Authors comments in reply to the reviewers' comments on "Technical Note: Alternative in-stream denitrification equation for the INCA-N model"

Anonymous Referee #1

1. **I think the authors should explain in the manuscript the reasons why the alternative approach, based on the mass transfer coefficient, gave better results during summer then the original INCA-N approach. They should discuss explicitly the mechanism that in their opinion allows better reproducing the low summer nitrate concentrations, but not other periods, such as the beginning of the wet season in September.**

   To this end, considering m_INCA (eq. 1) and m_alt (eq. 4), the mass transfer coefficient could be written as:

   ro_n=Rnh*

   Where ro_n is the mass transfer coefficient, Rn is the INCA-N original denitrification rate and h* is a factor that can be understood as an "effective" constant water depth for the volume of water stored in the reach. Therefore, we could say that an "effective" volume of water V*= (A h*) is calibrated when the equation 4 is used; where A is the estimated stream bottom area of the reach.

   The equations 1 and 4 of the manuscript can be written as follows:

   m_INCA = RnVC

   m_alt = Rn(Ah*)C = RnV*C

   Where C is the in-stream nitrogen-nitrate concentration on the previous day.

   Considering that all the terms of the equation 3 of the manuscript are exactly the same for the two approaches, being the denitrification term the only one that changes (as the authors stated clearly), we could say that the only difference between the results obtained and presented depends on the calibrated value for V* compared to the value of V simulated by the hydrological model. As a matter of fact, we can easily see from figure 1 that for most of the time the calibrated value for V* is greater than the simulated water volume V, since the dashed line representing the alternate equation is almost always lower than the continuous line representing the INCA-N model original simulation. During the summer period V* is much bigger than the simulated water volume V, so the difference

between the two lines is big, while during the wet period V* is much more similar to the simulated V so the differences between the two lines are not so significant.

In my opinion, this leads to think that the reason why the INCA-N model is not able to reproduce the observed nitrate concentrations should be searched somewhere else than the in-stream denitrification equation. Actually, it seems to be much more related to the hydrological component of the model than the in-stream denitrification process regardless the type of equation used by the authors. Can this also give some clues about why the calibrated value for the mass transfer coefficient needs to be higher than the range published by Birgand et al. (2007)?

I think the authors should discuss this point carefully, because even if the evaluation of alternate equations is always of interest and it may help to understand better a model behavior, they should be more prudent in drawing conclusions from this work if the premises are not the correct ones.

We agree that the differences between the two equations, the mechanisms that produced the different results, and the potential impact of the hydrological component were not discussed clearly in the original submission. Instead of using the approach suggested by the reviewer, we would like to look at the difference between the two equations from a different perspective. The NO_3-N concentration (C_1) in the INCA-N model is calculated using the following equation:

$$C_1 = \frac{1000 m_r}{V}$$

where m_r is the mass of NO_3-N in the stream reach (kg). If V is assumed to be equal to V_{t-1}, then the equation used to calculate the mass of NO_3-N removed via in-stream denitrification in the INCA-N model becomes:

$$m_{INCA} = R_n m_{r,t-1}$$

Although V is not always equal to V_{t-1}, this simplifying assumption is reasonable except immediately following a large precipitation event. This indicates that the simulated mass of nitrogen removed via denitrification is related to the mass of NO_3-N in the stream instead of the concentration. The concentration output from the model is related to the volume of water in the stream simulated by the hydrological component of the model, but does not impact the mass of nitrogen removed by in-stream denitrification.

In contrast, the alternate equation bases the simulation of in-stream denitrification on the NO_3-N concentration in the stream. Basing the in-stream denitrification on the concentration is important as the concentration gradient is one of the processes that drive the delivery of NO_3-N to the sites of denitrification in the stream sediment.

To improve the discussion of the mechanisms that caused the differences in the results, the following was added to the paper in addition to portions of the discussion above:

> "This may be an example of the simulated mass of nitrogen removed via in-stream denitrification being incorrectly inflated in the current model due to an increase in the mass of NO_3-N in the stream. At the peak concentration the simulated mass of NO_3-N in the stream was more than six times higher than prior to the event when using the current equation in the INCA-N model. The mass of NO_3-N increases by more than six times when the concentration increased only 2 times its pre-storm value because the volume of water in the stream also increased. The simulated mass of NO_3-N removed via denitrification with the current equation is more than six times higher at the concentration peak when compared to the mass of NO_3-N removed via denitrification at the pre-storm low concentration. The simulated mass of nitrogen removed via in-stream denitrification at the peak concentration increased only 3 times that of the value at the minimum concentration when using the alternate equation."

> "The lower rate of in-stream denitrification simulated by the current model during these periods is caused by the rate of denitrification being based on the low simulated mass of NO_3-N in the stream. The low removal of nitrogen via in-stream denitrification using the current method of modeling the process and the low volume of water in the reach result in elevated concentrations (Eq. 3)."

The following discussion about the alternate equation was added to the manuscript:

> "It is possible that the lower simulated NO_3-N concentrations during the periods with lower flow rates are a result of a constant stream bottom area being used. During these periods the stream bottom area may be too high when compared to the actual stream and the simulated mass of nitrogen removed via in-stream denitrification may be too high."

The potential impact of errors in the hydrological component of the model playing a role in the simulated NO_3-N concentrations was clarified in the paper by adding the following:

> "It is possible that during this low flow period, the simulated volume of water in the reach was too low. An increase in the simulated volume would result in a lower NO_3-N concentration due to dilution. Changes in the hydrologic portion of the model would also impact the results of the alternate equation, but a change in the calibrated mass transfer coefficient could potentially be used to compensate for the changes."

2. **To implement the alternate formulation the authors estimated the stream bottom area of the reach considered. I would have liked to see some sensitivity analysis results to understand how much this estimated area may affect the results, since I think there may be quite a lot of uncertainty related to this estimation.**

A sensitivity analysis was conducted where the stream bottom area was varied by +/- 20% and +/- 40%. These results are presented in section 3.3 of the revised manuscript.

3. **Another point I would like to highlight is that the authors do not present any type of validation for their conclusion. In fact, the data set considered for the model calibration is quite short itself. This, together with point 1, makes me doubt about the robustness and validity of the results presented. I would suggest to the authors to at least validate the model considering a different set before any publication.**

To address this comment and one made by the other reviewer, the area included in the model was expanded from a single sub-catchment in the Yläneenjoki catchment to four sub-catchments that have been used in previous applications of the model to this catchment. The calibration period was expanded to include all of 2004. The calibration was validated for 2001 for the same area. To prevent this technical note from expanding further in length, the results and discussion of the single sub-catchment for 9 months was replaced by the results for the full year and 4 sub-catchments.

4. **I could not understand very well what the authors wanted to say in chapter 3, lines 22-24, about the uncertainty associated to other parameters estimated. I suggest rephrasing the sentence and clarifying the idea.**

This portion was rewritten and is now contained in section 3.2.

Anonymous Referee #2

1. **This note deals with the difficult question of in-stream denitrification modelling at meso- and macro-scales. The aim of the paper is to assess two different equations inside a semi distributed catchment model. It is well written, clear and concise. Basically, the two equations are in the same form of proportionality to NO3 abundance in the streamwater. The difference is that, in the first case, the whole NO3 amount in a given reach is considered (concentration x volume of water in the reach), and the rate coefficient is calibrated (and temperature dependent), while in the second case, the concentration only is considered, and the rate coefficient depends in part on the interface area (i.e., the streambed area, considering that denitrification takes place in the sediment only). The authors should have stated this difference more clearly. It could have helped them to justify why this alternative formula might be more realistic, and more efficient in low flow conditions: if the denitrification rate depends on the total amount of nitrate in the reach, for a given temperature and a given concentrations, it will be higher in high flow conditions than in low flow conditions, whereas usually it is observed that the lower are the discharge and the height of the water column, the higher will be the denitrification rate.**

The difference between the two methods and the impact of this difference on the results has been expanded throughout the technical note. Examples can be seen in the response to comment 1 for the first anonymous reviewer.

2. **The fact that the mass transfer equation seems to "work" at lower concentrations than the theory is not really a problem: in detail, the variations for the very low concentrations do not seem very well simulated, what is relatively well simulated is the "bottom line" at low flow, and this is due to what happens previously, at concentrations higher than 1 mg/L.**

The variations at very low concentrations not being simulated well is a drawback of using a spreadsheet and the output from the INCA-N model. The lack of significant figures in the INCA-N model output makes the NO_3-N input used in the alternate equation simulation appear as a bulk input (10 kg) every 3rd or 4th day instead of a smaller input (2-4 kg) being added every day. This is the cause for the "sawtooth" pattern that is shown at very low concentrations. If the alternate equation was incorporated into the actual model, this "sawtooth" pattern would disappear.

3. **The authors also stated in the conclusion that introducing a new input (the streambed area A) in the model might be a drawback. However, even if this feature cannot be precisely quantify, the most important is that it almost always varies in a consistent way with respect to in-stream denitrification: the longer and the larger the reach, the higher will be the denitrification, in general. In**

practice, the errors on A could be compensated when calibrating the mass transfer coefficient. And one should remember that the "V" (reach volume) variable in INCA is also dependent of relatively poorly defined parameters: a simple comparative sensitivity analysis would have been welcome!

A sensitivity analysis was conducted where the stream bottom area was varied by +/- 20% and +/- 40%. These results are presented in section 3.3 of the revised paper.

4. **The comparison of the two formulae against observed values is definitively not a convincing demonstration: the poor fit of the model in one particular point of the river network can be due to many other parts of the model structure or to the calibration of many other parameters (and there are quite a few in INCA!) for this particular application. At least, a good test should include two contrasted catchments and data from a consecutive reaches within each catchment. Indeed, a definitive demonstration should include some sort of measured data for the process modeled itself (isotope data, retention experiments).**

To provide a better demonstration of the impact of using the alternate equation the calibration for a single sub-catchment for 9-months was removed. It was replaced by a 1 year calibration and 1 year validation period that was carried out for a catchment with 4 sub-catchments. Discussion of the consecutive reaches was limited by available data, but we think that the use of a validation period and its discussion shows that the alternate equation does not address all of the issues with the simulation of NO_3-N concentrations in the INCA-N model. In both the calibration and validation the alternate equation simulates the lowest NO_3-N concentrations during the growing season better than the current equation used in the model, which was the problem that we were hoping to address with this study.

5. **The figure is not very explicit, should separate concentration and discharge and include observed and simulated discharge. To conclude, this technical note raises interesting issues about in-stream process modeling. I encourage the authors to focus their paper on the significance of the equations rather than on the goodness of fit.**

Separate figures were used for concentration and discharge for both the calibration and validation periods in the revised manuscript.

Revised Manuscript

Technical note: Alternative in-stream denitrification equation for the INCA-N model

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Abstract

The Integrated Catchment model for Nitrogen (INCA-N) is a semi-distributed, process based model that has been used to model the impacts of land use, climate, and land management changes on hydrology and nitrogen loading. An observed problem with the INCA-N model is reproducing low nitrate-nitrogen concentrations during the summer growing season in some catchments. In this study, the current equation used to simulate the rate of in-stream denitrification was replaced with an alternate equation that uses a mass transfer coefficient and the stream bottom area. The results of simulating in-stream denitrification using the two different methods were compared for a one year simulation period of the Yläneenjoki catchment in Finland. The alternate equation (Nash-Sutcliffe efficiency = 0.63) simulated concentrations during the periods of the growing season with the lowest flow that were closer to the observed concentrations than the current equation (Nash-Sutcliffe efficiency = 0.63), but the results were mixed during other portions of the year. The results of the calibration and validation of the model using the two equations show that the alternate equation will simulate lower nitrate-nitrogen concentrations during the growing season when compared to the current equation, but promote investigation into other errors in the model that may be causing inaccuracies in the modeled concentrations.

1 Introduction

Catchment scale nutrient models can be used to predict the effect of changing land use and climate on nutrient export. The Integrated Catchment model for Nitrogen (INCA-N) is a catchment scale model that simulates both hydrology and mineral nitrogen processes (Wade et al., 2002; Whitehead et al., 1998). INCA-N has been applied to many European catchments, but one problem has been the overestimation of nitrate-nitrogen (NO_3-N) concentrations during the summer growing season (Jarvie et al., 2002; Rankinen et al., 2006). It is assumed that the current equations used in INCA-N to model in-stream denitrification also take into account other retention mechanisms (O'Shea and Wade, 2009), but other results indicate that a retention process such as macrophyte uptake is not accurately represented by the current equations for in-stream denitrification (Jarvie et al., 2002; Rankinen et al., 2006; Rankinen et al., 2013). Other potential causes of the overestimation of concentrations is too much NO_3-N being added from other sources such as groundwater (Wade et al., 2006; Wade et al., 2008) or the simulated volume of water in the stream being too low. With some simplification it can be shown that the current equation used to simulate in-stream denitrification assumes that the mass of nitrogen removed via in-stream denitrification varies linearly with the mass of NO_3-N in the stream (Section 2.1). This approach does not take into account the impact of dilution on the concentration gradient which drives the delivery of NO_3-N to the stream sediments where denitrification is most likely to occur (Reddy et al., 1978).

Birgand et al. (2007) proposed the use of a mass transfer coefficient (ρ) to quantify the in-stream NO_3-N retention in their extensive review of in-stream denitrification in agricultural catchments. The mass transfer coefficient multiplied by the NO_3-N concentration corresponds to the mass of nitrogen that would be removed from the water above a certain area of stream bed during a defined period of time. Birgand et al. (2007) recommended that the mass transfer coefficient be used in streams with NO_3-N concentrations above 1 mg L^{-1} based on the premise that above this threshold, the concentration gradient would be in a downward direction in accordance with the mass transfer coefficient theoretical application. The goal of this work was to test the equations proposed by Birgand et al. (2007) to determine their effectiveness in improving the INCA-N simulation of in-stream NO_3-N concentrations as the first step in the process of determining/addressing the issue of errors in the simulation of low NO_3-N concentrations during the growing season in the INCA-N model.

2 Methods

2.1 Estimation of in-stream denitrification as implemented in the INCA-N model

The INCA-N model is a dynamic model that uses a mass balance approach to track the movement of mineral nitrogen in a catchment (Wade et al., 2002; Whitehead et al., 1998). Wade et al. (2002) described the equations for in-stream denitrification that have been used in the model since version 1.6. INCA-N model version 1.11.10 was used in this study.

Equation (1) shows how the mass of nitrogen removed through in-stream denitrification is calculated in the INCA-N model:

$$m_{INCA} = \frac{R_n C_{1,t-1} V}{1000} \quad (1)$$

where m_{INCA} is the total mass of nitrogen removed through in-stream denitrification in a single reach (kg N day^{-1}), R_{n} is the temperature adjusted in-stream denitrification rate (day^{-1}), $C_{1,\mathrm{t-1}}$ is the in-stream NO_3-N concentration on the previous day (mg L^{-1}), and V is the volume of water stored in the reach (m^3).

The denitrification rate (R_{n}) is temperature dependent, so it varies daily. The relation between temperature and the denitrification rate in the INCA-N model are shown in Eq. (2).

$$R_n = 1.047 R^{(T-20)} \quad (2)$$

where R is the process rate before temperature adjustment (day^{-1}) and T is the in-stream water temperature (°C).

In the model, the water temperature is assumed to be the same as the air temperature, but a minimum water temperature is defined as a model input. In this simulation, the water temperature was not allowed to drop below 0 °C.

The NO_3-N concentration (C_1) in the INCA-N model is calculated using Eq. (3):

$$C_1 = \frac{1000 m_r}{V} \quad (3)$$

where m_{r} is the mass of NO_3-N in the stream reach (kg). If V is assumed to be equal to $V_{\mathrm{t-1}}$, then Eq. (1) becomes:

$$m_{INCA} = R_n m_{r,t-1} \quad (4)$$

Although V is not always equal to V_{t-1}, this simplifying assumption is reasonable except immediately following a large precipitation event. Based on Eq. (4), the simulated mass of NO_3-N removed via in-stream denitrification in the INCA-N model varies linearly with the mass of NO_3-N in the stream assuming a constant water temperature.

2.2 In-stream mass balance of NO_3-N as implemented in the INCA-N model

Equation (5) describes the in-stream mass balance calculations for NO_3-N used in INCA-N:

$$\frac{dm_r}{dt} = m_{in} - \frac{Qm_{r,t-1} \times 86400}{V} - m_{INCA} + \frac{R_i C_{2,t-1} V}{1000} \quad (5)$$

where m_{in} is the NO_3-N input mass from upstream and non-point sources in the watershed (kg N day^{-1}), Q is the reach discharge (m^3 s^{-1}), R_i is the temperature adjusted in-stream nitrification rate (day^{-1}), and $C_{2,t-1}$ is the in-stream NH_4-N concentration on the previous day (mg L^{-1}).

2.3 Estimation of in-stream denitrification using the mass transfer coefficient

Equation (6) was used to calculate the mass of nitrogen removed by denitrification using the mass transfer coefficient and the stream bottom area. Equation (6) was adapted from Birgand et al. (2007). The m_{INCA} in Eq. (5) was replaced with the m_{alt} value to model the in-stream NO_3-N mass balance:

$$m_{alt} = \frac{\rho_n A C_{1,t-1}}{1000} \quad (6)$$

where m_{alt} is the total mass of nitrogen removed via in-stream denitrification in a single reach calculated based on the mass transfer coefficient and the stream bottom area (kg N day^{-1}), ρ_n is the temperature adjusted mass transfer coefficient for NO_3-N removal through denitrification (m day^{-1}), and A is the stream bottom area of the reach (m^2).

The mass transfer coefficient is temperature dependent and is adjusted to temperature variations using an equation similar to Eq. (2). The assumption that the water temperature never drops below 0 °C was maintained for the mass transfer coefficient.

The equation using the mass transfer coefficient is different from the equation currently used in the INCA-N model because the mass of nitrogen removed via denitrification changes based on the NO_3-N concentration instead of the mass of NO_3-N in the stream. The stream bottom area is held constant in the model, which is discussed in section 2.4. Basing the mass of NO_3-N removed via in-stream denitrification on the NO_3-N concentration instead of the mass of NO_3-N in the stream more accurately represents the downward gradient which partially drives the delivery of NO_3-N to the sediments on the stream bottom where the conditions are most likely to be favorable for denitrification.

2.4 Model Calibration

The alternate equation was tested on a simulation of the River Yläneenjoki upstream of the Vanhakartano monitoring station for 2004 (Lepistö et al., 2008). The Yläneenjoki catchment is located in southwestern Finland and drains to Lake Pyhäjärvi. The portion of the Yläneenjoki catchment that is modeled was divided into 4 sub-catchments based on previous model applications (Lepistö et al., 2008; Etheridge et al., 2014). The modeled area is 197 km^2 with 33% of the land being in agricultural production. The main reach of the River Yläneenjoki has a length of 29 km in the modeled area.

The hydrology portion of the model was calibrated first, followed by the nitrogen portion of the model using the methods described in Granlund et al. (2004) and Etheridge et al. (2014). The hydrology portion of the model was calibrated to continuous flow data at the Vanhakartano monitoring station by adjusting the flow velocity parameters and time constants for the soil and groundwater zones. The nitrogen portion of the model was calibrated such that the in-stream nutrient concentrations followed the dynamics of the observed concentrations and were of similar magnitude. This was done by adjusting the nutrient process rates in the model. Data available related to nitrogen process rates ranging from fertilizer application data to rates of denitrification measured experimentally were used to reduce uncertainty in model results. More details about the Yläneenjoki Catchment and the general process used to calibrate the model can be found in Etheridge et al. (2014).

The in-stream denitrification and nitrification are the final two processes that alter nitrogen in the INCA-N model, so it was possible to change the in-stream denitrification calculations without changing the results from any other portion of the model. The order of calculations in INCA-N allowed the alternate equation calculations to be completed using a spreadsheet

instead of altering the model code. Simulations with the alternate in-stream denitrification equation were done using Excel 2007 (Microsoft, Redmond, WA, USA). Equation (5) is the in-stream mass balance equation for NO_3-N in the model. The input mass of NO_3-N (m_{in}), the reach discharge (Q), the reach volume (V), and the mass of nitrogen that is nitrified in the reach are all outputs of the model. These model outputs were taken directly from the calibrated model and were not altered in this work. The primary change that was made was replacing m_{INCA} with m_{alt} in Eq. (5), which changes the concentration of NO_3-N in the stream.

To make the calculations using the alternate equation, the stream bottom area (A) of the modeled reach was estimated using ArcGIS (ESRI, Redlands, CA, USA). The main sources of data were a raster map (1 m resolution) of all of the water areas in Finland and a map showing the streamline of the modeled reach. A buffer was created around the modeled streamline using the analysis tools in ArcGIS. All of the water area from the raster map located within this buffer was considered the stream bottom area input to the model. The stream bottom areas that were used in this simulation were 20,000 m^2, 80,000 m^2, 200,000 m^2, and 160,000 m^2 for the sub-catchments moving from upstream to downstream. This method may overestimate the stream bottom area of the primary reach as it includes both the stream bottom and the banks in the projected area. This error was considered reasonable because the entire stream bottom in the catchment was not included, but denitrification and other retention processes occur in the tributaries that feed the main channel.

Assuming a constant stream bottom area throughout the modeling period was not an ideal representation of the physical system because the stream width (i.e. submerged width of the stream) will increase with increasing depth and flow. This simplifying assumption was made so that extensive collection of channel dimensions was not required and model complexity was not further increased. The wetted stream bottom area in natural streams is dynamic, but increasing the wetted area does not necessarily increase denitrification during periods of higher flow due to the reduction in residence time. As stream flow and depth increase, the amount of time that NO_3-N rich water would be exposed to sites suitable for denitrification decreases, so an increase in the actual wetted stream bottom area does not always indicate an increased removal of NO_3-N via denitrification. Having a constant stream bottom area in the model may compensate for the effect of water residence time on in-stream denitrification.

When using the alternate equation to calculate the mass of nitrogen removed from the system through in-stream denitrification, the mass transfer coefficient was the only model input that was changed in the calibration process. An initial ρ was chosen based on values found in published results of many previous studies (Birgand et al., 2007). The calibration results were evaluated based on visual comparison to the observed data, the R^2 value, and the Nash-Sutcliffe (NS) efficiency. An NS efficiency greater than zero indicates that the model output is better than using the mean of the observed data (Nash and Sutcliffe, 1970). The ρ was adjusted to produce simulated NO_3-N dynamics which most closely followed the dynamics of the observed concentrations along with acceptable goodness-of-fit values.

2.5 Model Validation

Following calibration of the model, the model was validated for the same catchment for 2001 to evaluate the performance of the alternate equation. All of the parameters that were set during the calibration period remained the same for the validation period. The only thing that was changed was the time series of input data (e.g. temperature, precipitation, etc.) that was used in the simulations. The validation results were evaluated based on visual inspection, the R^2 value, and the NS efficiency.

2.6 Sensitivity Analysis

An added input that is not easily defined is not generally thought of as a model improvement. One drawback of using the mass transfer coefficient alternate equation in the INCA-N model is that it requires an added input of stream bottom area. The method used in this work to estimate the stream bottom area is quick and practical for modeling, but has a high degree of uncertainty. The amount of uncertainty varies depending on the data available for the catchment to be modeled. To better understand the impact that uncertainty in the estimated stream bottom area may have on the results a simple sensitivity analysis was carried out. In this sensitivity analysis the stream bottom area used in the model for each sub-catchment was varied by 20% and 40%. The impact of varying stream bottom area on the simulated NO_3-N concentrations and the mass of nitrogen removed via denitrification were evaluated.

3 Results and Discussion

3.1 Model Calibration

The outputs from the INCA-N model were compared to the results obtained using the alternate in-stream denitrification equation for the calibration period in Fig. 1A. Based on a visual inspection of the results, the alternate equation simulated the lowest observed concentration in 2004 better than the existing equation. The remainder of the results varied with each equation modeling certain observed concentrations better than the other. The observed concentrations above 3 mg L^{-1} prior to May 2004 are simulated better by the alternate equation, but this may be caused by an incorrect simulation of flow dynamics just prior to this event (Fig. 1B). The simulated flow is closer to the observed flow for the event in February 2004 where the NO_3-N concentration simulated using the alternate equation is closer to the observed concentration than the simulation using the current equation. This may be an example of the simulated mass of nitrogen removed via in-stream denitrification being incorrectly inflated in the current model due to an increase in the mass of NO_3-N in the stream. At the peak concentration the simulated mass of NO_3-N in the stream was more than six times higher than prior to the event when using the current equation in the INCA-N model. The mass of NO_3-N increases by more than six times when the concentration increased only 2 times its pre-storm value because the volume of water in the stream also increased. The simulated mass of nitrogen removed via denitrification with the current equation is more than six times higher at the concentration peak when compared to the mass of nitrogen removed via denitrification at the pre-storm low concentration. The simulated mass of nitrogen removed via in-stream denitrification at the peak concentration increased only 3 times that of the value at the minimum concentration when using the alternate equation.

These results show that the alternate equation simulates lower NO_3-N concentrations than the existing equation during the portions of the growing season with little flow. The lower rate of in-stream denitrification simulated by the current model during these periods is caused by the rate of denitrification being based on the low simulated mass of NO_3-N in the stream. The low removal of nitrogen via in-stream denitrification using the current method of modeling the process and the low volume of water in the reach result in elevated concentrations (Eq. 3). It is possible that during this low flow period, the simulated volume of water in the reach was

too low. An increase in the simulated volume would result in a lower NO_3-N concentration due to dilution. Changes in the hydrologic portion of the model would also impact the results of the alternate equation, but a change in the calibrated mass transfer coefficient could potentially be used to compensate for the changes. It is possible that the lower simulated NO_3-N concentrations during the periods with lower flow rates are a result of a constant stream bottom area being used. During these periods the stream bottom area may be too high when compared to the actual stream and the simulated mass of nitrogen removed via in-stream denitrification may be too high.

Using the alternate equation had a negligible impact on the goodness-of-fit values of the modeled results when compared to the observed concentrations. The original INCA-N equation produced a R^2 value of 0.63 and a NS of 0.60 when comparing the observed NO_3-N concentrations to the simulated concentrations. The alternate equation using the mass transfer coefficient produced a R^2 value of 0.63 and a NS of 0.61. The lack of improved goodness-of-fit values is indicative of the observation that each equation produced more accurate simulations at different points during the year.

The calibrated rate of in-stream denitrification in the INCA-N model was 0.145 day^{-1}. This resulted in a total nitrogen removal due to in-stream denitrification of 65000 kg for the 12 month modeling period in the 4 sub-catchments. This was equivalent to 30% of the nitrogen that entered the stream being retained by in-stream processes. A mass transfer coefficient of 0.21 m day^{-1} was used in the alternate equation as it produced the best results through calibration. The nitrogen removal via in-stream denitrification was 44000 kg or 20% of the total nitrogen that entered the stream for the alternate equation. The mass of nitrogen removed through denitrification was lower using the alternate equation because it did not simulate as much nitrogen removal during periods of high flow. The lower in-stream retention simulated by the alternate equation was closer to values of between 5 and 15% that have been estimated in Finnish catchments (Lepistö et al., 2006; Martikainen et al., unpublished). The mass transfer coefficient of 0.21 m day^{-1} used in this model application was within the range of plausible values based on the review by Birgand et al. (2007) as most of the values in the review were below 0.3 m day^{-1}.

3.2 Model Validation

The models using the two different equations were validated for 2001 and the results are shown in Fig. 2. The validation shows that neither the current model nor the model with the alternate equation adequately simulated the observed NO_3-N concentrations prior to June 2001 or after August 2001. This indicates that either the mass of NO_3-N input to the stream is too high or the volume of water simulated in the stream is too low during these periods. During the summer low flow periods, the alternate equation is able to simulate the lowest NO_3-N concentrations better than the equation currently used in the INCA-N model. This could be a result of the uncertainty related to other simulated processes (e.g. leaching) being lower during this period of time and an improved simulation of in-stream denitrification being shown by the improved simulation of NO_3-N concentrations. The low input of flow to the stream through surface water and groundwater would result in lower NO_3-N inputs to the stream; therefore the process most likely to impact the in-stream NO_3-N concentrations during this time is in-stream denitrification. Since in-stream denitrification is likely the dominant process an improved simulation of NO_3-N concentrations could be attributed to an improved simulation of denitrification. Basing the simulated mass of nitrogen removed via denitrification on the mass of NO_3-N in the stream accounts for the dynamics of lower peak concentrations and higher minimum concentrations simulated by the current equation when compared to the alternate equation. The R^2 values are similar with values of 0.45 and 0.48 for the current equation and alternate equation respectively. The NS efficiency in both cases was below zero.

Although Birgand et al. (2007) recommended using the mass transfer coefficient when the NO_3-N concentrations were greater than 1 mg L^{-1}, it appears that the alternate equation, using the mass transfer coefficient, simulates in-stream denitrification during low flow and low NO_3-N concentration conditions better than the current equations used in the INCA-N model. It was possible that a downward flux of NO_3-N continued to occur at concentrations below 0.5 mg L^{-1} and the alternate equation was still valid in this catchment.

3.3 Sensitivity Analysis

The impact of varying the stream bottom area by 20% on the NO_3-N concentrations during the calibration period is shown in Fig. 3A. The average of the NO_3-N concentration increased 0.2 mg L^{-1} when the stream bottom area was decreased by 20% and decreased 0.1 mg L^{-1}

when the stream bottom area was increased by 20%. The maximum difference in NO_3-N concentration based solely on changing the stream bottom area was a decrease in concentration of 0.4 mg L^{-1} when the NO_3-N concentration is decreasing following the spike in July 2004. The simulated mass of nitrogen removed via in-stream denitrification was 44000 kg, 49000 kg, and 39000 kg for the calibrated alternate equation model, the model with the stream bottom area increased by 20%, and the model with stream bottom area decreased by 20% respectively. These results indicate that a 20% change in the stream bottom area does not result in a 20% change in the simulated in-stream denitrification and that a decrease in the stream bottom area as would be expected during the low flow periods still does not raise the NO_3-N concentrations simulated by the alternate equation to the level of those simulated using the current equation in the model. Figure 3B shows that a change in stream bottom area of 40% does not account for the difference between the current equation used in the INCA-N model and the alternate equation, which indicates the influence of basing the mass of nitrogen removed via in-stream denitrification on the mass of NO_3-N in the stream versus the NO_3-N concentration. Uncertainty in the stream bottom area measurement can cause changes in the model results, but errors caused by inaccurate measurement of the stream bottom area are smaller than the errors in other portions of the model.

Using the alternate equation in INCA-N may improve the simulation of NO_3-N concentrations during the low flow portions of the growing season, but may not be addressing the root cause of the overestimation of NO_3-N concentrations. Improvements in the simulation of the volume of water in the stream during the summer could produce similar results. The validation period also shows that the mass of NO_3-N going into the stream is overestimated and needs improvement.

4 Conclusions

Using a short period of time to test the proposed in-stream denitrification equation is not as accurate as doing a multiple year calibration in the model, but this work shows that the use of alternate equation results in lower simulated NO_3-N concentrations during the growing season when compared to the alternate equation. During the calibration period the alternate equation shows promise for being able to better simulate peak concentrations. The influence of other factors such as the incorrect simulation of the volume of water in the reach or the mass of NO_3-N input to the stream also play a major role in the inaccuracy of the simulated NO_3-N

concentrations. Further investigation is required into the simulation of the other factors controlling in-stream NO_3-N concentrations, but this work provides evidence that the mass transfer coefficient equation should be considered as an alternate method of modeling the in-stream denitrification in the INCA-N model if the problem of simulating low NO_3-N concentrations during the growing season persists after other factors are investigated.

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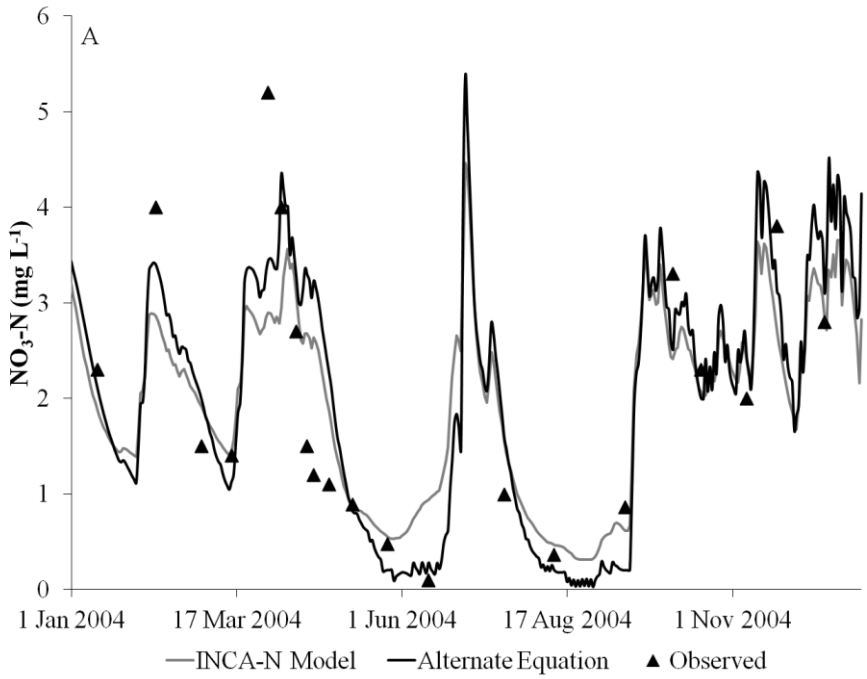

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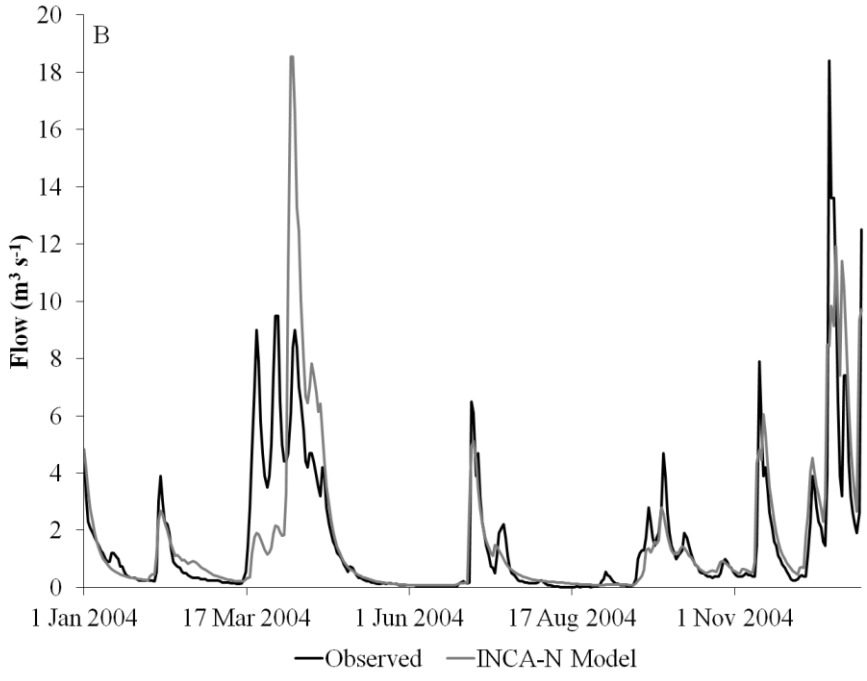

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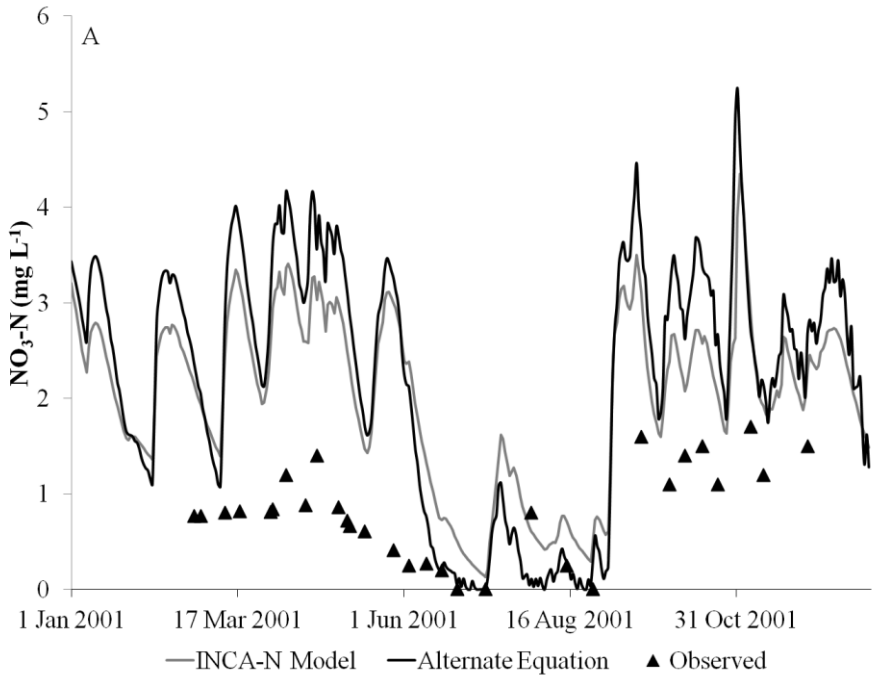
4 Figure 1. A. Graph comparing the INCA-N model results to the results with the alternate
5 equation for the calibration period in 2004. B. Graph of the simulated and observed flows for
6 the calibration period in 2004.



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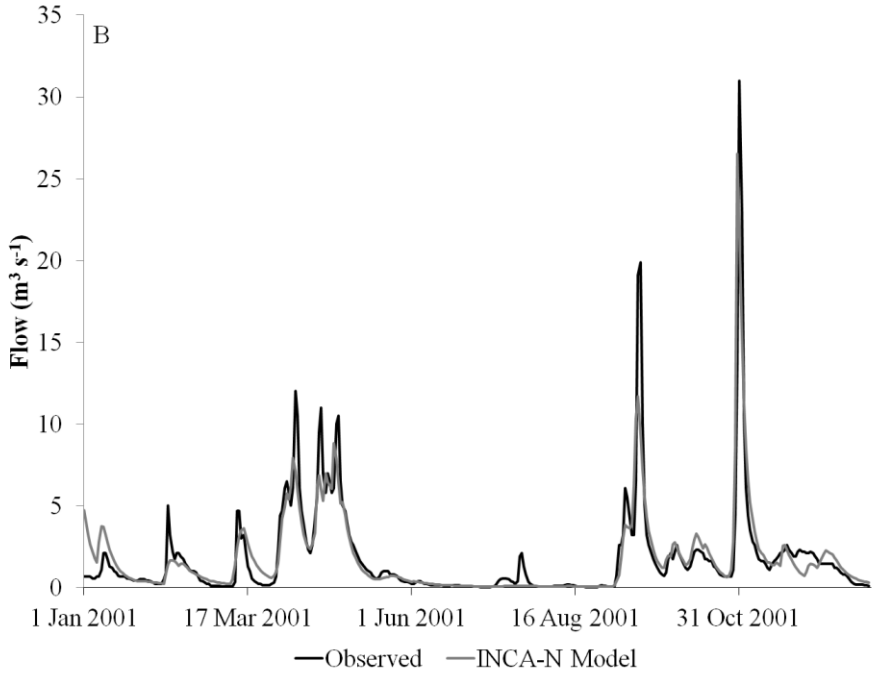

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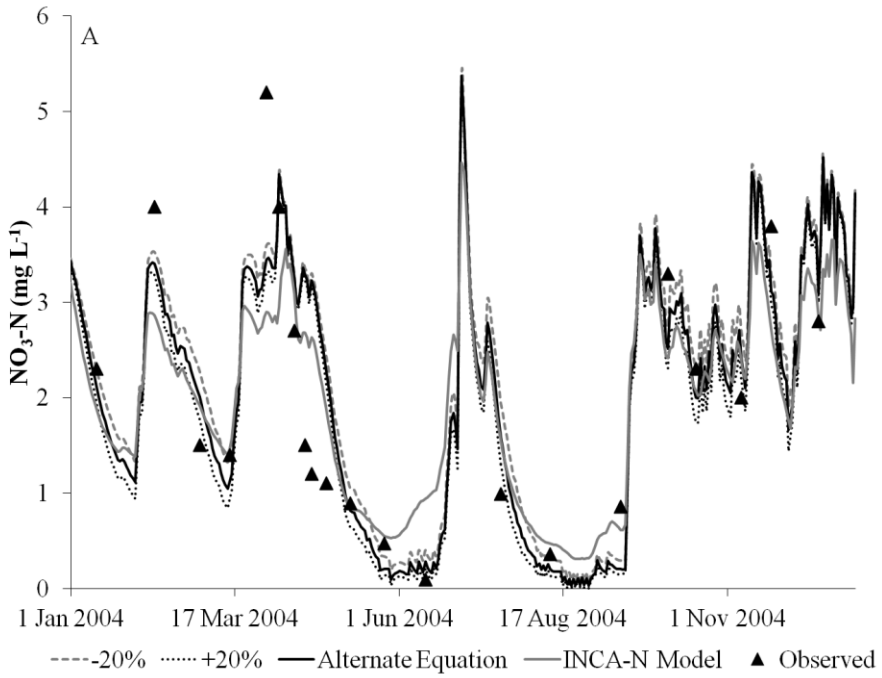
4 Figure 2. A. Graph comparing the INCA-N model results to the results with the alternate
5 equation for the validation period in 2001. B. Graph of the simulated and observed flows for
6 the validation period in 2001.



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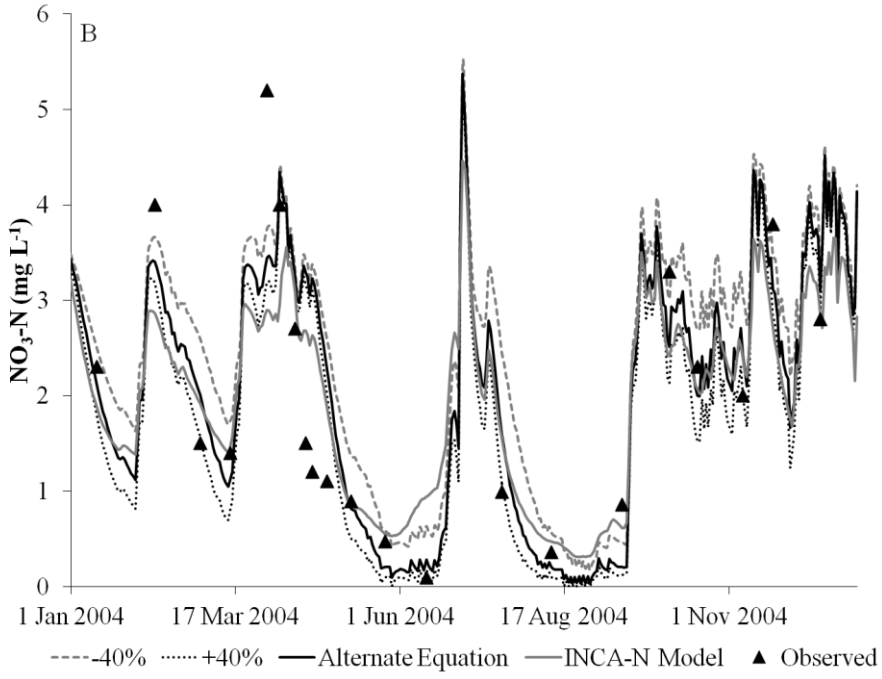

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4 Figure 3. A. Graph comparing the INCA-N model results to the results with the alternate
5 equation and the alternate equation with the stream bottom area varying +/- 20% for the
6 calibration period. B. Graph comparing the INCA-N model results to the results with the
7 alternate equation and the alternate equation with the stream bottom area varying +/- 40% for
8 the calibration period.