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Controls on inorganic nitrogen leaching from Finnish catchments assessed using a sensitivity and uncertainty analysis of the INCA-N model

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The semi-distributed, dynamic INCA-N model was used to simulate the behaviour of dissolved inorganic nitrogen (DIN) in two Finnish research catchments. Parameter sensitivity and model structural uncertainty were analysed using generalized sensitivity analysis. The Mustajoki catchment is a forested upstream catchment, while the Savijoki catchment represents intensively cultivated lowlands. In general, there were more influential parameters in Savijoki than Mustajoki. Model results were sensitive to N-transformation rates, vegetation dynamics, and soil and river hydrology. Values of the sensitive parameters were based on long-term measurements covering both warm and cold years. The highest measured DIN concentrations fell between minimum and maximum values estimated during the uncertainty analysis. The lowest measured concentrations fell outside these bounds, suggesting that some retention processes may be missing from the current model structure. The lowest concentrations occurred mainly during low flow periods; so effects on total loads were small.

Introduction

Improved computational resources and geographical information technology have enabled the development of complex distributed models to evaluate hydrological and nutrient processes on a catchment scale. As catchments are heterogeneous and hydrological processes are nonlinear, the use of these models has raised several questions concerning parameterization and calibration with important practical consequences for nutrient management (Beven and Binley 1992, Beven 2001, Blöschl and Grayson 2002, Vrugt *et al.* 2005).

Even if validation tests against independent data show that a model can perform tasks for

which it is intended, the model may be right for the wrong reasons. For example, errors in model structure can be compensated by errors in parameter values. The sources of uncertainty in modelling are commonly divided into categories related to model structure, parameter values and measured data (e.g. Ewen *et al.* 2006, Mantovan and Todini 2006).

Walker et al. (2003) characterized model uncertainty using criteria related to boundary conditions and problem formulation. Input uncertainty includes errors in input data sets like land-use maps, and driving forces like climate data. Structural uncertainty arises from the manner in which the conceptual structure of the model reflects reality, either in the current situation or future evolution of the system. Technical uncertainty arises from computer implementation of the model. Parameter uncertainty is related to parameter values, which may be universal constants e.g. π , or are unknown and must be calibrated by comparing the modelled output with observations. Model outcome uncertainty is thus the accumulated uncertainty caused by the previous factors. It is also called prediction error as it is the discrepancy between the measured value of an outcome and the model prediction.

A model with a simple structure does not often make the best use of available data but can sometimes be calibrated to correspond with observations. Conversely, a model with several parameters may be tuned to fit the calibration data but prediction error can still be dominated by parameter uncertainty (Walker *et al.* 2003). This problem is known as model over-parameterization (Refsgaard 1997, Beven 2001, Blöschl and Grayson 2002). Further, many models and many parameter combinations may give equally good fits to data, indicating that it is not possible to find a single optimal parameter set, an issue Beven and Binley (1992) refer to as equifinality.

Sensitivity and uncertainty analyses are primarily concerned with addressing the manner in which model outputs are affected by variability in parameters and input values. Sensitivity analysis (Hamby 1994) is the identification of parameters that predominately control the model behaviour, whereas uncertainty analysis relates prediction errors to uncertainties in model structure, parameters and input data. Good modelling practice requires that modellers provide an evaluation of the confidence in the model, possibly assessing the uncertainties associated with the modelling process and with the outcome of the model itself. Several guidelines for modelling or impact assessment prescribe sensitivity analysis as a tool to ensure the quality of the modelling or assessment (e.g. Refsgaard and Henriksen 2004, Refsgaard *et al.* 2005).

There are several different methods of performing sensitivity and uncertainty analysis. These methods vary from technically simple ones like stakeholder involvement to detailed statistical methods (e.g. Gallagher and Doherty 2007, Refsgaard et al. 2007). Parameter uncertainty can be assessed by local and global methods. In the simplest form of local sensitivity analysis, one parameter value is changed at a time while all other parameters are fixed. This method detects the net effect of a single parameter on model output. Global sensitivity analysis accounts for the whole range of possible parameter variations and for parameter interactions. In this method sensitivity indices are evaluated while varying all other factors. To conduct global sensitivity analysis for non-linear models advanced analytical methods including Generalized Sensitivity Analysis (GSA; Spear 1970, Spear and Hornberger 1980), Monte-Carlo analysis (Beven and Binley 1992, McIntyre et al. 2005, Rankinen et al. 2006, Futter et al. 2007 inter alia) or the Fourier amplitude sensitivity test (Saltelli et al. 1999) should be used. For example, Global Sensitivity Analysis based on the Fourier amplitude sensitivity test allows the contribution of each input factor to the output's variance. Different methods based directly on the Bayesian approach (Vrugt et al. 2003a, Vrugt et al. 2003b, Liu et al. 2008) or Bayesian thinking like GLUE (The Generalized Likelihood Uncertainty Estimation; Beven and Binley 1992, Rankinen et al. 2006) are both widely used and discussed (Mantovan and Todini 2006, Xiong and O'Connor 2008).

In recent years, different sensitivity and uncertainty analyses have been applied to distributed or semi-distributed hydrological and nutrient leaching models. Muleta and Nicklow (2005) reduced the number of parameters in an application of the SWAT (Soil and Water Assess-



Fig. 1. Locations of the study catchments in Finland. Savijoki on the left and Mustajoki on the right. Light grey: fields, medium grey: forests, dark grey: scattered settlements.

ment Tool) model by using GLUE to constrain stream flow and sediment concentration variables. Stream flow prediction was rather consistent but sediment yield prediction was highly uncertain. In an extensive regionalized sensitivity analysis of an INCA-N model application to a groundwater-dominated catchment, McIntyre et al. (2005) found that the model was generally insensitive to land-phase parameters, but very sensitive to groundwater and in-river parameters. They concluded that soil and groundwater nutrient and flow data are needed to reduce uncertainty in initial conditions, residence times and nitrogen (N) transformation parameters. Using GLUE, Rankinen et al. (2006) showed that equifinality of INCA-N simulations can be reduced by adding soft data (literature review of results from field studies of inorganic N leaching, vegetation N uptake and N mineralisation in soil) into the normal calibration method. A similar approach to assessing parameter sensitivity to the one presented in this study has been used previously (Futter et al. 2009a, 2009b) where the importance of hydrological, N-transformation and plant-growth related parameters in controlling INCA-N model output was shown.

One of the most important questions in environmental policy today is controlling agricultural nutrient loading. National and international water protection targets aim at reduction in nutrient loading to surface waters (in tonnes or percents per year) or lowering in-stream concentrations of nutrients (e.g. EEC 1991, Ministry of the Environment 2007, HELCOM 2011.

In the Euro-limpacs EU project (Kernan et al. 2010) the semi-distributed dynamic INCA-N (Integrated Nutrients from Catchments - Nitrogen) model (Whitehead et al. 1998, Wade et al. 2002, Wade 2004) was applied to two small catchments with an intention of simulating DIN (Dissolved Inorganic Nitrogen) loads under different scenarios of climate and land use change and agricultural practices. These study catchments represent typical land use and soil types in Finland. As especially climate change might lead to conditions outside the situation in which the model was calibrated, both parameter sensitivity and model structure were analysed in this study. The objectives were (1) to describe controls on DIN leaching from Finnish catchments; (2) to determine whether there are any processes missing in the current INCA-N model structure, and (3) to assess what additional data could improve simulations. In this study GSA (Spear 1970, Spear and Hornberger 1980) was used.

Material and methods

Study catchments

The INCA-N model was applied to two small catchments (Fig. 1 and Table 1) which represent typical land use and soil types in Finland. The Mustajoki catchment is a forest-covered head-water catchment (78 km², 103–180 m a.s.l.) in a drainage basin of Pääjärvi in southern Finland. The Savijoki catchment (15 km², 50–70 m a.s.l.)

represents intensively cultivated areas in southwestern Finland. Both catchments are located in the southern boreal vegetation zone. During winter, precipitation usually falls as snow and the soils are frozen. However, in Savijoki winters are somewhat milder than in Mustajoki.

There are no point sources of nutrients in the catchments, and the areas are sparsely populated. The main human influences are agriculture and forestry. Agriculture in Mustajoki is mainly cereal cultivation with a low proportion of sugar beets. In Savijoki, agricultural fields cover 39% of the catchment area and the rest is mainly forest and semi-natural. Main crops are spring cereals, which cover 23% of the catchment area (Table 1).

The INCA-N model

The INCA-N (Integrated Nutrients from Catchments — Nitrogen) model (Whitehead *et al.* 1998, Wade *et al.* 2002, Wade 2004) is a processbased and semi-distributed model that integrates hydrology, catchment and river N processes to simulate flow and daily concentrations of NO₃-N and NH₄-N in the river system. It has been tested in many European catchments with different ecosystems and used for e.g. scenario analyses investigating the impacts of deposition, climate and land-use changes on N dynamics on the catchment scale (e.g. Wade *et al.* 2004, Rankinen *et al.* 2006, Kernan *et al.* 2010).

Hydrological input in both catchments consisted of daily time series of hydrologically effective rainfall (HER), soil moisture deficit (SMD), air temperature and precipitation. Catchment hydrology was modelled with a three-box approach, including reservoirs of water in the reactive soil zone and deeper groundwater zone together with surface runoff. HER is the input to the soil water storage, driving water flow and N fluxes through the catchment system. Flows from the different zones are controlled by time constants, representing residence time in the reservoirs. Calculation of river flow is based on mass balance of flow and a multi-reach description of the river system (Whitehead *et al.* 1998).

A catchment can be divided into sub-catchments. INCA-N simulates key terrestrial N processes (nitrification, denitrification, mineralisation, immobilisation, N fixation and N uptake) in six land-use classes. Fertilisers and N deposition constitute the N inputs to the land-use units. Rate coefficients of N processes are temperature- and moisture-dependent. N processes in the river include nitrification and denitrification. Soil temperature was calculated with an empirical function from the ambient air temperature. The depth of the snow cover was calculated by a simple degree-day model.

The INCA-N model setup for the catchments

The hydrological input data were derived from the Watershed Simulation and Forecast System (WSFS, Vehviläinen 1994). The soil types were based on 25×25 m grid cells from the data of the Finnish Geological Survey. The land-use data were based on CORINE 2000 data at the same resolution. The detailed crop distribution for the Mustajoki catchment was based on an unpublished survey done by local agricultural advisers. The crop distribution and agricultural management data for the Savijoki catchment were obtained from the Survey of Finnish Agri-Environmental Programme (Mattila *et al.* 2007).

The INCA-N model was calibrated against the discharge nitrate-N (NO_3 -N) and ammonium-N (NH_4 -N) concentrations measured at the

 Table 1. Characteristics of the study catchments.

Catchment	Area	Annual	Annual	Land use (%)			Soils (%)			
	(Km²)	(mm)	temp. (°C)	Agriculture	Fallow	Forest	Till	Sand and silt	d silt Clay	Rocks
Mustajoki	78	234	4.5	13	19	68	68	11	1	20
Savijoki	15	369	5.2	39	3	61	51	0	49	0

catchment outlets. The INCA-N parameters were adjusted to improve the fit between the simulated and measured discharge and stream water DIN concentrations. Simulated annual terrestrial inorganic N process fluxes were compared with values reported in the literature or other smallcatchment studies (Rankinen et al. 2006). Snow dynamics was simulated by calibrating modelled snow water equivalents (SWE) against measured areal average values in the catchments. SWE is the average amount of water existing as snow (i.e. the mass of snow per unit area). It is determined by snow course measurements, which consist of a line laid out on a drainage area along which the snow is sampled at definite distances. Sampling occurs at appropriate times to determine snow depth, water equivalent and density.

The highest N concentrations in discharge from forest catchments are typically recorded just before snowmelt (Lepistö *et al.* 1995, Arheimer *et al.* 1996). During winter, inorganic N is accumulated in soil under the snow pack (Rankinen *et al.* 2004). After that, N is diluted due to the larger volume of meltwater. Uptake of N by natural vegetation starts at the same time, further lowering concentrations. However, high N-concentration values in autumn are typical in agricultural catchments, where agricultural practices, such as fertiliser or manure application and ploughing, can cause short-term N leaching during autumn rains.

The INCA-N model has previously been applied to Mustajoki (Bärlund *et al.* 2009) and Savijoki (Granlund *et al.* 2004). In general INCA-N simulations reproduced the seasonal pattern of runoff and DIN concentrations in both catchments. In this study, the models were re-calibrated for the period 1995–2004 to allow for comparison of model behaviour and sensitivity, and uncertainty analysis in similar climatic conditions.

Sensitivity/uncertainty analysis

In this study, the generalized sensitivity analysis of Spear (1970) and Spear and Hornberger (1980) was used. The method was applied in two stages as described by Futter *et al.* (2007). First, a set of Monte Carlo simulations with Latin hypercube sampling of different parameter combinations was performed in which parameter values were sampled from a rectangular distribution. Parameter sets were divided into behavioural and non-behavioural runs based on the goodness-of-fit value between observations and simulations. Second, a non-parametric Kolmogorov-Smirnov (KS) test (e.g. Zar 1999) was used to evaluate the difference in distribution of parameter values between sets of behavioural and non-behavioural model runs. In the analyses presented here, the KS statistic was used to test whether or not the distribution of behavioural parameter values deviated significantly from rectangular. The degree to which the distribution of values in the behavioural parameter set deviated from rectangular was interpreted as a measure of parameter sensitivity. Both site-specific and overall sensitivity analyses were performed. In the site-specific version, the calibrated parameter sets were used in the analysis, while in the general one a single parameter set covered the total range of parameter values of both catchments.

The starting point of the Monte Carlo simulations was the model application calibrated against measured discharge and NO₂-N concentrations. NO₂-N is the dominating N fraction in both rivers. In the site-specific sensitivity analyses, the parameters were allowed to vary by either (i) $\pm 20\%$ of the calibrated value, or (ii) the range between minimum and maximum measured values. Growth start day and fertilization addition day were fixed when these were applied as a part of an external time series (e.g. grass with multiple growing and fertilization periods), but were allowed to vary when the values were specified in the model parameter file (e.g. vegetation growth periods for natural vegetation such as forest and fallow). During Monte Carlo simulations, 250 iterations of a Latin hypercube with 20 divisions were produced for a total of 5000 simulations.

Parameter sets for the overall sensitivity analysis were defined in the following manner. In-stream and sub-catchment parameters were fixed at their best value from manual calibrations. Individual fertilizer time series and growth periods were used for each catchment. Only terrestrial N-process, vegetation uptake and snow cover parameters were allowed to vary. The lower bound for the parameter space was defined as 10% lower than the minimum value from the Mustajoki and Savijoki calibrations. The upper bound was defined as 10% higher than the maximum value from the two calibrations. The parameter space was sampled in an identical manner for both the Mustajoki and Savijoki overall sensitivity analyses. In each case, 10 000 simulations were performed. The 100 parameter sets giving the best correlation between measured and modelled NO_3 -N and NH_4 -N for Mustajoki and Savijoki were used to identify sensitive parameters.

Next, a non-parametric KS test was used to evaluate differences in parameter values between behavioural and non-behavioural model runs. This test was used to compare the distribution of values in behavioural model runs with those in non-behavioural runs. The KS test requires continuous distributions but does not set any requirements for the shape of the distribution. This allows the detection of differences in both shape and location of the distribution. The KS test is based on the maximum difference (D) between cumulative measured frequencies (S_1 and S_2):

$$D = \sup_{x} |S_{1}(x) - S_{2}(x)|$$
(1)

The maximum deviation D can then be used as a test quantity. The reference value D_{α} (Eq. 2) depends on the significance level α via K_{α} , where n_1 and n_2 are the numbers of behavioural and non-behavioural runs, respectively.

$$D_{\alpha} = K_{\alpha} \sqrt{\frac{n_1 + n_2}{n_1 \times n_2}} \tag{2}$$

Outputs from the Monte Carlo simulations include a list of input parameters ranked by the *D* value and uncertainty bounds (mean, minimum, maximum and quartiles) for predicted values from behavioural runs. Uncertainty bounds for daily values were calculated from the population of modelled values for that day. Because multiple statistical tests were performed, it was necessary to adjust estimates of statistical significance. Thus, analysis was restricted to parameters with a Bonferroni-adjusted α (Futter *et al.* 2009a, 2009b) equal to or greater than 0.15 (nominal $\alpha \approx 0.02$).

Results and discussion

Sensitivity analysis, general approach

The INCA-N model was successfully calibrated for both sites for the period 1995–2004. For Mustajoki, the Nash-Sutcliffe (NS) efficiency (Nash and Sutcliffe 1970) for simulated and measured discharge was 0.756; r^2 was 0.342 for NO₃-N and 0.355 for NH₄-N. In the Savijoki application, the NS efficiency for simulated and measured discharge was 0.872; r^2 was 0.317 for NO₃-N and 0.003 for NH₄-N. r^2 values are influenced by the fact that in reality farmers follow individual crop rotations but in modelling longterm average land-use allocation was used.

Model sensitivity was assessed separately for NO_3 -N and NH_4 -N concentrations in the discharge from each catchment. Thus, it was possible to explore differences in parameter sensitivity for the two determinants. Threshold correlations of between 0.33 and 0.34 were obtained for behavioural model runs simulating NO_3 -N for Mustajoki and Savijoki and NH_4 -N for Mustajoki (Table 2). Simulation of NH_4 -N concentration for Savijoki was more problematic, the behavioral correlation threshold was approximately 0.06.

The model performance when simulating both NO₃-N and NH₄-N concentrations in Savijoki and Mustajoki was sensitive to the estimated ammonium mineralisation rate in at least one land-cover class (Table 2). NO₂-N in Savijoki was more sensitive to parameters for spring cereal (mainly barley) and grass land-cover types while in Mustajoki, it was most sensitive to parameters from the forest land-cover type. Mustajoki and Savijoki have similar fractions of forest cover (68% vs. 61%) but there is more spring cereal (23%) in Savijoki than in Mustajoki (7%). It was not possible to get appropriate simulations of NH₄-N for Savijoki. NH₄-N in Mustajoki was sensitive to both mineralisation and immobilisation rates in forest, fallow and grass land-cover types.

Simulations of both NO_3 -N and NH_4 -N for Mustajoki and simulations of NH_4 -N for Savijoki were sensitive to the ammonium immobilisation rates in the forest land-cover type. This was because the initial Mustajoki parameter set simulated no immobilisation while the Savijoki initial parameter set included the immobilisation rate of $0.75 \text{ m } \text{d}^{-1}$. The median behavioural value for the ammonium immobilisation rate was close to 0 for behavioural simulations in all cases (Table 2).

As we did not include timing or amount of fertilizer application in the sensitivity analysis, the most important N input in the sensitivity analysis was the rate at which inorganic N is produced during mineralisation of the soil organic-N pool. This is described as a simple temperature- and soil-moisture-limited linear decay (kg ha⁻¹ day⁻¹) from an unlimited pool of soil organic-N. Retention processes (immobilisation, denitrification and vegetation uptake) were described by first order kinetics (1/day) and they were also limited by soil temperature and moisture. As first order kinetics depends on the input storage, these retention processes effectively limit the highest simulated concentrations. This has a significant effect on the r^2 values as the goodness of fit depends on how well the relatively few high observations are simulated. Further, very little measured data about immobilisation rates exist since most field studies report net mineralisation (gross mineralisation minus immobilisation).

Sensitivity analysis, site specific approach

In general, there were more influential parameters in the INCA-N model application to Savijoki (agricultural) than to Mustajoki (forest). In both applications, the number of influential parameters ranked by the test value D was about 10% of the total. The Mustajoki application seems to be more dominated by a few parameters but in the Savijoki application there were several equally influential parameters (Fig. 2). The parameter combinations based on the minimum and maximum parameter values led to simulated N process fluxes which covered the range of measured losses from the study fields, including individual years with exceptionally high or low losses (Table 3). However, the simulated fluxes in Table 3 represent long-term averages, and therefore some process fluxes (e.g. N leaching from sugar beet in Mustajoki, range 9–109) may be unrealistic.

The most influential parameters are listed in Table 4. The nominal α -values must be adjusted for multiple comparisons. A modified Bonferroni correction was employed in which the nominal α for the *n*th highest KS test value was tested against $p = 0.05^n$ (Futter *et al.* 2009a, 2009b). In both model applications, most of the influential parameters ($p_{adjusted} < 0.001$) were related to temperature-dependent N processes; these parameters range between 1 and 5. The base temperature varied between 10 and 35 °C, which corresponds to the temperature range of activity of psychrofilic and mesofilic microorganisms (e.g. Salkinoja-Salonen 2000).

In the Mustajoki catchment, the simulated discharge NO_3 -N concentration was most sensitive to parameters defining N cycling in the forest land-use class. Sensitivity in the Mustajoki application was also dominated by river flow velocity parameters *a* and *b*, which define the shape and level of the exponential equation used to calculate flow velocity from discharge. Nitrogen leaching from forests is low due to 'closed' internal N cycle. High N uptake by vegetation

Table 2. Sensitive model parameters in the ensemble of behavioural parameter sets (top 100) from the general sensitivity analysis where the same parameter range was used for both Mustajoki and Savijoki simulations. Coefficients of determination (r^2) indicate thresholds for behavioural simulations. Medians are the median parameter value for behavioural simulations.

Catchment	Process parameter	Median
Mustajoki		
$NO_3 - N(r^2 = 0.3)$	34)	
Forest	Ammonium immobilisation	0.0001
Forest	Ammonium mineralisation	0.44
Fallow	Ammonium mineralisation	0.51
$NH_4 - N(r^2 = 0.3)$	343)	
Forest	Ammonium immobilisation	0.02
Forest	Ammonium mineralisation	0.21
Fallow	Ammonium mineralisation	0.53
Grass	Ammonium mineralisation	0.88
Savijoki		
$NO_3 - N(r^2 = 0.5)$	33)	
Spring cereal	Denitrification	0.00082
Spring cereal	Ammonium mineralisation	0.62
Grass	Ammonium mineralisation	0.64
$NH_4 - N(r^2 = 0.0)$	062)	
Forest	Ammonium immobilisation	0.0001
Forest	Ammonium mineralisation	0.3
Fallow	Denitrification	0.0034



Fig. 2. *D* values of the ranked parameters in Savijoki and Mustajoki INCA-N model applications.

is covered mainly by N mineralisation from soil organic matter because anthropogenic N inputs were very low. The starting date of the growing period varies widely. For example the growing period started by 15 April in 1990 but not until 6 May in 1997 (Finnish Meteorological Institute).

In the Savijoki application, the six most significant parameters were related to N processes in the land-use class 'Spring cereals'. This is the most common fertilized crop-type in the catchment, covering 23% of the catchment area. Cereals were assumed to have an intensive N cycle with a high mineralisation rate, N uptake and leaching during the study period. Most Finnish farmers have participated in agricultural support schemes since 1995 (when Finland joined the EU) and have adopted environmentally sound management practices. However, conservation tillage practices have only recently become more common (Mattila *et al.* 2007). Three of the sensitive 'Spring cereal' parameters were related to N process-rate temperature dependence.

Initial DIN concentrations in groundwater or soil water influence both model applications. These values were calibrated against measured initial values in river water, and literature

Land use in catchment	N mineralisation (kg ha ⁻¹ a ⁻¹)		N uj (kg h	otake a⁻¹ a⁻¹)	N leaching (kg ha ⁻¹ a ⁻¹)	
	Min	Max	Min	Max	Min	Мах
Mustajoki						
Barley	3	77	77	126	27	35
Sugar beet	7	230	173	175	9	109
Grass	7	251	191	262	9	26
Fallow	4	126	11	40	6	15
Forest	1	42	9	36	5	7
Savijoki						
Spring cereal	3	84	83	93	7	48
Winter cereal	3	84	103	119	10	54
Grass	2	56	181	201	7	23
Fallow	2	49	5	41	4	9
Forest	3	67	5	32	2	3
Oilseed	3	84	92	102	7	48

Table 3. Process loads in the Mustajoki and Savijoki catchments calculated with the minimum ("Min") and maximum ("Max") parameter sets in the Monte Carlo simulations.

values of typical concentrations in ground water. In practice, their influence disappeared very quickly after starting the simulation, although aberrant values might have caused anomalies at the beginning of the simulation.

Uncertainty analysis

Uncertainty analysis was used to study the structure of the INCA-N model and to see how well it explains measured NO₂-N concentrations in river water. In both rivers, discharge was dominated by a spring snow-melt peak. Low-flow periods occur typically in summer or mid-winter. In general, measured NO₂-N concentrations in the rivers reflect land use. In the forest-covered Mustajoki catchment, the NO₂-N concentrations were low and the peaks did not exceed 5 mg l⁻¹. NO₂-N concentrations were lowest in the summer and rose throughout the winter so that the highest concentration occured just before snow melt. In the agricultural Savijoki catchment, the highest NO₃-N concentration peaks were close to 15 mg l⁻¹. The uncertainty analysis indicated that there was a risk of exceeding the Nitrates Directive limit for the NO₃⁻ concentration (50 mg l⁻¹) in the Savijoki water. Seasonal behaviour in Savijoki was not as clear as in Mustajoki, and the highest concentrations (> 5 mg l^{-1}) occured in autumn (October–November) rather than in early spring. Concentrations were lowest in both rivers during the growing season.

The highest, but not the lowest, measured NO_3 -N concentrations fell between the minimum and maximum uncertainty bounds in both model applications (Fig. 3). In the Mustajoki application, concentrations were underestimated, e.g. in winter 2002–2003. This period was exceptionally dry and the INCA-N model failed to correctly simulate low discharge, possibly because the input HER values were too low. As there was no leaching through the soil column, simulated concentrations did not rise. Simulated discharge is controlled by the input time series of HER and thus it did not vary much in the uncertainty analysis. Parameter values affect mainly the recession part and the height of the peaks.

In several years, the lowest measured NO_3 -N concentrations in the Savijoki fell outside the uncertainty bounds during the growing period. This is easily seen during early summer (April–June) when measured values are commonly below the minimum bound. This may indicate that one or more biological retention processes, for example retention in the riparian zone, are missing in the current model structure. Moreover, riverine plant uptake is not included.

Table 4. Most influential parameters in the individual catchment applications; nominal α of all the parameters is < 0.001.

Catchment	Parameter	D
Mustaioki	Forest mineralisation response to 10° change in temperature	0.551
	River flow b	0.369
	Forest growth start day	0.362
	Fallow mineralisation response to 10° change in temperature	0.283
	Base flow index	0.265
	Forest ratio of total to available water in soil	0.172
	River flow a	0.164
	Initial groundwater NO ₂ -N concentration	0.162
	Forest mineralisation base temperature response	0.161
Savijoki	Spring cereal mineralisation base temperature response	0.439
-	Spring cereal denitrification base temperature response	0.381
	Spring cereal max. nitrogen uptake rate	0.353
	Spring cereal ratio of total to available water in soil	0.275
	Spring cereal soil reactive zone time constant	0.268
	Spring cereal denitrification response to a 10° change in temperature	0.253
	Grass soil water flow initial condition	0.204
	Forest immobilisation response to a 10° change in temperature	0.189



Fig. 3. Measured and simulated mean NO₃-N concentrations with simulated maximum and minimum uncertainty bounds for the (a) Mustajoki and (b) Savijoki.

As lowest stream DIN concentrations occur mainly during low flow periods, the effect on total load is small. The measured daily NO₃-N loads fell in between simulated minimum and maximum loads (Fig. 4). In the Mustajoki application, measured loads were close to the minimum simulated values, and the maximum simulated values overestimated the load. In the Savijoki application, measured loads were in between the simulated maximum and minimum loads.

Effect of different parameter combinations on descriptions of terrestrial processes and river N export

The effect of two parameter combinations 'Best' and 'Worst' (highest and lowest accepted r^2) on modelled terrestrial N processes were also analysed. Fertilization levels of different crops were not changed and anthropogenic deposition was at a low level, so the main change happened in soil N processing.

In both catchments, the simulated minimum and maximum uptakes of different crops were representative of the measured annual values for these crops in Finland (Tike 2009). Further, leaching losses of main crops (spring cereals and grass) were relatively close to the measured values obtained from the literature. 'Best' case N leaching was overestimated ('Grass' in Mustajoki and 'Barley' in Savijoki). The largest differences between the simulated and measured annual loads were in mineralisation, which was underestimated in 'Grass' in Mustajoki and 'Barley' in Savijoki. In the Mustajoki application, the simulated N losses from forests were higher than the literature values. Because a large fraction of the catchment is covered by forest, the N losses were generally low. The measured values were based on small catchment studies in northern Finland, and leaching in southern Finland in more fertile areas with higher atmospheric deposition. On the other hand, in forest catchments there are usually peatlands at the outlet, and retention in these areas may be high.

Synthesis concerning scenario simulations

In this study, we analysed only the effect of parameter values on sensitivity and uncertainty. We did not include the effect of error or uncer-



Fig. 4. Simulated minimum and maximum river NO₃-N daily loads plotted against measured daily loads for (a) Mustajoki and (b) Savijoki INCA-N model applications. The lines indicates measured loads plotted as 1:1, assuming perfect model fit. Four lowest simulations are removed from **b**.

tainty in input values. The credibility of climate change simulations may be primarily dependent on hydrological input values, i.e. how well future temperature and precipitation is predicted. Another question is how land use, crops, etc. will vary due to climate change.

Climate change scenarios predict that in Finland by 2100 the mean annual air temperature and precipitation will increase by 3–7 °C and 13%–26%, respectively. Such changes in input values may alter the internal behaviour of the system (model structural uncertainty). Most of the climate change scenarios predict increase in temperature and precipitation especially in winter (Ruosteenoja and Jylhä 2007). Previous studies have shown that this would have a clear effect on discharge in such a way that current snow-melting peak in spring would level off to more even runoff throughout the winter, especially in southern Finland where the annual maximum flood typically occurs in spring and early summer (March–June) (Veijalainen *et al.* 2010).

Interestingly, in site-specific applications the temperature dependencies of N processes seem to be more important than process rates by themselves. Temperature dependency parameters are commonly described by the Q_{10} equation (Bunnel *et al.* 1977), which represents the factor by which the rate of a reaction increases for every 10 °C rise in temperature. In the sensitivity analysis, default values were allowed to change over a range which corresponds to activity temperatures of mesofilic and psychrophilic microorganisms. A small increase of soil temperature

may not change this behaviour but the decay is more dependent on the quality of organic matter than temperature dependency of microorganisms (Vanhala *et al.* 2008). Thus the Q_{10} equation calibrated against water quality parameters and reaction rates in current climate can be assumed to be valid in future climate as well. Soil moisture parameters are clearly less important than those of soil temperature as regulating factors in the model. Soil moisture deficit is given as input time series to the model and thus the direct effect is not included in the analysis.

Uncertainty analysis showed that the highest DIN concentrations are simulated by both model applications but not all of the lower ones in the Savijoki catchment. Most of these low concentrations occur during growing season, so possibly one or more retention process is missing (model structural uncertainty). Such processes may be important in an agriculturally-loaded river with intensive biological activities. River flow velocity played a large role in the uncertainty analysis presented here. In model calibrations, the simulated velocity corresponded well to the measured one close to the river banks rather than in the centre of the river. Therefore, it can be suggested that riparian-zone processes are partly modelled to occur in the river. A similar conclusion was reached during GLUE analysis of an INCA-N application to a large forest-covered river basin in northern Finland (Rankinen et al. 2006). This conclusion seems not to depend on the analysis method, the size of the catchment, or land use in the catchment. The other critical situation during low-flow periods occurs when, due to potentially erroneous input data, the hydrological sub-model underestimates runoff and there is no N leaching from terrestrial areas.

As the lowest DIN concentrations occur mainly during low flow periods, their effect on total load is small. Thus INCA-N can be used in scenario simulations when the interpretation of results is based on loads. This approach is especially important for mitigation of agricultural nutrient loading to water bodies, as targeted by different national and international water protection policies (e.g. EEC 1991, EEC 1992, WFD 2000, Ministry of the Environment 2007).

When effect of climate change on concentration levels is the question of interest, it should be kept in mind that INCA-N may overestimate concentrations during the growing season. Retention processes in a riparian zone and river should be added in case the detailed modelling of N concentrations of the discharge is intended. However, our analysis showed that high NO_3 -N concentrations, which are the major concern of the Nitrates Directive (EEC 1991), are satisfactorily modelled by INCA-N.

When the model was calibrated only against measured NO₂-N concentrations in river water, even a good calibration against NO3-N concentration in river (in terms of the r^2 value) could result in overestimating process loads due to over- or underestimated leaching from one or more land use classes. Thus when calibrating the model, also information about annual N process loads should be included. This was also an effective method to reduce equifinality in a study by Rankinen et al. (2006). Interestingly, for site-specific applications the INCA-N model tends to underrather than overestimate mineralisation process loads. In general, the INCA-N model is sensitive to retention processes (vegetation uptake, denitrification and immobilisation). Nitrogen immobilisation fluxes are seldom reported in the literature; any information concerning annual gross mineralisation and immobilisation would improve the reliability of simulations.

Conclusions

We used INCA-N to simulate inorganic N loads in two catchments in Finland. Our results show that the model was able to reproduce seasonal patters in concentrations and loads. However, the model performed poorly during low-flow periods as it either under- or overestimated the N concentrations. This may be a result of overlysimplistic process representations (i.e. the plant N uptake routines are not sensitive to soil moisture, in-soil processes may not respond linearly to soil moisture deficits and the representation of in-stream denitrification may need refinement). It is possible that the model should include instream N uptake and an explicit representation of the riparian zone. INCA-N results are sensitive to N-transformation rates, vegetation dynamics and descriptions of hydrological processes in soil and river. The overall sensitivity analysis showed that despite of the dominant land use type (forest *vs.* agricultural) parameters that control nitrogen mineralisation and retention (immobilisation and denitrification) processes are important for model performance. The site-specific sensitivity analysis revealed the differences between the catchments and ecosystem types.

Simulated loads and concentrations from INCA-N modelling can be used to evaluate policy-relevant scenarios which aim to reduce nutrient loads. Better hydrological input data and ongoing water-quality and discharge monitoring, especially during winter, are needed to improve model projections under a changing climate.

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