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Temperature Coefficient for Modeling Denitrification in Surface Water Sediments Using the Mass Transfer Coefficient

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Abstract

Watershed modeling has become an important tool for researchers with the high costs of water quality monitoring. When modeling nitrate transport within drainage networks, denitrification within the sediments needs to be accounted for. Birgand et al. developed an equation using a term called a mass transfer coefficient to mathematically describe sediment denitrification. This equation takes into account the effect that water column nitrate concentration and flow depth have on sediment denitrification. Water column temperature also has a marked effect on the rate of denitrification in sediment. A relationship of temperature to denitrification rate was developed using information presented by Dawson and Murphy. This relationship was inserted into the mathematical relationship developed by Birgand et al. to improve its' ability to prediction nitrate removal due to denitrification within drainage networks. The modified equation was tested by comparing measured nitrate concentrations over time from denitrification tanks with varying temperatures with predicted concentrations. Results show that the modified equation increased the accuracy of predicting nitrate removal through denitrification from sediment in drainage networks.

KEYWORDS. mass transfer coefficient, temperature, denitrification, modeling, watershed.

Introduction

Modeling has become an important tool for researchers with the scope and costs of water quality research at the watershed level. When modeling nitrogen transport within drainage networks, denitrification within the sediments needs to be accounted for as total nitrogen removal through denitrification can range from 1% to 66% (Birgand, 2000).

Under controlled conditions (constant temperature, denitrifier population, water column depth, amount of labile carbon present, and pH), water column nitrate removal through denitrification results in the typical exponential decay curve shown in Equation 1.

$$[C_1]= [C_0]*e^{(-k*t)} \quad (1)$$

Here $[C_0]$ is the concentration at the beginning of the time step, $[C_1]$ is the concentration at the end of the time step, t is the time step, and k is the decay coefficient. This relationship allows for the prediction of water column concentration over time rather than using a removal rate at a single concentration. Taking the natural log of both sides of Equation 1, it becomes a straight line relationship (Equation 2).

$$\ln[C_1]=-k*t + \ln[C_0] \quad (2)$$

Now k, the decay coefficient, is the slope of the straight line relationship relating time and concentration with $\ln[C_0]$ being the Y intercept.

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Denitrification rates have, and in some instances still are, being reported as an overall average in units of mass/unit area/time (e.g. $mg/m^2/day$) for a specific water column nitrate concentration. This gives a misrepresentation of denitrification as it varies with water column nitrate concentration, denitrifier population, temperature, water column depth, amount of labile carbon present, and pH.

Kelly et al. (1987) proposed a term called a mass transfer coefficient (ρ) to predict nitrate removal rates based on differing water column nitrate concentrations and to make comparisons of stream sediment denitrification rates possible. The mass transfer coefficient represents the straight-line relationship of the nitrate removal rate to the water column nitrate concentration Equation 3.

$$\rho = RR/[C] \quad (3)$$

Here ρ is the mass transfer coefficient (m/day), RR is the measured nitrate removal rate ($mg/m^2/day$), and [C] is the measured water column nitrate concentration (mg/m^3). The result is a useful term that is an averaged constant over the entire range of water column nitrate concentrations, allowing for easy comparisons of denitrification between different studies as well as predicting a nitrate removal rate for differing nitrate concentrations. This equation does not have a time step component for model application nor does it take into account the effects of denitrifier population, temperature, water column depth, amount of labile carbon present, and pH on the denitrification and thus results in only a rough approximation that is still fairly study specific.

Birgand (2000) derived an equation using Kelly's mass transfer coefficient concept (expanded from a removal rate to a mass removal) with a mass balance approach to nitrate removal rate, which contains a depth term (Equation 4).

$$[C_1] = [C_o]*e^{(-\rho*t/D)} \quad (4)$$

Here $[C_0]$ is the concentration at the beginning of the time step (mg/m^3), $[C_1]$ is the concentration at the end of the time step (mg/m^3), t is the time step (days), D is the depth of the water column (m), and ρ is the mass transfer coefficient (m/day). Birgand's equation is a version of the typical exponential decay equation (Equation 1) where k, the decay coefficient, is equal to the mass transfer coefficient divided by the depth term (ρ/D). By taking the natural log of both sides of the equation and rearranging, the equation can be solved for the mass transfer coefficient (ρ) (Equation 5).

$$\rho = Ln([C_1]/[C_0])/(-t/D) \quad (5)$$

Birgand's equation not only improved the accuracy of the mass transfer coefficient, it improved the ability to predict changes in water column concentration over a time step as needed for modeling. But this equation still did not address the effects of denitrifier population, temperature, amount of labile carbon present, and pH on a denitrification rate. Of these factors, temperature is the most variable over short periods of time and has the most effect on denitrification.

The objective of this study was to 1) improve the accuracy and applicability of Birgand's equation by incorporating a temperature term into it and 2) test the new equation using field data.

Temperature Coefficient Development

Denitrification in the sediments of drainage networks and natural streams, rivers, and lakes increases as the temperature increases. Dawson and Murphy (1972) conducted a study on the effect of temperature on the denitrification rate of a fixed population of denitrifying microbes. The results of that study showed an increase in denitrification as temperature increased that can be fitted with an empirical exponential curve (Figure 1) (Equation 6).

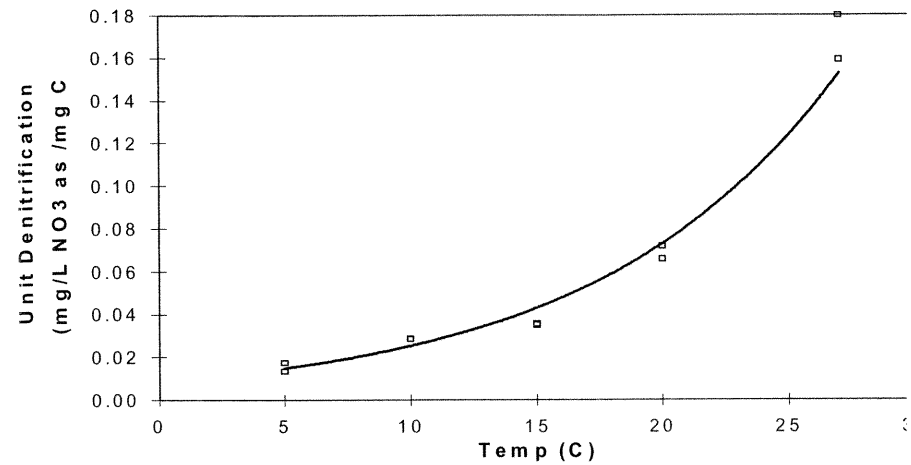

Figure 1. Relationship of temperature to denitrification rates using fixed denitrifying organism populations (from data from Dawson and Murphy, 1972).

$$D_{r,T} = 0.0087EXP(0.1059*T) \quad (6)$$

Here, $D_{r,T}$ is the denitrification rate (mg/L/h) at temperature T (°C). An assumption can be made that the relationship of two nitrate removal rates determined using the exponential model based on the fixed population of Dawson and Murphy (1972) is approximately equal to the relationship of the two nitrate removal rates of another population at the same two temperatures. With this assumption, Equation 7 can be written.

$$D_{r2,T2,Model} / D_{r1,T1,Model} = D_{r2,T2,P2} / D_{r1,T1,P2} = C_{T1-T2} \quad (7)$$

where: $D_{r1,T1,Model}$ = denitrification rate at temperature T1 of the modeled population (mg/L/h/mg cells), $D_{r2,T2,Model}$ = denitrification rate at temperature T2 of the modeled population (mg/L/h/mg cells), $D_{r1,T1,P2}$ = denitrification rate at temperature T1 of the population of interest (mg/L/h), $D_{r2,T2,P2}$ = denitrification rate at temperature T2 of the population of interest (mg/L/h), and C_{T1-T2} = correction factor for the change in the denitrification rate between the two temperatures (unitless).

It can also be assumed that the temperature correction factor (C_{T1-T2}) will be the same for denitrification rates based on units of mass/area/time (e.g. $mg/m^2/day$) as the conversion from units of mass/volume/time used in Dawson and Murphy (1972) to mass/area/time is a constant in this case. The denitrification rates (D_r) in units of mass/area/time can now be corrected for different temperatures by using Equation 8.

$$D_{rT2} = D_{rT1} * C_{T1-T2} \quad (8)$$

where: D_{rT1} = denitrification rate at temperature T1 ($mg/m^2/day$), D_{rT2} = denitrification rate at temperature T2 ($mg/m^2/day$), and C_{T1-T2} = correction factor for the differences in temperature (unitless).

The temperature correction factor can be inserted into Equation 4 in the following manner. Solving for D_{rT1} in Equation 8 results in:

$$D_{rT1} = D_{rT2} / C_{T1-T2}$$

which can be equated to Equation 3 also solved for D_{rT1} resulting in Equation 9.

$$D_{rT2} / C_{T1-T2} = \rho_{T1} * [C] \quad (9)$$

where: D_{rT2} = denitrification rate at temperature T2 (mg/m^2/day), $C_{T1\text{-}T2}$ = correction factor for the change in the denitrification rate between the two temperatures (unitless), ρ_{T1} = mass transfer coefficient for denitrification at temperature T1 (m/day), and [C] = nitrate concentration (mg/m^3). Rearranging Equation 9 results in Equation 10.

$$D_{rT2} = \rho_{T1} * [C] * C_{T1\text{-}T2} \quad (10)$$

The next step is to convert the denitrification rate (D_{rT2} in mg/ m^2/day) to a mass denitrified (R_{T2} in mg) by multiplying both sides by a sediment surface area (A - m^2) and a time interval (Δt - day).

$$A * \Delta t * D_{rT2} = \rho_{dT1} * [C] * C_{T1\text{-}T2} * A * \Delta t$$

This results in Equation 11 where R_{T2} is the mass of nitrate removed (mg) at temperature T2 during the time step Δt over the area A.

$$R_{T2} = \rho_{T1} * [C] * C_{T1\text{-}T2} * A * \Delta t \quad (11)$$

The mass of nitrate removed can also be determined using a mass balance of the nitrate at the beginning of the time step and the end of the time step (Δt) using the following equation,

$$R = ([C_o]-[C_1])*A*D,$$

where: R = mass of nitrate removed (mg), $[C_o]$ = initial nitrate concentration at the beginning of the time step Δt (mg/m^3), $[C_1]$ = final nitrate concentration at the end of the time step Δt (mg/m^3), A = sediment surface area (m^2), and D = depth of the water column (m). R is independent of temperature as temperature is not represented in the previous equation. In this case R at temperature T2 is of interest so R is determined for the temperature T2 (R_{T2} – the mass of nitrate removed at temperature T2 during the time step Δt over the area A. (mg)). This results in Equation 12:

$$R_{T2} = ([C_o]-[C_1]) * A * D. \quad (12)$$

Equation 11 can now be equated to Equation 12,

$$([C_o]-[C_1]) * A * D = \rho_{T1} * [C] * C_{T1\text{-}T2} * A * \Delta t$$

which can be reduced to:

$$([C_o]-[C_1]) * D = \rho_{T1} * [C] * C_{T1\text{-}T2} * \Delta t.$$

By rearranging the terms and multiplying through by -1 the equation is converted to

$$([C_1]-[C_0])/ \Delta t = (-\rho_{T1}*[C] * C_{T1\text{-}T2})/D.$$

Taking the limit as the time step approaches zero:

$$\text{Lim}(\Delta t \to 0)\ ([C_1]-[C_0])/ \Delta t = (-\rho_{T1}*[C] * C_{T1\text{-}T2})/D,$$

where:

$$\text{Lim}(\Delta t \to 0)\ ([C_1]-[C_0])/ \Delta t = dc/dt$$

the average change in concentration over the time interval resulting in differential equation:

$$d[C] / dt = (-\rho_{T1}*[C] * C_{T1\text{-}T2})/D.$$

Separating terms and integrating concentration and time over the intervals $[C_o]$ to $[C_1]$ and 0 to t:

$$\int_{C0}^{C1} dc/[C] = \int_0^t -\rho_{T1} * dt * C_{T1\text{-}T2}/D$$

resulting in:

$$\ln([C_1]) - \ln([C_o]) = (-\rho_{dT1}*t* C_{T1\text{-}T2})/D.$$

Rearranging the terms:

$$\ln\left([C_1]/[C_0]\right) = -\rho_{T1} * t * C_{T1\text{-}T2}/D$$

Raising both sides of the equation to the exponential (e^x) and rearranging, the equation to model denitrification in a system with a variable temperature is derived (Equation 13).

$$[C_1] = [C_o]*\text{EXP}(-\rho_{T1}*t* C_{T1\text{-}T2}/D) \quad (13)$$

By comparing Equation 4 and Equation 13, it can be deduced that the mass transfer coefficient (ρ) can easily be related to a change in temperature by Equation 14.

$$\rho_{T2} = C_{T1\text{-}T2} * \rho_{T1} \quad (14)$$

where: ρ_{T1} = mass transfer coefficient at original temperature T1 (m/day), ρ_{T2} = mass transfer coefficient at a second temperature T2 (m/day), and $C_{T1\text{-}T2}$ = correction factor for the change in temperature (unitless).

TESTING THE EQUATION

Methods

The field study was located in Washington County, near Plymouth, in the coastal plain of North Carolina (Figure 2). The 10,000 ha watershed drains into the Albemarle Sound through a five-mile stretch of Kendrick's Creek. The portion of the watershed used for this study consists of approximately 4,000 ha of managed forest. The soils of the study location are organic soils of the Belhaven series (Loamy, mixed, dysic, thermic Terric Medisaprists) (SCS, 1981).

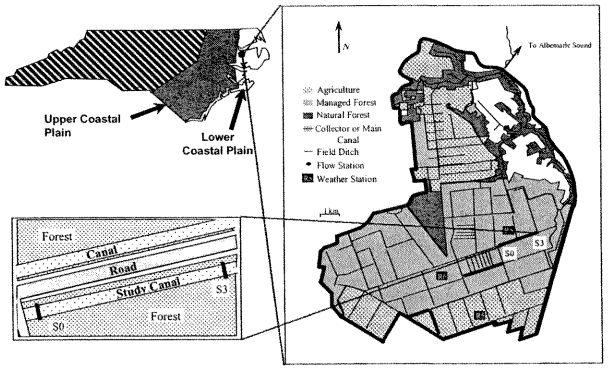

Figure 2. Location of Parker Tract watershed and canal study site.

A 1900 meter section of a forest drainage canal, from S0 to S3 (Figure 2), averaging four meters in top width, 1.4 meters in depth, average side slope of 1:1, and an overall bottom slope of 0.0003, was selected for the study. A litter layer (≈ 4 cm thick) and organic layer (≈ 20 cm thick) cover the bottom of the canal. Below ≈ 20 cm there is a thick sand layer underlain by an impermeable layer.

Water column nitrate depletion was measured in three in-stream tanks. The tanks were constructed of a section of PVC pipe 43 cm in diameter (Figure 3) and positioned in the center of the canal at three locations between S0 and S3 (Figure 2). A base for each tank was installed into the sediment during the dry season. An extension of the same diameter as the tanks was inserted into the sediment to a depth of 23 cm. An attached base plate at the top of the base rested on the sediment surface to keep the tanks from sinking into the sediment. A ring of the same diameter as the base protruded 7.5 cm above the sediment to serve as an attachment site for the tanks as they were placed in the canal, as well as to hold the tank in place and produce a seal between the tank and the base. A piece of neoprene rubber was attached to the base to ensure that water inside the tank would not mix with water outside the tank. The base allowed for the installation and removal of

the tanks without disturbing the sediments. The tanks were placed in the canal after each of two rainfall events to take advantage of the naturally occurring nitrate peak following each rainfall event. After the tanks were set in the canal, grab samples were taken periodically after tank placement (See Figure 4 for sampling dates). Samples were taken within the tank at mid-depth of the water column. Each sample consisted of 25 ml of water from the water column. All three tanks were sampled at the same time. Water samples were placed on ice immediately after collection and kept refrigerated until analysis. All samples were filtered through a 0.45 micron filter (Gelman Laboratory, Supor®-450) to remove particulate material. Each sample was analyzed for nitrate, ammonium, phosphate, dissolved organic, inorganic, and total carbon (Standard Methods, 1989).

Temperatures within the in-stream tanks varied with the ambient air temperature. Tanks were not continuously circulated due to the absence of a power source at the site. A companion study though showed that at this location there was no significant difference between the nitrate removal in circulated and non-circulated tanks (Appelboom, 2000). Dissolved oxygen, pH, and temperature were measured at mid-depth in the water column within the tank and in the open canal at each sampling.

The mass transfer coefficients were determined for this site using the companion study previously mentioned (Appelboom, 2000). Site specific mass transfer coefficients were used for each of the three locations where the in-stream tanks were placed. An overall average mass transfer coefficient was also used to determine how well the two equations perform using an average value.

Field collected water column nitrate concentrations were compared to predicted water column nitrate concentrations using both Equation 4 and Equation 13. All predicted concentrations were based on initial concentrations. Comparisons were conducted using regression analysis.

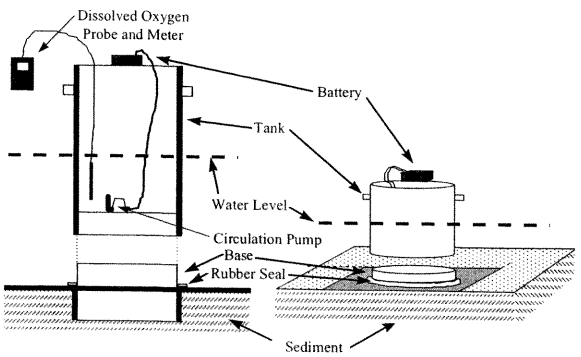

Figure 3. In-stream denitrification tank.

Results and Discussion

Temperatures within the in-stream tanks ranged from 6°C to 14°C during the first run and from 13°C to 20°C during the second run. The mass transfer coefficients (ρ_{T1}) used in Equations 4 and 13 were determined at 8°C.

During this study, Equation 4, without a temperature coefficient, overpredicted the nitrate concentration in all instances with the exception of the predicted concentrations using the average mass transfer coefficient (ρ) for the first run at Location 1 (Figure 4). The coefficient of determination R^2 ranged from 0.60 to 0.89 for the site specific mass transfer coefficient (ρ) and from 0.0.47 to 0.98 for the average specific mass transfer coefficient (ρ) (Table 1). The overpredicted concentrations are due to the mass transfer coefficient (ρ) being determined at a lower temperature than occurred during the runs, which results in a lower nitrate removal rate predictions and smaller changes in the concentration. Had the mass transfer coefficient (ρ) been determined at a higher temperature than occurred during the runs, Equation 4's concentration predictions would have been lower than the measured data. The predicted concentrations of the first run at Location 1 using the average mass transfer coefficient (ρ) resulted in a very close fit of the predicted to the measured data (R^2=0.98) (Table 1).

Equation 13 resulted in very close fits to the measured data when the site specific mass transfer coefficients (ρ) were used (R^2s ranged from 0.96 to 0.99 – Table 1) (Figure 4). When the average mass transfer coefficient (ρ=0.016) was used, there was still a good agreement among the individual runs (R^2s ranged from 0.82 to 0.98 – Table 1) with the one exception, run 2 at Location 1, which yielded R^2=0.66 (Table 1).

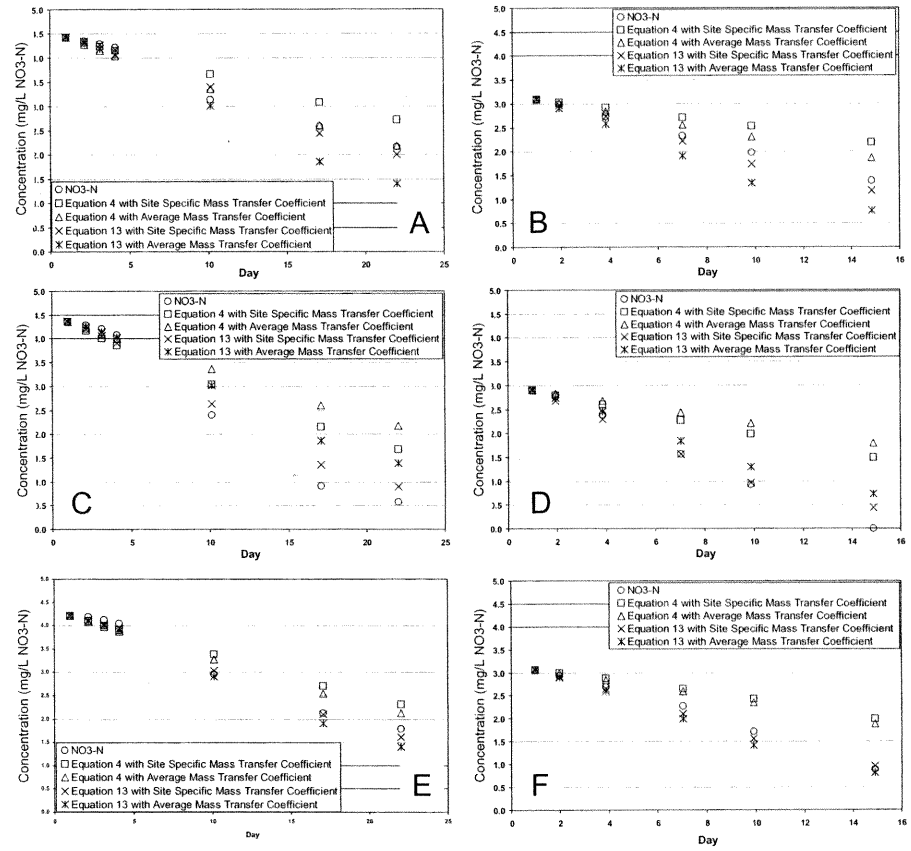

Figure 4. Measured and predicted (using Equation 4 and Equation 13 with both a site specific mass transfer coefficients and a study average mass transfer coefficient) water column nitrate concentrations in in-stream tanks over time: A, Location 1 - Run 1; B, Location 1 - Run 2; C, Location 2 – Run 1; D, Location 2 – Run 2; E, Location 3 – Run 1; F, Location 3 – Run 2. Site specific mass transfer coefficients (ρ) were: ρ=0.011 for Location 1, ρ=0.022 for Location 2, ρ=0.014 for Location3. The average mass transfer coefficient (ρ) was 0.016.

When the data points from all the runs were pooled into one regression analysis, Equation 13 showed a much higher correlation to the measured data than did Equation 4 using both the site specific and average mass transfer coefficients (ρ) (Figure 5). When the site specific mass transfer coefficient (ρ) was used, R^2 was 0.98 for Equation 13 as compared to 0.83 for Equation 4. When the average mass transfer coefficient (ρ=0.016) was used, the R^2 was 0.91 for Equation 13 as compared to only 0.78 for Equation 4.

The overall improved predictions resulting from the use of Equation 13 as compared to Equation 4 is attributed to the inclusion of the temperature term (C_{T1-T2}). This term allows the equation to change the nitrate removal rate as temperature changes between each time step resulting in a more accurate water column nitrate concentration prediction for the end of the time step. The improvement of the predictions using the site specific mass transfer coefficient (ρ) is due to the improved representation it gives the nitrate removal at each site as compared to the average mass transfer coefficient (ρ).

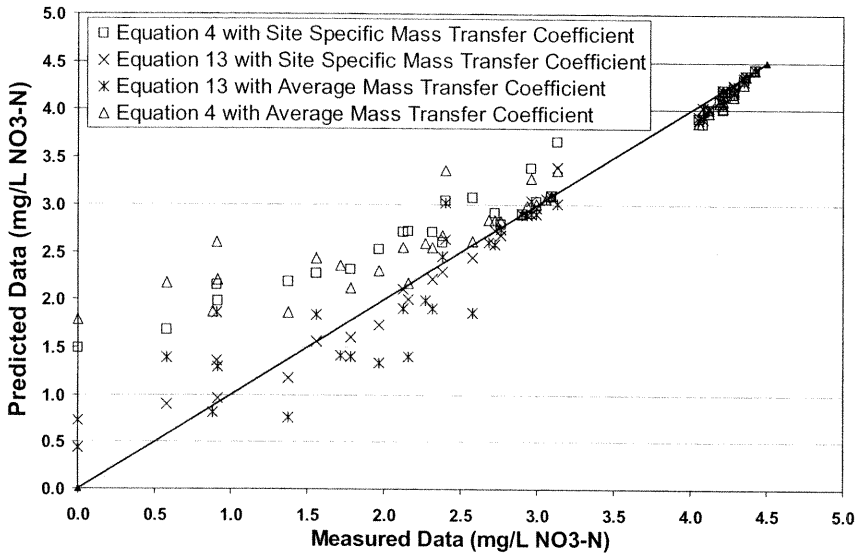

Figure 5. All data points from the two runs of the three in-stream tanks compared to their associated predicted nitrate concentrations using Equation 4 and Equation 13 with both a site specific mass transfer coefficients and a study average mass transfer coefficient.

Table 1. Regression analysis R2 values for the comparison of measured nitrate concentrations versus predicted nitrate concentrations over time using Equation 4 and Equation 13.

	Predicted Nitrate Concentrations Without Temperature Component (Equation 4)	Predicted Nitrate Concentrations With Temperature Component (Equation 13)
	R^2	R^2
Location 1, Run 1, Temp. 6°C to 14°C		
Location ρ[1] =0.011	0.88	0.98
Average ρ[2] =0.016	0.98	0.82
Location 2, Run 1, Temp. 6°C to 14°C		
Location ρ[1] =0.022	0.82	0.97
Average ρ[2] =0.016	0.68	0.89
Location 3, Run 1, Temp. 6°C to 14°C		
Location ρ[1] =0.014	0.89	0.99
Average ρ[2] =0.016	0.93	0.98
Location 1, Run 2, Temp. 13°C to 20°C		
Location ρ[1] =0.011	0.71	0.96
Average ρ[2] =0.016	0.88	0.66
Location 2, Run 2, Temp. 13°C to 20°C		
Location ρ[1] =0.022	0.60	0.97
Average ρ[2] =0.016	0.47	0.90
Location 3, Run 2, Temp. 13°C to 20°C		
Location ρ[1] =0.014	0.66	0.99
Average ρ[2] =0.016	0.71	0.97
All Locations, All Runs, Temp. 6°C to 20°C		
Location ρ[1]	0.83	0.98
Average ρ[2] =0.016	0.78	0.91

[1] Location ρ is the site specific mass transfer coefficient for the location the tank was placed.

[2] Average ρ is the average mass transfer coefficient for all the tank locations.

Conclusion

The introduction of a temperature term into the equation for predicting water column nitrate concentrations over time in surface waters, where denitrification is occurring in the sediments, improved the accuracy of the predicted concentrations when compared to the measured data. The use of the temperature coefficient improved the pooled coefficient of determination R^2 from 0.83 to 0.98 when the site specific mass transfer coefficient was used, and from 0.78 to 0.91 when the average mass transfer coefficient was used.

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