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Sjøeng

**The future impact of
nitrogen in the acidification
of surface waters;**

Modelling, empirical
and experimental
studies of changes in
nitrogen leaching

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The future impact of nitrogen in the acidification of surface waters;

*Modelling, empirical and experimental studies of changes in
nitrogen leaching*

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Dr. Scient thesis

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With courtesy of Petter Wang

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Oslo, mai 2008

Anne Merete S. Sjøeng

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Abstract

High nitrate (NO_3) leaching rates have been observed in mountain and heathland areas in Europe at sites receiving high levels of nitrogen (N) deposition. These areas are characterised by sparse vegetation on thin, patchy acidic soils and steep slopes and with relatively short growing season; they are therefore highly susceptible to NO_3 leaching. The main objective of this study was to contribute to increased knowledge about processes controlling N leaching in Norwegian mountain and heathland areas experiencing relatively high N load. To achieve these goals three research approaches have been used; empirical analysis, experimental studies and modelling.

The main objective of the paper I was to identify relationships between different vegetation cover (i.e. peat, heather and exposed bedrock) and N leaching on a seasonal and annual basis. As expected, highest NO_3 leaching was found for the exposed bedrock dominated catchments. The fraction coverage of exposed bedrock explained 70% of the variation in NO_3 concentrations during autumn and winter, but a much lower percent during the warmer seasons when biological processes exert higher control.

The field experiment was designed to test a proposed causal inverse relationship in surface water between NO_3 and dissolved organic carbon (DOC) concentrations. Paper II tested the hypothesis that increased availability of NO_3 (or N+P) would stimulate bacterial oxidation of DOC in the waterbody. As intended, the NO_3 concentrations increased from near zero up to 685 and 560 $\mu\text{g N l}^{-1}$ at the N+P and N manipulated ponds. Correspondingly, PO_4 concentration increased from below detection limit up to 32 $\mu\text{g P l}^{-1}$ after the first addition and to 58 $\mu\text{g P l}^{-1}$ after the second. The increase in N availability showed no effect on DOC, total organic carbon (TOC), bacteria or algae (measured as chlorophyll a) in the pond that received N alone. These results indicate that the inverse relationship between NO_3 and DOC in surface waters is probably not due to processes occurring within the waterbody. A possible explanation for the inverse NO_3 -DOC relationship can be related to differences in N deposition and the characteristic of catchment soils.

Despite the extensive use of the dynamic model MAGIC on annual basis, there have been few attempts using monthly time steps to examine seasonal variations. NO_3 , in particular, shows a pronounced seasonal pattern in many lakes and streams. In this study the objective was to apply the MAGIC model to the 12-year time-series from

Øygardsbekken using a monthly time step. The main goal was to test how well MAGIC could reproduce the observed long-term (1993-2004) and seasonal NO₃ pattern. The MAGIC application to Øygardsbekken satisfactorily simulated the seasonal NO₃ pattern over the 12-year record; the model explained almost 70% of the variation in monthly NO₃ concentrations and nearly 90% of the variations in flux.

In study IV the main objective was to use the MAGIC model as was calibrated on Øygardsbekken to simulate future NO₃ leaching from the catchment, implementing a future N deposition scenario combined with four different scenarios for climate change. Both seasonal and annual changes in NO₃ leaching were simulated. Implementing climate change scenarios for temperature and N deposition to the calibrated model at Øygardsbekken, resulted in increased future NO₃ leaching to surface water.

Catchment N stores have increased during several decades of elevated N deposition and retention. The long-term stability of this N accumulation is largely unknown. Internal ecosystem cycling of N greatly exceeds system inputs and outputs, and any disturbance of this cycle has the potential to obscure the relationship between N deposition and runoff.

The uncertainty in future chemical recovery from acidification is mainly related to the effects of climate change and future behaviour of N in the ecosystem. More research is needed on the long-term fate of N stored in soil under changing N deposition and climate. Release of N from this pool has potentially large effects in freshwater and coastal marine ecosystems.

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Papers included

Paper I

Sjøeng A.M.S., Ø. Kaste, K. Tørseth and J. Mulder. 2007.

N leaching from small upland headwater catchments in southwestern Norway.

Water, Air and Soil Pollution 179: 323-340

Paper II

Sjøeng, A.M.S, B. Kaasa, S. Larsen, B. L. Skjelkvåle and D.O. Hessen.

Effects of N and P addition on concentration of dissolved organic carbon in small humic lakes. Submitted May 2008 to Environmental Pollution.

Paper III

Sjøeng A.M.S., R.F. Wright, and Ø. Kaste.

Modelling seasonal nitrate concentrations in runoff of a heathland catchment in SW Norway using the MAGIC model I. Calibration and specification of nitrogen processes. Submitted May 2008 to Hydrology Research.

Paper IV

Sjøeng A.M.S., Ø. Kaste and R.F. Wright.

Modelling seasonal nitrate concentrations in runoff of a heathland catchment in SW Norway using the MAGIC model II. Simulation of future nitrate leaching given scenarios of climate change. Submitted May 2008 to Hydrology Research.

1. Introduction

1.1 General background of this thesis

During recent years regional monitoring of lakes has shown chemical recovery with increased pH and acid neutralizing capacity (ANC, defined as the equivalent sum of concentration of base cations minus the equivalent sum of strong acid anions), but acidification of surface water is still a problem in southwestern parts of Norway (SFT 2007). The primary cause of acidification is deposition of long-range transported sulphur (S) and nitrogen (N) compounds (Rohde et al. 1995) with sulphate (SO_4) being the largest contributor acting as a mobile anion in acidified soils (Seip 1980). Based on international agreements of reduction in N and S emissions (UN/ECE 1999) S concentration in precipitation in Norway has decreased by about 60-80% since 1980 with subsequent decrease in surface water concentrations. During the same time period there has been only a slight downward trend in N deposition (SFT 2007), thus the relative importance for N in acidification may have increased.

Over the past decades, vast areas have received increased atmospheric deposition of inorganic, bioavailable nitrogen (N), partly as oxidized N from combustion processes, partly as reduced N from agricultural activities (Vitousek 1994). Also increased temperature due to climate change may increase soil mineralization rates and liberate inorganic N that is organically bound in the soils (Rustad et al. 2001). In terrestrial ecosystems the increased loading of N may cause supply in excess of N demand in soil and vegetation, a phenomenon termed N saturation (Aber et al. 1989, Ågren and Bosatta 1988). In terrestrial catchments experiencing N saturation the excess N spills into aquatic ecosystems (Aber et al. 1989, Stoddard 1994) usually in the form of nitrate (NO_3). NO_3 leaching from soils may cause acidification of surface water and eutrophication in coastal marine areas where the supply for N often is limited (Granéli et al. 1986, Howarth et al. 1996, Ryther and Dunstan 1971). Most Norwegian surface waters are phosphorus (P) limited and thus the potential for eutrophication due to increased N availability is small (Faafeng and Hessen 1993, Hessen et al. 1997a). It is more likely that the N:P ratio in surface water to be skewed toward more extreme P-limitation (Jassby et al. 1995).

High NO_3 leaching rates have been observed in mountain and heathland areas in Europe at sites receiving high levels of N deposition (Allott et al. 1995, Curtis et al. 1998, Harriman et al. 1998, Kamari et al. 1992, Kaste et al. 1997). These areas are characterised

by sparse vegetation on thin, patchy acidic soils and steep slopes and with relatively short growing season; they are therefore highly susceptible to NO₃ leaching. Surface waters in these areas are often oligotrophic and lack sufficient base cations to neutralize acidic components from atmospheric deposition and soil, and are therefore particularly vulnerable to acidification (Skjelkvåle and Wright 1998). In a comparative study of NO₃ leaching in sub-catchments within the Bjerkreim river basin, Kaste et al. (1997) reported higher N leaching from catchments dominated by bare rock relative to forest and heathland. Studies in forested catchments have indicated high but limited capacity for N retention in soil and vegetation (Nadelhoffer et al. 1999) and a vast number of studies in forest ecosystems have increased our knowledge of how these systems respond to increased N deposition and climate change (see e.g. Vitousek et al. 1997). Comparably less is known about factors affecting N leaching due to high N deposition in mountain and heathland areas, and how perturbation due to climate change may change these systems. In Norway mountain and heathlands constitutes approximately half the total area, thus it is therefore important to achieve insight into how catchment characteristic is affecting N leaching here. This knowledge gives important information for modelling future changes in N leaching and critical loads that can be used when negotiating new international agreements emission reductions of N.

1.2 Objectives of the study

The main objective of this study was to contribute to increased knowledge about processes controlling N leaching in Norwegian mountain and heathland areas experiencing relatively high N load. More specifically, the objectives addressed in the accompanying collection of papers have been:

- To test for possible empirical relationships between catchment characteristics and N leaching in mini-catchments dominated by different land cover types (Paper I)
- Quantify N retention in different land cover types (bare rock, peatland, and heathland) with moderate and high N deposition, respectively (Paper I)
- To test for causality between NO₃ and dissolved organic carbon (DOC) by nitrogen N and P additions to small humic lakes (Paper II)
- To model seasonal NO₃ leaching in a heathland catchment using the model MAGIC with monthly time-step (Paper III)

- To predict future NO₃ leaching from a heathland catchment given different scenarios of climate change (Paper IV)

To achieve these goals three research approaches have been used; empirical analysis, experimental studies and modelling (Figure 1). Empirical relationships between different land cover types and N leaching have been obtained from measurements from the mini-catchments (paper I). An empirical relationship based on long-term data from regional monitoring of surface waters in Norway was put forward to be tested (paper II). A field experiment was designed and accomplished to obtain better insight into the relationship based on the empirical data (paper II). An existing model was calibrated on a heathland catchment included in the Norwegian monitoring programme using long-term data and with input from large-scale field experiments (paper III). Finally future N leaching from the calibrated catchment was simulated by implementing scenarios for climate change (paper IV). The new insights obtained from calibration can be used in future model evaluation and development. This is, however, out of scope for this study.

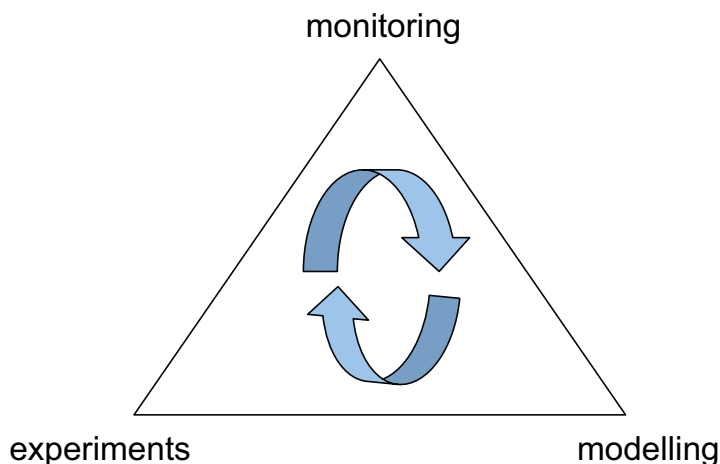
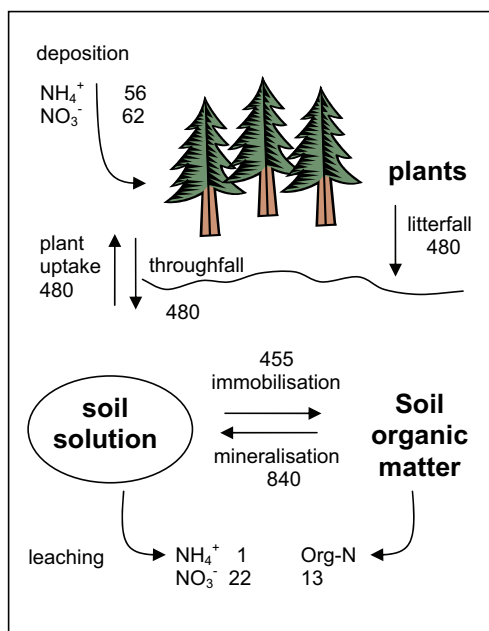


Figure 1. Schematic diagram showing the three research approaches used.

1.3 Nitrogen – a nutrient and component in acidification

1.3.1 The nitrogen cycle

The major part of atmospheric N deposition enters the terrestrial part of the catchment before reaching surface waters. N deposited is affected by a series of biological and chemical processes in the soil and enters the terrestrial N cycle (Figure 2). Major processes in the internal N cycle include assimilation by plants, litter fall, mineralisation of organically bound N into ammonium (NH_4), nitrification - oxidation of NH_4 to NO_3 , and microbial immobilisation. Denitrification – reduction of NO_3 to di-nitrogen (N_2 (g)), nitrogen-oxide (NO (g)) or di-nitrogen-oxide (N_2O (g)) occurs only under anaerobic conditions. N fixation of atmospheric N_2 into organic N performed by certain N fixing bacteria may counteract N losses from soil to the atmosphere from denitrification. NH_4



uptake is energetically preferred over NO_3 by plants and microbes, because NO_3 must be reduced before incorporated into the cells. Furthermore, due to the positive ionic charge NH_4 is absorbed to the negatively charged soil matrix. Taken together these processes are responsible for NO_3 rather than NH_4 leaching from the soil to surface waters.

Figure 2. N cycling ($\text{mmol m}^{-2} \text{ yr}^{-1}$) at the Øygardsbekken catchment. Leaching rates and deposition are measured mean annual values; immobilisation, and mineralization (=gross mineralization) are calculated from measured values and estimated rates from Wright et al. (1998). From paper III.

1.3.2 Nitrogen and acidification

Over the past 30 years acid atmospheric deposition has received considerable attention as an international environmental problem in Europe and North America. Polluted air masses containing S and N compounds travel long distances, cross national boundaries, and affect surface waters, ground waters and soils in other countries. The effect of N deposition in acidification of surface waters is dependent on the chemical form of N deposited and the

extent to which this N is being taken up through the internal soil N cycle. NO_3 ions are accompanied by cations when leached from the soil. If the soil is acidic, then a significant fraction of the accompanying cations are hydrogen- and aluminium acidic ions.

N deposition in Norway is almost evenly distributed between NO_3 and NH_4 (Tørseth and Semb 1997), and there are several possibilities in which NH_4NO_3 can be transformed through the internal soil N cycle (Figure 3). NH_4 can be either nitrified to NO_3 or taken up

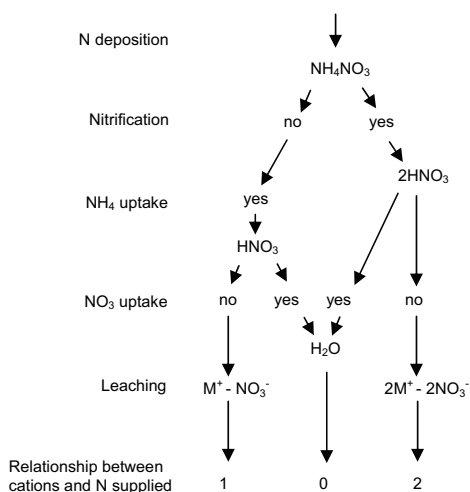


Figure 3. The effect of NH_4NO_3 deposition on the acidification of surface water. Adapted from Reuss and Johnson (1986).

in the soil. There are two possibilities if nitrified; 1) NO_3 is taken up in the soil and there is no acidification (Figure 3 right hand side, middle), or 2) NO_3 is leached unaltered to surface waters accompanied by 2 equivalents of cations (Figure 3, right hand side). There is no resulting acidification if NH_4 is taken up followed by NO_3 uptake (Figure 3, left hand side, middle), while one equivalent of cations can be released from the soil and leached if NO_3 is not taken up by the plants or microbes (Figure 3, left hand side).

Due to different soil N processes operating simultaneously, it can be difficult to predict the response of N deposition on affected receptors such as river and lakes. Monitoring is necessary. The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters) was established in 1985 and is based on existing monitoring programmes in the approximately 20 participating countries in Europe and North America (ICP waters 2003). The data collected provide useful information on dose-response relationships under different conditions and correlate changes in acidic deposition with the physical, chemical and biological status of lakes and streams. Trend analysis (during 1990-2001 and 1994-2004) performed on 189 sites within ICP Waters (ICP Waters 2007) showed no consistent rise or decline in NO_3 concentrations; some sites showed increased trends, some showed decreased trends while the majority did not show any change at all since 1990 (ICP Waters 2007). Despite reductions of S in surface water, the relative importance of NO_3 as an acidifying anion in Europe and North America does

not show any significant change (Figure 4). Only for about 14% of the European sites included in the study, NO_3 was more important in acidification of surface waters than SO_4 .

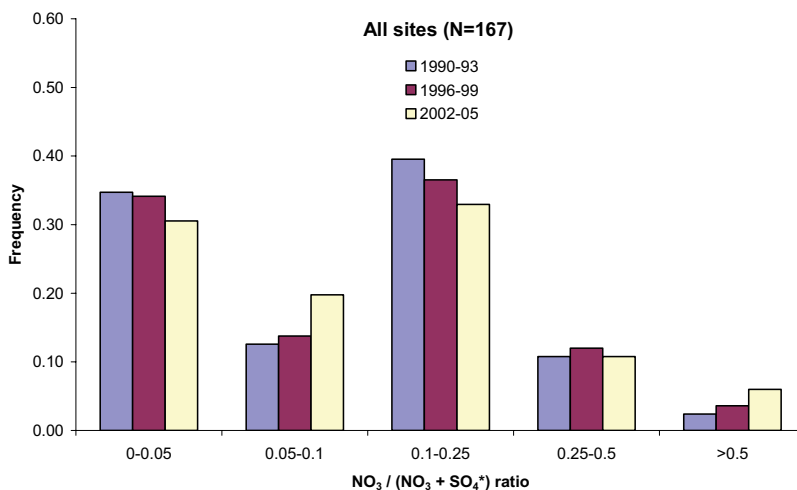


Figure 4. Relative importance of NO_3 in acidification at 167 ICP Waters sites in 1990-93 compared to the period 2002-05 for the same sites. From ICP Waters 2007.

1.3.3 Nitrogen and interaction with other nutrients

N is commonly the growth-limiting nutrient in temperate and boreal terrestrial ecosystems (Aersts et al. 1992, Chapin et al. 1986, Tamm 1991, Vitousek and Howarth 1991). The concept of nutrient limitation comes from agriculture and refers to the limitation of productivity of individual crop species due to insufficient supply of essential nutrients in the soil. If a N-saturated terrestrial ecosystem leaches a significant fraction of the incoming N, then another factor than N may be limiting to growth. Possible other factors are other nutrients such as phosphorous (P) or potassium (K). Fertiliser trials in forests, heathlands and wetlands indicate that although N is normally the growth-limiting nutrient, in areas receiving high N deposition or when N is applied as fertiliser, additional growth increases of vegetation are induced by P and/or K additions (Aerts and Berendse 1988, Aerts et al. 1992, Hayati and Proctor 1991). Fertilisation with P and K to a Sitka spruce stand in the UK also demonstrated significantly lower NO_3 concentration in soil solution (Stevens et al. 1993). Thus, increased P loading to the terrestrial part of N saturated systems may reduce N leaching and thus acidification surface waters.

Surface waters in mountain and heathland areas receiving high N load are generally P-limited. Moderate P additions to these oligotrophic waters may stimulate NO₃ assimilation by algae and plants (Davison 1995, Hessen et al. 1997b, Lyche-Solheim et al. 2001). When one equivalent of NO₃ is assimilated approximately one equivalent of acid is consumed resulting in decreased surface water acidity (Davison 1995). Increased retention of N in the aquatic part of the N saturated ecosystem may prevent eutrophication of receiving coastal areas.

Chronic N deposition leads to an enrichment of the N content in the soil organic matter. Data from European forests across a gradient of N deposition indicate that the C/N ratio in the forest floor is closely related to both N deposition and leaching of N from forests. Sites with low C/N ratios (N-rich sites) lose a substantial fraction of the incoming N (Gundersen 1995, Gundersen et al. 1998). The relationship between soil C/N ratio and NO₃ leaching has also been observed in moorland ecosystems in the UK (Curtis et al. 2004). The mechanism of N retention in both systems seems to be immobilisation by soil bacteria. Soil C/N ratio has also been used to successfully model riverine DOC on a local and global scale (Aitkenhead and McDowell 2000). The mechanism responsible for this relationship is not fully understood, due to the complex interaction between vegetation, microbes and climate that drive terrestrial C and N dynamics (Reich et al. 1997). It was suggested, however, that C:N may be a proxy for the climatic variables temperature and precipitation, each of which controls both the production and flux of DOC via biotic and hydrological pathways (Aitkenhead and McDowell 2000).

2. Site description

2.1 Øygard and Måkevatn

Øygard (2.55 km², 58°37'N, 6°08'E) is a small, semi-natural upland catchment in the Bjerkreim river basin, Rogaland County, south-west Norway (Figure 5). There is one major (Hedlevatn, 309 m.a.s.l) and several small lakes within the catchment that have a dampening effect of the surface water NO₃ concentrations at the catchment outlet (see figure 2, paper III for bathymetric chart of lake Hedlevatn). The catchment altitude ranges from 185-545 m a.s.l., with granitic-gneiss bedrock, thin and patchy podsollic soils mixed with areas of exposed bedrock. Dominating vegetation is *Calluna* heather, *Sphagnum* mosses, grasses and mountain birch. The climate is mild, humid with relatively high

amounts of annual precipitation ($>2000 \text{ mm year}^{-1}$) and annual mean (1993-2004) air temperature of $6.3 \text{ }^{\circ}\text{C}$. N deposition is about $20 \text{ kg N ha}^{-1} \text{ year}^{-1}$ and inorganic N output (mostly as NO_3) is about $5 \text{ kg ha}^{-1} \text{ year}^{-1}$ (Kaste et al. 1997).

The main stream at Øygard, Øygardsbekken, has been monitored since 1993, first as part of the project ‘Nitrogen from mountains to Fjords’ (Hessen et al. 1997c) and since 1995 as part of the Norwegian monitoring programme on long-range transboundary air pollution (SFT 2004). The 12-year NO_3 time series (1993-2004) from this stream served as basis for the calibration with MAGIC (paper III) and was used in future predictions of NO_3 leaching implementing climate change scenarios (paper IV).

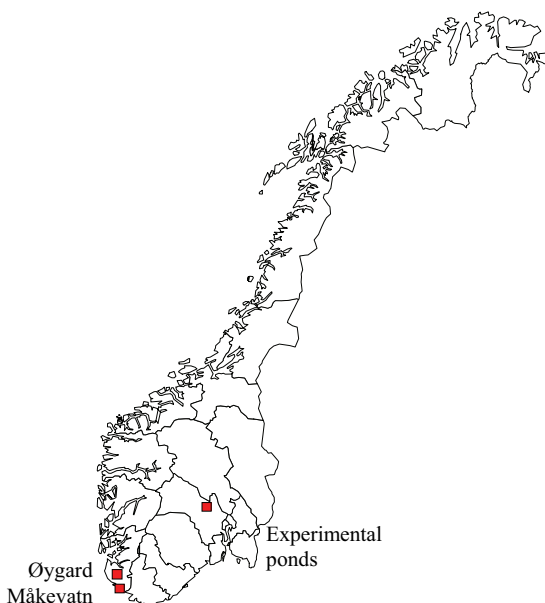


Figure 5. Map with location of the study sites in Norway.

Måkevatn ($58^{\circ}19'\text{N}$, $6^{\circ}23'\text{E}$) is located closer to the coast ($<5 \text{ km}$) and about 37 km southwest of Øygard (Figure 5). The two catchments have relative similar catchment characteristics, but Måkevatn has generally slightly higher share of exposed bedrock and Øygard has more heather vegetation (table II, paper I). The Øygard and Måkevatn catchments have moderate and high N deposition, respectively. At Øygard and Måkevatn six small, headwater catchments were chosen; two dominated by peat (Suffix M=Norwegian ‘myr’, MM1, MM2, ØM1 and ØM2), two dominated by heather (Suffix L=Norwegian ‘lyng’; ML1, ML2, ØL1 and ØL2) and two dominated by bare rock and grasses/sedges (Suffix F=Norwegian ‘fjell’; MF1, MF2, ØF1 and ØF2) (figure 1, paper I). The catchments also have various elements of the other ecotypes (table II, paper I). The rocky sites at both catchments have a high proportion of grasses and sedges.

2.2 Experimental ponds

Five small humic ponds situated in a peaty forested area of eastern Norway, Buskerud County were chosen for a field manipulation experiment (Figure 5). The ponds are located at 650 m a.s.l. within a radius of approximately 500 meters (figure 1, paper II). They are seepage fed and subjected to the same hydrological patterns and catchment properties. Dominant trees and vegetation are Norway spruce (*Picea abies*), Scots pine (*Pinus sylvestri*), blueberry bushes (*Vaccinium myrtillus*), heather (*Calluna vulgaris*) and *Sphagnum* mosses. This area has received low levels of atmospheric N deposition ($\approx 4.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, annual mean 1973-1990), and the ponds have previously been monitored for several years during the 1970's providing background data on natural TOC and NO_3 fluctuations (figure 2, paper II).

3. Methods

3.1 Field sampling and measurements in the mini-catchments

In a previous investigation Kaste et al. (1997) reported higher N leaching from catchments dominated by bare rock relative to forest and heathland. The main objective of paper I was to identify relationships between different vegetation cover (i.e. peat, heather and exposed bedrock) and N leaching on a seasonal and annual basis.

Surface water was sampled at the mini-catchment outlets approximately 8 times annually (from June 1999-July 2001) and analysed for major ions, but only N species (NO_3 , NH_4 (total inorganic N (TIN) = $\text{NO}_3 + \text{NH}_4$), total N (tot-N) and total organic N (TON) calculated by difference) and TOC were used in paper I. Fluxes of the various N species were calculated for each day using scaled areal water discharge and the corresponding chemical data from the catchments; either observed or linearly interpolated concentrations. N deposition was taken from the nearest monitoring station operated by the Norwegian Institute for Air Research (NILU).

Soil samples were taken from the surface (0–20 cm) of the organic horizon and analysed with respect to pH (H_2O), total content of C and N, and exchangeable acidity and cations. Cation exchange capacity (CEC) of the soil was calculated as sum of exchangeable base cations and exchangeable acidity. Only the soil C/N ratio data were used in paper I.

Simple annual input-output budgets of N species for each of the mini-catchments were calculated and related to the different vegetation types. Surface water NO₃ concentration data were grouped according to season (winter= December-February, spring= March-May, summer= June-August and autumn= September-November) and were related to the percent coverage of the different vegetation types.

3.2 Field manipulation experiment

The field experiment was designed to test a proposed causal inverse relationship in surface water (Goodale et al. 2005) between NO₃ and DOC concentrations (Evans et al. 2006, Goodale et al. 2005, Harriman et al. 1998, Skjelkvåle and Henriksen 1998, Konohira and Yoshioka 2005). The observed empirical inverse relationship might be caused by processes active in the terrestrial catchment, in the waterbody itself, or a combination of both. C and N are highly coupled through their soil nutrient cycles. Still no dose-response relationship has been demonstrated in terrestrial ecosystems by adding or removing N from deposition (i.e. no effect on DOC leaching to surface waters) (Moldan et al. 2006, Wright et al. 1993). Thus one might suspect that processes within the waterbody itself are responsible for the observed NO₃-DOC relationship. Paper II tested the hypothesis that increased availability of NO₃ (or N+P) would stimulate bacterial oxidation of DOC in the waterbody.

This hypothesis was tested in field manipulation experiments in which NO₃ (e.g. NaNO₃) up to a total concentration of about 600 µg N l⁻¹, was added to a DOC-rich pond. A combination of NO₃ and P (NaH₂PO₄) (to assure microbial stimulation) up to NO₃ and phosphate (PO₄) concentrations of about 700 µg N l⁻¹ and 40 µg P l⁻¹, respectively, was added to a second pond. In case of rapid incorporation of P in biota, P was added two times by the same amount with 3 days interval. The amount of nutrient to be added was based on bathymetric charts of the ponds (appendix 1, paper II) as obtained by manually sounding using a boat and Secchi disk, and measured temperature profiles (to estimate epilimnion volume).

Three additional ponds in close vicinity (less than 1 km) to the manipulated, served as untreated references. If the hypothesis is correct, a decline in DOC in the manipulated ponds relative to the unmanipulated ponds was expected. The experiments were conducted during August-October 2005. Autumn was chosen for the experiment because of organic carbon content is highest during this season (figure 2, paper II).

3.3 MAGIC calibration

Despite the extensive use of the dynamic model MAGIC on annual basis, there have been few attempts using monthly time steps to examine seasonal variations. NO₃, in particular, shows a pronounced seasonal pattern in many lakes and streams. In this study the objective was to apply the MAGIC model to the 12-year time-series from Øygardsbekken using a monthly time step. The main goal was to test how well MAGIC could reproduce the observed long-term (1993-2004) seasonal NO₃ pattern (paper III). The model calibration was then used to simulate future NO₃ leaching from this catchment, given future scenarios for climate change and N deposition (paper IV).

The calibration tested different ways of estimating monthly rates for each of the N and C processes included in MAGIC; decomposition of soil organic matter, gross N mineralization, plant N uptake, litterfall N and microbial immobilisation. The rates of these key ecosystem processes were assumed governed by temperature. Several trials were run to compare estimates of the different N processes (trials 1-4, Table 2, paper III). Then the effect of including a snowmelt routine was tested (trial 5). The trials also included tests of the effect of using either all or some of the input and parameter files with all years alike (i.e. input with long-term (1993-2004) monthly mean values for each year) both with and without the snowmelt routine.

3.4 MAGIC scenario simulation

In this study the main objective was to use the MAGIC model as was calibrated on Øygardsbekken to simulate future NO₃ leaching from the catchment, implementing a future N deposition scenario combined with four different scenarios for climate change (paper IV). We wanted to investigate both seasonal and annual changes in NO₃ leaching.

The scenarios comprised future estimates for temperature (increased by 2.1-3.7 °C), precipitation (10-34% increase) and N deposition (increase in TIN by 5-23%). The climate scenarios were based on dynamically-downscaled data from the Rossby Centre Regional Climate model (RCAO) driven by two scenarios of greenhouse gas emissions, A2 and B2, run with two global climate models, HadAM3 and ECHAM4/OPYC3, from the Hadley Center and Max Planck Institute, respectively.

Two different storylines for future rates of C and N processes were used. The first assumed a change in both vegetation and soil processes due to future warming and N deposition (SL2), while the other assumed changes only in soil processes (SL1). Future

process rates of N and C in the catchment were estimated based on the downscaled temperature scenarios, in the same manner as during model calibration.

A future warmer climate will also change the thermal regime in the small lake Hedlevatn, situated near the bottom of the catchment. This will affect the damping of seasonal pattern of NO₃ concentrations in runoff from the terrestrial parts of the catchment. Future changes in lake thermal regime have been estimated for lake Kolbotnvatn, a small lake in southeastern Norway (Tjomsland and Rohrlack 2008), and these estimates were used for lake Hedlevatn.

3.5 Statistical analysis

A multiple regression analysis was used to identify the main parameters explaining the variability in relative inorganic N leaching from the different vegetation types (paper I). Akaike's information criterion (AIC) was used as model selection tool, choosing the model with the lowest AIC (Akaike 1973). Simple linear regression was used on NO₃ concentration from the mini-catchments and percent cover of each vegetation type. The statistical programme JMP was used in these analysis.

To estimate differences between treatments during the field manipulation experiment (paper II), comparisons of calculated difference between each day during treatment and the last day prior to treatment were analysed with lake and time included as factors using one-way ANOVA followed by Tukey Honest Significant difference test (Tukey's HSD) (Appendix III, paper II). The statistical packages in R were used in this analysis (R Development Core Team 2006).

In evaluating model success in reproducing NO₃ surface water concentrations, efficiency, root mean square error (RMSE) and coefficient of determination (R^2) were calculated (equations 1-3, paper III) using general statistics in Microsoft Excel.

4. Main results

4.1 N leaching and vegetation cover (paper I)

The NO₃ concentrations in runoff from the mini-catchments showed clear seasonal patterns with high values in winter during the dormant season, and low values during the summer (figure 6). All catchments showed relatively much higher NO₃ concentrations during the

winter period of year 2001 compared to year 2000, probably due to soil freezing in 2001. NO_3^- levels varied considerably between catchments, especially at Øygard which in general also showed much lower levels compared to those at Måkevatn.

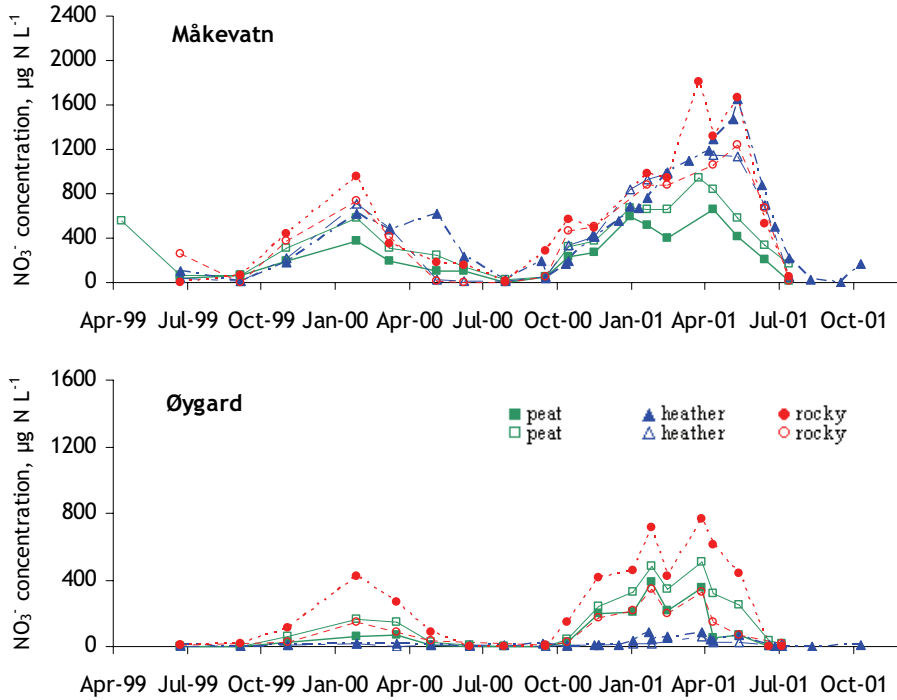


Figure 6. Seasonal NO_3^- concentrations in runoff from the mini-catchments at Måkevatn (top panel) and Øygard (bottom panel). Squares (open and solid), triangles (open and solid) and circles (open and solid) represent peat-, heather- and exposed bedrock dominated catchments, respectively (paper I).

As expected, highest NO_3^- leaching was found for the exposed bedrock dominated catchments. The fraction coverage of exposed bedrock explained 70% of the variation in NO_3^- concentrations during autumn and winter, but a much lower percent during the warmer seasons when biological processes exert higher control (figure 10, paper I).

Monthly NO_3^- fluxes showed analogous seasonal trends as concentrations (Figure 5 and 6, paper I). The large differences observed in maximum nitrate runoff concentrations between the two winter periods, however, were damped for fluxes due to lower flow in the spring of 2001 compared to 2000 (Figures 2d and 3d, paper I).

Calculated from year 2000, TIN deposition was 16.3 and 27.5 kg ha⁻¹ year⁻¹ at Øygard and Måkevatn, respectively. At Øygard and Måkevatn TIN leaching was 0.4-6.8 and 5.9-13 kg ha⁻¹ year⁻¹, respectively, representing relative leaching rates (compared to TIN input) of 3-42% and 22-47% (table III, paper I). When including annual data for fluxes (year 2000) from all mini-catchments (Øygard and Måkevatn) the fractional cover of exposed bedrock could explain 74% of the variation in inorganic N loss (figure 9, paper I).

Although the mini-catchments were classified according to the dominant vegetation (i.e. the vegetation type that constituted the largest fraction of each catchment), they were not homogenous (table II, paper I). This is because that although classified as e.g. a “heather” catchment, the percent share of heather was different from that at the other heather catchments. Furthermore, each catchment had a mixture of each of the other vegetation types thus complicating the picture. It was therefore not possible to distinguish between NO₃ leaching from the peat- and heather dominated catchments in this investigation. Although not presented in paper I, results indicated that the higher the catchment percentage of peat, the lower the NO₃ leaching.

4.2 Field manipulation experiment (paper II)

As intended, the NO₃ concentrations increased from near zero up to 685 and 560 µg N l⁻¹ at the N+P and N manipulated ponds (figure 3, paper II). Correspondingly, PO₄ concentration increased from below detection limit up to 32 µg P l⁻¹ after the first addition and to 58 µg P l⁻¹ after the second. The increase in N availability showed no effect on DOC, total organic carbon (TOC), bacteria or algae (measured as chlorophyll a) in the pond that received N alone (figure 3 and 4, paper II). After an initial depletion of the resulting high NO₃ concentrations following amendments, N concentrations stabilised at about 250 µg N L⁻¹ (in the N treatment). This is more than 100 µg N L⁻¹ higher than the concentration in the control ponds. In the pond receiving both N and P, however, there was a rapid decrease in NO₃ concentrations after the increased N availability due to amendments, resulting in large increase in the number of bacteria, algae and an increase in pH, but no change in DOC or TOC concentrations (figure 3 and 4, paper II). These results indicate that the inverse relationship between NO₃ and DOC in surface waters is probably not due to processes occurring within the waterbody.

4.3 MAGIC calibration (paper III)

The MAGIC application to Øygardsbekken satisfactorily simulated the seasonal NO_3 pattern over the 12-year record; the model explained almost 70% of the variation in monthly NO_3 concentrations (Figure 7) and nearly 90% of the variations in flux. The best set-up was when using all years alike for the deposition and nitrogen input files, but with inter annual variability in the runoff file, and with the snowmelt routine included (paper III).

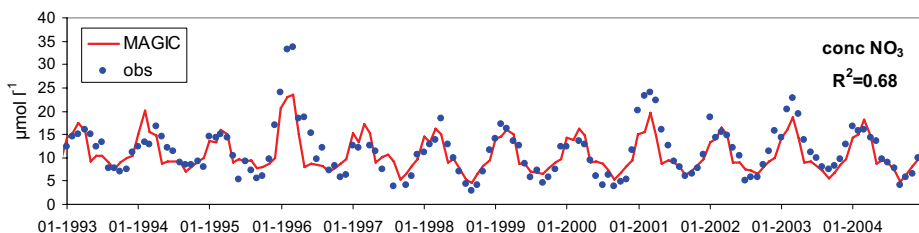


Figure 7. Observed NO_3 concentrations (solid circles) compared to MAGIC simulated (solid line) for the calibration period 1993-2004 (paper III).

4.4 MAGIC scenario simulation (paper IV)

Implementing climate change scenarios for temperature and N deposition to the calibrated model at Øygardsbekken resulted in increased future NO_3 leaching to surface water (paper IV).

Soil organic N pools increased by 10% for all scenarios irrespective of storyline, while for SL1 the soil organic C pool was reduced by 7-14% compared to only minor changes for the scenarios in SL2 (Figure 8, and table 4 paper IV). With the reduction and increase of the soil organic C and N pools respectively, the simulated soil C/N ratios were predicted to continue to decline under all scenarios, slightly more for SL1 compared to SL2.

The future simulated seasonal NO_3 patterns were different from present-day in both storylines (Figure 9). There were moderate changes in NO_3 levels and shape of the curves simulated for SL2, but the NO_3 concentrations were skewed towards highest leaching during spring, compared to winter at present. For SL2, MAGIC simulated large increases in NO_3 levels and the seasonal pattern levelled out (Figure 9).

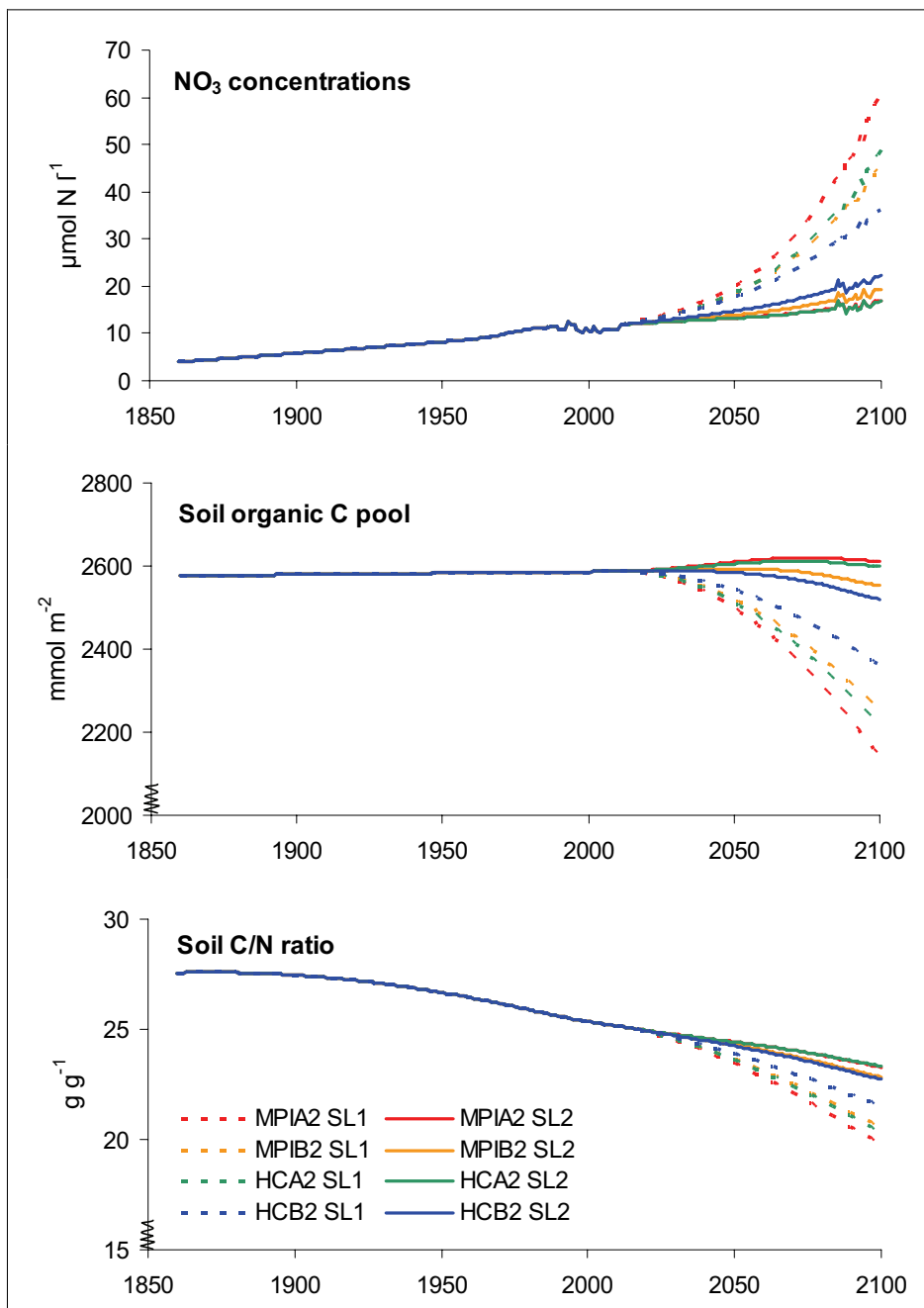


Figure 8. Simulated mean annual NO_3 surface water concentration, $\mu\text{mol l}^{-1}$ (upper panel), soil organic C pool, mmol m^{-2} (middle panel) and soil C/N ratio, g g^{-1} (lower panel) for SL1 (solid lines) and SL2 (dashed lines) during 1860-2100. Green, blue, orange and red lines represent HCA2, HCB2, MPIA2 and MPIB2 scenarios, respectively.

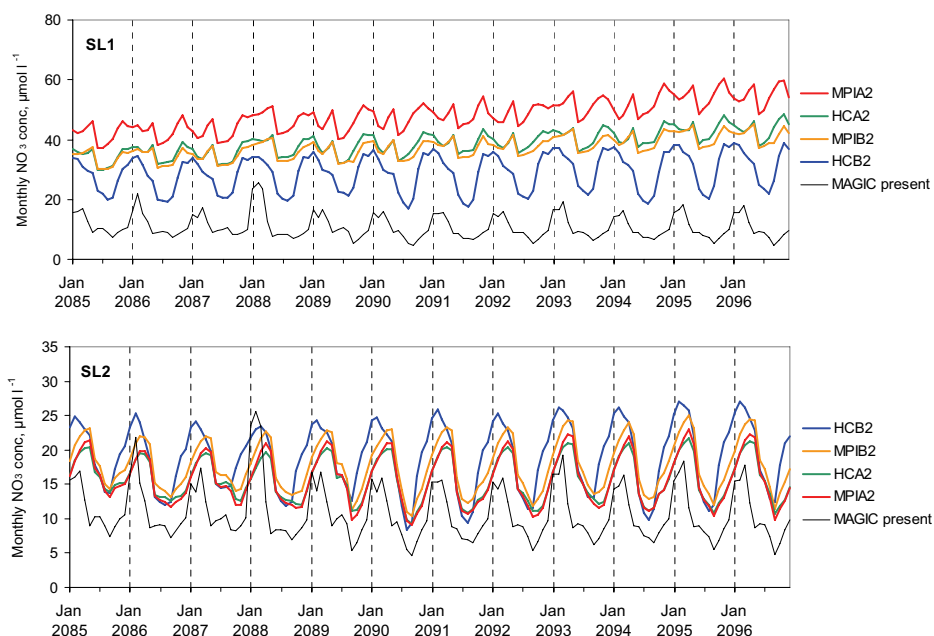


Figure 9. Simulated monthly seasonal NO_3 surface water pattern for SL1 (upper panel) and SL2 (lower panel) during the scenario period 2085-2096 for the different scenarios (coloured lines) compared to present-day simulations during 1993-2004 (black). Units are in $\mu\text{mol l}^{-1}$. Note different scaling on the y-axis (paper IV).

5. Discussion

5.1 Seasonal behaviour of NO_3 in surface water and N saturation

In N-limited terrestrial catchments, plant and microbial uptake lower the NO_3 concentrations in runoff during the growing season, often to levels below $5 \mu\text{g N l}^{-1}$ (paper I). During the dormant season, NO_3 concentrations are often higher due to low biological activity (low temperatures and poor light conditions) and higher precipitation and atmospheric N deposition rates. Thus, the seasonal NO_3 pattern often varies in phase with the general sinusoidal temperature pattern (paper III).

The seasonal behaviour of NO_3 is often used as an indicator of the catchment's ability to retain N from atmospheric deposition. Weak seasonal oscillation and generally high NO_3 concentrations in surface waters can be an indicator of N saturation which can imply limitation of biotic function by factors other than N (Aber et al. 1989, Stoddard

1994). This was the underlying assumption for the storyline, SL1 when modelling future changes in surface water NO₃ concentrations at Øygardsbekken (paper IV).

Based on the N saturation concept, Aber et al. (1989) proposed a hypothetical time course with recognisable stages (0-3) for a catchment response to chronic N additions. Some years later, Stoddard (1994) adjusted the concept for surface waters. The N saturation stage system reflects long-term and seasonal patterns of NO₃ concentrations in lake and stream water, as the catchments become more N-sufficient (figure10). In contrast to stage 0 (no saturation), the early stage of N saturation (1) is marked by increases in the severity and frequency of NO₃ episodes owing to increased N supply and reduction of the N limitation period within the growing season. The later stages (2 and 3) are marked by elevated NO₃ concentrations in surface waters also during the growing season, thus on an annual basis NO₃ may become a significant contributor to freshwater acidification. In these stages the period of N limitation during the growing season is much reduced, and the combined inputs of N from deposition and mineralisation with subsequent nitrification, can produce surface water NO₃ concentrations that exceed the input from deposition (stage 3).

Stoddard and Traaen (1995) proposed a set of distinct seasonal-dependent chemical criteria to allow a classification of water systems into different stages of N saturation. According to these criteria, the terrestrial headwater mini-catchments at Øygard and Måkevatn can be placed in stage 0 and 1, respectively (paper I). The placement of the Måkevatn mini-catchments into higher N saturation stage is due to the shorter period with low NO₃ concentration during summer compared to the Øygard catchments. Higher N deposition levels and lower soil C/N ratios measured here may have contributed to progression into higher N saturation stage. In contrast to the mini-catchments, the Øygard catchment as a whole is classified as stage 1 based in these criteria. At first sight, this can be taken as a sign of N saturation. However, it has been shown that lake sites with long water residence times show weak or even absent seasonal NO₃ variation at the lake outlet, even though brooks within the surrounding terrestrial catchment show distinct seasonal variation (Kaste et al. 2003). Thus, the classification of Øygard into stage 1 does not necessarily indicate progression into higher N saturation stage, but might be due to the dampening effect of the lakes within the catchment. Hence, there may not always be a distinct relationship between seasonal variations of NO₃ near the lake outlets and N saturation stage in the terrestrial catchment as demonstrated for Øygard (paper I and paper III).

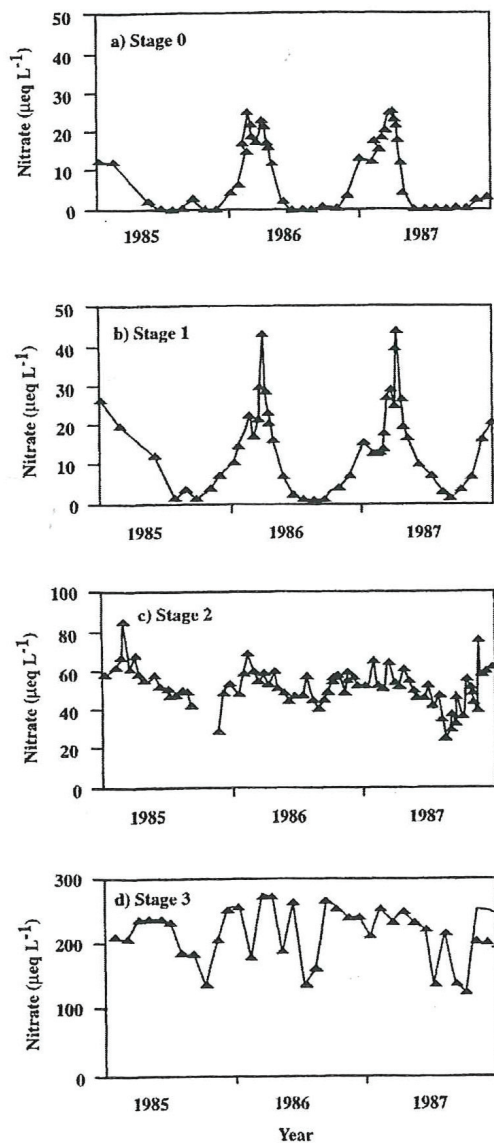


Figure 10. Expected changes of the seasonal long-term patterns of surface water NO_3 concentrations in response to the progressive development in N saturation (from Stoddard (1994)).

5.2 NO₃ leaching related to other elements

The biogeochemical cycles of C and N (and partly P) are highly coupled, impart because plant and microbes each require specific amounts of C, N and P for growth. Limitation of one of these elements can restrict plant or microbial growth or both, and may result in competition for nutrients. In the small humic ponds receiving N or N+P combined, P limitation for biological uptake of N was demonstrated (paper II). The recalcitrant nature of the organic C in these ponds may further have limited heterotrophic oxidation of DOC, as the nutrients added did not affect surface water DOC concentration despite large increase in both chlorophyll a (proxy for algal biomass) and bacterial number (paper II). The results from this study suggest that the commonly observed negative association between NO₃ and DOC is not likely caused by biological activity in DOC-rich surface waters.

Sobczak et al. (2003) tested the alternative from our hypothesis – namely that DOC additions cause reductions in NO₃ concentrations. Their study used water from high NO₃ streams in a series of experimental mesocosms. They found a marked decline in DOC concentrations and complete removal of NO₃ due to microbial uptake, thus demonstrating the potential for NO₃ removal in the water when bioavailable DOC is present. In light of the NO₃-DOC relationship this result indicates that microbial assimilation in the water may contribute to explain the observed NO₃-DOC relationship, but only if the DOC is bioavailable.

The empirical relationship between NO₃ and DOC shows that lower NO₃ leaching to surface water occurs in lakes characterised by high DOC concentrations (i.e. humic lakes), and the opposite, high NO₃ leaching occurs to low DOC lakes. A possible explanation for the inverse NO₃-DOC relationship can be related to differences in N deposition and the characteristic of catchment soils. Mountainous catchments are characterised by thin, patchy soils with high percentage of exposed bedrock and thus relatively low ability to retain N from atmospheric deposition (paper I). Mountainous lakes subject to high N depositions may therefore have high NO₃ content (figure 11, upper left quadrant). As demonstrated from the mini-catchments dominated by exposed bedrock, lower N leaching was observed at those located at Øygard receiving comparably lower N deposition than those at Måkevatn (paper I). Thus for lakes in mountain areas receiving low N deposition, NO₃ leaching would probably also be lower (Figure 11, lower left quadrant).

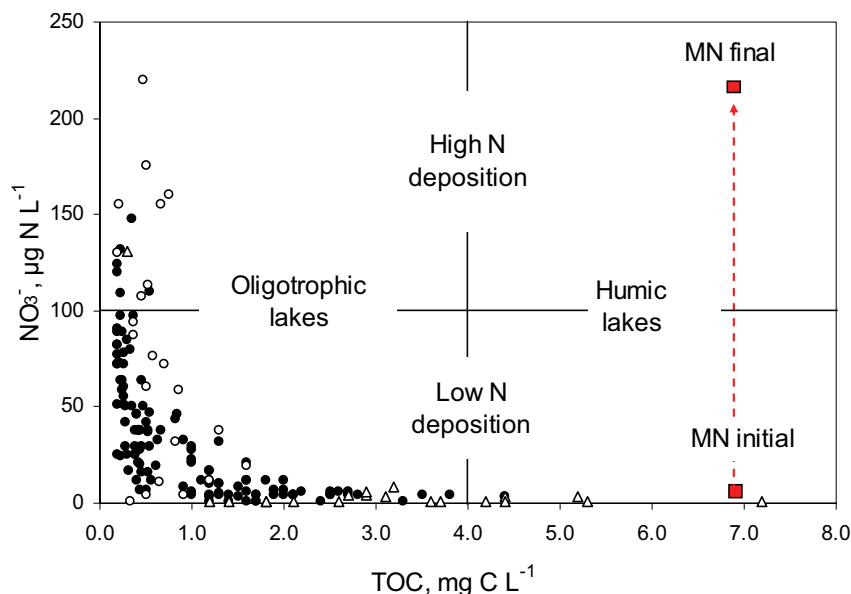


Figure 11. Schematic division of lakes based on the inverse NO_3 -DOC relationship in surface waters. Plotted data are from upland streams in Norway (from Skjelkvåle and Henriksen 1998). Also shown is the experimental pond MN, prior and after addition of NO_3 (paper II).

High DOC waters (figure 11, right side) are often located in peaty, forested areas and have deep soils with high capacity for N retention and result in low leaching of NO_3 to surface water. The ponds that were used in the manipulation experiment are examples of lakes with high DOC and low NO_3 concentrations (paper II). There are no observations in the upper, right quadrant (high NO_3 and DOC concentration combined) except for the experimental pond that received N alone (paper II).

5.3 Future NO_3 leaching to surface waters in response to climate change

Catchments N stores have increased during several decades of elevated N deposition and retention (Skjelkvåle et al. 1998). The long-term stability of this N accumulation is largely unknown (Vitousek et al. 1997, Wright 1998). Internal ecosystem cycling of N greatly exceeds system inputs and outputs (Figure 2), and any disturbance of this cycle has the potential to obscure the relationship between N deposition and runoff.

The time series of NO₃ concentrations used during calibration (paper III), and those from the mini-catchments (paper I) represent present-day situation at Øygard. With climate change increased temperature, precipitation and N deposition may alter this system in the future. Results from the modelling exercise implementing climate change scenarios for temperature and N deposition (paper IV), suggest larger differences and thus uncertainties between the two storylines compared to the differences between the scenarios (and thus the different GCMs) within each storyline (figure 4, paper IV). The underlying assumption for SL1 (i.e. no change in vegetation) is that elements other than N and temperature may limit vegetation growth. Those might be PO₄, potassium (K) or water. For SL2 the underlying assumption is that plant foliage will become enriched in N due to increased N uptake, and consequently litter C/N will decrease (Hobbie 2000, Norby and Cotrufo 1998). With these two storylines we have two contrasting results, i.e. large increased (SL1) and small increased (SL2) NO₃ leaching to surface water. The overall higher NO₃ leaching rates simulated for SL1 compared to SL2 are probably due to the lower soil C/N ratios under SL1. SL2 entails a higher supply of organic C in litter, which acts to maintain present-day soil C pool (figure 4, paper IV).

Based on MAGIC forecast simulations and according to Stoddard's N saturation criteria the Øygard catchment might progress towards stage 2 under the assumptions of SL2 (Figure 9). However, when assuming no change in vegetation in response to warming and increased N deposition (SL1), Øygard might progress towards the highest N saturation stage (3) (Figure 9). It is not a trivial task to decide which is the more likely storyline. Most biological processes are temperature dependent, thus increased temperature may speed up the different processes in the internal N cycle (e.g. Figure 2) making the "wheel" go faster than present. Increased N deposition may increase foliar mass and litter inputs. Whether plant uptake or net microbial mineralisation (=gross mineralisation – immobilisation) (figure 2) increases the most is not clear.

The humic ponds investigated during the field manipulation experiment (paper II) showed limitation of both N and P combined in the water. With climate change increased temperature may cause increased soil mineralisation (Rustad et al. 2001), and in combination with higher rates for N deposition, leaching of NO₃ to these waters may occur as the soils gradually becomes N saturated. Based on the result from the field manipulation experiment, however, increased N availability alone will have little impact on biological activity in humic waters, unless P also increases (paper II).

5.4 Uncertainties and shortcomings in dynamic modelling

Modelling the effect of increased temperature and N deposition for the next 100 years is fraught with large uncertainty. The accumulating evidence from single and multi-factor ecosystem-scale manipulation experiments has greatly improved our understanding of short-term responses of terrestrial ecosystems and many of their components to elevated atmospheric CO₂, warming, changes in water availability and N deposition (see e.g. Emmett et al. 1998, Hyvönen et al. 2007, Rustad et al. 2001, Stitt and Krapp 1999). For long-term simulations, however, experimental data are still lacking. For instance in areas that have experienced decades of elevated N deposition the long-term fate of the N retained and stored in soil is uncertain. Correspondingly, we do not know whether the net primary production (NPP) or soil decomposition will increase more with climate change, and thus there is high uncertainty associated with fate of the large store of C in soil.

Concern exists that the initial responses in ecosystem manipulations may be transitory, and caution should be used when attempting to extrapolate short-term experimental responses to infer longer-term effects (Norby and Luo 2004). Furthermore, data from these experiments may be difficult to generalize and transfer to other ecosystems as the responses induced by the perturbations may be site-specific and depend on the history and state of the ecosystem. To do the extrapolations to provide estimates for inputs to ecosystem models it will be necessary to improve the understanding of the change in response patterns over time, including alterations in the magnitude, direction, and rate of change of the response. These issues represent one of the biggest challenges in accurately predicting long-term changes in ecosystems and associated feedbacks to the atmospheric and climate system (Rustad 2006).

5.5 Nitrogen and climate change – confounding factors in recovery of acidification

Environmental factors other than acid deposition – so called ‘confounding’ factors – are expected to affect chemical and biological recovery of freshwaters in response to reduced acid deposition. Climate change is one of these factors. Climate contributes considerably to variability in surface water chemistry. Climate change may both enhance and delay recovery depending on region and variable considered.

N deposition is generally regarded as the main driver behind NO₃ leaching from soils to surface waters. Continued high deposition of N should tend to increase N saturation and

give increased NO_3 concentrations in runoff, thereby delaying recovery due to reductions in S-emissions. Replacement of declining SO_4 export by increasing NO_3 export as occurs in ecosystems that are approaching N saturation will thus nullify acidification recovery. The uncertainty in future chemical recovery from acidification is mainly related to the effects of climate change and future behaviour of N in the ecosystem.

But because internal ecosystem cycling of N greatly exceeds system inputs and outputs (Figure 2), any disturbance of this cycle has the potential to completely obscure the relationship between N deposition and runoff.

Results from the CLIMEX project (Wright and Jenkins 2001), in which ambient air and soil temperature were increased over three years, show increased leaching of inorganic N, probably due to increased mineralization and nitrification rates in the soils. Increased temperature due to climate change may thus increase nitrate in runoff and thereby also contribute to delay in recovery.

Climate change is also expected to lead to warmer winters. Warmer winters in areas where snow accumulation is common may contradictorily be associated with colder soils. This is because an unstable snowpack caused by frequent thaw periods isolates the soil less than a thick, continuous snowpack. Thus, soils during winter may become colder in an overall warmer climate with large effects on temperature-sensitive processes that drive N leaching. Groffman et al. (2001) suggest that a higher frequency of freeze-thaw cycles increase nitrate release from soils. Large pulses of nitrate have been observed in surface waters following severe winters in the UK and the US, possibly as a result of soil freezing (Mitchell et al. 1996, Monteith et al. 2000). Soil freezing may also have caused the doubling of NO_3 leaching rates at the mini-catchments during winter of 2001 compared to year 2000 (paper I). The frequency of such pulses may be expected to change in the future in response to altered climate.

6. Concluding remarks

There are still large uncertainties associated with future NO_3 leaching in a response to altered N deposition levels and possible changes in the global climate (Jenkins et al. 2001). Long-term monitoring and experiments in various ecosystem types under varying N deposition levels and climatic conditions are necessary to test for underlying mechanism of change. Further studies of individual N processes and rates are also needed to make better predictions of future NO_3 leaching using modelling as a tool for synthesis.

The uncertainty in future chemical recovery from acidification is mainly related to the effects of climate change and future behaviour of N in the ecosystem. More research is needed on the long-term fate of N stored in soil under changing N deposition and climate. Release of N from this pool has potentially large effects in freshwater and coastal marine ecosystems.

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