

Annual variability of nitrogen concentrations and export from forested catchments: A consequence of climatic variability, sampling strategies or human interference?

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This study was based on the data from 18 years of monitoring in six forested catchments. The aim was to find links between annual estimates of export and concentrations of NO₃-N and organic N and hydroclimatological factors, sampling strategy and human interference. A topography-based wetness index was used to assess whether the effects of forestry activities depended on prevailing wetness conditions. For organic N, annual runoff was the main explaining factor in three catchments. The flow condition during sampling was for organic N the main explaining factor in three and for NO₃-N in one catchment. Effects of clear-cutting of 14% in one catchment were observed. For organic N, the model could be improved by considering clear-cutting in wet areas only. The southernmost catchment, but also the northernmost catchment with the lowest deposition, showed links to atmospheric deposition, demonstrating that deposition can cause a significant direct response in streamwater concentrations in nutrient-poor catchments.

Introduction

The overall aim of environmental monitoring is to determine and predict the state and change of environmental variables with respect to the impact of human interference. However, in the as-

essment of trends and temporal variability, it is important to distinguish between human-induced changes and the impact of sampling programme design or climatological variability.

In addition to time series analyses from a usually rather limited set of available data, catchment-

based models can contribute to knowledge about the possible effect of changes of various environmental factors. Knowledge about linkage between temporal variation of nitrogen flow, and environmental factors that are easily available in a regional concept, are vital for the development and application of conceptual models of nitrogen (N) flow from forested catchments. The HBV-N model (Arheimer and Brandt, 1998), is a dynamic model for simulation of riverine N-transport, based on the hydrological catchment model HBV (Bergström 1976). HBV-N has been shown to give acceptable results in simulations of nitrogen transport from southern Sweden, where most of the export comes from agricultural areas (Arheimer and Brandt 1998). However, in large parts of Sweden and Finland, most of the land is covered by forest. Although the leakage from forest is much smaller as compared with that from agricultural areas, it is a significant contribution to the riverine N-transport, due to its large areal extent. In order to develop a conceptual tool for N-leaching from forests, it is therefore important to assess carefully the links between the temporal dynamics of N-flow and other, easily monitored environmental factors.

Substantial temporal variation exists in the concentrations of N in surface waters of forest ecosystems (e.g. Nicolson 1988, Creed 1998), and accurate prediction of N export is made difficult by the diversity of sources of N export.

Within a particular region or forest stand, mineralisation and nitrification rates may vary considerably in response to temperature and moisture. Global warming may thus be manifested in alterations in N dynamics, e.g. by increased mineralisation (Luekewille and Wright 1997). Temperature is also a critical factor for terrestrial assimilation, i.e. uptake and metabolic use of N by plants and soil microbes. Nitrification is thought to be responsible for nitrate production also at low temperatures, but root uptake only becomes significant at higher temperatures (Stevens *et al.* 1993, Arheimer *et al.* 1996).

Water flow paths and the transit time through the soil are crucial for the transport and retention of N. High levels of $\text{NO}_3\text{-N}$ during periods of increased runoff, increased saturated areas or surface flow, and flushing of N during snowmelt have been observed (Devito and Dillon 1993, Arheimer *et al.*

1996, Andersson and Lepistö 1998). Both negative and positive correlation between flow and concentration may exist, depending on whether the major effect of increased flow is dissolution or washout (Arheimer *et al.* 1996). A strong negative correlation between stream discharge and acidity is often found, and generally explained by the relationship between the movement of water through a catchment and the chemistry of the runoff that leaves the catchment. The episodic acidity of a water sample will thus reflect water pathways and transit times in the catchment (e.g. Davies 1989).

Due to variations in the composition of runoff that has followed different flow paths, concentrations can change rapidly, thereby making interpolations between sampling events rather uncertain, even when using simple flow-correction methods. A conscious or unconscious change of the hydroclimatological conditions which sampling represents could therefore have significant effects on annual estimates of average concentrations or exports (Kronvang and Bruhn 1996).

Measurements of elevated nitrate suggest that excess N deposition could saturate forest soils, thus leading to drastically increased inorganic N export (e.g. Aber *et al.* 1989, Dise *et al.* 1998). In Nordic areas (Sweden and Finland), with lower throughfall deposition, Lepistö *et al.* (1995) showed that forested catchments could still accumulate most of the incoming deposition.

Forest management practices may upset the N cycle by decreasing uptake by plants or by enhancing mineralisation and may cause accumulation of nitrogen in the soil, leaching and increased denitrification. Increases of inorganic N concentrations after clear-cutting can be drastic, but often decrease within a few years (Adamson and Hornung 1990, Wiklander *et al.* 1991). However, longer-term impacts (> 10 years) have also been detected (Ahtiainen 1992, Ahtiainen and Huttunen 1999). In the Nurmes study, it was shown that concentrations and loads of organic N increased considerably after drainage, due to increased erosion (Ahtiainen, 1992). The effect of drainage, together with soil ploughing and hummocking were clearly seen for $\text{NH}_4\text{-N}$ leaching, due to mineralisation. Saura *et al.* (1995) found that in the Kalliojärvi project, the leached amount of the fertilisation was 4%–5% in catchments with a mixture of mineral and organic

soils, and 10% in a catchment with only mineral soils. Most of the excess leaching of N was inorganic, and the amount decreased rapidly during the second year after the application.

Activities in recharge areas affect primarily the composition of groundwater, whereas those in discharge areas have a more direct effect on the surface or near-surface flow that reaches the stream with short transit times (Johnes and Heathwaite, 1997). It was therefore hypothesised that the impact varies according to where in the catchment the treatment (e.g. clear-cutting or fertilisation) takes place.

Trend analyses are best suited for detecting stable increases/decreases, e.g. due to gradual changes of atmospheric deposition. However, short-term effects of forestry management or hydroclimatological dynamics, and changes of sampling programmes, are all factors that may cause statistically significant trends, depending on which years are included in the analysis. The effects of such factors must therefore be carefully considered before drawing conclusions about long-term changes. For this study, data from six forested catchments in Finland were used to estimate annual variations of export and average concentrations of $\text{NO}_3\text{-N}$ and organic N, with the objective to assess:

- What effects does variability of (i) annual averages of climatological and hydrological factors and of (ii) climatic or hydrological conditions during sampling events, and of (iii) spatially rather limited forest management, and of (iv) fluctuations in atmospheric deposition have on the annual variability and trends of export and concentrations of $\text{NO}_3\text{-N}$ and organic N from forested catchments?
- Do the impacts of forest management practices depend on where in the catchment they are performed, e.g. in wet discharge areas, intermediate areas, or well-drained recharge areas?

Catchment database

The study was based on the data from a period of 18 years (1971–1988) from six forested catchments (0.7–23.3 km²) in Finland (Fig. 1) moni-

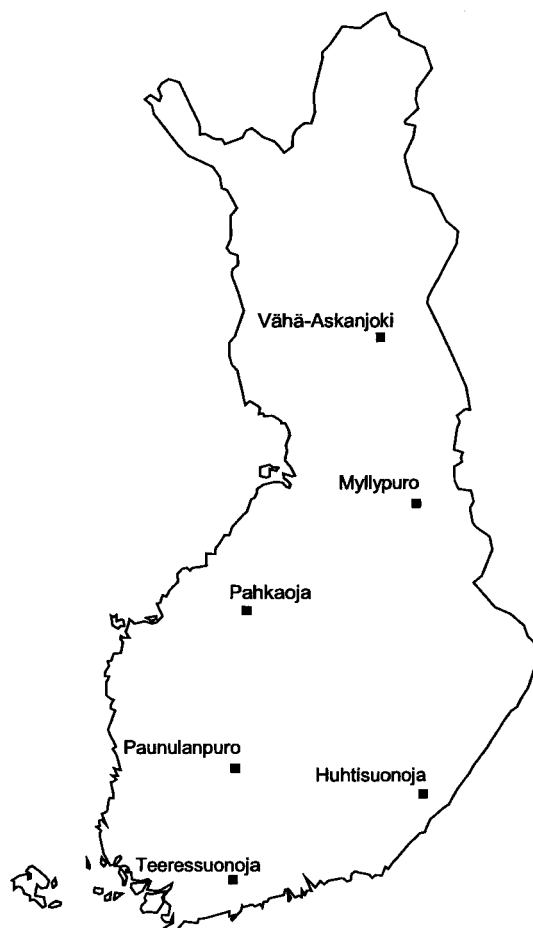


Fig. 1. Locations of the Finnish research catchments.

tored by the predecessor of the Finnish Environment Institute, the National Board of Waters and Environment. The selection of catchments and the time period were based on the availability of time series without significant breaks, and available maps showing locations of forestry activities. 1988 was chosen as the final year since national nutrient load monitoring was discontinued at two of the catchments at the end of the 1980s.

Geomorphological characteristics, soil types, average meteorological and hydrological conditions, average bulk deposition of inorganic N, and average concentrations and exports of $\text{NO}_3\text{-N}$ and organic N are presented in Table 1. Maps and tables of the temporal and geographical distribution of forestry activities in the form of ditching, fertilisation and cutting in the study catchments

Table 1. Geomorphological characteristics, soil types, average meteorological and hydrological conditions, average inorganic N deposition, and average volume-weighted concentrations and export of $\text{NO}_3\text{-N}$ and organic N in the study catchments. The period 1971–1988 was used for averages.

Catchment	Geomorphology				Soil types				Meteorology and hydrology				Streamwater concentrations and export			
	Area km^2	Altitude m	Relief m	Slope %	Stream density	Fine soils km^2	Organic soils %	Bedrock land %	Arable land %	Temp. $^{\circ}\text{C}$	Precipit. mm	Runoff mm	Inorganic N deposition $\text{kg km}^{-2} \text{a}^{-1}$	$\text{NO}_3\text{-N}$		Org.N
														$\mu\text{g l}^{-1}$	$\text{kg km}^{-2} \text{a}^{-1}$	$\mu\text{g l}^{-1}$
Teeressuonoja	0.7	42	59	10.2	2.6	7	13	2	0	3.9	613	266	770	365	95	463
Paunulanpuro	1.5	117	30	6.8	3.7	8	18	2	1	3.7	718	313	370	122	35	471
Huhtisuonoja	5.0	98	34	5.0	3.4	0	45	0	0	3.5	619	235	510	109	26	427
Pahkaaja	23.3	150	52	2.1	0.8	0	67	0	2	2.8	573	336	650	39	14	463
Myllypuro	9.9	178	81	7.4	1.8	0	27	0	2	0.5	599	365	460	16	6	425
Vähä-Askanjoki	16.4	168	215	10.9	1.1	0	17	0	0	-1.0	513	423	240	29	12	294
																132

were compiled from the records of local forest authorities (S. Saukkonen and P. Kortelainen unpubl.), and digitised into ArcInfo. The completeness of the forestry activity databases varied among the six catchments (Table 2).

Continuous streamflow monitoring with measuring weirs at the outlets of the catchments was available (Seuna 1983). From 1971 until 1980, streamwater samples of pH, total N, $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ (approximately 10–12 samples per year) were rather evenly distributed over the year. From 1981, the sampling was generally concentrated to the spring and autumn high flow periods in order to provide more accurate total export estimates (Rekolainen 1989), with limited sampling during low-flow periods. In one catchment (Teeressuonoja) in the late 1980s, the sampling increased to 40–60 samples per year, with a rather even distribution over the year. $\text{NO}_3\text{-N}$ was analysed by the cadmium amalgam method (Erkomaa *et al.* 1977), $\text{NH}_4\text{-N}$ was analysed by a spectrophotometric method with hypochlorite and phenol, and total N as $\text{NO}_3\text{-N}$ after oxidation with $\text{K}_2\text{S}_2\text{O}_8$ (National Board of Waters 1981). The organic-N concentrations were calculated as the difference between total and inorganic N.

Meteorological variables were obtained from local climatological stations, run by the Finnish Meteorological Institute. Soil temperature was not measured in the catchments, and air temperature was used as an index describing year-to-year variation in the intensity of biological processes. Atmospheric deposition of N was obtained from monthly bulk collections of nitrate and ammonium within the Finnish National Environment Programme, using averages of measurements from nearby stations (Järvinen and Vänni 1990).

Methods

GIS and TOPMODEL

In order to test whether the effects of clear-cutting and fertilisation depended on where in the catchments they were carried out, the distribution of a topography-based wetness index used by the TOPMODEL (Quinn *et al.* 1995) was calculated for each catchment. Digital terrain analysis was performed using $25 \times 25\text{-m}$ grids interpolated from

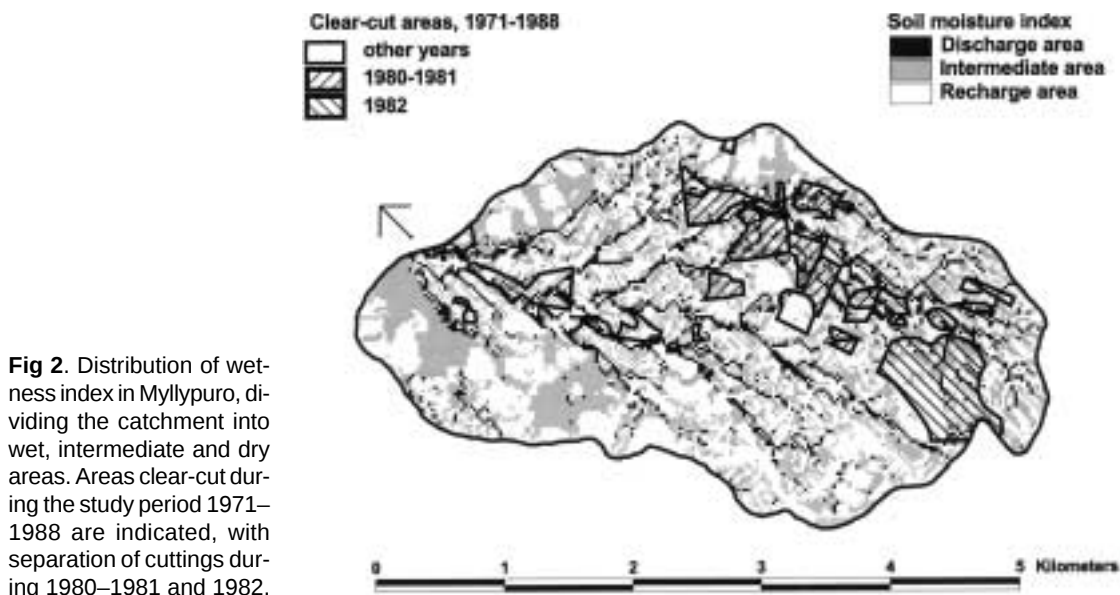


Fig 2. Distribution of wetness index in Myllypuro, dividing the catchment into wet, intermediate and dry areas. Areas clear-cut during the study period 1971–1988 are indicated, with separation of cuttings during 1980–1981 and 1982.

isolines of topographic maps (1:20 000) by the TIN-module in ArcInfo.

For each cell, the accumulated area being drained through that cell (α), and the average slope towards the lower situated neighbouring grids (β) was calculated to obtain the index value (Eq. 1).

$$\text{Topographic wetness index} = \ln (\alpha / \tan \beta) \quad (1)$$

A high index is obtained for cells with large accumulated upslope areas and low gradients to neighbouring cells, i.e. characteristics typical for wet areas. The catchments were divided into dry (wetness index < 8), intermediate (index 8–12) and wet areas (index > 12). The distribution of forest management into the different wetness classes was obtained from GIS overlays with the digitised clear-cut and fertilised areas (Fig. 2).

Estimates of average concentrations and exports

Annual averages of concentrations and annual exports were calculated by a volume-weighting method (Lepistö 1995). The sampled concentrations $c(t_i)$, 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 discharge to obtain annual export E (Eq. 2):

$$E = \frac{\sum_{i=1}^n c(t_i) q(t_i)}{\sum_{i=1}^n q(t_i)} q_{\text{year}} \quad (2)$$

Table 2. Forestry activities in the study catchments prior to the monitoring period (1960–1970) and during 1971–1988.

	Clear-cutting (%)		Fertilisation (Kg N km ⁻² a ⁻¹)		Drainage (%)	
	1960–1970	1971–1988	1960–1970	1971–1988	1960–1970	1971–1988
Teeressuonoja	0	0	0	0	0	0
Paunulanpuro	*	*	*	*	13	0
Huhtisuonoja	0	4	8 636	1 500	40	0
Pahkaoja	*	*	*	**	9	7
Myllypuro	3	14	64 545	121 667	3	19
Vähä-Askanjoki	*	*	*	*	3	6

* not known, ** N fertilisation not known, PK fertilisation in 1974

Regression and trend analyses

In order to explain annual variation, multiple regression analyses were performed, including a large set of factors describing hydroclimatological characteristics for the actual and the antecedent year, atmospheric N-deposition, forestry activities, and hydroclimatological conditions during sampling. All variables that were included in the selected multiple regression models are given in Table 3.

Hydroclimatological variables were calculated from annual variations of air temperature and runoff. N-deposition variables were calculated from annual bulk deposition of inorganic N, which was used as an index of total deposition.

Models were set up with different assumptions of the time lag of the maximum impact from forest activities (clear-cut, fertilisation and drainage) and the duration of the impact. Some models assumed a maximum impact during the year of the activity, whereas others assumed a delay of 1 or 2 years before the maximum impact occurred. The decline from maximum impact in the models varied from only impact during the year of the activity to a 12-year decline.

The impact ratio was multiplied by the area affected by the actual forest activity, and in the case of fertilisation, also by the amount of N-fertiliser used. For a certain year, the total index for the impact of a forest activity (e.g. clear-cut) was calculated as the integrated sum of activities during all antecedent years included in the selected model.

For clear-cutting and fertilisation, annual impact indices for forest activities were calculated both with inclusion of total areas, and with only the inclusion of affected areas located within intermediate or wet areas (wetness index > 8), or only within wet areas (wetness index > 12).

For the trend analysis, a non-parametric trend test (Hirsch and Slack 1984) was used. A flow-adjustment of observed concentration was performed using rank correlation between mean monthly concentration values and mean monthly flows (Grimvall *et al.* 1991). Time series of water quality are often characterised by seasonality, serial dependence and skewed distributions, and the above-mentioned non-parametric trend test has been shown to be suitable for the analysis of such

data. Correlation between daily streamflow and concentrations were calculated by Arheimer *et al.* (1996).

Results and discussion

Annual variation of NO₃-N export and concentrations

Variables included in regression equations for NO₃-N concentrations and exports are shown in Tables 3 and 4. For four of the catchments, trends in NO₃-N concentrations were reported by Lepistö *et al.* (1991). For two of these catchments (Myllypuro and Vähä-Askanjoki), no statistically significant trends ($P < 0.05$) remained when adding one more year (1989) to the time series. This demonstrates that trend analysis can be very sensitive even to slight changes in the time period analysed.

Effects of a fluctuating hydroclimate

Annual variability of water discharge could at most explain 40% of that of NO₃-N export. The inclusion of other explaining factors in addition to annual discharge increased the average R^2 from 0.18 to 0.68.

In one catchment (Teeressuonoja), high NO₃-N concentration in streamwater was correlated to low antecedent summer air temperature. At another catchment (Paunulanpuro), however, high concentrations and exports were significantly correlated with high summer air temperature. The effect of fluctuation in air temperature is thus not obvious, since the resulting effect on the nitrogen pool in the soil is due to the balance between mineralisation and biological uptake processes.

Recent studies have indicated that as a consequence of global warming, nutrient transport in Finnish basins might increase during the dormant season but decrease during the biologically active period (e.g. Bilaletdin *et al.* 1996). It is thus probable that in some catchments, the largest effect will be on mineralisation (causing higher annual average concentrations and export), whereas in others the overriding effect will be on the biological uptake (causing lower concentrations and exports).

Table 3. Variables used in the regression analyses, included in the selected multiple regression equations. C = concentrations. E = exports. (+) positive correlation, (–) negative correlation.

Variable	Used data/model	Significant for:
1. Annual water discharge	Annual recorded water discharge org-N (+)	E: NO ₃ -N (+)
2. Air temperature actual year	Average annual air temperature	C: org. N (–)
3. Air temperature, actual summer	Average air temperature Jun.–Aug. actual year	C: NO ₃ -N (+) E: NO ₃ -N (+)
4. Air temperature, previous summer	Average air temperature Jun.–Aug. previous year	C: NO ₃ -N (+,–), org. N (+) E: org. N (+)
5. Air temperature, dormant season	Average air temperature Sep. previous year to May actual year	C: org. N (–) E: org. N (–)
6. Washout in spring	Runoff Jan.–Jun., actual year divided by runoff from Jul. Previous year to Jun. actual year	C: NO ₃ -N (+), org. N (+) E: org. N (+)
7. Atmospheric N-deposition	Annual bulk deposition of NO ₃ -N and NH ₄ -N	C: NO ₃ -N (+) E: NO ₃ -N (+)
8. Accumulation of N-deposition in snowmelt	Bulk deposition of NO ₃ -N and NH ₄ -N in precipitation during the months before initiation of snowmelt with average air temperature below 0 °C	E: NO ₃ -N (+)
9. Concentration of N deposited in spring snowmelt	Average concentrations of NO ₃ -N and NH ₄ -N in precipitation during the months before snowmelt with average air temperature below 0 °C	C: NO ₃ -N (+)
10. Clearcut model (a)	All clearcut areas considered. Impact ratio 1.0 in the year of impact, multiplied by the clear-cut area	C: NO ₃ -N (+)
11. Clearcut model (b)	Total clearcut model considered. Impact ratio 1.0 in the year of impact, and 0.5, 0.25, 0.1 in the following years	E: NO ₃ -N (+)
12. Clearcut model (c)	Only clearcut in intermediate and wet areas considered (wetness index > 8). Impact ratio 1.0 in the year of impact and 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.35, 0.1 in the following years	C: org. N (+)
13. Clearcut model (c)	Only clearcut in wet areas considered (wetness index >12). Impact ratio 1.0 in the year of impact and 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.35, 0.1 in the following years	E: org. N (+)
14. Drainage model	Impact ratio 1.0 in the year of impact, and 0.5, 0.25, 0.1 in the following years	C: NO ₃ -N (+), org. N (+) E: org. N (+)
15. Flow during sampling	Average flow during sampling days	C: NO ₃ -N (+), org. N (+) E: NO ₃ -N (+), org. N (+)
16. pH during sample collection	Average pH during sampling days	C: org. N (–) E: org. N (–)
17. Flow increase during sampling	Percentage of samples collected during days with higher flow than the average of the three preceding days	C: org. N (+)
18. Biological activity during sampling	Percentage of samples collected during summer (Jun.–Aug.)	C: NO ₃ -N (–)

Table 4. The best multiple regression equations obtained for concentrations and exports for NO₃-N and organic N (1971–1988) in the study catchments. Variables are defined in Table 3. Adjusted R² is shown in parentheses. Type of variable is given in boldface.

	NO ₃ -N concentrations	N-exports	Organic N concentrations	Organic N export
Huhtisuonoja	Flow during sampling (+) (0.57)	Flow during sampling (+) (0.85)	pH during sampling (–) or flow during sampling (+) (0.34)	Annual discharge (+), pH during sampling (–) (0.85)
Myllypuro	Clear-cut model (a) (+) (0.79)	Clear-cut model (b) (+) (0.66)	Air temperature , previous summer (+), clear-cut , model (c) (+), air temperature , dormant season previous year (+) (0.56)	Air temperature , previous summer (+), washout in spring (+), clearcut , model (d) (+), (0.63)
Pahkaoja	Drainage (+), biological activity during sampling (–) (0.46)	Drainage (+), annual discharge (+) (0.53)	No statistically significant equation found	Annual discharge (+) (0.62)
Paunulanpuro	Air temperature , actual summer (+), air temperature , previous summer (+), washout in spring (+) (0.87)	Air temperature , actual summer (+), annual discharge (0.63)	Air temperature , actual year (–), drainage (+) (0.44)	Annual discharge (+) (0.93)
Vähä-Askanjoki	Atmospheric N-deposition (+) (0.64)	Accumulation of N-deposition in snowmelt (+) Annual discharge (+) (0.53)	Flow during sampling (+) (0.23)	Flow during sampling (+) (0.63)
Teeressuonoja	Wash-out in spring (+), concentration of N deposited in spring snowmelt (+), air temperature , previous summer (–) (0.70)	Atmospheric N-deposition (+) (0.55)	Air temperature , actual year (–), flow increase during sampling (+), washout in spring (+) (0.74)	Flow during sampling (+), air temperature , dormant season previous year (–), annual discharge (+) (0.73)

Fig. 3. Monitored and modelled average annual $\text{NO}_3\text{-N}$ concentrations from two catchments where N-deposition was included as a significant explaining variable (a) Vähä-Askanjoki ($R^2 = 0.64$), and (b) Teeressuonoja ($R^2 = 0.70$). Included variables are defined in Table 4.

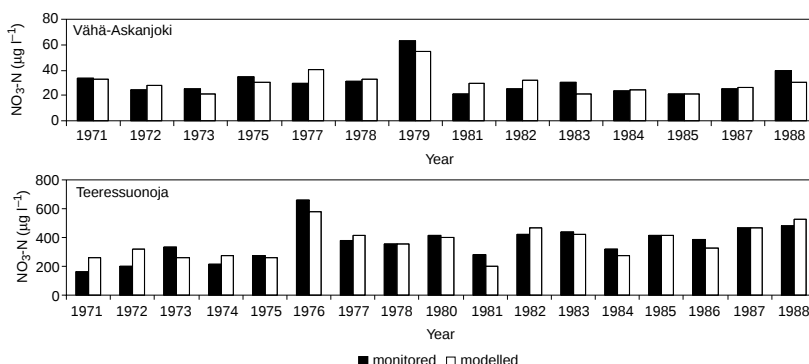
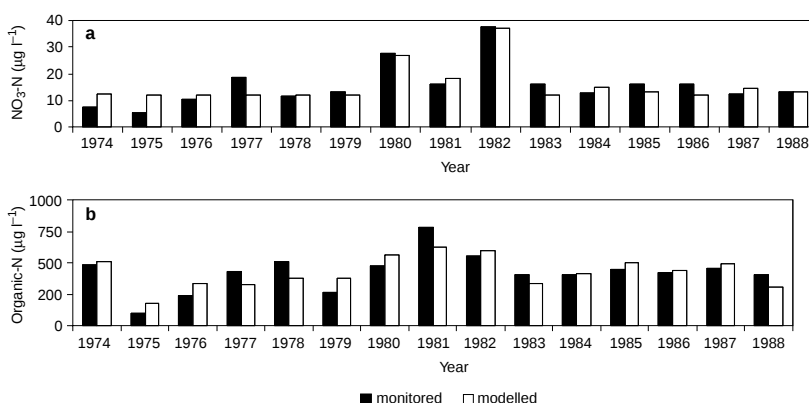


Fig. 4. Monitored and modelled average (a) annual $\text{NO}_3\text{-N}$ ($R^2 = 0.79$) and (b) organic N concentrations ($R^2 = 0.56$) in Myllypuro, where clear-cut was included in the regression models. Included variables are defined in Table 4.



Effects of fluctuating N-deposition

In two of the catchments (Vähä-Askanjoki and Teeressuonoja), a significant correlation was found between $\text{NO}_3\text{-N}$ concentrations and exports and variables related to atmospheric N-deposition (Tables 3 and 4, Fig. 3). Of the six studied catchments, Vähä-Askanjoki had the lowest inorganic-N deposition and the lowest streamwater export of $\text{NO}_3\text{-N}$, whereas Teeressuonoja had the highest (Table 1). This demonstrates that deposition on discharge areas close to the stream, and water surfaces, can cause a significant direct response in streamwater concentrations of $\text{NO}_3\text{-N}$ also in nutrient-poor catchments. Several authors (e.g. Govindaraju 1996, Creed 1998) highlighted the importance of variable source areas (discharge areas) in the prediction of the chemical composition of surface waters.

For Teeressuonoja, variability of concentrations was best explained when considering N-concentration in precipitation accumulated as snow (Table 4 and Fig. 3). The equation also included

high washout in spring, indicating high concentrations as a consequence of accumulation of $\text{NO}_3\text{-N}$ that is washed out rapidly during snowmelt when transit times to the streams are short (Table 4).

Effects of forestry activities

A total clear-cutting of only 14% of the catchment area in Myllypuro could explain a significant part of the annual variability of concentrations. The highest degree of explanation was obtained when using an impact model that only considered the cuttings during the actual year (Table 4 and Fig. 4). For exports, however, a direct effect that lasted for three years was indicated (Tables 3 and 4).

The effects of clear-cutting on $\text{NO}_3\text{-N}$ export have mainly been shown to be due to increased runoff volumes (Lepistö *et al.* 1995), which might explain why a longer duration of impact was found for exports than for concentrations.

No evidence was detected to indicate that the

wetness of cut areas was of significant importance for the $\text{NO}_3\text{-N}$ concentrations. This might be due to the fact that although the more superficial flow paths in wetter areas would favour higher concentrations in leakage, denitrification rates may be significant in the wetter areas. In forests, denitrification in riparian or poorly drained soils is typically greater than that in upland or more well drained soils (Groffman *et al.* 1991, Hanson *et al.* 1994).

In the peaty catchment Pähkajä, drainage works (7% of the catchment) were the main explaining factor for annual $\text{NO}_3\text{-N}$ concentrations and exports (Table 4). The selected model, assumed that the maximum impact occurred the year of the activity, followed by a 3-year decline.

The N-fertilisation, which was reported from two catchments (Myllypuro and Huhtisuonoja), did not show any significant correlation to the temporal variations of $\text{NO}_3\text{-N}$ concentrations and export, and did not increase the degree of explanation in multiple regression models. In Huhtisuonoja, also during the year with the maximum amount of fertilisation, the amount of inorganic-N added to the catchment was only 50% of the atmospheric deposition. In Myllypuro, however, during the year with the maximum fertilisation, the amount of inorganic N added to the catchment from fertilisation was more than four times larger than the amount added from atmospheric deposition. The fact that fertilisation was not shown to be significant for annual variability of N-leaching was probably due to the N limitation of these northern, boreal forest ecosystems. The retention of the inorganic N deposition (calculated as [(input-output)/input] of $\text{NO}_3\text{-N}$ and $\text{NO}_4\text{-N}$) was 98% for Myllypuro and 95% for Huhtisuonoja.

Effects of sampling strategies

Due to the change in the sampling strategy in all catchments from 1981 and onwards, with sampling concentrated to spring and autumn high flow periods; average runoff on the sampling days doubled when comparing the period 1981–1985 with the earlier period 1965–1974 (Rekolainen, 1989).

Low or high-flow biased sampling during individual years may have a significant impact on the estimated annual average concentrations and

loads, thereby making a flow-weighting method more favourable than an interpolation method. However, in spite of that a flow-weighting method was used, the flow during sampling was shown to be the most significant variable in one catchment (Huhtisuonoja) (Table 4).

In Huhtisuonoja, there was a significant positive correlation between the flow and $\text{NO}_3\text{-N}$ concentration ($P < 0.01$), and a positive trend for $\text{NO}_3\text{-N}$ concentrations ($P < 0.05$) was obtained as a consequence of the change of the sampling programme, in spite of that the trend test included flow adjustment.

If the correlation between the flow and $\text{NO}_3\text{-N}$ concentration is negative, however, a potential impact of increased N-deposition on concentration levels could instead have been suppressed by the change of the sampling programme.

Annual variation of organic-N export and concentrations

Variables included in the selected regression equations for organic N concentrations and exports are shown in Tables 3 and 4. Only in one of the catchments, Vähä-Askanjoki, was a statistically significant temporal trend detected for 1970–1988 ($P < 0.05$). However, this trend was not significant when adding one more year, 1989, to the time series.

Effects of a fluctuating hydroclimate

For organic N, the annual water discharge explained between 36% and 93% of the annual variations in export, i.e. a considerably higher degree compared to $\text{NO}_3\text{-N}$.

In Myllypuro, high concentrations and exports of organic N were correlated with high temperature during the previous summer (Table 4). This can be explained by biological activity within and in the vicinity of the aquatic environment, causing an accumulation of organic N that is flushed out during the following spring-flow.

In Paunulanpuro and Teeressuonoja, however, low air temperatures were linked to high annual organic N concentrations (and also to export in Teeressuonoja). A possible explanation is that there may have been less mineralisation during cold

years, leaving more N in its organic form. As in the case of $\text{NO}_3\text{-N}$, there is thus no simple relation to temperature, and further work should be conducted on relating links between catchment characteristics and differences in the response of temperature change on the N flow.

Effects of forestry activities

In Myllypuro, cuttings of 14% of the catchment explained a significant part of the annual variability of concentrations and exports (Table 4 and Fig. 4). In previous studies of Finnish catchments, it has been shown that a short-term impact on inorganic N leaching has been followed by a longer impact on organic N leaching (Ahtiainen and Huttunen 1999). In the present study a gradual 10-year decline of organic N export was included in the best regression model (Table 4).

Cuttings leave slash to be decomposed. In poorly drained soils, large lateral water flows are in close contact with organic matter, and increased groundwater levels and moisture contents could speed up the decomposition and transport of stored organic material. In contrast to $\text{NO}_3\text{-N}$, the degree of explanation increased if only cuttings in intermediate and wet areas (wetness index > 8) for concentrations, and for export, only wet areas (wetness index > 12) were considered. The effects of the cuttings carried out during 1982 were less pronounced than those during 1980–1981 (Fig. 4) because, although extending over large areas, they were concentrated to dry, well drained, areas (wetness index < 8) (Fig. 2).

Effects of a fluctuating hydroclimate

High flow (or low pH) during sampling was included in the multiple regression equations as the main explaining factor for annual variability of organic N concentrations in all of the three basins for which positive correlation between flow and concentrations were found. It was also the main explaining factor for exports from two of these three catchments (Table 4).

For Huhtisuonoja, where the highest correlation between flow and organic N concentrations were found, pH during sampling had a signifi-

cantly higher degree of explanation of annual variability on concentrations ($R = -0.70^{**}$), compared to water flow during sampling ($R = 0.59^*$). This was also the case for exports ($R = 0.54^*$ for flow and -0.70^{**} for pH during sampling). The fact that concentrations increased in times of low pH (and high flow) was probably due to that during acid events the flow was overwhelmed by precipitation or snowmelt that fed the stream as surficial runoff (Andersson and Lepistö 1998). Since concentrations had a higher correlation with pH than with the flow volume during the day of sampling, it can be assumed that for this catchment, pH was a better indicator of water flow paths than the flow during the day of sampling. However, there is obviously a risk in using pH as an indicator of flow paths, since the acidity might, in addition to its episodic variability, have a long-term trend that is co-variant to changes of the N dynamics in the catchment.

The correlation between flow during sampling and organic N concentration indicates that the found positive trend (1971–1988) was due to changes in the sampling strategies towards events with higher water discharge.

Conclusions

Time series from small catchments may provide a valuable tool in the assessment of the effects of human impact and climatic variability on concentration levels and exports of N. However, this study demonstrates that evaluations of long-term changes must carefully consider the fact that small catchments behave dynamically, with episodic flow patterns and changes in the chemical composition of the streamwater. The influence of the flow and climatic conditions during sampling events, the overall temporal variability of the climate, and the effects of human activities with varying impact periods, and changes of sampling strategies must be carefully assessed before drawing conclusions about long-term changes of water quality variables. The fact that adding one year to the time-series removed several of the detected trends demonstrates that, although statistically proven to be significant, trends can be caused by short-term variations of the monitored annual average concentrations. It must also be born in

mind that multivariate regression models, due to the complex interrelationships between the selected independent variables, can be used as a tool to indicate, but not prove, relationships between temporal variations of N concentrations or exports and selected variables.

For further development of conceptual catchment-based models of riverine nitrogen flow, the following conclusions could be drawn from the study.

- (i) Caution should be taken in assessment of effects of climatic change on N export, since the combined effect of changed mineralisation and biological uptake will probably differ significantly between catchments, depending on their characteristics.
- (ii) In all catchments for $\text{NO}_3\text{-N}$, but also in several catchments for organic N, temporal variations of environmental factors other than water discharge were shown to be more important than discharge in the explanation of annual variability of exports, indicating that significant errors may follow from using static, standard leakage concentrations.
- (iii) Links between $\text{NO}_3\text{-N}$ exports and atmospheric N deposition were found not only in the catchments with the highest, but also in the catchment with the lowest deposition. This demonstrates that deposition on discharge areas and water surfaces can cause a direct response in streamwater $\text{NO}_3\text{-N}$ concentrations and exports even in nutrient-poor northern catchments with very low concentrations and export levels of $\text{NO}_3\text{-N}$.
- (iv) In catchments where links between N deposition and annual variability of $\text{NO}_3\text{-N}$ were found, the content of $\text{NO}_3\text{-N}$ in snow seemed to be of critical importance. This demonstrates that in modelling of riverine $\text{NO}_3\text{-N}$, it should be considered that flow paths are short and thereby retention of N deposition is low during snowmelt.
- (v) The study indicates that, in the case of organic N, it is necessary to consider not only the size of the areas affected, but also their degree of wetness. For $\text{NO}_3\text{-N}$, it is possible that the shorter flow paths (and thereby low retention) were compensated by high denitrification in the wet areas. The wetness of ar-

reas affected by forest activities can be estimated by GIS-aided overlay of the distribution of a topography-based wetness index and maps of forestry activities.

- (vi) Even spatially rather limited (7%–14% of the catchment area) forestry activities were shown to have a significant, although usually short-term effect, on the chemical composition of the streamwater. There are, however, substantial methodological problems when upscaling the results from small catchment studies to larger river basins, since the effects of forest management are part of the overall noise from the integrated response within the basin. It must also be remembered that when modelling on a river basin scale, in addition to using the results from small catchment studies, a major effort should be devoted to a sound incorporation of retention processes within rivers and lakes.

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