

# Application of an integrated framework for estimating nitrate loads from a coastal watershed in south-east Sweden



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## ABSTRACT

Nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) loading from a 734 ha coastal watershed draining into the Baltic Sea off south-east Sweden was simulated using a simple modelling approach in which the nitrogen model DRAINMOD-N II and a temperature-dependent  $\text{NO}_3\text{-N}$  removal equation were incorporated into the Arc Hydro-DRAINMOD framework. Hydrology and water quality data collected during six periods between 2003 and 2007 were used to test Arc Hydro-DRAINMOD and its performance was evaluated by considering uncertainty in model parameters using GLUE methodology. The GLUE estimates (5th and 95th percentiles) and calculated monthly  $\text{NO}_3\text{-N}$  loads were in satisfactory agreement. There are some sources of errors that may affect the performance of the framework, such as  $\text{NO}_3\text{-N}$  load calculations, soil denitrification and in-stream removal of  $\text{NO}_3\text{-N}$ . Although additional measurements may help to improve the understanding of these processes and reduce uncertainty, they cannot completely eliminate the uncertainty in framework predictions. These uncertainties must be evaluated by some methodology, such as the GLUE procedure. Sensitivity analysis showed the framework to be most sensitive to changes in stream base-flow and N removal processes in the stream network. These results show that the Arc Hydro-DRAINMOD framework can be an effective tool to support water stakeholders in managing  $\text{NO}_3\text{-N}$  loading from small tile-drained watersheds at monthly time step.

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## 1. Introduction

In Sweden, N transport in lowland rivers has resulted in serious coastal eutrophication problems (Larsson et al., 1985; Stålnacke et al., 1999). This ongoing eutrophication has been the most pervasive anthropogenic alteration to marine coastal ecosystems, leading to widespread hypoxia and large permanently reducing bottom areas in the Baltic Sea (Vahtera et al., 2007). Special attention is required for coastal areas of southern Sweden including the island of Öland, which have been classified as particularly vulnerable to nitrogen (N) leaching from agriculture and identified as nitrate vulnerable zones according to the EU Nitrate Directive (SJV, 2006, 2007).

To counteract the undesirable consequences of excessive nutrient loads into aquatic systems, the processes controlling nutrient export from drained agricultural lands to downstream surface waters need to be better understood (Fenn et al., 1998). However, field studies have shown that the effects of improved drainage are difficult to quantify, where increasing drainage intensity on

agricultural land may have both positive and negative effects on hydrology and water quality (Skaggs et al., 1994). The development of hydrological models has allowed the description of the mechanisms of nutrient retention and release in these drained areas (Thomas et al., 1992). Modelling of the processes and interactions involved may explain how land use and management practices in coastal watersheds affect the recipient marine ecosystem (Valiela et al., 1992). Computer hydrological models have become an integral component of many drainage projects with outputs that may be used for planning, design, or operational decisions about matters in which hydrological information is relevant and useful (Skaggs et al., 2006). A number of models are available to predict the movement and fate of nutrients and pesticides at field-scale: CREAMS (Knisel, 1980), GLEAMS (Leonard et al., 1987), LEACHN (Hutson and Wagenet, 1991), RZWQM (Singh and Kanwar, 1995) and SOILNDB (Johnsson et al., 2002).

However, only a few models can be applied to quantify the effects of drainage system design and management on losses of agricultural chemicals, such as SOILNDB and DRAINMOD-N II. DRAINMOD-N II (Youssef, 2003; Youssef et al., 2005) was developed to simulate N dynamics under different management practices and soil and environmental conditions. It can be used with the water management model DRAINMOD (Skaggs, 1978, 1999) for

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the development and evaluation of methods that reduce N losses from drained agricultural land. DRAINMOD-N II has been tested by Salazar et al. (2009) at field-scale in a coarse-textured soil under cultivation in south-east Sweden, where predicted nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) load values have been found to be in good agreement with field data. The model has also been calibrated and validated for predicting edge-of-field N losses from drained crop and pasture lands in south eastern and Midwestern U.S. (Youssef et al., 2006; David et al., 2009; Thorp et al., 2009; Luo et al., 2010; Ale et al., 2012) and Germany (Bechtold et al., 2007).

The sum of N inputs to the stream network in a watershed usually exceed loads discharged at the outlet, where the stream network acts as a filter retaining and/or removing N by processes such as denitrification, sedimentation and plant and microbial uptake (assimilation) (Billen et al., 1991). Some researchers have reported that denitrification is the dominant nitrate ( $\text{NO}_3^-$ ) loss process in rivers, where  $\text{NO}_3^-$  is permanently removed through the formation and release of  $\text{NO}$  (g),  $\text{N}_2\text{O}$  (g) and  $\text{N}_2$  (g) into the atmosphere (Seitzinger, 1988; Saunders and Kalf, 2001). Several studies have estimated that a substantial amount of N (10–76% of total N input) can be removed during transport through the network of streams draining watersheds (Saunders and Kalf, 2001; Seitzinger et al., 2002; Birgand et al., 2007). Other studies show N retention values lower than 10%, mainly for coastal watersheds with practically no lakes (Lepistö et al., 2006; Appelboom et al., 2008).

It is important to consider that management of nutrient inputs to coastal ecosystems requires knowledge of both the magnitude of N losses from the watershed and the proportion of N removed during downstream transport in the watershed (Seitzinger et al., 2002). The N removal rate in the stream network has been included in several modelling approaches at the watershed scale, such as AGNPS (Bhuyan et al., 2003; León et al., 2004), a GIS-based model (Skop and Sørensen, 1998) and DRAINMOD-GIS (Fernandez et al., 2006). It has been represented either as a percentage of the total N input (Bhuyan et al., 2003; León et al., 2004) or as an exponential decay model (Skop and Sørensen, 1998; Fernandez et al., 2002, 2006). However, these approaches did not include temperature as a factor affecting N removal rate, whereas temperature has been identified as a key factor in N denitrification experiments (Dawson and Murphy, 1972; Appelboom et al., 2006). In contrast, a recent modelling study by Alexander et al. (2009) included temperature as an explanatory variable to estimate N losses by denitrification in river networks, based on about 300 published measurements from a variety of US streams.

Birgand et al. (2007) noted that the key to nutrient management at the watershed scale is understanding and quantifying the fate of nutrients, both at the field scale and after they enter the aquatic environment. Therefore, a distributed model that treats the watershed as a spatially variable physical system may be more realistic and have significant theoretical advantages that make them more useful (Ward and Robinson, 2000), for instance to estimate nutrient losses from fields within a small watershed.

Process-based nitrogen modelling usually requires a large number of difficult to measure parameters, which are usually estimated through model calibration. Estimated N parameter values have uncertainties that are propagated in each step of the calculations, an issue that should be assessed (Beck, 1987). Beven and Binley (1992) proposed the Generalised Likelihood Uncertainty Estimation (GLUE) methodology for calibration and uncertainty estimation of distributed models at watershed scale. This methodology has been used in several watershed modelling approaches and has been shown to be an applicable and formal basis for appropriate uncertainty estimation (Mo et al., 2006; Arabi et al., 2007; Choi and Beven, 2007; Blasone et al., 2008).

The aim of the present study was to extend the integrated Arc Hydro-DRAINMOD framework (Salazar et al., 2010) to

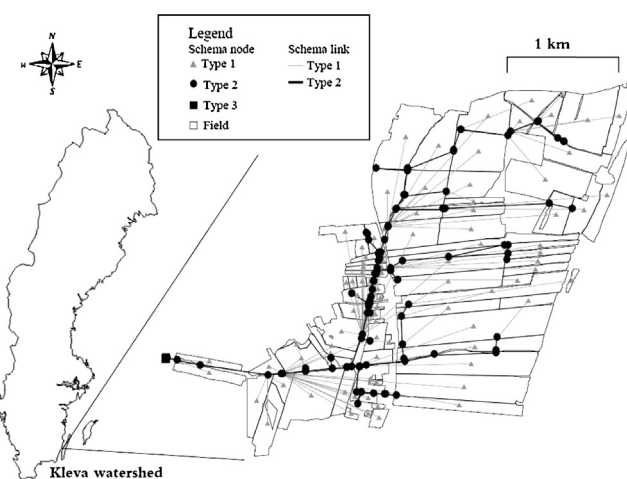


Fig. 1. Diagram of the study area in Kleva watershed with schematic network. Types of links and nodes are explained in Table 2.

predict  $\text{NO}_3\text{-N}$  loads at the watershed outlet using a relatively simple approach that can be used by local water stakeholders for managing  $\text{NO}_3\text{-N}$  loading. In this modelling approach the nitrogen model DRAINMOD-N II and a temperature-dependent  $\text{NO}_3\text{-N}$  removal equation were included to create an Arc Hydro-DRAINMOD framework for predicting  $\text{NO}_3\text{-N}$  loading. The performance of the framework was evaluated by considering the uncertainties in model parameters using the GLUE methodology. In addition, a sensitivity analysis was carried out using the GLUE results. The Arc Hydro-DRAINMOD framework was tested by comparing simulated results with calculated  $\text{NO}_3\text{-N}$  loads from a 734 ha artificially drained coastal watershed on Öland Island draining into the Baltic Sea off south-east Sweden for six periods between 2003 and 2007.

## 2. Materials and methods

### 2.1. Site description

The 734 ha artificially drained Kleva watershed is located on the coast of the Öland Island in the Baltic Sea, off south-east Sweden (latitude  $55^\circ 31' \text{N}$ , longitude  $16^\circ 23' \text{E}$ ) (Fig. 1). Land use in the watershed is predominantly agricultural. There are 95 fields in the watershed, ranging in area from 0.2 to 32 ha. A detailed description of area, soil texture and crop rotation for all fields is presented by Salazar et al. (2010).

The watershed soils, which are developed from glacial drifts, are predominantly coarse-textured with low water-holding capacity and high vertical saturated hydraulic conductivity ( $K_s$ ). There is a small area of peat-derived organic soil close to the outlet. The watershed is underlain by sedimentary rocks such as limestone, alum shale, sandstone and clay shale, which greatly restrict downward movement of water, where the bedrock is covered by Quaternary deposits of varying thickness ranging from 1 to 10 m in the watershed. The watershed drains to coastal waters in the Baltic Sea. It is characterised by flat topography, with average slope lower than 1%. Steep slopes (>10%) only occur on hills located on the eastern watershed boundary, where ground elevation is at its maximum (50 m a.s.l.).

The climate on Öland is Marine West Coast (Cfb) according to the Köppen–Geiger system (Peel et al., 2007). Average monthly temperatures at Mörbylånga, Öland, range from  $-1.4^\circ \text{C}$  in February to  $16.8^\circ \text{C}$  in July, with a mean annual temperature of  $7.4^\circ \text{C}$  and long-term average precipitation of 475 mm (Alexandersson et al., 1991).

**Table 1**  
Crop sequences, tillage practices and N fertilisation rates for crops in the Kleva watershed.

Crop/date	Activity	N rate (kg N ha <sup>-1</sup> )
Peas		
24 March	Ploughing	
31 March	Planting	
8 August	Harvesting	
	Total N application	0
Potatoes		
7 April	Ploughing	
14 April	Planting and first split N fertilisation	50
16 April	Second split N fertilisation	30
12 June	Third split N fertilisation	30
26 September	Harvesting	
	Total N application	110
Cultivated grassland		
19 March	Ploughing and manure application	60
26 March	Planting and N fertilisation	20
7 September	Harvesting	
	Total N application	80
Spring barley		
24 March	Ploughing	
31 March	Planting and N fertilisation	100
8 August	Harvesting	
15 August	Stubble cultivation	
	Total N application	100
Sugarbeet		
1 April	Ploughing and manure application	60
8 April	Planting and N fertilisation	55
10 October	Harvesting	
	Total N application	115
Winter wheat		
3 October	Ploughing	
10 October	Planting	
17 April	First split N fertilisation	120
12 June	Second split N fertilisation	30
4 September	Harvesting	
11 September	Stubble cultivation	
	Total N application	150

Data on the 2003–2007 crop rotation for each field were obtained from the Swedish Board of Agriculture statistical database and from farmers in the Kleva watershed. During the study period, crops were grown with conventional tillage, under rainfed conditions, fertiliser and pest management practices typical of the region. The main crops cultivated in the watershed were winter wheat (*Triticum aestivum* L.), sugarbeet (*Beta vulgaris* L. ssp. *vulgaris*), perennial ryegrass (*Lolium perenne* L.), spring barley (*Hordeum vulgare* L.), peas (*Pisum sativum* L.), potatoes (*Solanum tuberosum* L.) and bean (*Phaseolus vulgaris* L.). Crop sequences, tillage practices and N fertilisation rates for crops are summarised in Table 1.

The N sources to Kleva watershed are precipitation, synthetic fertilisers, animal manure and N fixation by leguminous crops. Using data on the average wet deposition of inorganic N (NH<sub>4</sub><sup>+</sup>+NO<sub>3</sub><sup>-</sup>) on Öland during 2003 and 2007 (Karlsson et al., 2008), precipitation was estimated to contribute on average 5.4 kg N ha<sup>-1</sup> year<sup>-1</sup> to the watershed. Nitrogen fertiliser and manure rates were estimated from national statistics reported for Kalmar County. Nitrogen fertilisers were generally applied at planting as nitrate in the spring, with rates ranging between 0 to 150 kg N ha<sup>-1</sup>. There is a pig farm close to the watershed and therefore pig slurry was assumed to be the main manure source. Approximately, 1 tonne ha<sup>-1</sup> (dry matter) of pig slurry was applied one week before grass cultivation and sugarbeet planting, delivering about 60 kg N ha<sup>-1</sup>. Atmospheric N<sub>2</sub> fixation by leguminous crops, such as peas and beans, was estimated by the DRAINMOD-II model as described in a subsequent section.

The watershed is drained by a network of field ditches and streams that drain into the Kleva river. Discharge was continuously measured at the watershed outlet (see details in Salazar et al., 2010). Drainage water grab samples were collected at the watershed outlet twice a month and analysed for nitrite plus nitrate as nitrogen (NO<sub>3</sub> + NO<sub>2</sub>-N) according to Swedish standards (Tecator, 1992). Since NO<sub>2</sub>-N is short lived in the soil–water–plant system, measured NO<sub>3</sub> + NO<sub>2</sub>-N were lumped together and considered to be in NO<sub>3</sub>-N form, which was used for comparison with framework-predicted NO<sub>3</sub>-N values. Daily values of NO<sub>3</sub>-N concentrations were estimated using linear interpolation of the measured values, as proposed by Kronvang and Bruhn (1996) for studies with discrete interval sampling in Denmark. Nitrate loads were calculated by multiplying measured daily discharge by estimated daily concentration.

## 2.2. Hydrological framework

ArcHydro-DRAINMOD is an integrated framework in which distributed predictions of watershed response are made based on the field-scale hydrological DRAINMOD model and the Arc-Hydro data model. A detailed description of the framework logic can be found in Salazar et al. (2010). The GIS software ArcGIS Info 9.2 (ESRI, 2004) is used as a common platform to embed model components and to store model input data. The Arc-Hydro data model (Maidment, 2002) describes the drainage patterns in the watershed and connects the DRAINMOD-simulated outflows from fields to the stream network. DRAINMOD version 5.1 (Skaggs, 1999) is used to simulate outflow from the fields.

The ROSETTA pedotransfer function model (Schaap et al., 2001) is used to estimate soil hydraulic properties required for running DRAINMOD. ROSETTA has the following advantages that: (i) it is included as a utility in the distribution package of DRAINMOD, (ii) coarse-textured soils, which dominate the Kleva watershed, are well represented in the ROSETTA database and (iii) DRAINMOD has been previously applied successfully on a coarse-textured soil in Sweden using soil hydraulic properties estimated by ROSETTA (Salazar et al., 2008).

DRAINMOD simulates drainage outflow and runoff on each field, which are stored in a time series of outflow. The outflow time series are routed from each field to the watershed outlet using a schematic network created by Arc Hydro tools, where the outflows from each field are summed through the stream network to predict the discharge at the watershed outlet. The model is also used to simulate the stream baseflow as a single run representing the conditions within the stream system that drains the watershed, which is summed to the stream network at the watershed outlet. This approach is based on a DRAINMOD application proposed by Northcott et al. (2002), who simulated stream base flow in DRAINMOD using the depth of the drainage system and the drain spacing to mimic the conditions within the stream system that drains the watershed. Thus, the watershed discharge is a combination of daily DRAINMOD-simulated outflow from each field and daily DRAINMOD-simulated stream baseflow.

## 2.3. DRAINMOD

DRAINMOD (Skaggs, 1999) version 5.1 is a field-scale computer simulation model that characterises the response of the soil water regime to various combinations of surface and subsurface water management, such as surface drainage, subsurface drainage, controlled drainage and subirrigation. The model simulates the effects of water management on water table depth by performing a one-dimensional water balance to a soil column located at the midpoint between adjacent drains, and extends from soil surface to the top of an impermeable soil layer. Subsurface runoff is computed using the



Hooghoudt equation during water table drawdown and Kirkham equation during surface ponding. Surface runoff is estimated as a function of a user defined surface depressional storage. Infiltration is approximated using the Green–Ampt equation. Simulated evapotranspiration ( $ET$ ) is computed from potential evapotranspiration ( $PET$ ) as limited by soil water availability. The model can internally calculate  $PET$  using the temperature-based Thornthwaite method or externally calculated by any other  $PET$  method and read by the model. A detailed description of DRAINMOD can be found elsewhere (e.g. Skaggs et al., 2012).

#### 2.4. DRAINMOD-N II

DRAINMOD-N II (Youssef et al., 2005) is a field-scale, process-based model that simulates C and N dynamics in the soil–water–plant system for a wide range of soil types, climatic conditions and farming practices. As the name implies, DRAINMOD-N II is a companion model to the drainage water management model DRAINMOD. DRAINMOD-N II simulates soil carbon (C) dynamics using a C-cycle adapted from the CENTURY model (Parton et al., 1987). It simulates a detailed N cycle that includes atmospheric wet deposition, application of mineral N fertilisers including urea and anhydrous ammonia ( $NH_3$ ), soil amendment with organic N (ON) sources including plant residues and animal waste, plant uptake, OC decomposition and associated N mineralisation/immobilisation, nitrification, denitrification,  $NH_3$  volatilisation, and N losses via subsurface drainage and surface runoff. DRAINMOD-N II simulates N reactive transport using a finite difference solution to a multi-phase form of the one-dimensional advection-dispersion-reaction equation. Model output includes daily concentrations of  $NO_3$ -N and  $NH_4$ -N in soil solution and drain flow, OC content of the top 20-cm soil layer and cumulative rates of simulated N processes on daily, monthly, and annual basis. A detailed description of DRAINMOD-N II can be found in Youssef et al. (2005).

#### 2.5. In-stream nitrate removal

In the present modelling application, in-stream nitrate removal was estimated based on the assumptions that the net loss in  $NO_3$ -N load as drainage water moved from fields to the watershed outlet was dependent on transit time and that denitrification was the only N removal process in the stream network.

Based on laboratory results, Dawson and Murphy (1972) found that denitrification rate in wastewater is positively correlated to temperature and that the temperature dependency of the denitrification rate may be approximated by the Arrhenius equation:

$$k_{den} = k_0 \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where  $k_{den}$  is the denitrification rate constant,  $k_0$  is the frequency factor,  $E$  is the activation energy ( $\text{cal g-mol}^{-1}$ ),  $R$  is the universal gas constant ( $\text{cal g-mol}^{-1} \text{K}^{-1}$ ) and  $T$  is the absolute temperature (K). As illustrated by Appelboom et al. (2006), the results of the Dawson and Murphy (1972) study can be fitted to an empirical exponential equation, where the denitrification rate depends on two decay coefficients ( $k_{c1}$  and  $k_{c2}$ ). Thus Eq. (1) can be represented on a daily basis as:

$$k_{den} = k_{c1} \exp(k_{c2}Tt) \quad (2)$$

where  $k_{c1}$  is the decay coefficient 1 (dimensionless),  $k_{c2}$  is the decay coefficient 2 ( $^{\circ}\text{C}^{-1} \text{day}^{-1}$ ),  $T$  is the daily average air temperature ( $^{\circ}\text{C}$ ), and  $t$  is the transit time (day) (Birgand, 2000).

#### 2.6. Application of ArcHydro-DRAINMOD to estimate nitrate-nitrogen

In a previous study, the hydrological framework Arc Hydro-DRAINMOD was used to simulate watershed discharge (Salazar et al., 2010). In the present study, the nitrogen model DRAINMOD-N II and temperature-dependent  $NO_3$ -N removal equations were incorporated into the Arc Hydro-DRAINMOD framework to predict  $NO_3$ -N loading.

DRAINMOD-N II simulated daily  $NO_3$ -N load for each field, with input based on the individual characteristics of each field (i.e. soil type, crop rotation and farming practices, and drainage system). Daily  $NO_3$ -N load predicted by the model was summed for each field and stored in a time series. The schematic network created by Arc Hydro tools for simulating watershed discharge was used to route the time series of daily simulated  $NO_3$ -N load from each field to the watershed outlet (Fig. 1). The schematic network included two types of links and three types of nodes (Table 2). The  $NO_3$ -N load routed from each field was summed through the stream network to predict the  $NO_3$ -N load at the watershed outlet on a daily basis.

Nitrate load by stream baseflow for the watershed was simulated with DRAINMOD-N II as an individual component, which represents the  $NO_3$ -N leaching downward until it reaches the groundwater reservoir and is then transported to the stream network by groundwater discharge into the Kleve river. The model was set to reflect the conditions within the stream systems that drained the watershed based on two assumptions: (i) the depth of the main stream was set at 2 m, which was the average depth of the Kleve river in the 2 km long reach upstream of the watershed outlet; and (ii) the distance between the river and the watershed boundary ranges from 500 to 2500 m, which was included in the GLUE analysis, as described in detail in a subsequent section. The  $NO_3$ -N load that reached the watershed outlet ( $\text{load}_{received}$ ) was a combination of daily DRAINMOD-simulated  $NO_3$ -N load from each field and daily DRAINMOD-simulated  $NO_3$ -N load by stream baseflow. Finally, the load that passed through the watershed outlet was reduced according to Eq. (3) as:

$$\text{load}_{passed} = \text{load}_{received} k_{den} \quad (3)$$

**Table 2**

Explanation of modules for links and nodes in the schematic network.

Type	Purpose	Process
<b>Links</b>		
1	To represent the field to stream network transport	DRAINMOD-N II $NO_3$ -N loss time series passed from field to stream network
2	To represent the along stream network transport	$NO_3$ -N loss routed along a stream segment to the watershed outlet
<b>Nodes</b>		
1	To represent a field	Store DRAINMOD-N II $NO_3$ -N loss time series
2	To combine DRAINMOD-N II field $NO_3$ -N losses	Sum DRAINMOD-N II $NO_3$ -N loss time series at a junction along the stream network to generate the $NO_3$ -N loss in the stream network flow
3	To combine DRAINMOD-N II $NO_3$ -N loss by stream baseflow with $NO_3$ -N loss by stream network flow at the watershed outlet	Sum DRAINMOD-N II $NO_3$ -N loss by stream baseflow time series and $NO_3$ -N loss by stream network flow at the watershed outlet

where  $load_{passed}$  is the downstream  $NO_3-N$  load ( $kg\ day^{-1}$ ),  $load_{received}$  is the upstream  $NO_3-N$  load ( $kg\ day^{-1}$ ) and  $k_{den}$  is the denitrification rate (Eq. (2)).

Arc Hydro-DRAINMOD was run for six periods for which complete datasets were available: October 2003–June 2004 (Period 1), July 2004–June 2005 (Period 2), July–September 2005 (Period 3), January–June 2006 (Period 4), January–June 2007 (Period 5) and July 2007–December 2007 (Period 6). The first three periods were used for the calibration process, while the last three periods were retained for model validation. Daily  $NO_3-N$  load estimated by linear interpolation and simulated daily  $NO_3-N$  load values were both aggregated to a monthly period. Model calibration and validation was based on the comparison of estimated and predicted monthly loads. The framework was not tested for predicting daily loads because of the high uncertainty in the estimated daily loads caused by the lack of high frequency measurement of  $NO_3-N$  concentration in drainage water.

### 2.7. Nitrate loading framework parameters

The DRAINMOD-N II parameters used in this simulation were based on those reported by Salazar et al. (2009), who calibrated and validated the model for the cold conditions of south-east Sweden and from ranges published in the literature. Climatological daily data (2003–2007) were obtained from the meteorological network stations in Kalmar County (SMHI).

Soil parameters for mineral soils (organic matter content <12%) were obtained from a soil survey in Kalmar county (Wiklert et al., 1983). Soil parameters for organic soils (organic matter content  $\geq 12\%$ ) were obtained from values reported by Ingevall (1984) and Kätterer et al. (2006). Soil hydraulic properties required by DRAINMOD were estimated using the ROSETTA pedotransfer model, as applied by Salazar et al. (2008). The estimated lateral saturated hydraulic conductivity ( $LK_s$ ) values were in the range of 1–4 times vertical saturated hydraulic conductivity ( $K_s$ ) values.

DRAINMOD-N II parameters are summarised in Table 3. Crop and management parameters used in DRAINMOD-N II simulations were similar to those used by Salazar et al. (2009) for winter wheat, sugarbeet and spring barley. For peas, beans, potatoes and ryegrass, crop and management parameter values were obtained from ranges published in the literature. Although potatoes were grown for tuber production and ryegrass as a cover crop, these were assumed to have a seed yield and seed N content (crop nitrogen). Assigning a seed N content is a requirement of the standard DRAINMOD N-II, which was originally developed for grain crops. Thus, the assumed seed N content was kept very small not to affect simulations. Similarly, harvest index and root/shoot ratio were adapted to consider seed yield as potential crop yield. For the fallow periods, weeds with a root depth of 5 cm were used to reflect the soil depth from which N may be taken up in the absence of a crop (green fallow). The nitrogen uptake tabulated function proposed by Youssef (2003) was used for the crops grown in the watershed. Table 3 lists common ranges for crop production parameters and plant biochemical composition parameters.

Nitrate removal estimation (Eq. (5)) used the measured daily average air temperature and the two decay coefficients. These decay coefficients are parameters that had to be calibrated using the GLUE methodology, as described in detail in a subsequent section.

### 2.8. Uncertainty estimation

The Generalised Likelihood Uncertainty Estimation (GLUE) methodology recognises the equivalence or near-equivalence of different model parameter sets as representations of hydrological systems, which is based on the concept of equifinality (Beven,

2006). A detailed description of the GLUE methodology can be found elsewhere (Beven and Binley, 1992; Beven and Freer, 2001). The GLUE procedure used in this study to quantify the uncertainty in monthly nitrate loss predictions was based on the assumptions presented by Salazar et al. (2010), which are summarised below.

The traditional statistical likelihood measure modelling efficiency ( $E$ ) was selected as likelihood function (Nash and Sutcliffe, 1970):

$$E = 1.0 - \frac{\sum_{i=1}^n (O_i - S_i)^2}{\sum_{i=1}^n (O_i - O')^2} \quad (4)$$

where  $O_i$  and  $S_i$  are the  $i$ th observed and simulated values, respectively,  $O'$  is the mean of observed values and  $n$  is the number of paired observed-simulated values. The value of  $E$  ranges from minus infinity to 1.0. The goodness of fit between observed and simulated values increases as the value of  $E$  increases. Modelling efficiency of 1.0 represents a perfect match between observed and simulated values, and zero  $E$  indicates that  $O'$  is as good a predictor as the model, whereas negative values indicate that the observed mean is a better predictor than the model. Although  $E$  has the disadvantage of amplifying the effect of large errors when squared (Eq. (4)), it was chosen because its interpretation is well known and has previously been used in many GLUE applications (e.g. Freer et al., 1996; Mo et al., 2006; Arabi et al., 2007; Choi and Beven, 2007; Salazar et al., 2013).

In this study, the following likelihood thresholds of acceptability were tested:  $E \geq 0.3$ ,  $E \geq 0.4$ ,  $E \geq 0.5$  and  $E \geq 0.6$ , to check which threshold ensured to bracket at least 60% of the observations. All the simulations with  $E$  values higher than the likelihood thresholds were retained for making predictions and were classified as behavioural simulations. Parameter sets with  $E$  values lower than the likelihood thresholds were classified as non-behavioural simulations and given a likelihood of zero.

When it is not possible to optimise all the parameters required in a modelling approach, most emphasis in the GLUE methodology must be placed on sensitive parameters that are important to give a good fit to the observed values (Beven, 2006). Sensitivity analysis conducted on DRAINMOD showed that the model is very sensitive to change in soil hydraulic properties (Anderson et al., 1987; Workman and Skaggs, 1994; Haan and Skaggs, 2003; Wang et al., 2006), in particular, lateral saturated hydraulic conductivity ( $LK_s$ ) in the soil layer where the drains are located (Haan and Skaggs, 2003). In this study nine parameters were calibrated using the GLUE methodology: lateral saturated hydraulic conductivity ( $LK_s$ ) (six replicates according to the textural classes found in the Kleva watershed), the distance between the river and the watershed boundary (DS) in the DRAINMOD-simulation of stream baseflow,  $k_{c1}$  and  $k_{c2}$  (Table 4). The last two parameters were included in the GLUE procedure because these were not measured and have few literature references.

The distribution of parameter values was defined on the basis of some prior knowledge about the watershed for  $LK_s$  and DS. Although the initial parameter distribution for  $k_{c1}$  and  $k_{c2}$  was subjectively defined, the range was refined by comparison of the predicted response within that range to define a suitable reference prior distribution. In this study, 9600 Monte Carlo parameter sets were simulated during Period 1 to Period 3 (calibration period).

For the present study, the 5th and 95th percentiles of the cumulative likelihood distribution were chosen as the uncertainty limits of the predictions. The 50th percentile was used as a measure of modal behaviour, which was compared with calculated  $NO_3-N$  load values.

The predicted  $NO_3-N$  load by each model run were ranked in order of magnitude and, using the likelihood weights ( $E$  values) associated with each run, a distribution function of the predicted

**Table 3**  
Summary of DRAINMOD-N II parameters in the Kleva watershed.

Soil physical and chemical properties						
	Soil type					
	Sand	Loamy sand	Sandy loam	Silty loam	Clay	Organic
Clay fraction <sup>a</sup>	0.01	0.05	0.06	0.09	0.61	0.33
Silt fraction <sup>a</sup>	0.06	0.16	0.21	0.65	0.33	0.31
Soil water content at wilting point (cm <sup>3</sup> cm <sup>-3</sup> ) <sup>a</sup>	0.03	0.06	0.09	0.07	0.26	0.23
Dry bulk density (g cm <sup>-3</sup> ) <sup>a</sup>	1.64	1.74	1.42	1.72	1.46	0.51
Distribution coefficient for NH <sub>4</sub> (cm <sup>3</sup> g <sup>-1</sup> ) <sup>b</sup>	1.42	1.76	1.84	2.09	6.40	4.08
Initial soil OC in the top 20 cm (μg C g <sup>-1</sup> ) <sup>a</sup>	9950	19,500	29,100	9550	20,850	243,000
Crop and management parameters						
	Peas	Potatoes	Ryegrass	Spring barley	Sugarbeet	Winter wheat
Potential yield grain/seed (kg ha <sup>-1</sup> )	2670 <sup>c</sup>	145 <sup>d</sup>	500 <sup>d</sup>	4730 <sup>c</sup>	1100 <sup>f</sup>	6740 <sup>c</sup>
Plant shoot dry matter (kg ha <sup>-1</sup> )	–	2000 <sup>d</sup>	3870 <sup>c</sup>	–	3000 <sup>f</sup>	–
Root/tuber dry matter (kg ha <sup>-1</sup> )	–	15,400 <sup>c</sup>	300 <sup>e</sup>	–	19,000 <sup>c</sup>	–
Harvest index	0.46 <sup>d</sup>	0.07 <sup>e</sup>	0.15 <sup>e</sup>	0.50 <sup>f</sup>	0.27 <sup>f</sup>	0.46 <sup>f</sup>
Root/shoot ratio	0.38 <sup>d</sup>	7.61 <sup>e</sup>	0.15 <sup>d</sup>	0.08 <sup>f</sup>	4.67 <sup>f</sup>	0.10 <sup>f</sup>
Crop nitrogen (%)	4.53 <sup>d</sup>	0.41 <sup>d</sup>	2.00 <sup>d</sup>	1.58 <sup>f</sup>	2.00 <sup>f</sup>	2.37 <sup>f</sup>
Shoot N (%)	2.11 <sup>d</sup>	4.06 <sup>d</sup>	2.63 <sup>d</sup>	0.59 <sup>f</sup>	2.30 <sup>f</sup>	0.73 <sup>f</sup>
Shoot C (%)	43.60 <sup>d</sup>	40.49 <sup>d</sup>	41.05 <sup>d</sup>	47.30 <sup>f</sup>	26.23 <sup>f</sup>	41.50 <sup>f</sup>
Shoot lignin (%)	7.40 <sup>d</sup>	7.45 <sup>d</sup>	3.00 <sup>d</sup>	6.10 <sup>f</sup>	4.20 <sup>f</sup>	5.70 <sup>f</sup>
Root/tuber N (%)	2.37 <sup>d</sup>	1.40 <sup>c</sup>	1.58 <sup>d</sup>	1.80 <sup>f</sup>	0.76 <sup>f</sup>	0.86 <sup>f</sup>
Root C (%)	42.2 <sup>d</sup>	–	39.60 <sup>d</sup>	39.20 <sup>f</sup>	–	36.50 <sup>f</sup>
Root lignin (%)	14.6 <sup>d</sup>	–	7.90 <sup>d</sup>	23.10 <sup>f</sup>	–	9.50 <sup>f</sup>
Transport and transformation parameters <sup>f</sup>						
Longitude dispersivity (cm)	5					
Tortuosity	0.5					
Critical pH	7.5					
	Nitrification			Denitrification		
V <sub>max</sub> (μg N g <sup>-1</sup> soil d <sup>-1</sup> )	9			4		
K <sub>m</sub>	170			30		
Optimum temperature (°C)	20			25		
Threshold water-filled pore space	–			0.8		
Optimum water-filled pore space range	0.5–0.6			–		
Organic matter parameters <sup>f</sup>						
Optimum temperature (°C)	30					
Optimum WFPS range	0.5–0.6					
Litter pools	C/N ratio		Decomposition rate (d <sup>-1</sup> )			
Surface structural	150		1.0685 × 10 <sup>-2</sup>			
Surface metabolic	15		4.0548 × 10 <sup>-2</sup>			
Surface microbes	8		1.6438 × 10 <sup>-2</sup>			
Below-ground structural	150		1.3425 × 10 <sup>-2</sup>			
Below-ground metabolic	15		5.0685 × 10 <sup>-2</sup>			
SOM pools	Initial OC assigned to pool (%)		C/N ratio		Decomposition rate	
Active	2		15		2.0000 × 10 <sup>-2</sup>	
Slow	28		20		5.4795 × 10 <sup>-4</sup>	
Passive	70		10		1.2329 × 10 <sup>-5</sup>	

<sup>a</sup> Estimated from ranges published in the literature (Wiklert et al., 1983; Ingevall, 1984; Kätterer et al., 2006).

<sup>b</sup> Estimated according to Knisel et al. (1993).

<sup>c</sup> Data from the Swedish Board of Agriculture.

<sup>d</sup> Estimated from ranges published in the literature.

<sup>e</sup> Calculated considering seed production.

<sup>f</sup> Reported by Wesström (2006) and Salazar et al. (2009).

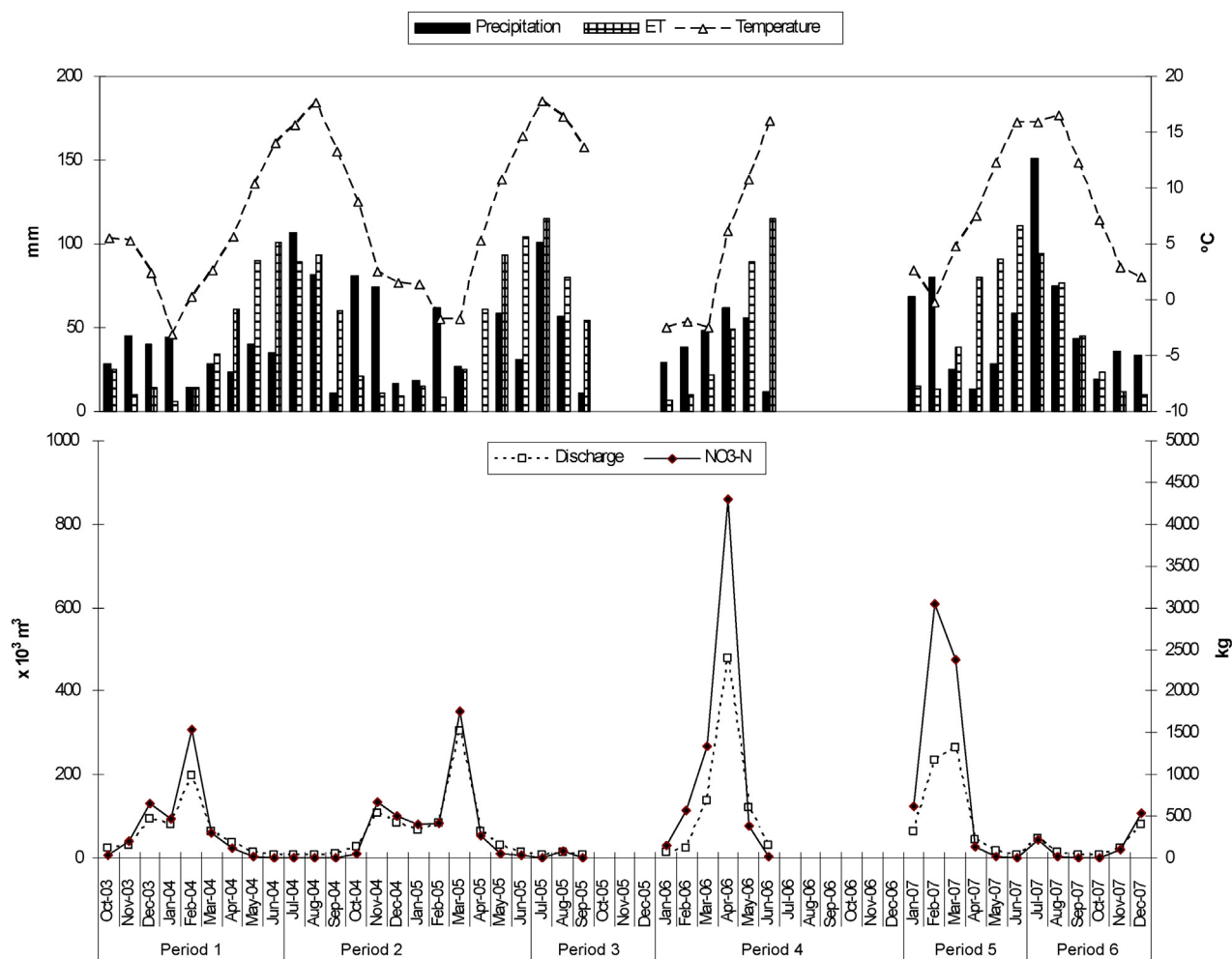
NO<sub>3</sub>-N load was calculated. The likelihood associated with each model run and the predicted percentiles (5th and 95th percentiles) were updated as each new period of data was included into the analysis from Period 1 to Period 3 (calibration period), using the Bayes equation (Beven and Binley, 1992).

The posterior likelihood distribution determined after Bayesian updating was used to validate Arc Hydro-DRAINMOD by

comparison with observed data that were not used in the likelihood updating. This was done for Period 4 to Period 6 using the posterior likelihood distribution calculated for Period 1 to Period 3. In model calibration/validation, monthly loads calculated by linear interpolation and predicted 5th and 95th percentiles NO<sub>3</sub>-N loads were compared by calculating the NO<sub>3</sub>-N load deviation ( $E_d$ ). This statistical measure determines the percentage when the

**Table 4**  
Parameter ranges used in Monte Carlo simulations for the Kleva watershed.

Parameter	Description	Minimum value	Maximum value
$S-LK_s$ [ $\text{cm h}^{-1}$ ]	Lateral $K_s$ in soils with sand textural class	160	643
$LS-LK_s$ [ $\text{cm h}^{-1}$ ]	Lateral $K_s$ in soils with loamy sand textural class	105	420
$SL-LK_s$ [ $\text{cm h}^{-1}$ ]	Lateral $K_s$ in soils with sandy loam textural class	38	152
$SIL-LK_s$ [ $\text{cm h}^{-1}$ ]	Lateral $K_s$ in soils with silty loam textural class	18	72
$C-LK_s$ [ $\text{cm h}^{-1}$ ]	Lateral $K_s$ in soils with clay textural class	15	60
$ORG-LK_s$ [ $\text{cm h}^{-1}$ ]	Lateral $K_s$ in organic soils	8	32
DS [m]	Distance between the river and the watershed boundary for stream baseflow simulation	500	2500
$k_{c1}$	The decay coefficient 1 in Eq. (6)	0.5	1
$k_{c2}$ [ $^{\circ}\text{C}^{-1} \text{day}^{-1}$ ]	The decay coefficient 2 in Eq. (6)	0.001	0.005



**Fig. 2.** Monthly sum of measured precipitation ( $P$ ), calculated potential evapotranspiration ( $PET$ ), average air temperature ( $T$ ), river discharge and nitrate load ( $\text{NO}_3\text{-N}$ ) in the Kleva watershed for Periods 1–6.

model simulated 5th and 95th percentiles bracket the observations and was adapted from the acceptability variables proposed by Thorndahl et al. (2008):

$$E_{d,p} = \frac{\sum_{i=1}^n S_{i,p} - \sum_{i=1}^n O_i}{\sum_{i=1}^n O_i} \quad (5)$$

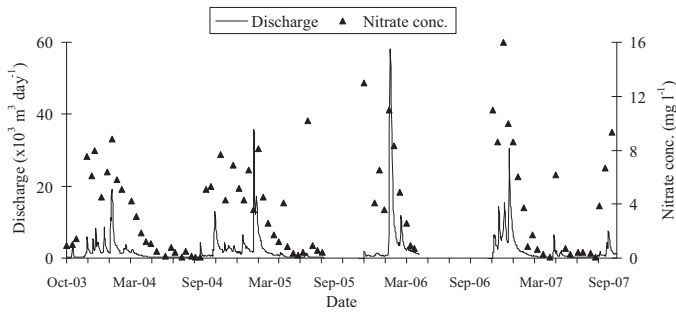
where  $O_i$  is the individual observed value at time  $i$ ,  $S_{i,p}$  is the individual simulated value at time  $i$ ,  $p$  is the percentile (5th or 95th) and  $n$  is the number of paired observed-simulated values. The value of  $E_{d,5\text{th}}$  should be negative for a model, showing that the prediction is less than the observation and that overprediction is prevented. Correspondingly,  $E_{d,95\text{th}}$  should be positive for a model showing that the

prediction is larger than the observation and that underprediction is prevented.

### 2.9. Sensitivity analysis

A sensitivity analysis was carried out for all nine parameters selected in the Monte Carlo simulations (Table 4) using the GLUE results. This methodology was proposed by Hornberger and Spear (1981) and adapted by Beven and Binley (1992) to consider the likelihood weights for the behavioural simulations. In the present study, the sensitivity analysis was performed by comparison of the cumulative distribution for the final behavioural simulations after all Bayesian updating of likelihood weights and





**Fig. 3.** Daily discharge and measured nitrate (NO<sub>3</sub>-N) concentrations for the study period.

non-behavioural simulations. The parameters that showed a strong deviation between behavioural and non-behavioural cumulative distributions across the same parameter range were considered the most sensitive. In contrast, parameters that were uniformly distributed were considered less sensitive to changes in parameter values. In addition, the non-parametric Kolmogorov–Smirnov *d*-statistic ( $d_{K-S}$ ) was used as a measure of the sensitivity (Hornberger and Spear, 1981). The  $d_{K-S}$  calculates the maximum distance between the behavioural and the non-behavioural cumulative distributions. The value of  $d_{K-S}$  ranges from 0 to 1, where a parameter with  $d_{K-S} = 1$  indicates a high sensitivity, whereas a parameter with  $d_{K-S} = 0$  indicates non-sensitivity.

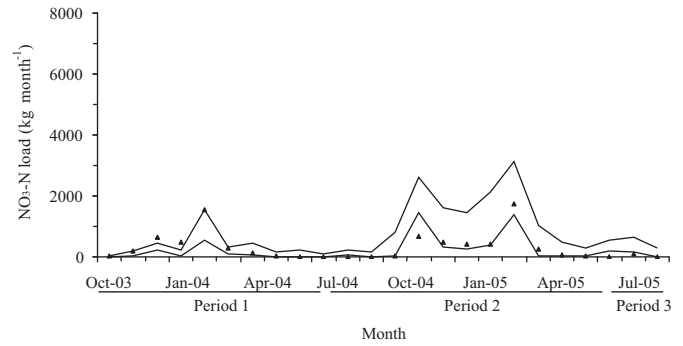
### 3. Results and discussion

#### 3.1. Discharge and nitrate load

Within the hydrological year (1st October to 30th September), discharges from Kleva watershed were highly seasonal because of fluctuations in rainfall, temperature, evapotranspiration and snow melt. There were two distinct phases of discharge from the watershed, a phase of high discharge during winter and spring, and a phase of low discharge during summer and autumn. Seasonally, 36% and 41% of the overall discharge from the watershed was recorded during winter and spring, respectively (Fig. 2), during snow melting events as explained by Salazar et al. (2010). Similarly, 42% and 47% of the overall NO<sub>3</sub>-N load were recorded in winter and spring, respectively. Thus, the movement of NO<sub>3</sub>-N was strongly dependent on the movement of water in the watershed, with the highest NO<sub>3</sub>-N concentrations measured during intense discharge events in winter and spring seasons (Fig. 3).

#### 3.2. Framework calibration, validation and sensitivity analysis

The previously described GLUE procedure was performed to measure the uncertainty in Arc Hydro-DRAINMOD predictions of NO<sub>3</sub>-N loading. After all Bayesian updatings of likelihood weights during the calibration period, 60% of the simulations were retained as behavioural using a threshold of  $E \geq 0.3$ . The predicted 5th and 95th percentiles defined during the calibration period (Periods 1 to 3) are shown in Fig. 4. In the calibration period, the uncertainty bands included a high percentage (about 71%) of the monthly calculated NO<sub>3</sub>-N loads by linear interpolation values, showing good agreement between the GLUE estimates and calculated monthly NO<sub>3</sub>-N loads. This is consistent with the Arc Hydro-DRAINMOD predictions of discharge during the calibration period, when the uncertainty bands also bracketed a high percentage of the monthly observed values, about 88% (Salazar et al., 2010). Similar trends were generally observed in the different periods, with comparisons of the percentage of time when the calculated NO<sub>3</sub>-N loads were bracketed by the uncertainty bands yielding 67%, 83% and 33% in



**Fig. 4.** Predictive uncertainty for results from calibration period (Period 1 to Period 3). Triangles indicate calculated monthly NO<sub>3</sub>-N load and dashed lines indicate 5th and 95th percentiles.

**Table 5**

Deviation in nitrate load between calculated by linear interpolation and simulated 5th ( $E_{d,5th}$ ) and 95th ( $E_{d,95th}$ ) percentiles during calibration period (Periods 1 to 3) and validation period (Periods 4 to 6).

Period	<i>n</i> <sup>a</sup>	$E_{d,5th}$ <sup>b</sup>	$E_{d,95th}$ <sup>c</sup>
1	9	-0.7	0.1
2	12	-0.1	2.4
3	3	3.1	15.1
Overall 1–3	24	-0.3	1.5
4	6	-0.3	0.9
5	6	-0.6	-0.1
6	6	-0.3	0.7
Overall 4–6	18	-0.4	0.5

<sup>a</sup> Number of months.

<sup>b</sup> A positive value indicates that the NO<sub>3</sub>-N loads are outside the prediction interval (overprediction).

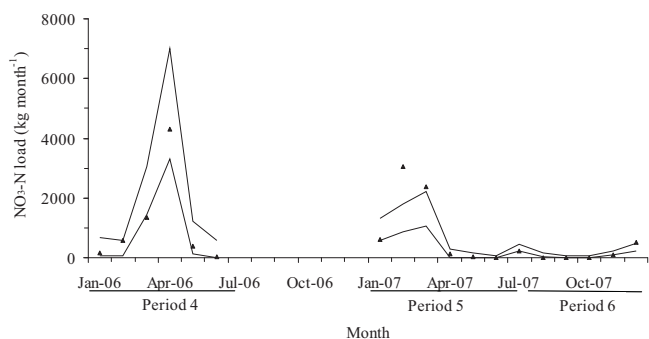
<sup>c</sup> A negative value indicates that the NO<sub>3</sub>-N loads are outside the prediction interval (underprediction).

Periods 1, 2 and 3, respectively. The average width of the bands for the calibration period was 0.78 kg NO<sub>3</sub>-N ha<sup>-1</sup>, ranging from 0.04 kg NO<sub>3</sub>-N ha<sup>-1</sup> (October 2003) to 2.37 kg NO<sub>3</sub>-N ha<sup>-1</sup> (March 2005). This indicates that the uncertainty in predictions was higher during periods of higher NO<sub>3</sub>-N load, such as spring periods.

The overall NO<sub>3</sub>-N load deviation ( $E_d$ ) showed good agreement between the GLUE estimates and calculated monthly NO<sub>3</sub>-N loads for the calibration period (Table 5). However, compared with calculated values, the NO<sub>3</sub>-N load deviation at 5% ( $E_{d,5\%}$ ) showed a positive value during Period 3. This positive value was caused by overprediction of the GLUE estimates during July–September in Period 3. This can also be observed in Fig. 4, where the calculated NO<sub>3</sub>-N loads were below the uncertainty bands in Period 3. It is possible that in Period 3 the framework might have predicted lower denitrification in the stream network or higher NO<sub>3</sub>-N loads from the stream baseflow. Although, a lower agreement in Period 3 was found between the GLUE estimates and calculated monthly NO<sub>3</sub>-N loads, the period only included three months and those had a much lower weight on the overall performance of the framework during calibration period which included 24 months.

Fig. 5 shows the predicted 5th and 95th percentiles for the validation period (Period 4 to Period 6), which were defined using the posterior likelihood distribution calculated for the calibration period. In the validation period most of the calculated NO<sub>3</sub>-N loads (around 67%) were within the uncertainty bands and the performance of the GLUE estimates in describing the NO<sub>3</sub>-N load resembled that in the calibration period. Comparing the percentage of time when the calculated NO<sub>3</sub>-N loads were bracketed by the uncertainty bands yielded 83%, 67% and 50% in Periods 4, 5 and 6, respectively. Similarly, the uncertainty bands included a high percentage of monthly observed discharges in the validation period,





**Fig. 5.** Predictive uncertainty for results from validation period (Period 4 to Period 6). Triangles indicate calculated monthly  $\text{NO}_3\text{-N}$  load and dashed lines indicate 5th and 95th percentiles.

about 75% (Salazar et al., 2010). The width of the bands was on average 19% higher in the validation period than in the calibration period, indicating increasing uncertainty in prediction during the validation period.

The overall  $\text{NO}_3\text{-N}$  load deviation ( $E_d$ ) for the validation period also showed good agreement between the GLUE estimates and calculated monthly  $\text{NO}_3\text{-N}$  loads (Table 5). However, the  $\text{NO}_3\text{-N}$  load deviation at 95th ( $E_{d,95\text{th}}$ ) showed a negative value compared with calculated values during Period 5. This negative value was caused by underprediction of the GLUE estimates during January–March in Period 5 as can also be observed in Fig. 5, where the calculated  $\text{NO}_3\text{-N}$  loads were above the uncertainty bands during January–March in Period 5. Errors in predicting  $\text{NO}_3\text{-N}$  loads during this period might be attributed to errors in predicting field outflow volumes, with DRAINMOD overpredicting discharge due to errors in snow accumulation and melt in this mild winter period. Other possible explanations are that in contrast to errors in the warmer Period 3, the framework might have predicted higher denitrification in the stream network or lower  $\text{NO}_3\text{-N}$  loads from the stream baseflow in the winter Period 5. However, measurements of these processes would be necessary to confirm these hypotheses.

Comparing results from the sensitivity plots in Fig. 6, DS and  $k_{c1}$  showed a strong deviation between behavioural ( $E \geq 0.3$ , 60% of the simulations) and non-behavioural ( $E < 0.3$ , 40% of the simulations) cumulative distributions. Similarly, the Kolmogorov–Smirnov  $d$ -statistic ( $d_{K-S}$ ) indicated that DS had the highest value (0.52), followed by  $k_{c1}$  (0.33) (Fig. 6), and these were found to be the most sensitive parameters. The DS affects the  $\text{NO}_3\text{-N}$  transport in the stream baseflow that reaches the river and the  $k_{c1}$  affects the N removal process in the stream network. It is evident that these processes were the most unknown during this framework evaluation because of the unavailability of measurements and the few number of published studies investigating these processes.

DRAINMOD-N II predictions, which are based on the output of the DRAINMOD hydrology model, depend directly on the performance of DRAINMOD (Youssef et al., 2006). Although in our study the  $\text{NO}_3\text{-N}$  loads were strongly dependent on discharge rates, lateral saturated hydraulic conductivity ( $LK_s$ ) values, which have been identified as a very sensitive parameter affecting DRAINMOD field outflow predictions (Haan and Skaggs, 2003; Wang et al., 2006), did not show a strong deviation between behavioural and non-behavioural cumulative distributions. A possible explanation is that the effect of  $LK_s$  on watershed discharge was modulated by the stream hydraulics, as reported by Fernandez et al. (2006) when using the DRAINMOD-GIS model to predict  $\text{NO}_3\text{-N}$  loads at watershed-scale.

**Table 6**

Comparison between calculated by linear interpolation and simulated (5th, 50th and 95th percentiles)  $\text{NO}_3\text{-N}$  loads during Periods 1–6.

	$\text{NO}_3\text{-N}$ load <sup>a</sup> ( $\text{kg ha}^{-1}$ )	$E^b$
5th	0.44	0.68
50th	0.60	0.76
95th	1.28	0.37
Calculated	0.69	

<sup>a</sup> Overall  $\text{NO}_3\text{-N}$  load during Periods 1–6.

<sup>b</sup> Modelling efficiency comparing calculated by linear interpolation and simulated monthly  $\text{NO}_3\text{-N}$  loads.

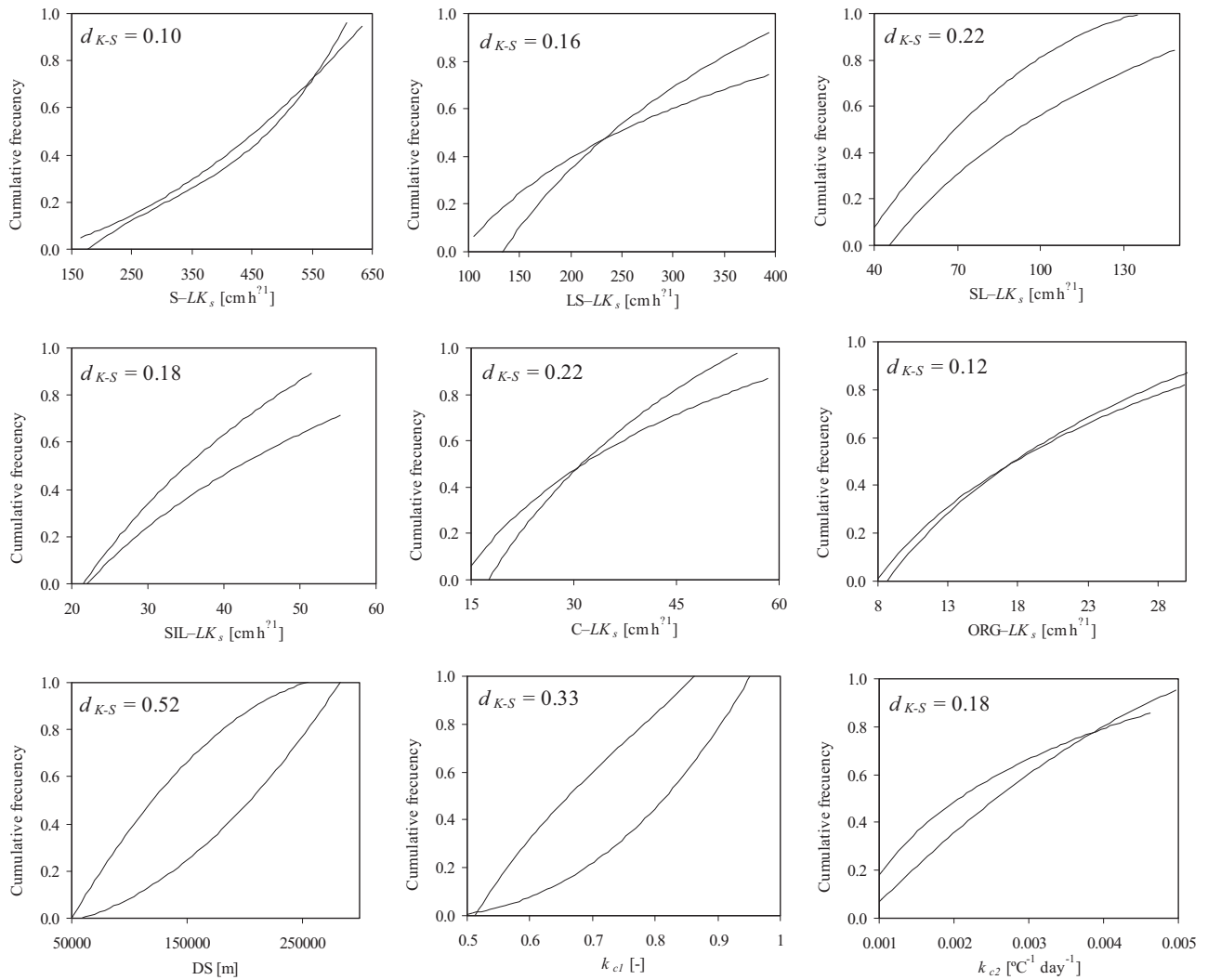
### 3.3. Simulating nitrogen processes in the watershed

The temporal trend and magnitude of calculated monthly  $\text{NO}_3\text{-N}$  loads were well predicted by the framework during the study period. The monthly  $E$  values for the GLUE estimates (5th and 95th percentiles) ranged from 0.37 to 0.76, with the highest value for the 50th percentile (Table 6), which indicates acceptable agreement between predicted and calculated monthly  $\text{NO}_3\text{-N}$  loads for the Kleva watershed.

Simulated N removal in the stream network ranged from 3% to 44% for the 95th and 5th percentiles, respectively. Results from the 50th percentile GLUE estimate showed that 25% of the  $\text{NO}_3\text{-N}$  load was removed in the stream network and 75% of the  $\text{NO}_3\text{-N}$  load passed through the watershed outlet (Table 7).

The Arc Hydro-DRAINMOD 50th percentile GLUE estimates were used to estimate the relative magnitude of  $\text{NO}_3\text{-N}$  load contributions from each soil type to the field total  $\text{NO}_3\text{-N}$  load, and from each soil texture and stream baseflow to  $\text{NO}_3\text{-N}$  load received at the watershed outlet (Table 7). Sandy fields were the principal source of  $\text{NO}_3\text{-N}$  load (36%) to the total field  $\text{NO}_3\text{-N}$  load, followed by sandy loam fields (31%). The total field  $\text{NO}_3\text{-N}$  load from coarse-textured fields (sand, loamy sand, sandy loam), about 73%, was directly proportional to the percentage of coarse-textured fields in the watershed area (75%). Although organic soils represented only 9% of the soils in the watershed, they accounted for 26% of the total field  $\text{NO}_3\text{-N}$  load. In contrast, silty loam soils occupied 16% of the watershed area, but delivered only 2% of the total field  $\text{NO}_3\text{-N}$  load. It is in agreement with literature that concludes that the movement of N- $\text{NO}_3$  is directly related with the percolation of water on the soil, where clearly the displacement of water is generally greater for sandy soils than finer-textured soils. On the other hand, organic soils have an important amount of organic N that may have a high impact on N loads in the watershed when mineralisation process is favoured by climatic factors (mainly soil water content and temperature). Most of the  $\text{NO}_3\text{-N}$  load received at the watershed outlet was delivered from fields (92%), with a small contribution to the stream baseflow (8%).

The Arc Hydro-DRAINMOD simulations also provided an estimate of the effects of different crop rotation and management on the N balance in each field. Table 8 shows simulations of inputs and outputs from sandy fields with different crop rotations during Period 1 to Period 6 (2003–2007). In this example, the highest net N mineralisation was predicted for Field 24, which received the highest applications of organic material (pig slurry) containing high N relative to C. The highest N losses by drainage and denitrification were in Field 12, which had the highest N fertilisation. Nitrogen fixation was predicted for Field 21, which had a pea crop, where nodule bacteria fixed on average  $158 \text{ kg N ha}^{-1} \text{ year}^{-1}$ . This value appears reasonable with respect to the N fixation values for peas of  $34\text{--}200 \text{ kg N ha}^{-1} \text{ year}^{-1}$  reported by Havlin et al. (1999). Simulated wet deposition loads of  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  were in agreement with the  $5.6 \text{ kg N ha}^{-1} \text{ year}^{-1}$  reported for Öland Island 2003–2007 by the Swedish Environmental Research Institute (Karlsson et al., 2008). Plant uptake was the main N removal mechanism from the



**Fig. 6.** Sensitivity plots for all parameters included in the GLUE procedure (see Table 4). Solid lines indicate behavioural parameter distributions and dashed lines indicate non-behavioural parameter distributions.  $d_{K-S}$  is the Kolmogorov–Smirnov test (parameter with  $d_{K-S} = 1$  indicates a high sensitivity, whereas a parameter with  $d_{K-S} = 0$  indicates non-sensitivity).

fields. The volatilisation process was favoured by high soil pH value at the site (7.5) and the highest volatilisation losses occurred after application of  $\text{NH}_4$ -forming pig slurry. Thus as shown previously by Arheimer et al. (2004), Arc Hydro-DRAINMOD can be used to simulate different scenarios in Swedish agricultural drained watersheds

in order to identify the changes in agricultural practices, such as the timing of fertilisation and ploughing, that may be the most effective and least expensive in reducing N transport from land to sea.

Model results presented in Tables 7 and 8 corresponded to model estimates obtained through this model application exercise,

**Table 7**

Contribution of each soil type to field  $\text{NO}_3\text{-N}$  load and of each soil type and stream baseflow to  $\text{NO}_3\text{-N}$  load received at the watershed outlet, and  $\text{NO}_3\text{-N}$  load that passed through after  $\text{NO}_3\text{-N}$  removal using the 50% percentile GLUE estimate.

Source of $\text{NO}_3\text{-N}$ load	Percentage of soil type to watershed area (%)	Percentage of soil type to field $\text{NO}_3\text{-N}$ load (%)	Percentage of $\text{NO}_3\text{-N}$ load to watershed $\text{NO}_3\text{-N}$ load received (%)	Percentage of $\text{NO}_3\text{-N}$ load to watershed $\text{NO}_3\text{-N}$ load passed (%)
Field soil type				
Sand	24.8	35.6	32.9	
Loamy sand	14.9	5.8	5.3	
Sandy loam	34.7	31.0	28.6	
Silty loam	16.3	1.5	1.4	
Clay	0.5	0.4	0.4	
Organic	8.8	25.8	23.8	
Total field $\text{NO}_3\text{-N}$ load	100.0	100.0	92.3	
Stream baseflow				
Total stream baseflow			7.7	
Watershed $\text{NO}_3\text{-N}$ load received			100.0	
$\text{NO}_3\text{-N}$ removal				25.0
Watershed $\text{NO}_3\text{-N}$ load passed				75.0

**Table 8**  
Comparison of nitrogen inputs and outputs from sandy fields with different crop rotations during Periods 1–6 (2003–2007).

Field	Rotation <sup>a</sup>	Input <sup>b</sup>				Output <sup>b</sup>			
		Net N mineralisation (kg N ha <sup>-1</sup> )	Fertilisation and manure (kg N ha <sup>-1</sup> )	N fixation (kg N ha <sup>-1</sup> )	Wet deposition (kg N ha <sup>-1</sup> )	Plant uptake (kg N ha <sup>-1</sup> )	Denitrification (kg N ha <sup>-1</sup> )	Volatilisation (kg N ha <sup>-1</sup> )	Drainage loss (kg N ha <sup>-1</sup> )
12	WW-SB-SU-SB-WW	77	615	0	23	337	237	12	43
21	SB-PO-PE-WW-PE	198	360	315	23	432	128	19	3
24	CG-CG-CG-CG-CG	223	400	0	23	264	141	13	17
25	FA-FA-FA-FA-FA	78	0	0	23	72	28	0	3

<sup>a</sup> CG: cultivated grassland; FA: green fallow; PE: peas; PO: potatoes; SB: spring barley; SU: sugarbeet; WW: winter wheat.

<sup>b</sup> kg N ha<sup>-1</sup> in 5 years.

although simulated values for N dynamics in soil and water were not confirmed by in situ measurements, these may be used to define a priori some nitrate vulnerable zones where future research has to be carried out to confirm these N losses.

This distributed approach, which used fields as units to store data, was an effective method for upscaling the DRAINMOD-N II model from field scale to watershed scale. It was possible due to the data available from the Swedish agricultural database, where the field is the main unit used by farmers to report yield, fertiliser and manure applications. Thus our distributed model approach was a more realistic method of accounting for watershed spatial variability than the current cell-based approach utilised in hydrological models integrated with GIS tools.

Limited data were available to estimate N transport by stream baseflow and N removal from the stream network, which were identified as the most sensitive parameters in this study. To increase accuracy in prediction of NO<sub>3</sub>-N load, it is necessary to measure parameters that could offer an accurate characterisation of both the stream baseflow and N removal process in the stream network, which would help reduce uncertainty. In addition, future framework evaluations should include the uncertainty in soil denitrification predictions. For instance Wang et al. (2005) conducted a sensitivity analysis for DRAINMOD-NII parameters at field scale and showed that the model is sensitive to the denitrification parameters which are very difficult to measure and usually obtained by calibration.

It is important to note that uncertainty is added in this modelling approach when NO<sub>3</sub>-N concentration from grab samples with lower-frequency observations are used to estimate monthly loads. Littlewood and Marsh (2005) in a comprehensive study of N loads in rivers of Great Britain found that when sampling regime is essentially manual and taken at nominally regular intervals, it can affect the quality of computed mass loads. They noted that recorded concentrations can be highly aperiodic, sometimes exhibiting an interesting frequency distribution of the time between consecutive samples, which introduced an additional source of error. Similarly, Martin et al. (1992) reported that grab samples under-represented concentrations of suspended sediment and some sediment-associated constituents, thus limiting the applicability of such data. In addition, Fogle et al. (2003) concluded that failure to account for diurnal variability when collecting a grab sample may also produce unacceptable error in mass load estimates. On the other hand, Stone et al. (2000) compared different water sampling methods, and found that flow-proportional sampling predicted significantly greater N mass loading rates than grab samples. They suggest that an appropriate sampling method should adequately weight sampling of both storm and base flows. However, simple surface-grab sample data are usually more available in water quality studies in Sweden, and its use for nutrient mass load estimation should be considered as a measurement error of any uncertainty analysis.

Other important source of error that may affect the performance of the framework is the linear interpolation between observed NO<sub>3</sub>-N concentrations to estimate NO<sub>3</sub>-N loads. For instance, Tiemeyer et al. (2010) used linear interpolation to estimate NO<sub>3</sub>-N loads in an artificially drained watershed area similar to our study area in Germany, where they found that this method performed well, but it still tended to underestimate the actual NO<sub>3</sub>-N loads.

Although the Arc Hydro-DRAINMOD framework showed promising results for monthly NO<sub>3</sub>-N load predictions, it is clear that a better characterisation of the travel time (time lag) of water and nitrate from the field edge to the watershed outlet is necessary in future versions of the framework for improving the framework performance. Clearly, if the NO<sub>3</sub>-N loads are higher during winter-spring than autumn-summer period, the framework and monitoring improvements should be focused on the processes that occur in the first period.

However, very often complex models are not used by water stakeholder agencies at local level, due to the lack of specific inputs or coefficients that are not either easily field measured or available from the literature. It is important to note that our main aim was to develop a simple framework, based on physical, chemical and biological processes, but that could be used by stakeholders using available information from Swedish agencies to evaluate best management practices to reduce NO<sub>3</sub>-N loads. In this sense, the current framework may have limitations and its application is only recommended for small tile-drained watersheds with low retention time.

#### 4. Conclusions

The nitrogen model DRAINMOD-N II and a temperature-dependent NO<sub>3</sub>-N removal equation were included into the Arc Hydro-DRAINMOD framework in order to estimate NO<sub>3</sub>-N loads. The estimates obtained were evaluated using hydrological and water quality data from a coastal watershed with agricultural land use located in south-east Sweden for six periods between 2003 and 2007.

GLUE methodology showed that the temporal trend and magnitude of monthly calculated NO<sub>3</sub>-N loads were well predicted by Arc Hydro-DRAINMOD, with 71% and 67% of “measured” loads bracketed within the GLUE estimates during calibration and validation periods, respectively.

Major discrepancies in predicting monthly NO<sub>3</sub>-N loads could be attributed to errors when NO<sub>3</sub>-N concentration from grab samples with lower-frequency observations were used to estimate NO<sub>3</sub>-N loads. Other possible explanations were that the framework might have predicted lower NO<sub>3</sub>-N loads from stream baseflow or higher denitrification in the stream network. The parameters with the highest sensitivity values were the distance between the river and the watershed boundary (DS) for stream baseflow simulation and the decay coefficient 1 ( $k_{c1}$ ) for the N removal equation.

In this application, Arc Hydro-DRAINMOD proved to be capable of evaluating the effects of different crops on the N balance as regards the spatial variability within the watershed, which will allow framework users to evaluate the impact of each field management option to nitrate pollution in the watershed. Arc Hydro-DRAINMOD can be used to evaluate best management practices (BMPs) to reduce NO<sub>3</sub>-N loads within the watershed and to prioritise BMPs in fields more prone to nitrate losses, such as fields with coarse-textured and organic soils.

The results show that Arc Hydro-DRAINMOD can be used to predict NO<sub>3</sub>-N loads from coastal watersheds in south-east Sweden. To improve model performance as regards NO<sub>3</sub>-N load simulation, the framework needs to be tested on the basis of field measurements, particularly of stream baseflow and N removal in the stream network. Although additional measurements may help to improve the understanding of these processes and reduce uncertainty, they cannot completely eliminate the uncertainty in framework predictions. These uncertainties must be evaluated by some methodology, such as the GLUE procedure.

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