxes as a function of geomorphological, meteorological, hydrological, deposition and forest management variables, and in order to predict the average export of different nitrogen fractions from forested catchments in the Nordic conditions. A combination of high inorganic N deposition or air temperature and a low extent of organic soils was related to (R^2=0.63–0.64) high losses of NO_3-N. A strong correlation between N deposition and air temperature makes it difficult to distinguish the effects of one variable from the other. High losses of NH_4-N had the strongest correlation with forestry activities. A combination of drainage percentage and temperature was related to (R^2=0.53) losses of NH_4-N. The most important factors explaining spatial variability of organic N losses were clearly forestry activities. A combination of high percentage of drainage and clear-cutting was clearly related to (R^2=0.81) high organic N losses.

7 Concluding remarks

A high percentage of organic soils seemed to be a factor contributing to high amounts of recent, event water, but low amounts of released nitrate N from a catchment. It seems probable that increase of the contributing area fraction increases possibilities for leaching, but only to a certain limit, above which retention processes start to dominate the N cycling. The results of this study suggest that retention of deposited nitrogen is still high in most of the catchments. Particularly in organic soils retention is very effective. In Finland, losses of nitrate to watercourses are expected to increase mainly from the most fertile forest ecosystems (MT and OMT site type) in southern and central parts of the country where N deposition is also highest. Further efforts to develop NO_x emission controls in order to reduce the effects of N deposition are needed.

It seems obvious that only by using integrating distributed models together with experimental studies, including tracers and hydrochemical variables, and internal variables such as groundwater levels and extensions of saturated areas, can a more detailed understanding of physical processes behind streamflow generation be reached. Since the main objective for increasing knowledge about streamflow generation processes and incorporating this information into hydrological models is to reach a better understanding of hydrochemical processes, it is a great advantage if physical, chemical and biological processes can be studied simultaneously.

Saturated, contributing areas along the streams (riparian zones) may have a high potential to regulate nutrient fluxes between upland areas and the stream. Groundwater is frequently present at a shallow depth beneath the riparian area, and vegetation and soil processes may therefore modify the chemistry of groundwater before it enters the stream. These areas play an important role, having a potential to capture nitrate leached from upper parts of catchments either by nutrient uptake or denitrification, or to transport it further to watercourses. More effort should be devoted to studies of these areas, using models, GIS and empirical methods, and to the incorporation of the information into practical forest management and water pollution control.

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To my wife and children
To my parents

Helsinki, January 1996 Ahti Lepistö

Yhteenveto

Hydrologiset prosessit – veden alkuperä, kulkureitit ja viipymä valuma-alueen maaperässä – vaikuttavat merkittävästi valumaveden laatuun ja ravinteiden huuhtoutumiseen. Mitä suurempi on 'uuden' lumensulamis- ja/tai sadeveden osuus valunnassa, sitä herkemmin alueen voidaan arvioida reagoivan muutoksiin laskeuman määrässä. Valunnan muodostumisprosesseilla ja -alueilla on merkitystä sekä puhtaasti hydrologisessa mielessä että tarkasteltaessa aineiden huuhtotumista metsämaaperästä vesistöihin. Isotooppimäärityksiin perustuvia valunnan erotusanalyyseja tehtiin toisaalta lumensulamis- ja sadetapahtumille, toisaalta vuositasolla. Valuntaan vaikuttavan alueen dynamiikkaa tarkasteltiin perustuen isotooppimäärityksiin ja mallinnukseen. Typpipitoisuuksien vuodenaikaisvaihtelua, sekä huuhtouman ajalliseen ja alueelliseen vaihteluun vaikuttavia tekijöitä selvitettiin. Seuraavassa on lyhyt yhteenveto päätuloksista:

1. Moreenivaltaisella metsävaluma-alueella (Teeressuonoja, Vihti) osoitettiin isotooppitutkimuksiin perustuen, että sulamisvalunta oli suureksi osaksi (75–85%) *esivettä*, ennen sulamista maaperässä ollutta vettä, joka purkautui vesiuomiin yhdessä sulamisvesien kanssa. Tutkimusvuosina sulamishuiput olivat pienempiä kuin pitkällä aikajaksolla keskimäärin havaitut. Voidaan olettaa, että suurempien sulamishuippujen yhteydessä uuden, lumensulamisesta välittömästi peräisin olevan veden, *uusiveden*, osuus (joka nyt oli 15–25%) olisi jonkinverran suurempi.

2. Suovaluma-alueella (Liuhapuro, Nurmes) uusiveden osuus oli lumensulamiskausina selvästi suurempi kuin edellä, 55–65 %. Lumen määrä oli tärkein eroon vaikuttava tekijä eri vuosien välillä. Suoalueen pintakerrosten vedenvarastointikapasiteetti on vähäinen, joten voimakas sulamisen intensiteetti johti valuntaan turpeen pintakerroksissa. Pääosa esiveden ja uusiveden sekoittumisesta tapahtui näillä tasaisilla, lähes maanpintaan asti kyllästyneillä turvealueilla.

3. Pyrkimyksenä alueellistaa valunnan jakautumiseen vaikuttavia tekijöitä, em. tuloksia sulamiskausilla verrattiin Rodhen (1987) tuloksiin ruotsalaisilta valuma-alueilta. Tarkastelussa oli mukana kaikkiaan 12 valuma-aluetta ja 21 sulamisjaksoa. Uusiveden kokonaisvaihteluväli oli 10–65 %, osuuden lisääntyessä epälineaarisesti,valuma-alueen suoprosentin ja kevättulvan volyymin kasvaessa. Suoprosentti selitti vaihtelusta 42 % ja suurin havaittu vuorokausivalunta sulamisjaksolla vastaavasti 60 %.

4. Sadetapauksia tutkittiin kolmella moreenivaltaisella valuma-alueella (Rudbäck, Siuntio). Ainoastaan huomattavan rankkojen sateiden seurauksena (n. 80 mm d^{-1}) 'uusi' sadevesi dominoi valuntaa uomissa. *Uusiveden* osuus lisääntyi sademäärän ja sateen intensiteetin lisääntyessä. Vuositasolla uusiveden, jonka viipymä maaperässä on alle kuukausi, osuus oli 10–20 % kokonaisvalunnasta eräällä osavaluma-alueista (8 Rudbäck), jonka maakerrokset ovat suhteellisen ohuita ja kalliopaljastumien osuus suuri. Osuuden vaihtelu eri kuukausina oli 0–35 %, lukuunottamatta elokuuta 1991, jolloin 180 mm:n sadanta johti 65 %:n osuuteen valunnasta.

5. Purkautumisalueilla on merkittävä rooli valuma-aluehydrologiassa, ne voivat toimia alueina, joilla maaperästä purkautuva esivesi, ja 'uusi' sade- tai sulamisvesi sekoittuvat. Pintavalunta orgaanisessa kerroksessa vedellä kyllästyneellä alueella, ja maanalainen valunta valuma-alueen ylemmistä osista, ovat tärkeitä valunnan syntymekanismeja boreaalisilla luonnontilaisilla, moreenivaltaisilla metsäalueilla.

6. Purkautumisalueiden, valuntaan vaikuttavien alueiden, dynamiikkaa tarkasteltiin vertaamalla topografisen TOPMODEL- valuma-aluemallin ja isotooppimenetelmän tuloksia (Rudbäck'in alue Siuntiossa) kuukausittain. Eri menetelmillä päästiin samansuuntaiseen tulokseen, mutta yksittäisinä kuukausina havaittiin eroja eri menetelmien välillä. Keskimäärin purkautumisalueiden osuus oli 4–5 % alueen pinta-alasta vastaten suon (6 %) osuutta alueesta. Arvioitu osuus vaihteli kuukausittain välillä 0–17 %.

7. Nitraattitypen vuosivaihtelua kuvattiin kaksikomponentti -mallilla: purkautumisalueella (contributing area) kerrotaan deposition pitoisuus, sekä oletetaan valuma-alueen muista osista huuhtoutuvalle typelle kyllästyneestä vyöhykkeestä mitattu vakiopitoisuus. Malli perustuu yksinkertaistukseen, että kaikki deposition nitraattityppi huuhtoutuu nopeasti uomiin vedellä kyllästyneillä purkautumisalueilla, kun taas valuma-alueen muissa osissa, imeytymisalueilla, kaikki infiltroituu tai pidättyy biomassaan. Mallilla pystyttiin kuvaamaan pitoisuuden dynamiikkaa tyydyttävästi, mikä viittaa purkautumisalueiden merkitykseen myös ainevirtojen kannalta.

8. Valunnan ja vuodenaikaisvaihtelun vaikutusta typpipitoisuuksiin tarkasteltiin kymmenen vuoden pitoisuus- ja valunta-aineistosta, 20 metsävaluma-alueelta (0,3–42 km^2) Suomessa ja Ruotsissa. Seitsemällä valuma-alueella NO_3-N -pitoisuudet olivat merkitsevästi korkeampia valunnan lisääntyessä, verrattaessa tilanteisiin joissa valunta on stabiili tai laskeva. Tähän vaikuttaa maaperään talven aikana kertyneen nitraatin huuhtoutuminen sekä lumipeitteeseen kertyneen typpilaskeuman fraktioituminen ja huuhtoutuminen vesiuomiin.

Kahdella kolmasosalla valuma-alueista NO_3-N -pitoisuudet kesäalivalumakausina olivat kasvillisuuden ravinteidenoton takia merkitsevästi pienempiä. Syys-talvikaudella nitraattityppi on peräisin joko maaperästä, mineralisaation ja nitrifikaation seurauksena, tai laskeumasta. Neljä valuma-aluetta, joilla ei havaittu merkittäviä eroja kasvukauden ja syys-talvikauden (dormant season) pitoisuustason välillä, olivat alttiina suuremmalle typpilaskeumalle.

9. Aikaisemmassa selvityksessä (Lepistö ym. 1991) havaittiin, että viidellä metsävaluma-alueella 15:sta nitraattitypen pitoisuuksissa oli nouseva trendi jaksolla 1971–1988. Typpihuuhtouman ajallista vaihtelua tutkittiin yksityiskohtaisemmin kahdella lähes luonnontilaisella metsävaluma-alueella Etelä-Suomessa 1960-luvulta vuoteen 1990. Toisella alueista (Yli-Knuutila) valunnalla painotettu nitraattitypen keskimääräinen pitoisuus oli vuosina 1980–90 yli kaksinkertainen (1350 $\mu g\ l^{-1}$) verrattuna jaksoon 1969–79 (580 $\mu g\ l^{-1}$). Suurin nousu pitoisuuksissa havaittiin jaksolla 1970-luvun puolivälistä 1980-luvun puoliväliin. Kokonaistypen huuhtouma kasvoi lähes kolminkertaiseksi, keskimääräisestä arvosta 1,1 kg N $ha^{-1}a^{-1}$ vuosina 1969–79 arvoon 2,9 kg $ha^{-1}a^{-1}$ vuosina 1980–90. Verrattaessa vastaavia jaksoja havaittiin, että nitraattitypen osuus kokonaistypen huuhtoumasta lisääntyi 56 %:sta 68 %:iin. Viereisellä valuma-alueella (Teeressuonoja) nitraattitypen pitoisuustaso on matalampi, mutta nouseva, merkitsevä trendi havaittiin vastaavasti kuin Yli-Knuutilan alueella.

10. Epäorgaanisen typen ainetaseessa kuvastui vähenevä laskeuman pidättyminen Yli-Knuutilan valuma-alueen maaperään; huuhtouma (output) jaettuna laskeumalla (input) kasvoi 12 %:sta 1970-luvulla 24 %:iin 1980-luvulla. Typen nettoakkumulaatiossa puuston biomassaan ei ollut merkittäviä muutoksia 1970- ja 1980 -luvuilla. Lisääntyvä nitraattitypen huuhtoutuminen indikoi typpilaskeuman vaikutusta metsäekosysteemiin. Verrattaessa 1970- ja 1980-lukuja, havaittiin että lisääntyvä huuhtoutuminen erityisesti kesäkuukausina viittaa ekosysteemin 'kyllästymiseen' typellä, jolloin kasvillisuus ei enää pysty pidättämään kaikkea ylimääräistä typpeä. Lisääntyvä huuhtoutuminen syys-talvikaudella ja lumensulamisen yhteydessä, jolloin veden viipymä metsämaaperässä on lyhyempi, indikoi sitä, että suurempi osuus epäorgaanisen typen laskeumasta huuhtoutuu vesiuomiin. Yli-Knuutilan valuma-alue on metsätyypiltään pääosin käenkaali-mustikkatyyppiä (OMT), joka on toiseksi rehevin metsätyypeistämme ja kattaa 16 % metsämaaperästä Etelä-Suomessa.

11. Kahdeltakymmeneltä metsävaluma-alueelta (0,3–42 km^2) Suomesta ja Ruotsista kerättiin

aineisto alueiden ominaispiirteistä, eräistä meteorologisista ja hydrologisista muuttujista, metsätaloustoimenpiteistä ja epäorgaanisen typen laskeumasta, jaksolla 1979–1988. Aineistoon perustuen muodostettiin empiirisiä monimuuttujayhtälöitä selittämään typpihuuhtoutuman alueellista vaihtelua. Yhtälöitä voidaan käyttää pohjoismaiden olosuhteissa arvioitaessa huuhtoutumista alueilla, joilta ei ole käytettävissä havaintoaineistoa. Nitraattitypen huuhtoutumasta selitettiin 63–64% korkean epäorgaanisen typen laskeuman tai ilman lämpötilan ja orgaanisten maiden vähäisen osuuden avulla. Mitä enemmän valuma-alueilla oli turvemaita, sitä vähemmän nitraattityppeä huuhtoutui pidättymisprosessien takia. Tämäntyyppisellä analyysillä ei voida erottaa toisistaan laskeuman ja lämpötilan vaikutusta, jotka korreloivat keskenään merkitsevästi. Ammoniumtypen ja orgaanisen typen huuhtoutumalla oli voimakkain korrelaatio metsätaloustoimenpiteiden (hakkuut, ojitukset) osuuteen alueella. NH_4-N -huuhtoutumasta selitettiin 53 % ojitusprosentin ja lämpötilan avulla. Orgaanisen typen huuhtoutumasta vastaavasti selitettiin 81 % avohakkuu- ja ojitusprosentin avulla.

Suuri orgaanisten maiden osuus valuma-alueella on tekijä, joka vaikuttaa merkittäviin 'uuden' veden osuuksiin valunnassa, mutta toisaalta pienehköihin nitraattitypen huuhtoutumiin. Vaikuttaakin mahdolliselta, että kasvava purkautumisalueiden osuus valuma-alueilla lisää huuhtoutumisriskiä tiettyyn rajaan asti, minkä ylittyessä happitilanteen huonontuessa pidättymisprosessit, mm. nitrifikaation estyminen ja denitrifikaatio, alkavat dominoida typen kiertoa. Suurimmalla osalla valuma-alueita, etenkin alueilla joilla on merkittävästi turvemaita, laskeumana tullut typpi pidättyy yhä tehokkaasti. On todennäköistä, että nitraattitypen huuhtoutumat tulevat lisääntymään rehevimmiltä metsämailta (MT ja OMT) Suomen etelä- ja keskiosissa. Typen emissoiden rajoittamiseksi tarvitaan lisäpanostusta. Jos ilmasto muuttuu kosteammaksi ja lämpimämmäksi, riski typen huuhtoutumiseen kasvaa entisestään, mm. mineralisaation ja nitrifikaation kiihtymisen takia.

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Appendix 1

Glossary of hydrological terms

Contributing area *Valuntaan vaikuttava alue* The area of a catchment contributing to storm (or snowmelt) runoff

Contributing area of the event water *Uuden veden lähdealue valuma-alueella* The area of a catchment contributing to snowmelt or storm runoff of event water

Discharge area *Purkautumisalue* An area in which the flow is directed out of the groundwater zone (upward flow in the uppermost groundwater)

Event water *Uusivesi* Liquid water entering the catchment during the event, i.e. new rain- or meltwater

Infiltration excess overland flow (Horton) *Pintavalunta kyllästymättömällä alueella* Overland flow in unsaturated areas, occurring when the rain or snowmelt intensity exceeds the infiltration capacity of the soil

Macropore flow or **Pipeflow** *Huokosvirtaus* Flow through a network of large pores, macrochannels or pipes

Overland flow *Maanpäällinen valunta* Flow of water on the ground

Pre-event water *Esivesi* Liquid water existing in the catchment prior to an event

Recharge area *Imeytymisalue* An area in which the flow is directed into the groundwater zone (downward flow in the uppermost groundwater)

Return flow *Purkautumisvalunta* Infiltrated water which returns to the land surface after flowing for a short distance in the upper soil horizon (Dunne and Black 1970)

Saturated area *Vedellä kyllästynyt alue* Area in which the saturated zone reaches the ground surface

Saturation excess overland flow *Pintavalunta vedellä kyllästyneellä alueella* Surface runoff occurring where the storage capacity of the soil is completely filled, so that all subsequent additions of water are forced to flow over the surface (Kirkby 1988). This occurs frequently when soils become saturated from below, by rising water tables

Soil matrix flow *Suotovirtaus* Movement of soil moisture in response to a gradient of hydraulic potential. If it is laminar, the flow conforms to Darcy's law. Soil matrix flow may occur under both saturated and unsaturated conditions.

Subsurface flow *Maanalainen valunta* Unsaturated or saturated flow in the soil or bedrock with flow paths directed towards the discharge area

Subsurface stormflow *Maanalainen välitön valunta* Subsurface flow that contributes significantly to the stormflow hydrograph in the stream

Transmissivity *Maaperän lateraali vedenjohtavuus* Lateral flow through the saturated profile of a soil profile

Oxygen-18 as a tracer

The relative deviation of the isotopic ratio of the sample from that of a reference water SMOW (Standard Mean Ocean Water) (Craig 1961) is denoted as $\delta^{18}O$:

$$\delta^{18}O = \frac{R_{sample} - R_{SMOW}}{R_{SMOW}}$$

where the R's are the isotopic ratios, i.e. the ratios between the number of atoms of the two isotopes, ^{18}O / ^{16}O. The δ -value is commonly expressed in o/oo.

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Book chapters:
Tamminen P. & Starr M. 1990. A survey of forest soil properties related to soil acidification in Southern Finland. In: Kauppi P., Anttila P. & Kenttämies K. (eds.), *Acidification in Finland*, Springer, Berlin, pp. 237-251.

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