Estimating Nutrient Uptake in Streams with Pulse Release

by

Chao Song

(Under the direction of Daniel B. Hall)

Abstract

Anthropogenic activities greatly accelerate the nutrient input into ecosystems. Rivers and streams not only transport nutrients between terrestrial and oceanic ecosystems but also transform nutrients and control the nutrients export from watersheds. Thus, a robust technique of estimating nutrient uptake rate in streams is necessary. Using pulse release of solutes to estimate nutrient uptake rates is an logistically easy experimental approach but a proper statistical method for analyzing such data is lacking. In this study, we analyzed the theoretical and practical issues of the current methods and propose a new method of estimating nutrient uptake rate from pulse release data based on the solute dynamics described by the advection–dispersion equation. The new method allowed us to estimate the dynamics of nutrient uptake with explicit assumptions. We implemented the estimation routine in R (`https://github.com/songchao1986/Nutrient-uptake`) for easy application.

Index words: Nutrient uptake, Nutrient spiraling, Partial differential equation, Nonlinear model

Estimating Nutrient Uptake in Streams with Pulse Release

by

Chao Song

B.A., Peking University, China, 2009

B.S., Peking University, China, 2009

M.A., University of Kansas, 2011

A Thesis Submitted to the Graduate Faculty

of The University of Georgia in Partial Fulfillment

of the

Requirements for the Degree

Master of Science

Athens, Georgia

2016

Estimating Nutrient Uptake in Streams with Pulse Release

by

Chao Song

Approved:

Major Professor: Daniel B. Hall

Committee: Nicole A. Lazar
Jaxk H. Reeves

Electronic Version Approved:

Suzanne Barbour
Dean of the Graduate School
The University of Georgia
December 2016

Acknowledgments

I would like to express my deepest appreciation to my major professor Dan Hall, who has the attitude and the substance of a truly great advisor. He continually guided me to improve my statistical skills, and convincingly conveyed a spirit of excellent scholarship. This thesis would not be possible without his guidance. I would like to thank my committee members, Nicole Lazar and Jaxk Reeves, for their insightful advice in the thesis research. In addition, I would like to thank all the collaborators in this thesis project, Ford Ballantyne, Lauren Koenig, Walter Dodds, and John Vinson. This work would not be possible without their excellent collaboration.

Table of Contents

List of Figures

List of Tables

Chapter 1

Methods of Analyzing Nutrient Uptakes Rate in Streams

Streams play a critical role in transporting and transforming nutrients globally. In streams, nutrients are continually taken up by the biological activities and temporarily retained in stream ecosystems as they are physically transported. Recent research suggested that nutrient uptake and transformation due to biological activities in streams has a profound control on the nutrient export out of the watershed and therefore influences the nutrient input to the receiving ecosystems (Peterson et al, 2001; Mulholland et al, 2008). As anthropogenic activities have greatly accelerated nutrient input into ecosystems, nutrient loading has exceeded the holding capacity of many ecosystems, resulting in deleterious impacts to the ecosystems (Vitousek et al, 1997). Therefore, understanding nutrient uptake in streams is not only of great scientific interests, but also relates to practical issues in ecosystem management. Hence, it is critical to investigate the characteristics of nutrient uptake in streams. A robust method of estimating nutrient uptake rate in streams is particularly important and will be our focus in this thesis.

Researchers have employed various methods to measure nutrient uptake rate in streams. The first approach is a constant injection approach. A concentrated solute solution containing conservative tracer and reactive tracer (nutrient) is injected into the stream at a constant flow rate until the concentration of both tracers reaches steady state. The relative decrease in concentration of the nutrient compared to the conservative tracer when moving downstream is then used to estimate the nutrient uptake rate (Webster and Ehrman, 1996). A second common approach is similar to the constant injection method but uses isotope labeled

nutrient tracers (Newbold et al, 1981; Peterson et al, 2001; Mulholland et al, 2008). A concentrated solution of isotope labelled nutrient tracer and conservative tracer is injected into the stream with a constant flow rate. After sufficient time for the stream to reach steady state in the isotope tracer concentration, isotopic signature in various forms of nutrients can be determined. The downstream decrease in isotopic signature is then used to estimate nutrient uptake rates. A third approach uses a pulse release of conservative and nutrient tracers to estimate nutrient uptake (Covino et al, 2010). Specifically, a small volume of concentrated solution with both conservative and nutrient tracers is released in the stream as a pulse. The concentration of each tracer is monitored at a downstream location. The concentration of each tracer over time, often referred to as the breakthrough curve, is then used to estimate the nutrient uptake rate.

Both constant injection method and the isotope method require a constant injection of concentrated solute solution in streams until concentration in stream reaches equilibrium. The equilibrium often requires long time to achieve. It is thus logistically inconvenient to apply these methods. Methods based on constant injection are also limited to application in small streams because a high injection flow rate and a large reservoir of concentrated solute solution are required in large streams and rivers, which are not always feasible in the field. In addition to being logistically challenging, the isotope approach requires measurements of isotope signature of water samples. The high cost of isotopically enriched material and sample analysis by mass spectrometry limit the use of this technique. In contrast to the logistical difficulty with methods based on constant injection, the pulse release method is logistically easy to perform in the field. Releasing a pulse of concentrated solutes and monitoring the breakthrough curves downstream are quick and easy. Thus the pulse release method has been increasingly accepted as the preferred method to measure nutrient uptake rate by stream ecologists.

Covino et al (2010) proposed a method to estimate nutrient uptake rate from pulse release data. The method they proposed consists of the following steps. Here we use chloride (Cl)

and nitrogen (N) as examples of conservative and nutrient tracers to illustrate the method proposed by Covino et al (2010):

1) Release a pulse of concentrated solution of Cl and N with known mass of each solute. At the downstream location with known distance to the release location, take samples of stream water and measure concentrations of both Cl and N in the sample.

2) Subtract the background N and Cl concentrations from the sample concentrations and obtain a background corrected N/Cl ratio for each sample. At time 0, the background corrected N/Cl ratio at the release location is the ratio of the release solution. At the time of sampling, we have a background corrected N/Cl ratio of the sample. For each sample, perform a linear regression of the log transformed background corrected N/Cl ratio on time using the two points for each sample. The slope of the regression is the per time uptake rate for that sample. Repeat this procedure and obtain a per time uptake rate for each sample.

3) Calculate the uptake rate (in the unit of concentration of nutrient per time) for each sample by multiplying the per time uptake (in the unit of per time) rate calculated in step 2 and the measured N concentration of each sample. The uptake rate and the nutrient concentration for each sample is then used as data and fit to an assumed function describing the concentration dependence of uptake rate. For example, the Michaelis–Menten function is a general function describing concentration dependence of chemical reaction rate

$$rate = \frac{V_{max}}{K_m + C} \ . \tag{1.1}$$

Here, V_{max} is the maximum uptake rate, K_m is the half saturation constant and C is the nutrient concentration. Alternatively, one can fit a first order uptake

$$rate = KC \ . \tag{1.2}$$

Here K is the per time first order uptake rate. The choice of the uptake function can be made based on the understanding of the system or based on visual examination of the calculated uptake rate–concentration relationship.

Although the approach proposed by Covino et al (2010) provides a convenient recipe to analyze nutrient uptake rate from pulse release data, the theoretical justification of this method has not been thoroughly investigated. It remains unclear what assumptions about solutes transport and uptake are implicitly made when performing such calculation. Thus, there is a pressing need to theoretically evaluate this method to verify its validity.

Chapter 2

Issues with the Current Method

2.1 Inconsistent assumptions on the form of nutrient uptake

The key step in estimating nutrient uptake rate as proposed by Covino et al (2010) is using the regression of log(N/Cl) over time to estimate an per time uptake rate for each sample. Although the reasoning of such calculation is not explicitly presented by Covino et al (2010), we attempt to derive their calculation procedure by analyzing the dynamics of solute transport and uptake in streams. Through such analysis, we shall see the assumptions made implicitly when using the method by Covino et al (2010). This allows us to evaluate the validity and the scope of application of their method.

The solute concentration change at any time and location is the result of advection (i.e. solutes movement with water flow), dispersion (i.e. solutes diffusion over concentration gradients) and biological production and uptake based on mass balance. Thus, solute dynamics in streams can be described by a one dimension advection–dispersion–decay model. Here, we use Cl and N as examples of conservative and nutrient tracers. If we assume that the nutrient production rate is constant and uptake rate follows a first order uptake function, the transport and uptake of Cl and N after a pulse release can be modeled as:

$$\frac{\partial C}{\partial t} = -U\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - KC + I \ . \tag{2.1}$$

Here C is the solute concentration, U is the velocity of water flow, D is the dispersion coefficient and K is the first order nutrient uptake rate per time, I is the nutrient production rate, t is time and x is distance. Both Cl and N have the same parameters except that the per time uptake rate K and production rate I for Cl are 0. In particular, because dispersion

in streams is dominantly turbulent dispersion, the dispersion coefficient is determined by flow conditions instead of characteristics of the solutes. Thus, dispersion coefficient for N and Cl should be equal. The initial condition that models a pulse release is that the tracers are injected uniformly across the cross-section over an infinitesimally small width along the flowing direction. To specify such an initial condition, we use the Dirac delta function

$$C(x,0) = \frac{M}{A}\delta_0(x) \ . \tag{2.2}$$

Here, M is the total mass of injected tracer, A is the cross section area and $\delta_0(x)$ is the Dirac delta function. We assume that there is a stable background concentration of tracers (C_0) before pulse release by specifying the boundary condition as

$$C(\pm\infty, t) = C_0 \ . \tag{2.3}$$

We further assume that the background tracer concentration before pulse release is stable, meaning that the production and uptake balance each other at the background concentration. Thus,

$$I = KC_0 \ . \tag{2.4}$$

We can analytically solve the model specified above and obtain the concentrations of both Cl and N over time t at the sampling distance x (O'Loughlin and Bowmer, 1975; Genuchten et al, 2013):

$$C_{Cl}(x,t) - C_{Cl,0} = \frac{M_{Cl}}{A\sqrt{4\pi Dt}} \exp\left[-\frac{(x-Ut)^2}{4Dt} \right] , \tag{2.5}$$

$$C_N(x,t) - C_{N,0} = \frac{M_N}{A\sqrt{4\pi Dt}} \exp(-Kt) \exp\left[-\frac{(x-Ut)^2}{4Dt} \right] . \tag{2.6}$$

If we take the log ratio of equation 2.6 and 2.5, we obtain the log ratio of background corrected tracer concentration as

$$\log\left[\frac{C_N(x,t) - C_{N,0}}{C_{Cl}(x,t) - C_{Cl,0}}\right] = \log\left[\frac{M_N}{M_{Cl}}\right] - Kt \ . \tag{2.7}$$

Equation 2.7 justifies why the regression of background corrected log(N/Cl) on time (step 2 of the Covino et al (2010) method) gives an estimate of uptake rate K. Equation 2.7 is

the result of equation 2.1–2.4. To arrive at equation 2.7, it is necessary to assume a first order uptake (equation 2.1), i.e. uptake rate is proportional to the nutrient concentration. Therefore, when using equation 2.7 to estimate uptake rate as proposed by Covino et al (2010), one implicitly assumes that uptake is first order. This is in direct contradiction to the third step proposed by Covino et al (2010), where they proposed to use a Michaelis–Menten function to describe the uptake–concentration relationship. It is inherently inconsistent to assume one form of uptake in one step and another form of uptake in another step. The inconsistent use of assumption invalidate the method proposed by Covino et al (2010).

The analysis of solute dynamics above also shows that the approach by Covino et al (2010) is solely based on solute dynamics in the stream main channel. However, it is well known that the porous benthic sediments, often referred to as transient storage zone, interact with solutes in the stream channel, temporarily store the solutes and delay the downstream transport of solutes. Consequently, the presence of transient storage zone could significantly alter how solute concentration in water changes over time and space (Runkel, 2002). It is therefore important to include transient storage in modeling nutrient uptake in streams. Given the common presence of transient storage zone in streams, a model focusing solely on solute dynamics in stream channel is likely very limited in its scope of application.

2.2 Vulnerability to inaccurate background concentration measurements

A second deficiency of the Covino et al (2010) method arises from the fact that background concentration of solutes is needed to estimate nutrient uptake rate. Specifically, to calculate the uptake rate for each sample, one needs to subtract the background concentration of solutes from the measured concentration of solutes in each sample. Thus, an accurate measurement of background solute concentration is necessary. However, chemical analysis of solutes concentration has limitations. For example, in streams with low background concentration of N, there is often substantial inaccuracy in measuring the background concen-

tration due to a detection limit of the chemical assay. Inaccurate background concentration may cause error in the estimate of nutrient uptake rate.

To demonstrate potential influences of inaccurate background concentration measurements, we first simulated breakthrough curves of Cl and N assuming first order uptake following equation 2.5 and 2.6, and then calculated the uptake rate following the steps proposed by Covino et al (2010) using a slightly inaccurate background concentration. In the simulation, we assumed that we released 4g N (M_N) and 1000g Cl (M_{Cl}) and monitored solute concentration every 2 seconds at 10m downstream from the release point. The flow velocity (U) is 1m/s and dispersion coefficient (D) is 0.1m^2/s. The cross section area of the stream (A) is 1m^2. We set the uptake rate (K) at 0.05/min. We set the background concentration of N at 5 μg/L. We followed the steps in the method proposed by Covino et al (2010) but used a background N concentration of 4.9 μg/L in the calculation (step 2). It is worth mentioning that a deviation of 0.1 μg/L is a fairly conservative magnitude of inaccuracy given the precision of measuring N concentration in water samples. For example, Sororzano (1969) first proposed the widely used phenolhypochlorite method for ammonia determination and reported a coefficient of variation of 0.023. Given that we simulated the solute concentration using equation 2.5–2.6, we assumed that the uptake rate is proportional to the concentration and thus expected a linear relationship between uptake rate and concentration. However, the calculated uptake–concentration relationship using a slightly inaccurate background N concentration showed a nonlinear relationship (Fig. 2.1). This contradicts the assumption of first order uptake, which was used to simulate the data. The parameter values we chose in this simulation are comparable to realistic range of values commonly found in nutrient uptake experiments. Thus, the simulation suggests that the estimated nutrient uptake rate based on the method proposed by Covino et al (2010) is sensitive to slight inaccuracy in background concentration measurements, limiting its application to real field data.

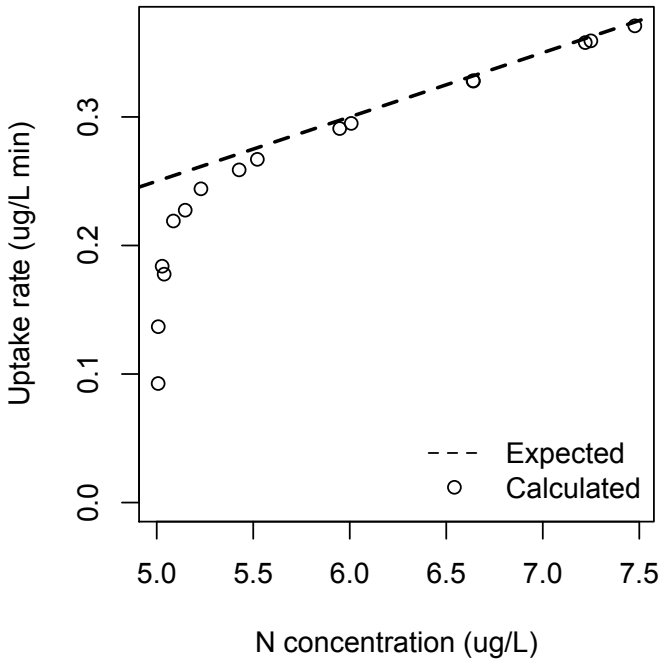

Figure 2.1: Inaccuracy in background concentration results in unexpected nonlinear dependence of uptake rate on concentration

2.3 Inappropriate error propagation

A third deficiency with the method proposed by Covino et al (2010) is improper error propagation. Because measurement error of solute concentration always occurs, the estimated per time uptake rate from regression of log(N/Cl) over time (step 2) contains uncertainty. However, the regression of calculated uptake rate on nutrient concentration (step 3) does not properly incorporate the uncertainty in estimated per time uptake rate. Thus, uncertainty of parameter estimates, i.e. standard error of V_{max} and K_m, cannot be reliably evaluated.

In summary, the method proposed by Covino et al (2010) is theoretically flawed with inconsistent assumptions. Practically, the method suffers from high sensitivity to measurement inaccuracy and does not allow for proper evaluation of uncertainty. Thus, we argue

that such method should not be adopted and a new method to analyze the pulse release data needs to be developed.

Chapter 3

A new method of estimating nutrient uptake with pulse release

The analyses of the method by Covino et al (2010) suggest two major directions of improvements. First of all, estimates of nutrient uptake rate in streams should rely on explicitly specified underlying model of solute dynamics in water and assumptions of the form of uptake. Assumptions of the model need to be consistently used throughout. Second, the source and distribution of error need to be specified and explicitly incorporated in model fitting. This enables us to obtain meaningful estimates of the uncertainty in nutrient uptake rate. This also allows for model comparison to select proper form of nutrient uptake.

3.1 Model specification

Based on the insights gained from analyzing the existing approach, we propose a new method to estimate nutrient uptake from pulse release data. First, we specify the model describing how concentration of solutes change over time based on solute transport and forms of nutrient uptake. In generally, the solute dynamics in flowing water can be described by an advection–dispersion–decay model (Stream Solute Workshop, 1990). In addition, solutes in the main channel of a stream may exchange with the sediments at the bottom of the channel, which is often referred to as transient storage zone (Bencala, 1983). Thus, a general model describing the dynamics of nutrients in streams is the advection–dispersion–decay model with transient storage (Runkel, 2007).

$$\frac{\partial C}{\partial t} = -U\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} + I - f(C) - \alpha(C - C_s)\ , \tag{3.1}$$

$$\frac{\partial C_s}{\partial t} = \frac{A}{A_s}\alpha(C - C_s)\ . \tag{3.2}$$

Here, C and C_s are concentration of solutes in the main channel and transient storage respectively, U is flow velocity, D is dispersion coefficient, A/A_s is the ratio of cross section area of the main channel and the transient storage zone, α is the exchange rate between main channel and transient storage zone, I is the constant nutrient production rate in the stream channel. The assumption of constant nutrient production rate is justified because nutrient production rate is unlikely to change significantly during the short period of pulse release experiment. The function $f(C)$ is chosen to be suitable for describing nutrient uptake rate in the stream channel. Nutrient uptake is an enzymatic catalyzed reaction and thus the concentration dependence of nutrient uptake rate in stream channel can be generally described by the Michaelis–Menten function

$$f(C) = \frac{V_{max}C}{K_m + C} \, . \tag{3.3}$$

Here, V_{max} is the maximum uptake rate, and K_m is the half saturation constant. Michaelis–Menten function is a general form describing concentration dependence of uptake rate. When nutrient concentration is low ($C \ll K_m$), Michaelis–Menten uptake is approximately first order. Thus, we have an alternative choice of function describing the nutrient uptake rate in the stream channel, namely the first order uptake function

$$f(C) = KC \, , \tag{3.4}$$

where K is the per time uptake rate.

While we have modeled the pulse release by assuming that the tracers are injected uniformly across the cross-section over an infinitesimally small width, such initial condition as specified by the Dirac delta function (equation 2.1) is difficult to implement if we have to numerically solve the partial differential equation model for solute dynamics (equations 3.1–3.3). Thus, we modified the initial condition slightly by assuming that the tracers are injected uniformly over a short length of x_0. Mathematically, the initial condition can be

expressed as

$$C(x,0) = \begin{cases} C_0, & x < 0 \text{ or } x > x_0; \\ C_0 + \frac{M}{x_0 w d}, & 0 \leqslant x \leqslant x_0. \end{cases} \tag{3.5}$$

Here, M is the mass of injected tracer, C_0 is the background concentration, w is the width of stream and d is the depth of stream. The volume of water at which the tracers are injected into initially is thus x_0wd, assuming that the cross section of the stream is roughly rectangular. Given that the tracer solution is often released quickly, an arbitrary choice of a short x_0 is likely reasonable. Because dispersion is the major process responsible for the spread of the initial pulse, the choice of a short injection time should not influence the modeled dynamics of solutes significantly (See appendix). We further assume a stable background concentration of tracers during the period of pulse release experiment. This gives rise to the boundary condition

$$C(\pm\infty, t) = C_0 \ . \tag{3.6}$$

The assumption of stable background concentration also suggests that the concentration of solutes is equal in the channel and transient storage zone

$$C_0 = C_{s,0} \ . \tag{3.7}$$

and the input and uptake balance each other in the main channel

$$I = f(C_0) \ . \tag{3.8}$$

In summary, with equations 3.1–3.8, we use observed concentration of solutes to estimate parameters in the model (U, D, α, A/A_s, C_0, V_{max} and K_m or K). Equations 3.1–3.8 offer multiple choices of models describing solute dynamics in streams. The combination of different forms of nutrient uptake (choosing among equations 3.3 and 3.4) and whether we include transient storage zone ($\alpha = 0$ or $\alpha \neq 0$) offers four candidate models: 1) main channel model with Michaelis–Menten uptake; 2) main channel model with first order uptake; 3) transient storage zone model with Michaelis Menten uptake; and 4) transient storage zone

models with first order uptake; A model selection procedure can then be performed to choose the most proper model for a particular data set.

We assume a normal distributed measurement error, i.e. the difference between modeled and measured solutes concentrations follows independent and identical normal distribution. Thus we can use least squares as the criteria for model fit.

3.2 Computational considerations

Fitting the partial differential equation model as specified in equations 3.1–3.8 leads to a few considerations of computation. First of all, the partial differential equation model for nutrient dynamics (equations 3.1–3.8) usually does not have a closed form analytical solution (van Genuchten et al, 2013) and needs to be solved numerically to obtain the trajectory of solute concentration over time. One reliable method of solving partial differential equation numerically is the method of lines. For partial differential equation with two independent variables, method of lines first divides space into finite number of segments and solve the partial differential equation as a sequence of ordinary differential equations defined on the segment (Schiesser, 2012). In this study, we used the method of lines implemented in R package `ReacTran` to numerically solve the partial differential equation (Soetaert et al, 2010; Soetaert and Meysman, 2012).

One particular issue when numerically solving partial differential equation is numerical dispersion. Numerical dispersion refers to the dispersion–like behavior of nutrient pulse solely caused by inaccuracy of the numeric method of solving partial differential equation. When solving partial differential equation numerically, a pulse will appear to spread even without diffusion. Such behavior is undesirable. We employed two strategies to tackle the problem of numeric dispersion. First, we used the algorithm proposed by Fiadeiro and Veronis (1977) to reduce the amount of numeric dispersion when numerically simulating partial differential equations. The algorithm switches between backward differencing and central differencing to achieve a compromise between stability, accuracy and reduced numerical dispersion. Second,

we divided the space in finer resolution to reduce numeric dispersion. Since the degree of numeric dispersion depends on the relative magnitude of advective and dispersive transport, it is impossible to propose a general rule of setting spatial resolution. Thus, we tested the simulation with different spatial resolution until the degree of numeric dispersion does not affect parameter estimates when fitting the model.

A second consideration is the choice of algorithm for nonlinear least squares fitting. We chose a variant of Levenberg–Marquardt algorithm (Levenberg, 1944; Marquardt, 1963) implemented in R function `nlfb` in package `nlmrt` because this method is robust to ill conditioned problems and provide the ability to put upper and lower bound of parameter estimates (Nash, 1990).

A third consideration is the starting values of parameters as bad starting values can lead to slow or no convergence, or possibly convergence to the wrong solution. Since the general advection–dispersion–decay model with transient storage is not analytically solvable, it is difficult to analyze the behavior of the model to obtain starting values of parameters. Instead, we analyze the behavior of the model without transient storage zone to obtain rough estimates of starting values for a subset of parameters. In equations 2.5 and 2.6, the observed solute concentration when $t \to 0$ and $t \to \infty$ is approximately the background concentration. Thus the average of measurements at the beginning or towards the end of pulse release experiments is a reasonable starting value for background concentration. Equation 2.5 suggests that conservative tracer concentration is the highest at $t = U/x$. Thus we use the time it takes the peak to arrive at the sampling location and the distance between injection and sampling locations to obtain a starting value for U. It is difficult to obtain starting values for other parameters by analyzing the model. We thus simulate the model (equations 3.1–3.8) with various combination of parameters until it visually fits the observed data. These values are then used as the starting value for nonlinear least squares fitting.

3.3 Evaluating the new method with simulated data

To evaluate whether the model and algorithm discussed above can correctly estimate the nutrient uptake rate, we applied the proposed new method to simulated data sets. In particular, we simulated breakthrough curves of Cl and N assuming transient storage and first order uptake (equations 3.1, 3.2, 3.4–3.8). The parameter values used to simulate the data were $C_{Cl,0}$=6mg/L, $C_{N,0}$=3μg/L, D=0.3m^2/s, U=1.5m/s, α=0.03/s, A/As=2, and K 0.05/s. For initial condition (equation 3.5), we assumed that the tracers were injected uniformly over a length of 0.5m. The Cl and N concentration immediately after the pulse release was 1g/L and 2mg/L respectively. We sampled 68 pairs of N and Cl concentrations from the breakthrough curves at 40m downstream of the releasing location. As discussed above, we used method of lines to numerically solve the partial differential equation. Thus, we need to discretize space for this numerical method. In this simulation study, we divide the stream into segments of length 0.5m. We added random error drawn from a normal distribution with mean 0 and standard deviation 0.5 to the simulated Cl and N concentration. We then fit the proposed new models with different specifications to the data. The candidate models we fit to the data were 1) main channel with first order uptake (equations 3.1 with $\alpha = 0$, 3.4–3.6, 3.8), 2) main channel with Michaelis–Menten uptake (equations 3.1 with $\alpha = 0$, 3.3, 3.5, 3.6, 3.8), 3) transient storage with first order uptake (equations equations 3.1, 3.2, 3.4–3.8), and 4) transient storage with Michaelis–Menten uptake (equations 3.1–3.3, 3.5–3.8). We also used the method by Covino et al (2010) to compare its performance to the new method. Specifically, we calculated the uptake rate for each sample (step 2) using the correct background concentration for correction and assumed a first order update (step 3). Due to long computation time for numerically solving partial differential equation, we performed the simulation 200 times. The mean, variance and mean square error of the parameter estimates are fully summarized in Table 3.1.

Table 3.1: Mean, standard deviation (SD) and root mean square error (RMSE) of parameter estimates in the simulation study

	$C_{Cl,0}$	$C_{N,0}$	D	U	α	A/A_s	K	V_{max}	K_m
True parameters values									
	6.00	3.00	0.30	1.50	0.03	2.00	0.05		
Main channel with first order uptake									
Mean	5.35	2.94	0.88	1.43			0.052		
SD	0.26	0.16	0.032	4.7×10^{-3}			1.5×10^{-3}		
RMSE	0.69	0.17	0.58	0.073			2.3×10^{-3}		
Main channel with Michaelis–Menten uptake									
Mean	5.38	2.73	0.88	1.43				2.4×10^4	4.8×10^5
SD	0.28	0.21	0.029	4.7×10^{-3}				303.3	164.3
RMSE	0.68	0.35	0.58	0.074					
Transient storage with first order uptake									
Mean	6.00	2.99	0.30	1.50	0.03	2.00	0.05		
SD	0.066	0.078	7.4×10^{-3}	2.7×10^{-3}	5.6×10^{-4}	0.045	6.7×10^{-4}		
RMSE	0.066	0.079	7.4×10^{-3}	2.7×10^{-3}	5.6×10^{-4}	0.046	6.7×10^{-4}		
Transient storage with Michaelis–Menten uptake									
Mean	5.94	2.92	0.31	1.50	0.03	1.98		2.4×10^4	4.8×10^5
SD	0.064	0.073	7.1×10^{-3}	2.6×10^{-3}	5.4×10^{-4}	0.051		114.0	25.9
RMSE	0.065	0.073	7.1×10^{-3}	2.6×10^{-3}	5.5×10^{-4}	0.052			
Covino et al (2010) method									
Mean							0.041		
SD							1.6×10^{-3}		
RMSE							8.9×10^{-3}		

The data sets were generated from a model with transient storage zone and a first order uptake in the main channel (equations equations 3.1, 3.2, 3.4–3.8). For each iteration of simulation, we fit the four candidate models to the simulated data and obtained an AIC for each model. The model with the same structure as the one used to generate the data set had the lowest AIC 100% times in our simulation, and correctly recovered the parameter values used to simulate the data set as evidenced by small MSE and bias (similar variance and MSE of parameter estimates) (Table 3.1). Visually, this model resulted in a good fit to data (Figure 3.1). On the other hand, the estimated uptake rate based on Covino et al (2010) differs significantly from the true parameter value used in simulating the data sets (Table 3.1). This finding confirms our analysis that the method proposed by Covino et al (2010) is based on first order uptake in the stream channel and is not applicable to streams with transient storage zone.

3.4 Application to field data

The data we used to demonstrate the application of the new method come from a pulse release experiment in the Luquillo Experimental Forest in northeastern Puerto Rico. We performed the experiment in a first order stream within the Rio Mameyes watershed. During the pulse release experiment, we added 667g NaCl as conservative tracer and 3g NH_4Cl as the nutrient tracer. We monitored the solute breakthrough curve 48.9m downstream of the pulse release location. The background Cl concentration measured immediately prior to the release experiment was 8mg/L. The N background concentration was below the detection limit of 5μg/L. We collected 28 water samples throughout the solute breakthrough curve. We measured N and Cl concentration for each sample.

We fitted all four candidate models to the data and used AIC to select the best fit model. We assumed that the injected solutes were uniformly distributed over a 0.5m length of the stream initially. We set a higher limit of estimated background Cl and N concentration at 12 mg/L and 5μg/L, given the measurements of background concentration prior to the

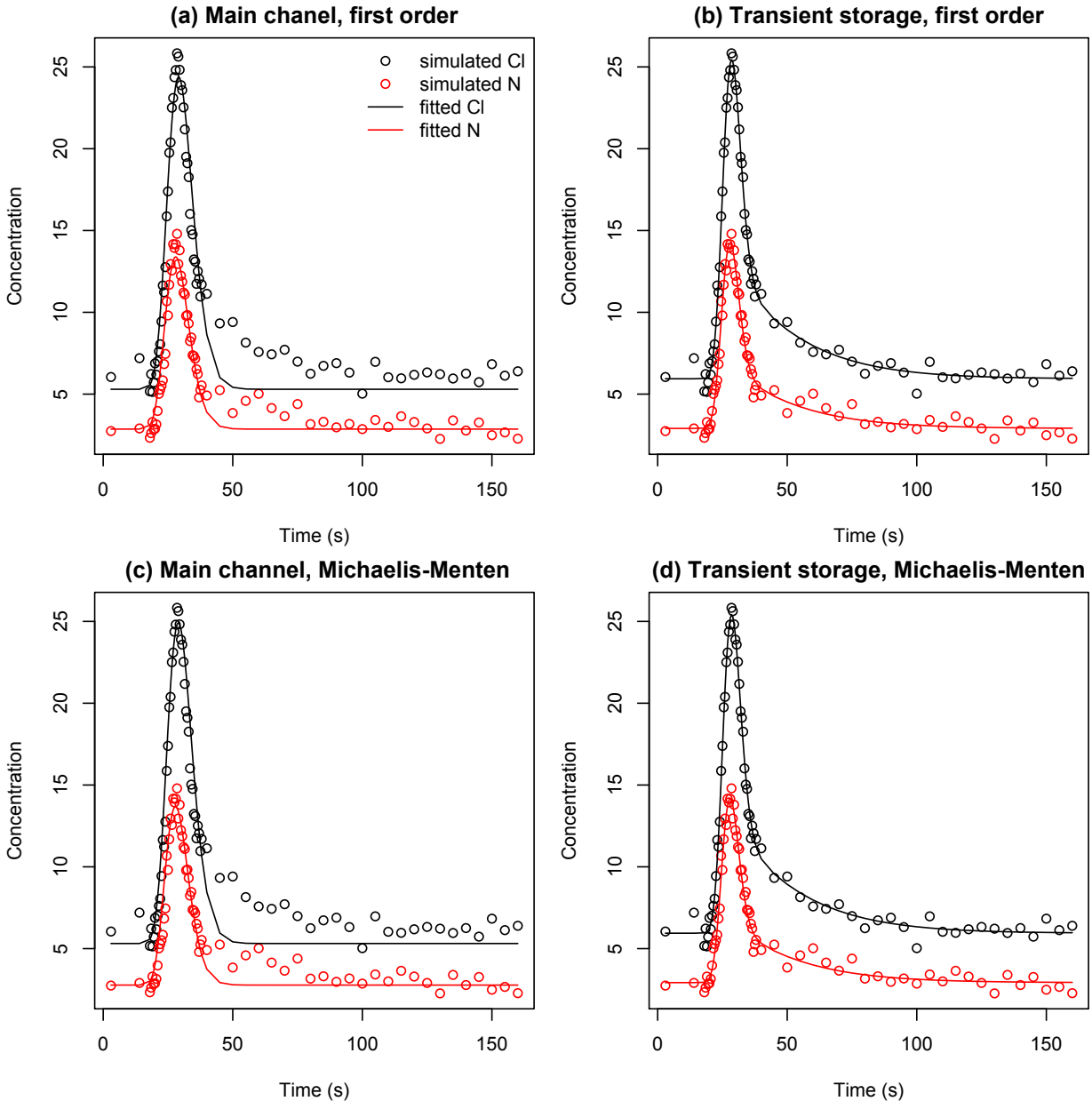

Figure 3.1: Model fits to the simulated data set

release experiment. The parameter estimates and AIC for each candidate model are listed in Table 3.2 and fitted curves are displayed in Figure 3.2). We found that models including transient storage zone had a significant better fit to the data. Based on AIC, model with transient storage and first order uptake of nutrient is the best model. We also found that the Michaelis–Menten uptake and first order uptake result in very similar residual sum of square. The estimated half saturation constant K_m in Michaelis–Menten uptake function is much higher than the observed N concentration in breakthrough curve. Because Michaelis–Menten uptake is approximately equal to a first order uptake when the actual nutrient concentration is much lower than half saturation constant K_m, The similar fit between these two models is expected. It suggests that the Michaelis–Menten uptake is not necessary and first order uptake is sufficient to describe the nutrient uptake dynamics in this data set.

We also estimated uptake rate following the method by Covino et al (2010). Given that this method inherently assumes a first order uptake, and the first order uptake model is found to be the best model in our model comparison (Table 3.2), we first obtained a per time uptake rate for each sample (step 2) and regress the uptake rate on concentration following a first order uptake (step 3). In the experimental data set, the background Cl concentration is 8mg/L and the background N concentration measured prior to the pulse release experiment is below the detection limit of 5μg/L. We thus follow the convention to use half detection limit, i.e. 2.5μg/L, as the background N concentration in the Covino et al (2010) method. We found that the resulting estimate of per time uptake K differs significantly from that estimated based on the advection-dispersion models (Table 3.2). The Covino et al (2010) method also does not allow us to assess the uncertainty in the parameter estimates due to its improper error propagation.

Table 3.2: Parameter estimates (standard error) and AIC of models fitted to the experimental data set

Model	$C_{Cl,0}$	$C_{N,0}$	D	U	α	A/A_s	K	V_{max}	K_m	AIC
main channel	11.72	4.81	1.12	1.11			0.045			407.6
first order	(0.17)	(0.069)	(0.00083)	(0.0055)			(0.0004)			
main channel	11.72	4.81	1.12	1.11				45176	1000551	409.6
Michaelis–Menten	(0.18)	(0.23)	(0.0088)	(0.0054)				(1004)	(3050)	
transient storage	9.18	0.87	0.075	1.62	0.14	1.69	0.056			324.3
first order	(0.15)	(0.024)	(0.0031)	(0.014)	(0.0057)	(0.036)	(0.0014)			
transient storage	9.23	0.93	0.075	1.62	0.14	1.69		56420	1×10^6	326.3
Michaelis–Menten	(0.063)	(0.052)	(0.0061)	(0.0025)	(0.00048)	(0.028)		(444.9)	(8087)	
Covino et al (2010)							0.039			

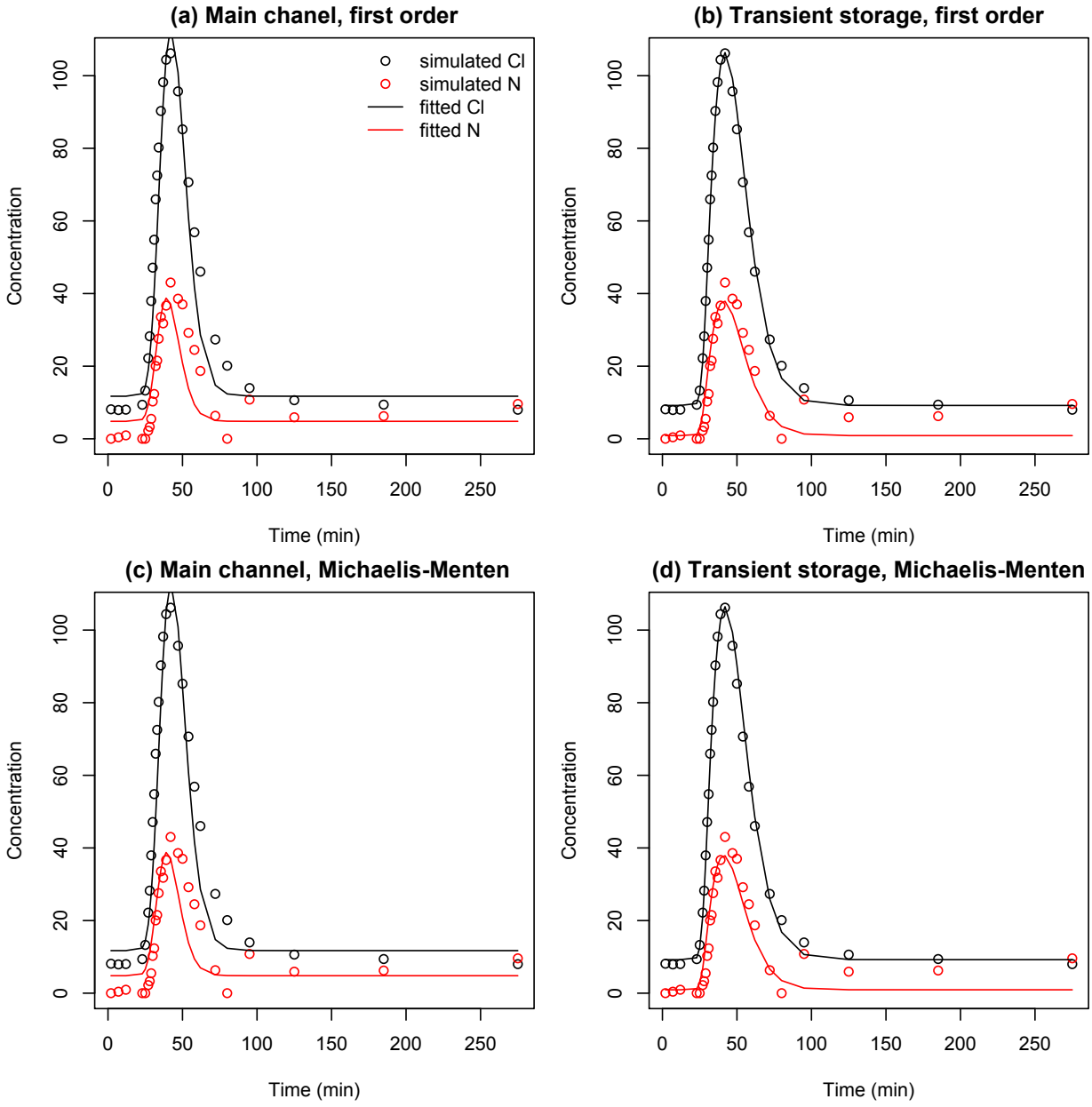

Figure 3.2: Model fits to the experimental data set

Chapter 4

Conclusions

We evaluated the existing method through theoretical analyses and fitting to simulated data set. We found that the existing method had inconsistent use of assumptions and is sensitive to slight inaccuracy in solute concentration measurements. The existing method is based on nutrient dynamics in the stream main channel and does not include the influences of transient storage. These problems suggest that the existing method has severe methodological flaws and is inadequate to deal with the complexity in real data sets. We developed a new method based on description of the solute dynamics in streams and tested this method with both simulated and experimental data sets. Our method allows for inclusion of transient storage zone and different forms of nutrient uptake function, and thus provides a flexible model to estimate nutrient uptake from pulse release experiment in streams.

One limitation of the new method is that the starting values of parameters used for nonlinear least square fitting are difficult to obtain. It is well known that good starting values are critical for convergence to correct parameter estimates in nonlinear models. While we can get rough estimates for flow velocity based on the timing of peak concentration in the breakthrough curves and background concentration based on sample measurements prior to the pulse solute release, it is difficult to obtain estimates of other parameters in the model. Currently, we recommend testing various starting values of parameters and compare the resulting model fit. Future research should aim to develop a robust method for obtaining starting values of the parameters.

The new method we developed requires numerically solving the partial differential equation that describes the solute dynamics in streams. Accurately solving partial differential

equation is time consuming. Consequently, processing large amount of nutrient release data likely requires dedicated computing facility and implementation of parallel computing.

Despite the limitations discussed above, this new method is the first attempt to provide a flexible and logically consistent method to estimate nutrient uptake from pulse release experiments. The new method is based on sound and well understood mechanisms of solute dynamics. The R code we implemented for this method (`https://github.com/songchao1986/Nutrient-uptake`) provides a convenient tool to analyze nutrient uptake data for stream ecologists.

Bibliography

Bencala KE (1983) Simulation of solute transport in a mountain pool-and-riffle stream with a kinetic mass transfer model for sorption. Water Resources Research 19(3):732–738

Covino TP, McGlynn BL, McNamara RA (2010) Tracer additions for spiraling curve characterization(tascc): Quantifying stream nutrient uptake kinetics from ambient to saturation. Limnology and Oceanography: Methods 8(9):484–498

Fiadeiro ME, Veronis G (1977) On weighted-mean schemes for the finite-difference approximation to the advection-diffusion equation. Tellus 29(6):512–522

van Genuchten MT, Leij FJ, Skaggs TH, Toride N, Bradford SA, Pontedeiro EM (2013) Exact analytical solutions for contaminant transport in rivers 2. transient storage and decay chain solutions. Journal of Hydrology and Hydromechanics 61(3):250–259

Genuchten MT, Leij FJ, Skaggs TH, Toride N, Bradford SA, Pontedeiro EM, et al (2013) Exact analytical solutions for contaminant transport in rivers 1. the equilibrium advection-dispersion equation. Journal of Hydrology and Hydromechanics 61(2):146–160

Levenberg K (1944) A method for the solution of certain non-linear problems in least squares. Quarterly of applied mathematics 2(2):164–168

Marquardt DW (1963) An algorithm for least-squares estimation of nonlinear parameters. Journal of the society for Industrial and Applied Mathematics 11(2):431–441

Mulholland PJ, Helton AM, Poole GC, Hall RO, Hamilton SK, Peterson BJ, Tank JL, Ashkenas LR, Cooper LW, Dahm CN, et al (2008) Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature 452(7184):202–205

Nash JC (1990) Compact numerical methods for computers: linear algebra and function minimisation. CRC Press

Newbold JD, Elwood JW, O'Neill RV, Winkle WV (1981) Measuring nutrient spiralling in streams. Canadian Journal of Fisheries and Aquatic Sciences 38(7):860–863

O'Loughlin EM, Bowmer KH (1975) Dilution and decay of aquatic herbicides in flowing channels. Journal of Hydrology 26(3-4):217–235

Peterson BJ, Wollheim WM, Mulholland PJ, Webster JR, Meyer JL, Tank JL, Martí E, Bowden WB, Valett HM, Hershey AE, et al (2001) Control of nitrogen export from watersheds by headwater streams. Science 292(5514):86–90

Runkel RL (2002) A new metric for determining the importance of transient storage. Journal of the North American Benthological Society 21(4):529–543

Runkel RL (2007) Toward a transport-based analysis of nutrient spiraling and uptake in streams. Limnology and Oceanography: Methods 5(1):50–62

Schiesser WE (2012) The numerical method of lines: integration of partial differential equations. Elsevier

Soetaert K, Meysman F (2012) Reactive transport in aquatic ecosystems: Rapid model prototyping in the open source software R. Environmental Modelling and Software 32:49–60

Soetaert K, Petzoldt T, Setzer RW, et al (2010) Solving differential equations in r: package desolve. Journal of Statistical Software 33(9):1–25

Sororzano L (1969) Determination of ammonia in natural waters by the phenolhypochlorite method. Limnology and Oceanography 14:799–801

Stream Solute Workshop (1990) Concepts and methods for assessing solute dynamics in stream ecosystems. Journal of the North American Benthological Society pp 95–119

Vitousek PM, Mooney HA, Lubchenco J, Melillo JM (1997) Human domination of earth's ecosystems. Science 277(5325):494–499

Webster J, Ehrman T (1996) Solute dynamics. In: Hauer F, Lamberti G (eds) Methods in Stream Ecology, vol 2, Academic Press: New York, pp 145–160

Appendix

Influence of initial conditions

To numerically solve the partial differential equation, we replace the initial condition specified by a δ function with

$$C(x,0) = \begin{cases} C_0, & x < 0 \; or \; x > x_0; \\ C_0 + \frac{M}{x_0 w d}, & 0 \leqslant x \leqslant x_0. \end{cases} \tag{1}$$

Here, M is the mass of injected tracer, w is the width of stream and d is the depth of stream. The volume of water at which the tracers are injected into initially is thus x_0wd, assuming that the cross section of the stream is roughly rectangular. We argue that an arbitrary choice of a short x_0 should not influence the simulated breakthrough curves. To prove this point, we simulated three breakthrough curves of Cl using the same parameter sets we used in the simulation study. Specifically, The parameter values used to simulate the data were $C_{Cl,0}$=6mg/L, D=0.3m^2/s, U=1.5m/s, α=0.03/s and A/As=2. We monitor the concentration at 40m downstream from the release point. For initial conditions, we simulated three scenarios. The first scenario assumes that the tracer is injected uniformly over a length of 0.5m. The Cl concentration immediately after the pulse release was 1g/L. The second scenario assumes that the tracer is injected uniformly over a length of 0.25m and the initial concentration of Cl after release is 2g/L. The third scenario assumes that the tracers injected uniformly over a length of 0.2m and the initial concentration of Cl after release is 2.5g/L. We ensure the total amount of tracer injected remains the same in the three scenarios. The breakthrough curve for each scenario is shown in Figure 1. We see that choosing different values of x_0 does not alter the simulated breakthrough curve significantly.

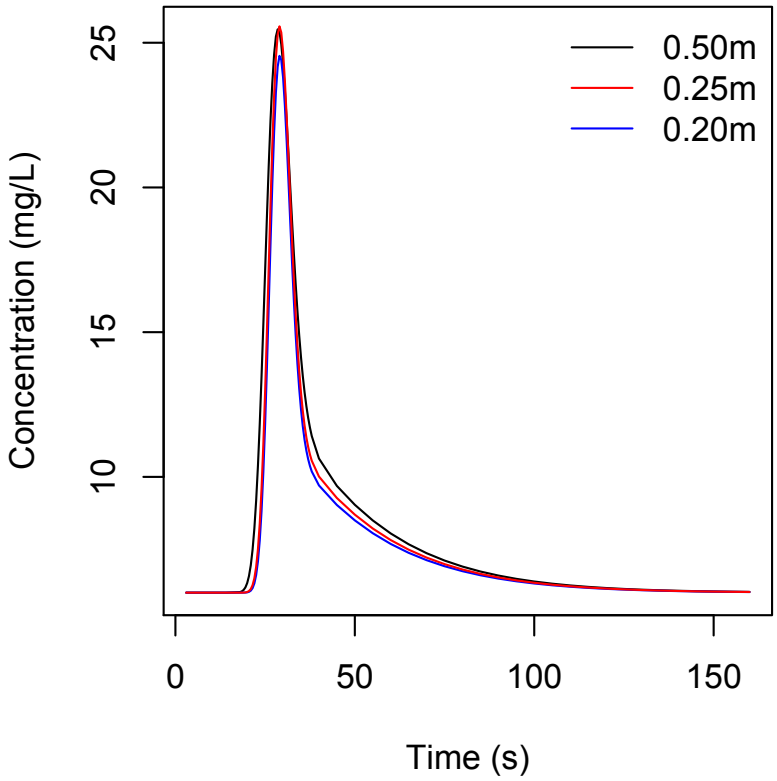

Figure 1: Simulated breakthrough curve of Cl for different x_0