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Combined nitrogen retention in an agricultural river system

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Combined nitrogen retention in an agricultural river system

By

Christopher Allaway

Thesis submitted to the
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Abstract

Since combined nitrogen is a pollutant in streams, rivers and coastal areas, conditions that favour nitrogen removal were identified. The importance of stream depth as a predictor of a reach's capacity to remove nitrogen was tested in the South Nation watershed (3915 km^2), an agricultural watershed in eastern Ontario. Combined nitrogen (N) retention was estimated in 48 reaches across the watershed which varied in discharge (0.0008 – 118 $m^3 s^{-1}$), length (350 m to 5.2 km) and size from headwaters to the outflow of the South Nation River at the Ottawa River. Retention dynamics were also investigated within a few sites over the summer season.

Retention efficiency (expressed as a percentage of inputs) varied widely for nitrate from almost complete removal within a reach to reaches acting as a net source. A narrower range in percent retention and loading was observed for total nitrogen (TN) among the sites suggesting that some forms of combined nitrogen are relatively inert. An exponential decline in percent nitrogen retention with increasing stream depth was observed for TN, but not for nitrate. The lack of a significant relationship for nitrate was likely due to the several occurrences of a net increase in nitrate along the length of the reach (-ve retention values). These unexpected net increases in nitrate could be due to the sampling methodology and less likely to nitrification or groundwater inputs within the reach. More of the variability of nitrogen retention was explained when percent N retention and depth were log transformed (removing sites with –ve retention values) which resulted in a significant linear decrease in nitrate and TN retention with depth.

In addition to depth, turbidity explained a low, but significant portion of total Kjeldahl-N (TKN) and TN percent retention, while planktonic chl *a* explained a portion of TKN percent retention. It appears that percent TKN retention increases with decreasing levels of turbidity over the length of the reach (sedimentation) and TKN loading occurs with growth of suspended algae.

A seasonal study showed that discharge is an important factor in determining N retention, with percent N retention (%) and areal N retention (g m^{-2} d^{-1}) decreasing as the discharge increases and the water residence time of the reach decreases.

There was a highly significant positive relationship between areal retention of nitrate and TN with their respective areal N loading (g m^{-2} d^{-1}) across sites. The results in the South Nation span the range of areal retention and loading seen in the literature for rivers and produced a highly significant regression when combined with the literature data. Data from the current study and literature showed that summer N retention appeared to drop off substantially when loading exceeded 2 g m^{-2} d^{-1}.

Résumé

De nouvelles inquiétudes concernant la pollution par l'azote des rivières et des régions côtières ont mené à des recherches sur le potentiel de rétention et d'élimination d'azote de ces plans d'eau. La capacité d'élimination de l'azote en fonction de la profondeur fut étudiée dans la Rivière Nation Sud (3915 km^2), un basin versant agricole dans l'est de L 'Ontario. La rétention d'azote fut évaluée sur 48 tronçons différents, situés tout au long du bassin versant. Ces tronçons variaient en taille et en débit (0.0008-118 m^3 s^{-1}) des tributaires en amont jusqu'à la confluence avec la Rivière des Outaouais. Ces phénomènes de rétention furent également étudiés à différents sites au cours de l'été.

L'efficacité de rétention de nitrate (exprimée en pourcentage des apports) varient grandement, allant d'une rétention presque totale à des tronçons agissant comme sources de nitrate. Par contre, une variabilité plus faible parmi les sites a été observée entre le pourcentage de rétention et le pourcentage de charge positive de l'azote totale (NT) suggérant qu'un fraction de l'azote total est relativement inerte. Un déclin exponentiel du pourcentage d'azote retenu en fonction de l'augmentation de la profondeur du ruisseau fut observé pour le NT, mais non pour le nitrate. Cette relation peu significative fut probablement causeé par la méthode d'échantillonnage plutôt que par la nitrification ou même l'ajout d'azote par le biais d'eaux souterraines. Une grande partie de la variabilité de la rétention d'azote est expliquée lorsque les pourcentages de rétention de N, ainsi que les données de profondeur furent transformées de façon logarithmique (éliminant les sites sources de N). Ceci met en relief le déclin linéaire et significatif de nitrate et de NT en fonction de la profondeur.

En plus de la profondeur, la turbidité explique une partie significative du pourcentage de rétention du Kjeldahl-N total (KNT) et de NT, tandis que la chl-*a* planctonique explique une partie du pourcentage de rétention du KNT. Il sembler que le pourcentage de rétention du KNT augmenterait en fonction d'une baisse du niveau de la turbidité et que les apports de KNT se produiraient simultanément à la croissance d'algues suspendues.

Une étude saisonnière indique que le débit fut un facteur important dans la détermination de la rétention de N; le pourcentage de rétention de N et de la rétention de N par unité de surface baisse avec une augmentation du débit et une décroissance du temps de passage de l'eau dans le tronçon.

Une relation significative a été observée entre la rétention calculée par unité de surface de N et la quantité d'apports estimée par unité de surface d'azote. D'ailleurs, d'autres études sur les rivières présent des résultats semblables. De plus, ces résultats produisent une régression significative lorsque jumelés avec les données provenant de la littérature. De plus, les résultats de cette recherche ainsi que ceux de la littérature suggèrent que la rétention de N diminue à partir de 2 g m^{-2} par jour d'azote.

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Chapter 1

Introduction

Rivers are not just simple conduits for nutrients, particularly during the summer months. Biological and physical processes cause a retention and recycling of nutrients as they travel downstream, cause a transformation of nutrient chemical composition and a permanent removal from the aquatic system (Peterson *et al.* 2001).

Many factors affecting nitrogen (N) loss within rivers have been elucidated including, chemical (carbon, oxygen and nutrient) sediment characteristics, temperature, vegetation cover, water residence time and flow (Jansson *et al.* 1994b, Cooper 1990, Seitzinger 1988). However, reported estimates vary widely between rivers and studies. Emphasis has been placed on quantifying and explaining retention at specific locations, while variables that can explain differences in retention seen for different sizes of river have yet to be explored.

1.1 Anthropogenic impacts on the nitrogen cycle

Nitrogen is an essential element for all life forms in terrestrial and aquatic systems and when in short supply can limit algal and plant growth. However, when in surplus it is a pollutant. In addition to natural N fixation, human activities can also add new sources of fixed N to the global cycle through industrial fertilizer production through the Haber-Bosch process, fossil fuel combustion and nitrogen fixing agricultural crops. This has resulted in humans currently doubling the rate of atmospheric nitrogen transfer to bioavailable forms in terrestrial systems (Vitousek *et al.* 1997). Human activities also

contribute indirectly to the global nitrogen (N) cycle by mobilizing long term biological storage of nitrogen from biomass burning, land clearing and wetland drainage (Vitousek *et al.* 1997). A portion of this increased nitrogen input to terrestrial systems makes it to groundwater and surface waters through the drainage basin and direct atmospheric deposits resulting in an increase of riverine N loads (Turner and Rabalais 1991, Caraco and Cole 1999, Jaworski *et al.* 1997). Howarth *et al.* (1996) estimated that total riverine N fluxes may have increased 2 – 20 fold from pre-industrial times for most temperate regions surrounding the North Atlantic Ocean. The average nitrate concentration and nitrate flux in the lower Mississippi River has increased 2.3 and 3.3 fold in the last 30 – 40 years, respectively (Justic *et al.* 2003).

Agriculture accounts for ~ 86 % of anthropogenic N inputs to the global cycle and nearly matches that of natural terrestrial N fixation (140 Tg yr^{-1}) (Vitousek *et al.* 1997). Alexander *et al.* (2000) modeled the sources of total nitrogen (TN) from major watersheds in the Mississippi River Basin and found that agriculture accounted for 64 % of the TN flux delivered to the Gulf of Mexico. Fertilizer alone accounted for nearly half (49 %) of the N exported from the basin. The atmosphere contributed 17 %, non-agricultural non-point sources 12% and point sources 6 %. Kronvang *et al.* (1999) found that agriculture was the main source of riverine nitrogen in the Gjern river basin, Denmark, contributing 76 % of the total export. This result is similar to the findings in Svendsen and Hansen (1995) that agriculture contributed 78 % of the nitrogen mass to streams and lakes in Denmark for the year 1995.

This increased nitrogen loading to surface waters poses a number of environmental and health concerns. High nitrate concentrations (>10 mg L^{-1}) in drinking

water can cause methoglobinemia (blue baby syndrome) that is harmful to both newborn humans and livestock. Nitrogen may cause acidification of freshwaters directly through nitric acid and indirectly from biological uptake and nitrification of ammonium which produces hydrogen ions (Vitousek *et al.* 1997). Increased nitrogen loading, alone or in conjunction with increases in phosphorous, can cause eutrophication of freshwaters which, similar to acidification, results in decreased plant and animal diversity (Schindler 1994).

The U.S. National Research Council (NRC 2000) has concluded that eutrophication of coastal marine waters from riverine N export the greatest pollution problem facing these ecosystems. Eutrophication may cause anoxia or hypoxia, a loss in benthic and planktonic community diversity, growth of nuisance or toxic algae and a decline in coastal fisheries, as reported in Vitousek *et al.* (1997) and Carpenter *et al.* (1998). Nitrogen loading from the Mississippi River, resulting in increased algal production, has caused an annual mid-summer hypoxic (< 2 mg O_2 L^{-1}) area in the northern Gulf of Mexico which covered an area of 16 000 to 20 700 km^2 between 1993 – 2001 (Rabalais *et al.* 2002).

1.2 Nitrogen forms and cycling

Nitrogen enters biological pathways beginning with the assimilation (fixation) of molecular nitrogen (N_2) by cyanobacteria and some bacteria into particulate organic nitrogen (PON), mostly as amino acids and peptides. Organic nitrogen also exists in

dissolved forms as dissolved organic nitrogen (DON) from wastes excreted by organisms, cell leakage or from the degradation of PON.

Nitrogenous compounds follow numerous transformation pathways due to their existence in a range of oxidation states allowing them to act as both an electron donor and receiver in a variety of oxidation-reduction reactions. Dissolved inorganic nitrogen (DIN) compounds include ammonia (NH_3), ammonium ion (NH_4^+), nitrite ion (NO_2^-) and nitrate ion (NO_3^-). These compounds are formed from the decomposition of organic-N, first to ammonia through the process of ammonification then to nitrate through nitrification when oxygen is present. Nitrite is an intermediate product in many reactions including the first stage of nitrification (oxidation of NH_4^+) and denitrification (reduction of NO_3^-). Nitrite rarely accumulates in oxic surface waters as it is rapidly converted to nitrate through nitrification. However, nitrite may accumulate under nearly anoxic conditions because the oxidation of ammonium (nitrification) will terminate at the NO_2^- or N_2O stage (Downes 1988). Ammonia is found in sewage, fertilizer and is produced during the process of ammonification. Ammonia is a weak base ($pK_b = 4.75$) and is typically found in the ionized form (NH_4^+) in the pH range of most natural waters (Wetzel 2001). Total Kjeldahl-N (TKN) is an operationally defined fraction that includes both particulate and dissolved organic-N and NH_4^+. In the Kjeldahl method, organic-N is converted to NH_4^+. Organic-N is calculated by subtracting NH_4^+ (determined separately) from TKN. Total nitrogen (TN) can be derived from the addition of DIN, DON and PON or TKN plus nitrate and nitrite.

In a river, nitrogen undergoes multiple cycles of biotic/abiotic uptake, storage, and regeneration back to the water column ultimately resulting in a permanent loss from

the stream or river through denitrification or export. The principal site for nitrification, and the closely coupled process of denitrification, is at the oxic-anoxic interface of the water column and sediment (Peterson *et al.* 2001). Ammonification of organic matter provides a large supply of ammonium for nitrification. The nitrate produced from nitrification may diffuse into the anoxic sediment where it acts as the terminal electron acceptor during the oxidation of organic matter by heterotrophic, facultative anaerobic bacteria (Knowles 1982). However, the supply of nitrate from the overlying water column, rather than nitrification, has commonly been found to be the dominant source of nitrate for denitrification (Christensen and Sørensen 1988, Christensen *et al.* 1990). The process of denitrification results in the loss of fixed nitrogen from the aquatic environment to the atmosphere primarily as molecular nitrogen (N_2) and some nitrous oxide (N_2O).

1.3 Nitrogen concentrations in rivers

Typically nitrogen concentrations are higher in freshwater systems than marine systems. From a survey of Ontario and western Quebec rivers, summer total nitrogen concentrations ranged from 0.20 to 6.63 mg L^{-1} with a median value of 0.54 mg L^{-1} (Chételat *et al.* 2005). The range in river discharge was 0.1 – 1197 m^3 s^{-1} with a median discharge of 9 m^3 s^{-1}. Mean annual nitrate concentrations (1990 – 1994) in Ontario rivers were similar for both agricultural (n=11) and urban watersheds (n=8) (~ 3 mg L^{-1}) and lowest for undisturbed sites(n=5) (0.47 mg L^{-1}) (Fleming and Fraser 1999).

Land use influences the stream concentration of nitrogen. In east-central Illinois, Royer *et al.* (2004) monitored five headwater streams located in an area of extensive row-crop agriculture. Stream nitrate and TN concentrations during the summer were < 1 mg L^{-1} and 1.5 mg L^{-1} respectively, and on average 10 - 11 mg L^{-1} during the late fall, winter and spring (Royer, Tank, and David 2004). Long term (14 yr) monitoring of 10 small agricultural streams in Sweden revealed a median TN concentration of 5.5 mg L^{-1} (Ulén *et al.* 2004).

Dodds *et al.* (1998) used published data to calculate a median TN concentration of 0.89 mg L^{-1} from over 200 streams/sites ranging from pristine to nutrient enriched, low-order to large rivers from North America and New Zealand in mainly temperate areas during the summer season. The median TN concentration was found to be 6.4 times greater than the estimated median background (atmospheric deposition-corrected and pristine habitat) concentration of 0.14 mg L^{-1} for rivers of all sizes and locations across the U.S. (Smith *et al.* 2003).

Land use also influences the relative importance of nitrogen fractions. Undisturbed catchments export most of the total nitrogen as dissolved organic N, while the nitrate fraction of total nitrogen appears to increase with human population (Howarth *et al.* 1996). In 100 unpolluted first-order streams in Chile and Argentina, the DON fraction comprised 80 % of total dissolved nitrogen, while nitrate comprised 5 % and ammonium 15 %. In contrast, in three "chronically" polluted old growth forests in eastern North America, DON comprised roughly 20 % of the total nitrogen and nitrate between 70 – 86 % (Perakis and Hedin 2002). In addition, the nitrate levels in North America were 40 – 95 times greater than the highest concentrations in South America

(Perakis and Hedin 2002). From an analysis of 102 forested streams in the north eastern U.S., Binkley *et al.* (2004) reported that nitrogen forms were about 45 % NO_3, 45 % DON and 10 % NH_4.

A study of the world's largest rivers showed that as TN concentrations increased, almost all of the increase was in the form of nitrate (Turner *et al.* 2003). In five agricultural eastern Illinois streams, nitrate comprised only 37 % of TN during low summer concentrations (1.5 mg TN L^{-1}) but rose to 94 % when TN concentrations rose in the fall, winter and spring (average 10.8 mg TN L^{-1}) with organic-N comprising the remainder of the TN (Royer *et al.* 2004).

The nitrate fraction tends to form most of the TN in agricultural watersheds (Keeney and Deluca 1993). A long term study on the influence of agricultural activity on stream chemistry revealed an increasing gradient in nitrate concentrations from pristine prairie uplands to the fertilized-cropland lowlands, with the minimum nitrate concentrations in the agricultural lowlands greater than any upland prairie concentrations (Kemp and Dodds 2001).

1.4 Nitrogen retention: mechanisms and measurement

Retention in this thesis refers to the observed loss of nitrogen (temporary and permanent) from the mass-balance approach. Removal indicates a permanent loss of N from the aquatic system.

Several river mass balance studies have shown that nitrogen input (i.e. loading) to a system is larger than the output (i.e. export), indicating that nitrogen is retained or denitrified within river systems (Behrendt and Opitz 2000, Boyer *et al.* 2002, Howarth *et*

al. 1996). In two English rivers, the Great Ouse and Trent, a close agreement was found between inorganic nitrogen loading to the rivers and downstream export during the winter, spring and late autumn (Owens *et al.* 1972). However, summer export of inorganic nitrogen was substantially smaller than the loading indicating that retention mechanisms (plant uptake and denitrification) removed a substantial fraction of the nitrogen load to the rivers.

Nitrogen retention in wetlands, lakes and rivers stems from three main mechanisms: uptake by aquatic plants, burial or sediment sorption, and denitrification. Denitrification is especially important in rivers because it represents the only mechanism responsible for the permanent removal of nitrogen from the system. Uptake by plants and sediment burial/sorption are only temporary retention mechanisms during the summer and are considered to be a negligible component of nitrogen removal on an annual basis (Svendsen and Kronvang 1993). However, sediment sorption and organic matter burial are important nitrogen sinks in lakes, ponds and possibly wetlands (Jansson *et al.* 1994a).

Rates of denitrification measured in rivers ranges over two orders of magnitude (Appendix I). Factors that control denitrification rates include the supply of nitrate, the amount of organic matter, temperature and oxygen concentrations (Seitzinger 1988). Denitrification rates generally increase with an increasing supply of nitrate and/or organic carbon and warmer water temperatures and may be limited by any one of these factors. Decreasing nitrate flux (nitrate supply) to the sediments during the summer limited denitrification rates in Gelbæk stream, Denmark, whereas the low organic content of sediments of Rabais Bæk limited denitrification rates throughout the year (Christensen and Sørensen 1988). Pattinson *et al.* (1998) found that denitrification rates increased

from upstream to downstream sites along a 145 km stretch of the Swale-Ouse river system, England. The increase in denitrification rates was attributed to a pattern of increasing downstream water column nitrate concentrations and carbon content in the sediments, however this pattern was not a significant explanatory variable for observed denitrification rates.

Nitrogen loss in aquatic systems is commonly assessed through mass-balance studies and denitrification measurements. A mass-balance study captures all three retention mechanisms, however, this "black-box" approach does not distinguish between the individual contributions of each mechanism towards the observed retention. Measuring denitrification, in addition to a mass-balance study, allows an estimate of the fraction of nitrogen removal that is permanent versus the fraction that is only retained temporarily through storage in the sediments and plant biomass.

Mass-balance studies calculate the gain or loss of nitrogen by comparing the mass of N entering the reach from upstream and lateral inputs (tributaries and groundwater) to the mass leaving the reach (mass in – mass out = Δm). The change in mass along a reach (Δm) is usually expressed as a percentage of the inputs (% retention = Δm / mass in). Retention can also be expressed on an areal basis (g m^{-2} d^{-1}), thus facilitating comparisons between reaches of different sizes.

1.5 Nitrogen retention at the reach scale

Published areal rates of nitrate retention ranges from 0.005 g NO_3-N m^{-2} d^{-1} to 0.70 g NO_3-N m^{-2} d^{-1} (Table 1). Percent N retention ranges from to <1 – 75 % during the summer with annual retention generally below 8 %. Low annual retention efficiencies

for lotic systems are due to negligible late autumn, winter and early spring N retention when flows are high and water temperature is too low to support biological uptake. Potentially high summer retention has a small effect on annual nitrogen processing because typically, only a small fraction of nutrient transport occurs during summer low flow conditions (Hill 1979) and most nitrogen stored in sediments and vegetation over summer low flow periods is resuspended and transported in the fall (Svendsen and Kronvang 1993).

The relative importance of plant uptake or denitrification as the main agent responsible for retention varies between studies. Annual nitrogen budgets, in a headwater New Zealand stream, attributed in-stream N retention primarily to plant uptake (Cooper 1990). Highest removal efficiencies were found to occur during months with high plant cover while a denitrification experiment conducted in one month of this annual study showed that it accounted for only 15 % of the areal uptake of nitrate. In a different headwater New Zealand stream, approximately 60 % of nitrate retention was attributed to the vegetation (a grassed channel consisting of *Glyceria fluitans*) and 20 % to denitrification in a New Zealand headwater stream (Cooper and Cooke 1984). Conversely, Hill (1981) used estimates of algal biomass and daily growth rate to conclude that benthic algae were responsible for 20 % of the nitrate retention and denitrification roughly 65 % in Duffin Creek, Ontario. Kaushik and Robinson (1976) used an estimate of macrophyte standing crop and N yields in watercress plants to conclude that vegetation was only responsible for 1.4% of the summer nitrate retention in Swift's Brook, Ontario, over the summer.

Owens *et al.* (1972) estimated that denitrification could possibly remove 3 times more nitrate than vegetation in the Great Ouse and 115 times more in the River Trent, England. Hill (1983) found similar results in the Nottawasaga river, Ontario, to Duffin Creek in that 63% of the nitrate retention determined from the mass-balance was removed permanently due to denitrification. Jansson *et al.* (1994b) attributed 30 – 60 % of summer TN retention and 20 -50 % of the annual retention in a Swedish river-pond system to denitrification. The authors suggest that vegetation was primarily responsible for the remainder of summer retention not accounted for by denitrification.

However regardless of the mechanism, the main driver determining how much nitrogen a reach will retain (on a mass basis) and at what efficiency (% retention), is discharge. Saunders and Kalff (2001) performed a literature analysis of nitrogen retention in freshwater systems from North America, Europe and Israel and found that differences in retention efficiencies between wetlands (n = 23), lakes (n = 23) and rivers (n = 5) were related to differences in discharge (average discharge 0.1, 0.7, and 18.6 $m^3 s^{-1}$, respectively). Once the data were standardized for discharge there was no significant difference in retention. Jansson *et al.* (1994b) found that the percent TN retention declined exponentially with increasing discharge in the River Råån, Sweden. Significant nitrogen retention only occurred when the discharge was less than 0.2 to 0.3 $m^3 s^{-1}$, or the water residence time was between 1 to 2 days in the 7 km reach. Royer *et al.* (2004) found that denitrification only had a strong influence on nitrate loss under low flow and low nitrate concentrations (July - September) and concluded that hydrology was the primary control of how much nitrate was exported from four eastern Illinois agricultural streams.

Retention efficiency decreases with increasing nitrogen loading (N input to a channel in terms of mass per unit time) and discharge (Jansson *et al.* 1994b, Cooper 1990, Burns 1998, Pind *et al.* 1997). The nitrate retention efficiency for a reach in Duffin Creek, dropped from roughly 30 % (9-12 kg retained per day) when the loading was 30 – 40 kg d^{-1} to less than 5 % (< 5 kg d^{-1}) when loading was > 100 kg d^{-1} and another stream showed a decline from 70% retention to less than 15% over a similar range in inputs (Hill 1988). Even with low retention efficiencies at high discharges, the mass of nitrogen retained within a reach (Δm) increases with loading and/or discharge due to the large supply of nitrogen (Seitzinger *et al.* 2002). Nitrate concentration and loading typically shows a strong positive correlation with discharge (Cooper 1990, Hill 1988, Pind *et al.* 1997, Pind *et al.* 1997) especially in agricultural watersheds where a significant portion of the stream N load may originate from tile drainage (David *et al.* 1997, Mitchell *et al.* 2000).

Discharge affects retention efficiencies because of its effect on water column depth and water residence time. The water residence time (WRT) is the ratio of discharge to water body volume and is a measure of how quickly the volume of water is renewed in a given reach (Mitsch and Gosselink 1986). As the discharge increases, water will spend less time within a reach before being flushed out or renewed. A shorter water residence time means that there is less time available for retention processes to operate within the reach. In addition, an increase in depth associated with higher discharges would decrease the probability of contact between nitrogen in the water column and the stream bed where nitrogen removal primarily occurs.

1.6 Nitrogen retention models

Because of concerns over nitrogen as a pollutant in rivers and coastal waters, several models have been developed to predict N transport along a river continuum. Alexander *et al.* (2000) used a mass-balance model (SPARROW; Smith *et al.* 1997) to estimate the in-stream removal of nitrogen for various sizes of water channel. The model included terms of point source inputs, land use delivery factors and data from 374 U.S. monitoring stations in the Mississippi river basin. They found that the rate of in-stream loss decreased with increasing stream depth from 45 % day^{-1} (retention within the reach was divided by the water residence time) for streams < 1 m deep to 0.5 % day^{-1} for rivers > 4 m in depth. They compared their results with literature estimates of loss rates and found that they "agree reasonably well" with the model and that the comparison provided "limited confirmation of the validity of the SPARROW rates of nitrogen loss".

Seitzinger *et al.* (2002) used published nitrogen removal data from rivers and lakes to develop a model (RivR-N) that would predict the proportion of nitrogen input removed by a river (% removal) based on the ratio of depth (m) to water residence time (yr^{-1}) in 16 drainage networks in the eastern U.S.. The 10 river studies used in the model were conducted over a range of channel sizes from 1 to 6 Strahler order and 0.08 km to 120 km in length, included watersheds that were mostly in pasture, agriculture, forest or a combination of these land use types and used either a mass balance approach or denitrification measurements on sediment cores to estimate N removal within the reach. According to the model, nitrogen removal efficiency (% removal) decreased with increasing stream order but the total amount of nitrogen removed (kg) per metre of stream length increased with higher stream orders. No field studies were conducted to

validate the model and the authors stated that independent studies were needed as comparisons to the model predictions.

1.7 Thesis objectives

Most studies examining the factors controlling nitrogen retention are typically done within a single section of river. Few studies have been conducted *in situ* over an entire stream/river system. Studying a short section of river makes it difficult to determine where nitrogen removal is primarily taking place within a river network and makes understanding the factors that control N removal difficult because channel characteristics tend to remain fairly uniform within a short reach.

The overall objective of this thesis was to test the influence of depth on nitrogen retention within a single riverine network (from headwaters to outflow). A secondary objective was to see evaluate the influence of other in-stream characteristics, such as, discharge, water residence time, nitrogen loading to reach, oxygen concentrations and reducing conditions on nitrogen retention. Where retention is occurring, how much, and which in-stream variables influence retention were examined. I tested the prediction that nitrogen retention (expressed as a percentage of inputs) decreases with increasing stream depth.

Knowing the distribution of nitrogen retention within an entire riverine system is useful for understanding how lotic systems process nitrogen. Understanding the retention capacity of different reaches and the factors that influence retention are important tools for developing strategies to reduce nitrogen levels in rivers. Knowledge of what makes a reach a good nitrogen "remover" could be used to enhance N retention within a

watershed and conversely, considerations can be taken to reduce the amount of N loading to reaches that are known to be poor at retaining nitrogen.

Table 1. Areal nitrogen retention as nitrate (g NO_3-N m^{-2} d^{-1}) and percent retention (retention as a percentage of inputs) of nitrate and total nitrogen in rivers. Areal retention is calculated by mass balance technique and represents summer values (except where noted). The method used to derive percent retention and the specific mechanism responsible for retention (when reported) is recorded in the "% removal attributed to" column. All estimates of % N removal were performed on discrete reaches of river from Sites are roughly organized according to increasing discharge. (NO_3^-) nitrate, (TN) total nitrogen, (a) annual, (s) summer, (w) winter, (bf) baseflow, (US) upstream, (DS) downstream, (MB) mass balance, (AI) acetylene inhibition, (ND) NO_3^- decrease in concentration, (NS) nutrient spiralling.

River/Stream Location	Discharge m^3 s^{-1}	Areal removal (g NO_3-N m^{-2} d^{-1})	% N removed		Experimental approach and % removal attributed to	Reference
			annual	summer		
Purukohukohu, NZ*	0.001a, 0.0008s	0.005 - 0.01	8 (NO_3^-)	30 (NO_3^-)	MB, AI;	Cooper 1990
Walker Br., TN**	0.005 - 0.01bf		0.03 (TN)		MB, AI; 100 % denitrification	Martin *et al.* 2001
Noland Creek, N.C.**	0.001bf		1.5 (TN)		MB, AI; 100 % denitrification	Martin *et al.* 2001
Swift's Brook, Ont.*	0.003s	0.43		56 (NO_3^-)	MB; plant uptake ~ 1 %	Kaushik and Robinson 1976
Swift's Brook, Ont.*	0.003s	0.26 - 0.48	20 (TN)		MB;	Robinson *et al.* 1979
Neversink (US), N.Y.*	0.06s	0.06 - 0.17		16	MB;	Burns 1998
Neversink (DS), N.Y.*	1.4	0.12 - 0.25		15	MB;	Burns 1998

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River/Stream Location	Discharge $m^3 s^{-1}$	Areal removal (g NO_3-N $m^{-2} d^{-1}$)	% N removed annual	% N removed summer	Experimental approach and % removal attributed to	Reference
Gelbæk, DK*	0.02s, 0.1-0.4w		< 1 (TN)	10 (TN)	MB, AI; 100 % denitrification	Christensen and Sørensen 1988
Rabais Bæk, DK*	0.12 yr round		< 1 (TN)	10 (TN)	MB, AI; 100 % denitrification	Christensen and Sørensen 1988
Gelbæk, DK**	0.1a, 0.03s			1 - 11 (TN)	MB; 100 % sediment storage	Svendsen and Kronvang 1993
Gjern, DK**	1.46a, 0.92s			12 - 16 (TN)	MB; 100 % sediment storage	Svendsen and Kronvang 1993
W. Duffin Crk., Ont. *#	0.55s	0.10 - 0.41		12 - 26 (NO_3^-)	MB;	Hill 1988
4 streams in Illinois*	0.5		< 5 (NO_3^-)		NS; 100 % denitrification	Royer *et al.* 2004
Swale-Ouse, UK**	1 – 3		Negligible	5 (TN)	AI; denitrification only	Pattinson *et al.* 1998
Råån, SE*	1.8a	0.14 - 2.74 †	< 2 (TN)	-4 - 24 (TN)	MB, AI; 30 – 60 % denitrification	Jansson *et al.* 1994b
Duffin Crk., Ont. *$	2.5a	0.04 - 0.30	5 - 6 (TN)	50 (TN), 75 (NO_3^-)	MB, ND; 100 % denitrification	Hill 1979
Nottawasaga, Ont.*	3.3s	0.06	1 (NO_3^-)	13 (NO_3^-)	MB, ND: 63 % denitrification	Hill 1983
South Platte River Colorado*	3.5a, 2.5-5.7s	0.53 – 0.70	49 (NO_3^-)	56 – 64 (NO_3^-)	MB: 100% denitrification	Sjodin *et al.* 1997

* estimate of % N removed is for discrete reaches ranging in length from 586 m (Neversink (US)) to 100 km (South Platte River)

** estimate of % N removed is for entire river

range in areal removal and % N removed is for 3 contiguous reaches, A, B and C, of West Duffin Creek

$ range in areal removal is for 6 connected reaches of east and west branches of Duffin creek and estimates of % N removal is for the combined 6 reaches

† areal retention is for TN not NO_3-N and is on an annual basis. Estimate is higher than most summer estimates because of high winter loading and areal retention includes contribution from a pond

Chapter 2

Materials and Methods

2.1 Study area

South Nation watershed

The South Nation watershed in Eastern Ontario, Canada, was chosen as the study area because of its location in a largely agricultural landscape (57 % of land use) (Statistics Canada 1999). This watershed was chosen because the high concentrations of nutrients typically seen in agricultural watersheds were thought to facilitate the study of nitrogen retention due to the detectable presence of N, especially the nitrate fraction.

The South Nation River commences close to the St. Lawrence River near Brockville and flows in a north-easterly direction until its confluence with the Ottawa River near the village of Plantagenet (Fig. 1, Pg. 34). The river is 177 km long and drains 3915 km^2 of land. The river drops by only 84 m over its length through a flat landscape, which combined with extensive clay soils results in generally poorly drained soils and turbid water. The historical annual average discharge of the South Nation at Plantagenet is 42.1 $m^3 s^{-1}$ (Environment Canada 1990). The South Nation has four major sub-watersheds; The Castor (733 km^2), Bearbrook (487 km^2), Scotch (272 km^2) and the Payne (152 km^2).

Wetlands were once a predominant characteristic of the watershed, forming up to 48% of the land in some municipalities (Snell 1987). Today, wetlands cover 4.7% of the watershed with some municipalities having 90% of original wetlands, mostly from land

conversion to agriculture. The area of highest agricultural land-use occurs near the centre of the watershed around Winchester and Chesterville with roughly 78 – 87 % of the land being used for agriculture, while the lowest percentage of farmland (~ 38%) occurs in the headwaters near Spencerville (Statistics Canada 1999). Cropland (corn, soya, wheat) accounts for 70 % of farmland and 40 % of the total land in the watershed.

In 1996, the population of the South Nation was 134 866 persons (excluding municipalities that border or are only partially in the watershed). The total number of farm animals was 167 540, of which 80% were cattle (Statistics Canada 1999).

Site selection

In order to test the role of depth, sites were selected to obtain a broad range in depths from several centimetres to several metres. More shallow sites were sampled than deep sites because a previous study had indicated that retention in headwater streams is more variable (Alexander *et al.* 2000). It was also assumed that there would be more between reach variation (i.e. between reaches of different depths) than variation within a reach at a given depth.

Reaches were selected to minimize within reach variables (depth, water residence time, discharge) while maximizing between reach differences. Reaches were selected with no major tributaries, tile drains or diversions. It was observed that under summer baseflow conditions, tributaries and tile drains were almost always dry and no overland flow was observed. Three sites, North Castor (Hwy 31), North Castor (Sale Barn) and Dump Creek, had tributaries located close to the upstream location representing 0.006 %, 11 % and 15 % of the upstream flow, respectively. Contributions from these tributaries were considered when calculating the upstream loading of chl *a*, nutrients, DOC and

turbidity. One site, Scotch (Concession 15 Road) was not used in any analysis because numerous tributary inputs made the calculation of upstream loading unreliable.

Reaches in a variety of land-use types were sampled in an attempt to achieve a range in nitrogen loading. Sites were also selected based on their road access and the ease of measuring discharge.

2.2 Sampling and field methods

Sampling was conducted during baseflow conditions from June to September 2003 and 2004 (See Appendix II for site names, sampling dates and location). Sampling was not done during periods of precipitation and whenever possible five previous rain free days were preferred.

A total of 29 sites were sampled in 2003. Most sites were sampled once, however, 12 of the sites were sampled 2 - 4 times each (Appendix II). In the summer of 2004, two new sites and one site from 2003 were sampled six times each (Appendix II).

Seven reaches were chosen and sampled along the main stem of the South Nation River in (Fig. 1). Major tributaries of the South Nation River were also sampled, including, the Castor River, Bearbrook, and the Scotch River.

Shallow sites (~ 15 - 50 cm deep) were accessed by foot and were roughly 1 km in length. Medium depth sites (~ 50 cm - 2 m) were sampled by canoe or motor boat and were roughly 1 – 4 km in length, and deep sites (> 2 m) were sampled by motor boat and were 4 – 5 km in length. Reach lengths varied so that they were long enough to observe a change in chemistry, but short enough to minimize the impact of groundwater entering

the reach and to reduce the probability of encountering tributaries. The reach length was based on the lengths used for various stream depths from the literature and preliminary field work.

A general description of the sampling procedure is as follows; each reach is comprised of an upstream (US) and downstream (DS) location defining the length in between. For the walk-in and canoe sites, the DS site was sampled first followed by the US site in order to avoid sample contamination by sampling the same water mass. This was not considered to be a problem at deep sites because of the long water travel times (greater than the time taken to sample) between US and DS locations, so sampling began at either the US or DS site.

At each location, three water samples were collected (see section 2.2.1) and discharge was estimated (see section 2.2.2). A Hydrolab Minisonde 4a multiprobe was used to measure specific conductivity (SpC), oxidation reduction potential (ORP), temperature, pH, and dissolved oxygen (DO) at both the US and DS sites on most of the sampling dates. For some sampling dates, specific conductivity and temperature were recorded using a YSI model 33 S-C-T meter and with DO, pH and ORP not recorded.

Between the DS and US locations, length, width and depth measurements were made in order to estimate the water residence time, benthic surface area and the average depth for the reach. Once the appropriate reach length had been achieved, the US location was sampled in an identical manner as the DS location.

In 2004, the diel (24 hour) variability in nitrogen retention and water chemistry was investigated during two studies conducted at different locations and stream depths. The North Castor River at Parkway Road was roughly 30 cm in depth while the South

Nation River at Plantagenet was 2.77 m deep. One water sample was collected every three hours over a 24 hour period at both US and DS locations. Duplicate water samples were collected at one sampling time (mid-day), resulting in a total of 20 water samples per diel study. Hydrolab readings were measured (temperature, SpC, ORP, DO) and turbidity and planktonic chl *a* levels were determined for each sampling time. Separate Hydrolabs were used at the US and DS locations. Measurements were corrected to a single instrument by making measurements with both machines at both the US and DS locations at North Castor at the surface (shallow site) and at the 0.5 m and 2 m water depths at the US Plantagenet location.

The downstream location at North Castor was sampled 1 hour and 20 minutes after the upstream sampling had occurred. This delay corresponded to the estimated water residence time of the reach (see section 2.2.4 for calculation). The water residence time was estimated from a sampling date in 2003 which had a similar to the discharge during the diel study. Verification of the estimated WRT was conducted after the diel sampling by adding 8 kg of common table salt (previously dissolved in roughly 15 L of water) to the US location and awaiting detection at the DS location with a conductivity meter (Hydrolab). The sampling times were staggered in an attempt to sample the same water parcel. The sampling times at South Nation (Plantagenet) were not staggered because the water residence time exceeded the length of the diel study, 24 hours.

2.2.1 Water collection

Grab samples were obtained at the shallow sites. For medium depth sites, a 1 L Nalgene bottle was attached to a pole and lowered at a constant rate through the water column. For deep sites, a tube sampler was used to obtain a vertically integrated sample.

All bottles were rinsed three times with site water prior to collection and care was taken to avoid disturbing the sediment or surrounding vegetation. Collected bottles were placed in a cooler with ice packs. In 2003, three water samples were collected at US and DS locations and two samples in the middle for longer reaches (medium and deep sites). Two samples at the US and DS locations and one sample at the middle location were analyzed for nutrients (NO_3^-, TKN, and total phosphorous (TP)). In 2004, four samples were collected at the US and DS locations and 3 – 4 samples in the middle for the two L. Castor sites and three US and DS samples and two middle samples at Plantagenet. All L. Castor samples were for nutrient chemistry (NO_3^- and NH_4^+). All US and DS samples at Plantagenet and one sample at the middle site were analyzed for nutrients (NO_3^-, NH_4^+, TKN, reactive phosphorous (RP) and TP). All samples in 2003 and 2004 were analyzed for planktonic chl *a*, and turbidity.

2.2.2 Discharge measurement and calculation

Discharge was measured using the velocity-area method (Herschy 1985). The cross-sectional area of the stream was measured and multiplied by the average velocity passing through that cross section. Discharge was calculated as:

$$Q = V \times A,$$

Where Q = discharge ($m^3\ s^{-1}$), V = average velocity ($m\ s^{-1}$), and A = cross-sectional area of the channel (m^2). The channel cross-section was divided into segments that were separated by verticals. At each vertical, depth and velocity were measured, averaged with adjacent verticals and multiplied by the width between the verticals to obtain the discharge for that segment. The total discharge was then obtained by summing

the discharge for each segment. For example, the discharge passing through segment 5 - 6 using the mean-section method (Herschy 1985) was calculated as follows;

$$q_{5\text{-}6} = ((\upsilon_5 + \upsilon_6) \div 2) \times ((d_5 + d_6) \div 2) \times (b_6 - b_5)$$

Where, $q_{5\text{-}6}$ = discharge through segment 5 - 6

υ_5, υ_6 = mean velocities at verticals 5 and 6

d_5, d_6 = depth at verticals 5 and 6

b_6, b_5 = distance from initial point on the bank to verticals 5 and 6

Discharge measurement sites were chosen in a straight section of the reach where the flow path was parallel with the bank. Sinuous flow patterns and river bends were avoided. Streambeds containing obstructions, such as, large rocks, woody debris and vegetation were avoided due to the turbulence, eddies and dead water zones that they create. Pools and riffles were avoided due to their low velocities and irregular streambed profile, respectively. Runs with a smooth water surface and uniform bed profile or the entrance to a riffle were preferred measurement sites. An attempt was made to have the US and DS discharge sites as similar as possible with respect to cross-sectional area, shape and streambed substrate, thus facilitating comparisons between US and DS discharge.

Once a site had been selected, a tape measure was stretched across the stream at right angles to the bank. Between 15 – 20 verticals were measured across the channel unless the stream was too narrow. Verticals were spaced so that roughly the same amount of water passed through each segment. Vertical spacing decreased as the channel became deeper and/or if the water velocity increased. An attempt was made for each segment to contain no more than 5 – 10 % of the total flow (Herschy 1985). For streams

less than 0.6 m in depth the water velocity was read at a depth of 0.6 times the stream depth starting from the surface. For example, if the stream depth was 0.35 m then the velocity was measured at 0.21 m from the water surface (0.6 × 0.35 m) or 0.14 m from the stream bottom. When the depth exceeded 0.6 m, measurements were made at 0.2 and 0.8 of the stream depth from the surface and the average was taken as the mean velocity (Herschy 1985). Flow was measured using a Swoffer c-140 wading rod. This unit consists of a propeller mounted on a sliding rod. The machine was set to display a velocity that was averaged over 30 seconds. The MDL of the unit is 0.03 m s^{-1}, however the machine displayed velocities as low as 0.01 m s^{-1} which were recorded.

For tributaries entering a study reach that were too shallow to permit the use of the Swoffer unit (~2 cm), velocity was estimated by recording the time necessary for a float to travel a known distance. For tile drainage and small tributaries with a waterfall, discharge was calculated by recording the amount of time necessary to fill a container of a known volume.

All discharge measurements were made by wading into the stream except for the South Nation River at Highway 9 on August 7, 2003. On this date, the water velocity was sufficiently high to permit US and DS discharge measurements from a boat. The method is the same as outlined above.

Slow water velocities (< 0.01 m s^{-1}) along the main channel of the South Nation River did not always permit both US and DS discharge measurements except at South Nation River at Ventnor, which was a long riffle zone, and South Nation (Hwy. 9) as mentioned above. Flow for the South Nation at Hyndman, Sandy Row Rd., Chesterville and Lemieux was measured in abnormally shallow sections and at only one location

within each reach. Discharge for the main stem of the South Nation River at Plantagenet, where velocities were too low to allow measurement, was obtained from the Water Survey of Canada (http://www.wsc.ec.gc.ca) continuous gauging site (station # 02LB005) located around 4 km US of the reach. Discharge for the South Nation (Hwy. 9) on September 23, 2003 was obtained from the discharge relationship between South Nation (Hwy. 9) and station 02LB005 located around 11 km DS, on August 7, 2003.

2.2.3 Reach dimension measurements and calculations

Numerous width, depth and length measurements were made in each reach to calculate the depth, water residence time and benthic surface area for the reach. Measurements were made once for each site. For sites that were sampled more than once, only the nitrogen retention results obtained the day of the measurements were used in the analysis since depth, WRT and benthic surface area would change from one sampling date to another due to changes in river discharge. An exception to this were sites where the stream depth was continuously monitored. Known changes in stream depth allowed adjustments to the original measurements to reliably calculate depth, WRT and surface area for different dates.

Depth loggers (pressure transducers) were installed in both L. Castor sites in 2004 to monitor stream depth. Corrections to reach measurements made for South Nation (Plantagenet) and South Nation (Hwy. 9) were obtained from water level recordings made at station 02LB005.

Measurements were made whenever the reach changed shape markedly in width and/or depth, i.e. from pool to run. This was roughly every 15 – 50 m for shallow sites.

For larger reaches, the shape generally remained fairly constant and was measured roughly every 200 m for medium depth sites and every 400 – 500 m for deep sites.

Length measurements were recorded with a Norpak hip chain for all sites except for the South Nation River at Chesterville, Lemieux, Plantagenet, and Hwy. 9 due to their long length. For these sites, the location of the width and depth measurement sites were recorded with a GPS unit and the length between measurement sites was obtained using GIS software (ArcMAP 9.0).

Width and depth were measured with a tape measure and metre stick, respectively, at shallow and medium depth sites. For deep sites, width was measured using a Norpak hip chain and depth was recorded using a 5 m pole marked off at 5 cm intervals. For shallow sites and some medium depth sites (generally less than 10 m in width), depth was recorded at ¼, ½ and ¾ the channel width (placement by eye). For wider channels, generally 8 -12 depth measurements were recorded. Width and depth measurements were collected to calculate the channel cross-sectional area.

The volume of the reach was obtained by summing up the volume of individual segments. Each segment volume was calculated by multiplying the length between two cross sections with the average area of those two cross sections.

The weighted mean depth for the reach was calculated by multiplying the length between two cross sections with the average of the mean depth from each cross section. This value was summed over all cross sections and then divided by the total length of the reach. The mean depth for each cross-section was calculated by dividing the cross-sectional area by the channel width. Multiplying the mean depth by the length over which it occurs weighs the contribution of that depth over the length of the reach.

The benthic surface area of a reach was calculated by multiplying the length between two cross sections with the average of the channel width along the bottom from each cross section. The channel width along the bottom was calculated using the existing cross-sectional measurements (surface width and depth) and the Pythagorean Theorem ($c^2 = a^2 + b^2$) solving for the length of the hypotenuse (streambed) of a right sided triangle. Pythagorean Theorem was also used to determine the length along the bottom of the channel between two cross sections.

2.2.4 Water residence time calculation

The water residence time (WRT) is the time it would take for the reach to fill up if it were empty at a given discharge. It was calculated by dividing the volume of the reach (V_R) with the average of the US and DS discharge (Q), or by a single discharge if only one was measured;

$$WRT = V_R / Q \quad (1)$$

2.3 Laboratory Analysis

2.3.1 Nutrients

Samples collected in 2003 were analyzed for total phosphorous (TP), total Kjeldahl nitrogen (TKN) (TKN includes dissolved organic-N, particulate organic-N and $NH_3 + NH_4^+$) and nitrate + nitrite ($NO_3^- + NO_2^-$). Nitrate and nitrite were measured together and are presented singly as NO_3^- because nitrite levels are typically very low compared to nitrate. Plantagenet 2004 samples were also analyzed for reactive phosphorous (RP) and ammonia + ammonium ($NH_3 + NH_4^+$), determined separately from

the TKN fraction. Samples were analyzed within 24 hours at the Robert O. Pickard Environmental Centre Laboratory (city of Ottawa) using standard methods (Regional Municipality of Ottawa-Carleton 1993). All nitrogen fractions are expressed as mg N L^{-1}. The method detection limit (MDL) were; 0.003 mg L^{-1} for $NH_3 + NH_4^+$; 0.003 mg L^{-1} for $NO_3^- + NO_2^-$, 0.02 mg L^{-1} for TKN; 0.002 mg L^{-1} for RP; and 0.005 mg L^{-1} for TP.

All samples collected in 2004 were analyzed for $NO_3^- + NO_2^-$, expressed solely as NO_3-N, at the University of Ottawa on a Lachat QuikChem FIA+ 8000 series autoanalyzer according to QuikChem Method 10-107-04-1-C (Lachat Instruments 2000), MDL 0.002 mg L^{-1}. Samples were filtered upon return to the lab from field collection through 0.45 μm Sartorius cellulose acetate filters (11106-47-N) and were either refrigerated and analyzed within 24 hours or frozen for analysis at a later date.

Both Little Castor sites were also analyzed for $NO_3^- + NO_2^-$ and NH_4^+ at the Eastern Cereal and Oilseed Research Centre (ECORC), Agriculture Canada, Ottawa. Analysis was performed on a similar Lachat autoanalyzer according to the same method for nitrate and QuikChem Method 10-107-06-01-J (Lachat Instruments 2001) for ammonium with an MDL of 0.002 mg N L^{-1}. The samples were filtered as mentioned above and immediately frozen until analysis at Agriculture Canada.

2.3.2 Turbidity

All samples were analyzed for turbidity with a Lamotte 2020 Turbidimeter. The machine type is a nephelometric meter calibrated in NTU. Accuracy is 0.05 or ± 2 %, whichever is greater.

2.3.3 Chlorophyll

Suspended chlorophyll samples were collected by filtering 300 – 500 ml of sample water through Whatman 934-AH glass microfibre filters (1.5 μm particle retention). Pigments were extracted with dimethyl sulfoxide (DMSO) heated to 65°C for 10 minutes. The glass fibre filter paper was then ground and filtered with 90 % acetone (Burnison 1980). Chlorophyll *a* pigment concentrations were calculated using the equations of Jeffrey and Humphrey (1975).

2.4 Retention and loading calculations

Retention refers to what is retained within the reach as a particular substance passes through the reach. Retention represents a loss that may either be permanent and/or temporary. Reaches may also act as a source with more substance leaving the reach than initially entered, resulting in a net increase to the river network.

Retention was calculated for turbidity, chl-*a*, and nutrients. A positive number indicates retention within the reach (a net loss), whereas negative numbers reflect loading along the reach (a net gain).

Retention efficiency was calculated as the change in nitrogen concentration over the reach expressed as a percentage of the inputs to the reach;

$$\text{Retention (\%)} = (([US] - [DS]) \div [US]) \times 100\% \quad (2)$$

In certain analyses, the percent retention was normalized to account for the large differences in reach size with percent retention being expressed on a per m^2 basis.

The variability associated with the percent retention value was calculated as the Standard Error of the Ratio and was expressed as a percent;

$$SE_R\ (\%) = \sqrt{((SEd_{iff} \div diff)^2 - (SE_{US} \div [US])^2)} \times (([US] - [DS]) \div [US]) \times 100\% \quad (3)$$

Where, SEd_{iff} is the standard error of difference between the upstream and downstream means (Zar 1999;pg. 124), diff is the upstream average concentration minus the downstream average concentration, SE_{US} is the standard error of the upstream mean (Zar 1999; pg 77), [US] and [DS] is the average concentration at the upstream and downstream location, respectively.

The amount of nitrogen on a mass basis (g) retained within a reach was expressed on an areal basis (m^2) according to the equation;

$$\text{Areal retention } (g\ m^{-2}\ d^{-1}) = ([US] - [DS]) \times Qavg \div B.S.A. \quad (4)$$

Where, [US] = upstream concentration, [DS] = downstream concentration, Qavg = the average of the upstream and downstream discharge, B.S.A. = benthic surface area. The equation was multiplied by 86400 seconds to express the rate per day.

The standard deviation for the areal retention was calculated according to the rules of subtracting, multiplying or dividing standard deviations. The fractional standard deviations (standard deviation divided by value) for each term in equation (4) were squared, summed and then the square root was taken to get the fractional total deviation. The total error was then derived by multiplying the retention value calculated in equation (4) by the fractional total deviation according to the following equation;

Standard deviation of areal retention ($g\ m^{-2}\ d^{-1}$)

$$= X \times \sqrt{((S_{diff} \div diff)^2 + (S_{Qavg} \div Qavg)^2)} \quad (5)$$

Where, X = value calculated in equation (4), S_{diff} = standard deviation of the difference between upstream and downstream concentrations (see equation 6), diff = difference between upstream and downstream concentration, S_{Qavg} = standard deviation surrounding discharge measurements which was determined to have an error of 3.8 % (see pg. 36 and Appendix III). The error surrounding the measurement of benthic surface area was not determined and is therefore not included in the equation.

The standard deviation for the difference between the upstream and downstream concentration (S_{diff}) was determined by squaring the standard deviations of the upstream and downstream chemistry, summing them and then taking the square root;

$$S_{diff} = \sqrt{(S_{[US]}^2 + S_{[DS]}^2)} \quad (6)$$

The nutrient loading entering the reach was determined by;

$$\text{Areal Loading } (g\ m^{-2}\ d^{-1}) = [US] \times Qavg \div B.S.A. \quad (7)$$

Explanation of the terms is the same as equation (2). The calculation of the standard deviation surrounding areal loading is similar to equation (3);

Standard deviation of areal loading ($g\ m^{-2}\ d^{-1}$) =

$$X \times \sqrt{((S_{US} \div [US])^2 + (S_{Qavg} \div Qavg)^2)} \quad (8)$$

A new upstream concentration was calculated for the three shallow sites that had tributary inputs. The stream and tributary concentrations were multiplied by their respective discharge and summed to calculate the total mass entering the reach per second. This value was then divided by the combined discharge (reach plus tributaries) to arrive at a new upstream concentration that was used in equation 2 and 4.

2.5 Statistical Analysis

All statistical analysis was performed with Systat version 11 (SPSS Inc.). Maps were created using ArcMap version 9.0 (ESRI Inc.). All literature data used in figure 25 and some points in figures 26 and 27 were obtained from published figures using GetData version 2.21 (S. Federov).

Two tailed two sample t-tests assuming equal variance and an alpha level of 0.05 were used to determine whether there was a significant difference between upstream and downstream chemistry for each reach. The power of the t-test to detect deviations from the null hypothesis and the sample size required to achieve a power of roughly 0.8 was determined using power analysis in Systat or GPOWER version 2.0 (F. Faul and E. Erdfelder, 1992) when the sample size in each group was uneven. When there was no variance at either upstream and downstream locations, the t-test was calculated by hand using an estimated variance based on the average nutrient coefficient of variation of all the sites in 2003.

Simple linear, non-linear and multiple regressions of nitrogen retention (expressed as either as a percent or areal basis) versus possible explanatory variables such as depth, areal N loading (N entering the reach from upstream) or percent turbidity and/or chl *a* retention were performed and the residuals were tested for normality using the Kolmogorov-Smirnov and Lilliefor's tests. Equal variance of the residuals was assessed with the scatterplot of residuals versus expected model estimates.

Non-linear decay models and parameters were initially estimated using SigmaPlot, then the best model (highest r^2) was run in Systat where the model assumptions were tested (same as linear regression).

Logarithmic transformations were primarily used to eliminate data that displayed N loading (-ve value in retention formula) and to improve the fit of the model. Arcsine transformation of percentage data did not improve any of the statistical models.

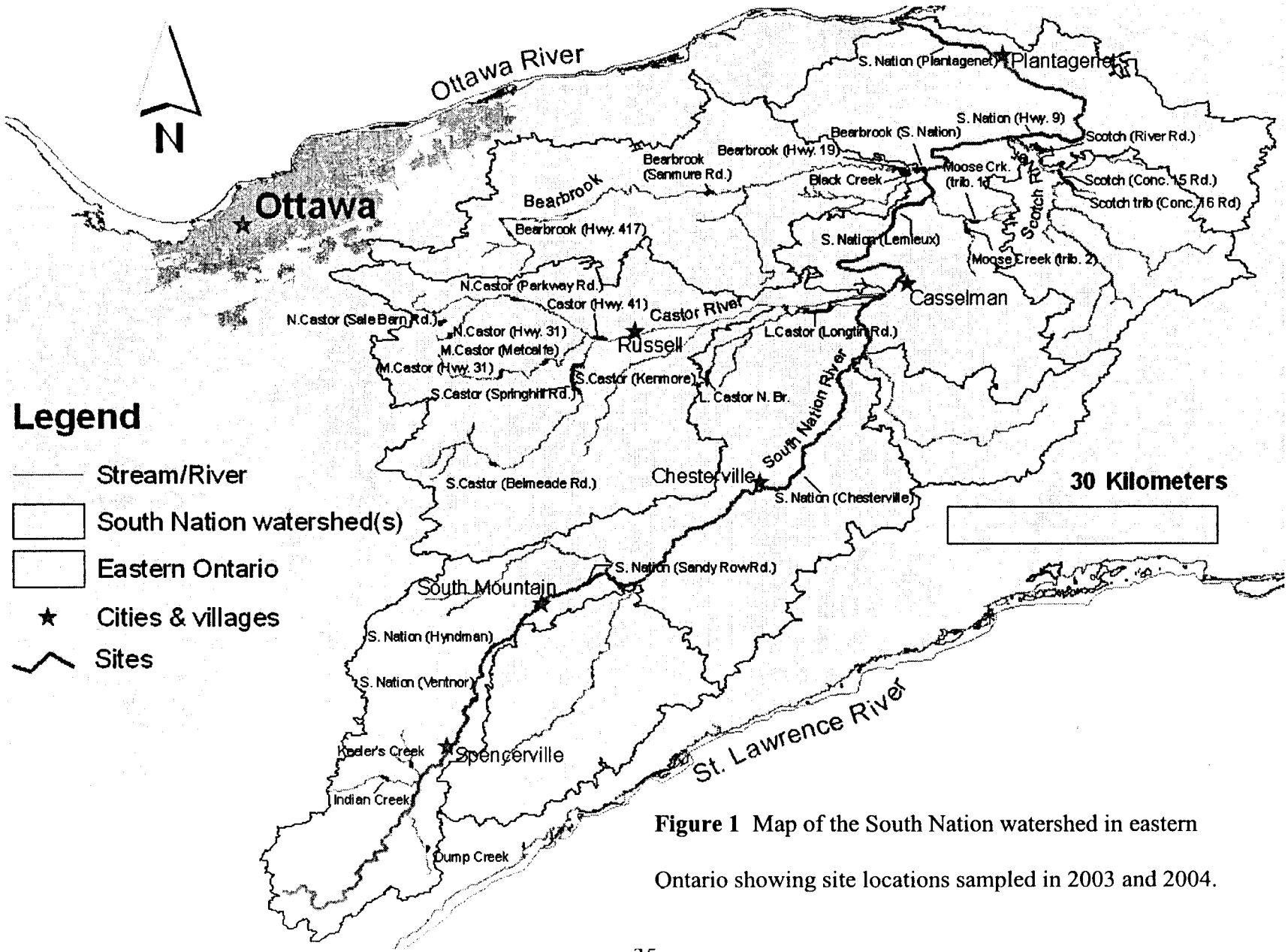


Figure 1 Map of the South Nation watershed in eastern Ontario showing site locations sampled in 2003 and 2004.

Chapter 3

Results

3.1 Physical characteristics of sites in 2003

Study sites ranged in size from a tributary of the Scotch River 0.08 m deep and 0.9 km long to a reach with a depth greater than 2.5 m and 4.8 km in length on the main branch of the South Nation River at Plantagenet. A total of 28 different sites were sampled: 22 sites < 0.50 m in weighted mean depth, 4 sites between 0.6 – 2 m and 2 sites > 2 m. Some sites were sampled more than once bringing the total number of data sets to 46 (see Appendix II). Analyses involving water residence time, depth or streambed surface area have fewer than 46 data points because these variables were not estimated for sites that were sampled more than once, except for the South Nation River at Hwy. 9 and Plantagenet which were continuously gauged. A summary of the physical, biological and chemical characteristics of the sites sampled in 2003 is provided in Table 2. The water column was generally well oxygenated with most concentration falling within 5 to 15 mg O_2 L^{-1}.

The prediction of decreased nitrogen removal efficiency with increasing stream depth is assumed to be due to the increase in water volume relative to bottom area as streams get deeper. Figure 2 shows that the volume of a reach of uniform width and depth increased exponentially with depth. The benthic surface area (the main site for nitrogen removal) also increased exponentially with increasing depth, but not to the same

extent as volume (results not shown). As a result, there is less contact between the water column and sediments as a stream deepens. Figure 3 shows that the benthic area available to process each cubic metre of water declined exponentially with increasing depth. For example, a 0.09 m deep headwater site on the North Castor had 12.6 m^2 of sediment available to process each cubic metre of water, whereas, close to the outflow of the South Nation River at Plantagenet (depth 2.76 m) there was only 0.36 m^2 to process each cubic metre of the water column. Figure 3 does not take into account current velocity and thus the amount of time available to process each cubic metre of water. A similar pattern is observed as in figure 3 when the ratio of benthic surface area to volume is divided by the water residence time.

Discharge measurements between the sites ranged over four orders of magnitude in 2003 (Table 2). The discharge at shallow sites (< 0.5 m) displayed a great deal of variation and ranged anywhere from roughly 0.001 $m^3 s^{-1}$ to close to 0.4 $m^3 s^{-1}$.

Two main sources of error surrounding the discharge values are the measurement error and the sampling error associated with site characteristics. The low gradient of the South Nation posed a significant challenge in measuring discharge. Difficulties in obtaining precise values of discharge were primarily due to low water velocities and instrument detection limits. The measurement error was determined by repeating discharge measurements three times at identical vertical positions at four different locations on three different streams (Appendix III). The average coefficient of variation for all sites was 3.8 %. Sampling error was influenced by the specific channel properties at the site. Obstructions, such as rocks, an uneven streambed profile and aquatic vegetation can alter flow patterns and affect the precision of the measurement. The size

of the channel (in terms of cross-sectional area) can also affect the precision of the discharge measurement. Two locations close to each other along a stream should display the same discharge if there are no additional surface or groundwater inputs. However, it was noted that measurements made in riffles led to higher discharge values than measurements made in adjacent runs or slow moving pools. Discharge was measured at two locations close together (1 to 50 m apart) on three different streams which displayed a range in discharge between 0.007 $m^3 s^{-1}$ to 0.396 $m^3 s^{-1}$. The coefficient of variation for the three pairs of measurements ranged from 3 % to 12 %. This sampling error was larger than the measurement error and appeared to be related to the size of the channel cross section with the smaller cross sectional area consistently having the higher discharge value. The lower discharge values associated with a larger cross sectional area is probably due to detection problems of the instrument at low velocities that arises when a given volume of water passes through a relatively larger channel area compared to another site close by with a smaller cross sectional area. Installation of a weir would produce more precise measurements of discharge with greater accuracy and would reduce the sampling error associated with in discharge measurements. This was not possible considering the number of sites visited in 2003, as well as the cost and regulatory approval necessary for weir construction.

Discharge was measured manually at the village of Plantagenet on July 16, 2003. The measured discharge of 3.018 $m^3 s^{-1}$ was the same as the value reported from the Water Survey of Canada discharge station (02LB005) located 2.5 km upstream of Plantagenet for the same day (3.02 $m^3 s^{-1}$).

3.2 Chemical characteristics of sites in 2003

Total combined nitrogen and nitrate ranged from 0.46 mg L^{-1} to 8.67 mg L^{-1} and 0.003 mg L^{-1} (detection limit) to 7.82 mg L^{-1}, respectively across the sites (Table 2). Nitrate concentrations showed no pattern with respect to stream size (Fig. 4). High nitrate levels were found in both tributaries and in the lower portion of the South Nation River (north of the village of Casselman), while the upper reaches of the main branch of the South Nation River had low or below detection levels. The highest nitrate concentration (7.82 mg L^{-1}) was observed at Dump Creek. This site was located about 800 m downstream from a public landfill site outside the village of Maynard. Total Kjeldahl-N (TKN) levels did not appear to be affected by the presence of the landfill (Fig. 4).

Total Kjeldahl-N showed higher levels along the main branch of the South Nation River (1 - 1.5 mg L^{-1}) than tributaries within the watershed (< 1 mg L^{-1}) with the exception of Keeler's Creek which displayed the highest concentration of TKN in the watershed (2.3 – 2.4 mg L^{-1}) based on two sampling dates (Aug. 13th and June 26th) (Fig. 4).

Similarly to nitrate, TN showed no pattern with respect to stream size. However, in contrast to nitrate, TN was consistent (1- 2 mg L^{-1}) along the length of the South Nation River (Fig. 5) due to high TKN levels.

In general, TN was dominated by TKN within the watershed (Fig. 6). Total Kjeldahl-N usually formed the dominant fraction when TN concentrations were less than 1.5 mg L^{-1} while nitrate became the dominant form as TN levels increased (Fig. 7). An exception was the headwater site Keeler's Creek which displayed unusually high levels

of TKN for the given concentration of TN. Both nitrate and TKN concentrations increased with increasing TN concentrations, however, TKN appeared to level off at around 1.5 mg L^{-1}, while nitrate continued to increase (Appendix IV and Fig. 7).

Total phosphorous concentrations generally increased downstream in both the South Nation River and Bearbrook. The Scotch River, Moose Creek and Keeler's Creek showed high TP levels despite their low stream order (Fig. 5).

Headwater conductivity was highly variable (223 – 1109 mS cm^{-1}) compared to sites along the South Nation River (400 to 600 mS cm^{-1}) (Appendix V). The main branch of the South Nation River displayed the highest overall concentrations (20 – 30 mg L^{-1}) of dissolved organic carbon with tributaries generally below 15 mg L^{-1} (Appendix V). Exceptions are Keeler's Creek which had the highest concentration in the watershed (55 mg L^{-1}) and both Moose Creek tributaries which have areas of peat within their headwaters. Turbidity was highest north of the village of Casselman where there is an extensive deposit of Leda clay (rock flour produced by glacial abrasion) (Appendix VI). Planktonic chlorophyll *a* concentrations increased downstream along the main branch of the South Nation River (Appendix VI). High levels of chl *a* at three headwater sites were probably attributed to the site being located within or directly below a damned up area which resulted in an increase in stream volume and water residence time.

3.3 Nitrogen retention across sites in 2003

Both retention and loading were observed for all nitrogen forms across the 28 different study reaches sampled in 2003, that is, less nutrients left the downstream end of the reach than had entered (retention) or more left the reach than had entered at the

upstream end (loading). Headwater and deep sites displayed a similar range in the percent increase or decrease of nitrogen over the length of the reaches (Appendix VII). Nitrate retention (as a % of inputs) at the two deep sites (Scotch-Paxton and Jessup-Plantagenet) ranged from – 20 to 70 %, while headwater sites ranged from -25 to 91 %. Total Kjeldahl-N at the two deep sites experienced loading between by 5 to 22 % while headwaters ranged from 12 % loading to 24 % retention. The largest nitrate retention (91 %) occurred over a 2 km reach roughly 0.30 m deep where the nitrate concentration dropped from 0.08 ± 0.01 mg L^{-1} to 0.01 ± 0.005 mg L^{-1}. Two different sites experienced the highest nitrate loading of 25 %. Both sites were 0.41 m deep and roughly 800 m in length; the nitrate concentration increased from 0.12 ± 0.003 mg L^{-1} to 0.15 ± 0.003 mg L^{-1} at Moose tributary # 2 and from 0.02 ± 0.003 mg L^{-1} to 0.03 ± 0.01 mg L^{-1} at Middle Castor (Metcalfe), but the difference was not significant at the latter site. Some sites showed extremely high loading values (i.e. M. Castor Metcalfe, Aug. 22, at 567 %) because the upstream chemistry was at detection resulting in a very small denominator in the calculation of % retention (Eq. 2) (Appendix VII). Sites with upstream or downstream chemistry at detection were not used in the data analysis.

For nitrate, 13 sites displayed retention, 1 no change and 10 sites indicate loading; for TN, 18 sites displayed retention, 1 no change and 11 sites loading (Appendix VII).

Upstream and downstream chemistry (Appendix VII) were compared using a two sample t-test (two-tail assuming equal variance, $\alpha = 0.05$) to examine if the observed retention or loading was significant. In cases where the replicate water values at both upstream and downstream locations were the same, the variance was estimated by multiplying the average concentration of each location with a coefficient of variation

(CV) of 4.1 %. This is the average CV for nitrate replicates sampled in 2003. This average CV is a high estimate of the chemistry variability because the median CV was considerably lower (approximately 0 %).

For nitrate and TN, about half of the sites showed a difference between US and DS locations (Appendix VII). Post-hoc power analysis revealed that an increase in sample size from duplicates to 3-5 samples collected at each upstream and downstream location would have achieved a high probability (0.8) of detecting a difference in around a third of the non-significant nitrate comparisons and two-thirds for TN. The alternative hypothesis (H_1) in the power test is that the difference between the two means does not equal zero.

When percent retention was standardized by benthic surface area to account for the different sizes of reaches (roughly 850 m^2 to 780 000 m^2), nitrate and TN retention appeared to decrease exponentially and approached 0 % at the deeper sites (Fig. 8 and 9, respectively). Six sites were not included in Figure 8 because nitrate concentrations were at detection at the upstream and/or downstream locations thus not allowing for a correct estimate of percent retention standardized for reach size (i.e. the point along the reach where the concentration dropped to detection was unknown). In addition, a site which resulted in insignificant model parameters was removed from Figures 8 and 9 because of high nitrate and TN loading that may have been the result of a dam at the downstream end which created a watercourse that was more similar to a pond than stream.

There was no significant relationship (i.e. exponential decline) between percent nitrate retention and depth ($p = 0.31$). Percent retention of total nitrogen displayed a significant exponential decay with depth ($p = 0.0003$), however the residuals were not

normal. Arcsine transformation did not improve the normality or variance of the residuals. However, nitrate and total nitrogen displayed a significant decrease in percent retention per square metre with increasing stream depth when the data were log transformed, resulting in the loss of sites with negative retention, i.e. loading (Fig. 10 and 11, respectively). In Figure 10, there were no data points around 1 m depth because at one site (at 0.69 m deep) nitrate was at the detection limit upstream and downstream, while the other site (at 1.12 m) displayed retention but the downstream was at the detection limit and was therefore not included in the analysis.

On an areal basis (g m^{-2} d^{-1}), nitrate and TN retention did not appear to decrease with depth. The highest areal nitrate retention (0.73 g m^{-2} d^{-1}) was observed at a deep site, Scotch-Paxton August 7, which had a moderate retention (9 %) between the upstream and downstream locations (Appendix VII). This high areal retention was driven by an extremely large discharge (29 m^3 s^{-1}) (see equation 4).

Areal retention generally increased with more loading (input to a reach) (Fig. 12). Nutrient loading to a site provides a reasonable estimate of areal N retention when a sub-set of the data in figure 12 was used that only included sites that retained nutrients (Fig. 13 and 14). More nitrogen is retained the larger the nitrogen load across different sites. When a statistical outlier was removed from Figure 13, the r^2 increased to 0.78 and the p value decreased to 0.0001. The outlier site was the shortest reach sampled (277 m) and sampling such a short length could have possibly increased the error around the estimated retention.

Percent TN retention displayed a significant positive relationship with percent retention of turbidity (Fig. 15) ($r^2 = 0.25$, $p = 0.0007$). Two statistical outliers were

removed that both displayed large leverage. One site was more similar to a pond than stream (same site removed from figures 8 and 9), while the other site was a forested headwater stream. Inclusion of the outliers still produced significant results. A positive significant relationship with percent retention of turbidity was also found for percent TKN retention ($y = 0.12\ (x) - 1.20$; $r^2 = 0.21$, $p = 0.002$, $n = 42$) and percent TP retention ($y = 0.33\ (x) + 0.05$; $r^2 = 0.38$, $p < 0.0001$, $n = 42$). The same data points removed in the TN analysis were also removed for these analyses, while inclusion of outliers still produced a significant result for TKN but not for the TP regression. Percent nitrate retention did not show a significant relationship with percent retention of turbidity.

Percent TKN retention showed a significant positive relationship with percent retention of planktonic chl *a* (Fig. 16) ($r^2 = 0.17$, $p = 0.008$, $n = 40$). Four data points with large leverage were removed. Three of these points were from the same site, Plantagenet, which displayed lake like conditions of long water residence times and high nutrients compared to most other sites. In addition, the US end of the Plantagenet reach had unusually low chl *a* concentrations for a river of that size most likely due to filtering of chlorophyll in a large riffle zone just US of the study reach. The fourth site was a forested headwater stream. Inclusion of all outliers still produced marginally significant results. Percent nitrate, TN or TP retention showed no significant relationship with percent retention of chl *a*.

Percent nitrate retention showed a significant relationship with changes in reach redox potential (Fig. 17). Positive numbers on the x-axis in figure 17 indicate that the redox potential in the water column has decreased over the length of the reach. As an example if the US redox potential is 303 mV and the DS is 289 mV, then the percent

change in redox potential over the reach is (303 mV – 289 mV) / 303 mV × 100% = 4.6 %. No significant relationship was seen between changes in redox potential and retention of TKN, TN or TP. There were no observed relationships between percent nitrate, TKN, TN or TP retention and changes in oxygen concentration (expressed as a %) or absolute oxygen concentrations. There was no relationship between oxygen concentrations and depth, discharge, temperature or ORP.

Multiple regressions including both turbidity and chl *a* explained more of the variability in TKN retention ($r^2 = 0.38$, $p = 0.0002$, $n = 38$) and TP retention ($r^2 = 0.53$, $p < 0.0001$, $n = 38$) than either independent variable alone. The sites removed in the multiple regressions were the same of those removed in the two separate simple linear regressions of turbidity and chl *a* with percent TKN retention. A Pearson correlation matrix of percent retention of turbidity and chl *a* showed that the two variables were not correlated ($r = 0.26$, $p = 0.12$, $n = 38$). Multiple regressions were not significant with nitrate and TN.

3.4 Seasonal characteristics at three sites in 2004

Seasonal changes in physical, biological, chemical and retention values were examined at three locations in 2004 (see Appendix II and Fig. 1). These sites were chosen as examples of shallow, medium and deep reaches. The Little Castor North Branch site was roughly 12 km upstream from the Little Castor site at Longtin Road. A large tributary enters the L. Castor between to two L. Castor sites (see Fig. 1). The third site was on the main branch of the South Nation River at Plantagenet which was also sampled in 2003. The average depth at L. Castor N. Br., Longtin and Plantagenet was

0.24 m, 0.56 m and 2.73 m, respectively and the lengths were 1.85 km, 2.8 km and 4.8 km, respectively. A summary of the physical, biological and chemical characteristics of the sites sampled in 2004 is provided in Table 3. For L. Castor N. Br. and L. Castor Longtin, only nitrate and ammonium were processed due to difficulties encountered in TKN and TP sample analysis at Agriculture Canada (Appendix VIII).

At L. Castor N. Br., there were 10 observed tile drains and three tributaries originating from ditches. On July 13th at L. Castor N. Br., all 13 tile drains and tributaries were flowing and the stream nitrate concentration increased dramatically from 0.59 mg L^{-1} at the upstream end to 3.38 mg L^{-1} at the downstream end 1.85 km away. The tile drainage nitrate concentration on this date ranged from roughly 8 mg L^{-1} to 15 mg L^{-1}. On the other sampling dates at L. Castor N. Br. there were fewer tile drains flowing with smaller flow and lower nitrate concentrations (roughly 3 mg L^{-1} to 4 mg L^{-1}). When tile drains and tributaries were flowing into L. Castor N. Br., the upstream nitrate concentration of the reach was recalculated taking into account the contributions from the inflows and it was found that these inputs influenced the upstream concentration from no change to roughly a 7 % increase. The data from the 13th of July were not used in the analysis due to the loading uncertainty associated with so many inputs.

Longtin displayed the greatest temporal variation of the three sites in terms of depth, discharge, and nitrate concentration (Table 3). Nitrate was at detection during low flow at Longtin and showed the highest recorded value within the South Nation watershed (8.32 mg L^{-1}) at its highest flow (Fig. 18 B). Both L. Castor N. Br. and Longtin showed a significant positive relationship between nitrate concentration and flow (Fig. 18 A and 18 B, respectively). The highest discharge data point at Longtin displayed

large leverage, however, it was retained because it was probably an outlier due to the lack of data points between 0.3 and 0.9 $m^3 s^{-1}$. The relationship was no longer significant for Longtin (Fig. 18 B) when the highest discharge data point was removed ($r^2 = 0.35$, $p = 0.30$). There was no significant linear relationship between nitrate concentration and discharge at Plantagenet (Fig. 18 C).

At Plantagenet in 2003 and 2004, nitrate, TKN, TN, TP and turbidity all showed a large range in values for low discharge values (< 5 $m^3 s^{-1}$) while the largest values for each variable were always at the highest discharge (118 $m^3 s^{-1}$). Total Kjeldahl-N and TP at Plantagenet showed a significant positive linear relationship with discharge in 2004 ($n = 5$) ($r^2 = 0.95$, $p = 0.004$ and $r^2 = 0.89$ $p = 0.02$, respectively) which experienced a large range in discharge (3 to 118 $m^3 s^{-1}$); there were no significant relationships in 2003 because of the low range in discharge (Appendix IX). Without the highest discharge data point in 2004, there was no significant relationship between TKN or TP with discharge. Downstream chemistry showed similar results with respect to discharge.

Total Kjeldahl-N and TP concentration increased with turbidity at Plantagenet in 2003 and 2004 (Appendix X), except for TKN at the downstream location ($r^2 = 0.37$). There was no significant relationship between nitrate and turbidity.

The nitrate concentration at Plantagenet in 2003 and 2004 displayed a significant linear relationship with TN concentration ($r^2 = 0.98$, $p < 0.0001$), while TKN showed no relationship with either nitrate or TN ($r^2 = 0.14$, $p = 0.32$ and $r^2 = 0.25$, $p = 0.17$, respectively) (Appendix XI). Results are similar for the upstream location for each year analyzed separately.

3.5 Seasonal nitrogen retention at three sites in 2004

Nitrate retention at each site varied from June to September (Fig. 19). L. Castor N. Br. experienced the highest seasonal average retention, of 18 ± 13 %, while L. Castor Longtin had the lowest retention (overall loading) at -7 ± 48 %. The large error for Longtin on August 26 (Julian day 239) was due to roughly half the nitrate samples being at detection.

The percent nitrate retention decreased significantly ($r^2 = 0.91$, $p = 0.01$) over a narrow range of depth for L. Castor N. Br. (Fig. 20 A). L. Castor (Longtin Rd.) also showed a general pattern of decreasing nitrate retention and even loading with increasing channel depth (Fig. 20 B). The deepest site, Plantagenet, showed no relationship between depth and nitrate retention (Fig. 20 C). Percent nitrate retention also displayed a negative correlation with discharge and nitrate concentration for L. Castor N. Br. (Appendix XI).

The percent nitrate retention at L. Castor N. Br. increased when the amount of time that water took to travel through the reach increased (Fig. 21). Percent nitrate retention decreased with increased loading (Fig. 22). Increasing discharge was negatively correlated to water residence time and positively correlated to areal nitrate loading to a reach (Appendix XII). Nitrate retention on an areal basis showed a marginally insignificant decline ($r^2 = 0.70$, $p = 0.08$, $n = 5$) with increased areal nitrate loading (Fig. 23). Maximum retention at L. Castor N. Br. occurred during periods of low nitrate loading and high water residence time.

Similarly to the 2003 data, upstream and downstream chemistry were compared using a two sample t-test to see if the observed loading or retention was significant. Retention at L. Castor N. Br. was significant except for August 9, 2004 (Julian day 222)

due to high variability in US chemistry (Appendix VIII). Three dates displayed a significant difference between US and DS chemistry at L. Castor (Longtin), two dates were not significant and one date, 29 June (Julian day 181), showed no change in concentration between upstream and downstream locations (Appendix VIII). Half the dates at Plantagenet showed a significant difference between upstream and downstream chemistry (Appendix VIII).

3.6 Diel variability in chemical characteristics and nitrogen retention

Two diel experiments were conducted in 2004. One at a deep site, Plantagenet (weighted mean depth 2.78 m) and one at a shallow site, Parkway (0.30 m). Diel changes in conductivity (SpC), pH, oxidation reduction potential (ORP), temperature and dissolved oxygen (DO) for Plantagenet and Parkway are summarized in Table 4 (raw data in Appendix XIII and XIV).

Plantagenet and Parkway both showed a diel variation in surface DO concentration. Minimum values were observed in early morning ~ 6 – 7 am and rose throughout the day reaching a maximum ~ 6 – 7 pm, then declined overnight. At Plantagenet, the DO concentration close to the river bottom remained relatively unchanged throughout the day and was significantly lower than the surface DO at both the US and DS locations (paired t-test, $p = 0.0001$ and $p = 0.005$, respectively). The ORP and pH also showed a significant difference between top and bottom of the water column at Plantagenet (paired t-test, all comparisons $p < 0.003$). For all variables that displayed a significant difference between surface and bottom readings at Plantagenet, the p value was less significant downstream. In addition, the DO declined significantly over the

length of the reach at Plantagenet (both surface and bottom) while there was only a small increase in temperature (significant increase for the bottom). The surface temperature showed diel variation at Plantagenet with a late afternoon peak while the bottom water temperature remained relatively unchanged and significantly lower (paired t-test, $p < 0.05$ both locations). The temperature at Parkway increased over the duration of the study due to warmer air temperatures during the diel compared to the preceding 24 hours.

Diel changes in nitrate and TKN concentrations for Plantagenet and Parkway are presented in Figures 24 and 25 and Table 5. Downstream sampling at Parkway started at 4:20 pm to coincide with an estimated water residence time of 1 hour and 20 minutes. A salt addition at 4 pm on September 21 showed that the actual water residence time was around 1 hour and 15 minutes (Appendix XV).

The diel experiments were primarily conducted to estimate the variability in nitrogen retention and water chemistry over a 24 hour period. The variance in diel nutrient concentrations were compared to the variance associated with sampling duplicates or triplicates at a single point in time to assess whether sampling at one point in time underestimated the error (standard error of the ratio, eq. 3) associated with the retention estimate. Diel estimates of percent retention were used to assess the precision of the sampling method i.e. whether sampling at different times of the day produced similar values in retention and to determine whether sampling the same water parcel as it travels through the reach produces similar retention values as unrelated upstream and downstream water pairings.

A comparison of the diel variance in stream or river water chemistry with duplicate or triplicate sampling at one point in time (grab sampling) is presented in Table

5. At Plantagenet, the range and upstream average coefficient of variation (CV) of nitrate concentration for sampling conducted over 2003 and 2004 (excluding the diel sampling) was 0 – 4 % and 1.8 %, respectively; the downstream range and average was 0 – 10.8 % and 1.6 %, respectively. The upstream range and average CV of TKN concentration at Plantagenet over the same period was 0 – 3.4 % and 2 %, respectively; the downstream range and average was 0.9 – 10.5 % and 4.1 %, respectively. At Plantagenet, the diel CV for nitrate and TKN concentrations fell within the average CV and standard deviation for grab sampling conducted on several dates over the summer in 2003 and 2004, and thus sampling at one point in time would not appear to underestimate the standard error of the ratio.

The diel CV at Parkway for nitrate or TKN, upstream or downstream, was greater than that found at Plantagenet and the duplicate samples collected at Parkway the preceding year (Table 5).

The range and average CV for nitrate concentration across all sites in 2003 was 0 – 64.3 % and 4.1 %, respectively. This is similar to the Parkway and Plantagenet diel values, however around half of the nitrate CVs at the US and DS locations in 2003 were 0 % resulting in a median nitrate CV of 0 %. This indicates that for roughly half the US and DS locations in 2003, duplicate sampling probably underestimates the daily nitrate variability, which according to the diel studies ranges between 1 – 7 %, resulting in an underestimation of the standard error of the ratio. The range (0 – 16 %) , average (2 %) and median CV (1.2 %) for TKN in 2003 were similar to the diel results for Plantagenet and Parkway and indicate that overall, sampling duplicates or triplicates at one point in

time would not appear to appreciably underestimate standard error of ratio for this fraction of nitrogen.

Estimates of nitrate and TKN retention and associated error at Plantagenet and Parkway are presented in Table 6. Comparing US and DS chemistry by collecting duplicate samples at the same time (Duplicates; Table 6) or comparing the average US and DS chemistry over a 24 hour period (Diel; Table 6) produced similar estimates of the standard error of the ratio for nitrate and TKN at Plantagenet and TKN at Parkway. Many estimates of retention were performed over a 24 hour period with different pairings of US and DS water chemistry (pairs; Table 6). The "real" pairing (Real pairs; Table 6) matches the same water parcel as it travels from US to DS, while "instantaneous" pairing (Inst. pairs; Table 6) matches unrelated water parcels sampled at roughly the same point in time (collected minutes to 1 - 2 hours apart). There was no difference in the average nitrate or TKN retention when comparisons of US and DS chemistry were between the same water parcel, "real", or between unrelated water parcels, "instantaneous", at Parkway.

The diel experiment suggests that the standard error of the ratio for percent nitrate retention, but not TKN, may be underestimated by sampling at one point in time within the day. Upstream and downstream comparisons of the same or unrelated water parcel produced, on average, a similar estimate of retention, however, it appears that individual comparisons over a 24 hour period vary with respect to their estimate of retention despite their being a small standard error.

Table 2. Physical, biological and chemical characteristics of 29 sites sampled in the South Nation watershed in 2003. Weighted mean depth, velocity and water residence time (WRT) were averaged over the reach, all other variables were measured at both upstream and downstream locations. ORP = oxidation reduction potential, SpC = specific conductivity, NTU = nephelometric units, chl *a* = chlorophyll *a*, NO_3^- = nitrate, TKN = total Kjeldahl-N, TN = total nitrogen, TP = total phosphorous.

Site Characteristics	Range	Mean / Median
Reach length (km)	0.277 – 5.244	1.854 / 0.935
Weighted mean depth (m)	0.08 – 2.76	0.54 / 0.30
Discharge ($m^3 s^{-1}$)	0.0008 – 29.58	1.169 / 0.115
Velocity ($m s^{-1}$)	0.001 – 0.20	0.05 / 0.04
WRT (hr)	1 – 365	43 / 10
pH	6.97 – 8.73	7.84 / 7.85
ORP (mVolts)	244 - 379	340 / 341
Dissolved Oxygen ($mg L^{-1}$)	1.31 – 19.74	8.83 / 8.19
Temperature (°C)	13.62 - 28.86	21.9 / 22
SpC ($mS cm^{-1}$)	222 - 1192	665 / 680
Turbidity (NTU)	0.12 – 175	14.1 / 5.42
chl *a* ($\mu g L^{-1}$)	2 – 149.3	9.2 / 5.8
NO_3^- ($mg L^{-1}$)	0.003 / 7.82	0.63 / 0.08
TKN ($mg L^{-1}$)	0.31 – 2.75	1.03 / 1.01
TN ($mg L^{-1}$)	0.46 - 8.67	1.67 / 1.32
TP ($mg L^{-1}$)	0.005 - 0.233	0.069 / 0.057

Table 3. Physical, biological and chemical characteristics of the three sites sampled in the South Nation watershed in 2004. Weighted mean depth, velocity and water residence time (WRT) were averaged over the reach on the specific sampling day, all other variables were measured at both upstream and downstream locations (except discharge at Plantagenet). ORP = oxidation reduction potential, SpC = specific conductivity, NTU = nephelometric units, chl *a* = chlorophyll *a*, NO_3^- = nitrate, NH_4^+ = ammonium, TKN = total Kjeldahl-N, TN = total nitrogen, RP = reactive phosphorous, TP = total phosphorous.

Site Characteristics	L. Castor N. Br.		L. Castor Longtin		Plantagenet	
	Range	Mean / Median	Range	Mean / Median	Range	Mean / Median
Weighted mean depth (m)	0.22 – 0.26	0.24 / 0.24	0.40 – 0.85	0.56 / 0.55	2.78 – 3.54	2.95 / 2.81
Discharge ($m^3 s^{-1}$)	0.0201 – 0.0784	0.0410 / 0.0379	0.0075 – 0.9467	0.1901 / 0.1330	3.10 – 118.0	28.05 / 6.42
Velocity ($m s^{-1}$)	0.03 – 0.05	0.04 / 0.04	0.00 – 0.06	0.03 / 0.03	0.00 – 0.24	0.06 / 0.02
WRT (hr)	6.87 – 17.6	11.89 / 11.25	12.2 – 197.0	67.3 / 25.9	5.5 -155.8	82.0 / 87.6
pH	7.65 – 8.94	8.05 / 8.00	7.53 – 8.17	7.83 / 7.85	7.60 – 8.88	7.99 / 7.97
ORP (mVolts)	209 - 501	389 / 429	400 -493	440 / 435	371 - 544	438 / 442
Dissolved Oxygen ($mg L^{-1}$)	5.46 – 13.70	8.55 / 8.26	4.23 – 12.70	6.81 / 7.00	3.54 – 13.80	6.92 / 6.5
Temperature (°C)	13.55 – 21.62	16.66 / 16.32	17.89 – 21.63	19.43 / 19.41	17.03 – 24.57	20.94 / 20.89
SpC ($mS cm^{-1}$)	562.0 – 762.6	691.1 / 692.6	620.8 – 771.0	707.0 / 707.0	372.3 – 611.5	529.7 / 565.5
Turbidity (NTU)	6.68 – 53.5	19.7 / 17.1	2.03 – 8.55	4.10 / 3.81	5.48 – 51.3	22.5 / 19.5
chl *a* ($\mu g L^{-1}$)	2.6 – 13.8	6.3 / 5.9	2.8 – 22.3	5.7 / 4.9	2.9 – 91.2	12.6 / 5.0
NO_3^- ($mg L^{-1}$)	0.30 – 1.20	0.71 / 0.65	0.003 – 8.32	1.43 / 0.51	0.44 – 2.35	1.36 / 1.31
NH_4^+ ($mg L^{-1}$)	0.002 – 0.045	0.013 / 0.007	0.002 – 0.033	0.015 / 0.013	0.011 – 0.160	0.074 / 0.070
TKN ($mg L^{-1}$)					0.92 – 1.49	1.11 / 1.03
TN ($mg L^{-1}$)					1.43 – 3.81	2.48 / 2.30
RP ($mg L^{-1}$)					0.029 – 0.125	0.082 / 0.077
TP ($mg L^{-1}$)					0.057 – 0.183	0.110 / 0.105

Table 4. Physical and chemical characteristics at upstream (US) and downstream (DS) locations over a 24 hour period at North Castor (Parkway Rd.) and South Nation River (Plantagenet). Plantagenet measurements were recorded at the surface (S = 0.5 m) and bottom (US = 2.2 m; DS = 2.5 m). Depth of sediments at Plantagenet US was 3.2 m and DS 2.7 m. Sample size = 9 at each US and DS location. SpC = specific conductivity, ORP = oxidation reduction potential, DO = dissolved oxygen. Turbidity and chl *a* were depth integrated with a tube sampler. See Appendix VII and VIII for Plantagenet and Parkway raw data, respectively.

Site	Variable	Range		Mean ± Standard deviation	
		US	DS	US	DS
Parkway					
	SpC (mS cm^{-1})	1107.0 – 1149.0	1108.2 – 1149.0	1131.9 ± 17.0	1131.4 ± 16.4
	pH	8.24 – 8.39	8.32 – 8.43	8.34 ± 0.05	8.37 ± 0.03
	ORP (mVolts)	462 – 518	470 – 510	492 ± 22	499 ± 16
	Temperature (°C)	11.76 – 14.13	11.74 – 14.45	12.42 ± 0.74	12.60 ± 0.92
	DO (mg L^{-1})	8.72 – 10.5	8.92 – 10.34	9.55 ± 0.65	9.64 ± 0.54
	Turbidity (NTU)	7.11 – 10.8	7.10 – 11.20	8.90 ± 1.46	9.06 ± 1.32
	chl *a* (µg L^{-1})	1.6 – 3.5	2.3 – 3.3	2.8 ± 0.7	2.8 ± 0.3
Plantagenet					
S	SpC (mS cm^{-1})	565.5 – 575.5	565.8 – 567.5	570.1 ± 3.7	566.9 ± 0.6
B		570.0 – 573.6	565.5 – 566.8	571.4 ± 1.2	566.2 ± 0.4
S	pH	8.29 – 8.88	8.07 - 8.41	8.5 ± 0.19	8.2 ± 0.11
B		7.88 – 8.18	7.92 – 8.12	8.03 ± 0.09	8.01 ± 0.06
S	ORP (mVolts)	451 – 523	449 – 544	488 ± 25	495 ± 36
B		475 -534	450 - 543	512 ± 19	500 ± 35
S	Temperature (°C)	19.28 – 23.56	20.61 – 23.38	21.20 ± 1.49	21.71 ± 1.04
B		19.33 – 19.92	20.67 – 21.00	19.58 ± 0.17	20.88 ± 0.11
S	DO (mg L^{-1})	7.42 – 11.75	5.47 – 7.84	8.95 ± 1.44	6.41 ± 0.79
B		5.03 – 7.00	4.32 – 5.61	5.84 ± 0.63	5.03 ± 0.43
	Turbidity (NTU)	25.0 – 35.0	18.9 – 23.3	30.6 ± 3.2	21.5 ± 1.3
	chl *a* (µg L^{-1})	6.5 – 21.5	5.1 – 16.9	12.8 ± 5.1	10.1 ± 4.2

Table 5. Nitrate and total Kjeldahl-N average concentration, standard deviation and coefficient of variation at North Castor (Parkway Rd.) and South Nation River (Plantagenet). Diel results are highlighted in grey.

Site	Nutrient	Sampling Date	US			DS	
			n	Average ± St. Dev.	CV	Average ± St. Dev.	CV
		Parkway, Sept. 20-21, 2004					
	NO_3^-	29-Jul-03	2	0.49 ± 0.00	0.0	0.54 ± 0.00	0.0
		20,21- Sep-04	9	0.28 ± 0.02	7.1	0.27 ± 0.02	7.4
	TKN	29-Jul-03	2	0.57 ± 0.00	0.0	0.58 ± 0.01	1.7
		20,21- Sep-04	9	0.49 ± 0.02	4.1	0.43 ± 0.02	4.7
		Plantagenet, Sept. 2-3, 2004					
	NO_3^-	16-Jul-03	3	1.79 ± 0.03	1.7	2.15 ± 0.01	0.5
		25-Aug-03	2	0.37 ± 0.00	0.0	0.11 ± 0.00	0.0
		04-Sep-03	2	0.47 ± 0.01	2.1	0.27 ± 0.00	0.0
		10-Sep-03	2	0.56 ± 0.01	1.8	0.30 ± 0.00	0.0
		28-Jun-04	3	1.24 ± 0.05	4.0	1.39 ± 0.15	10.8
		16-Jul-04	3	0.45 ± 0.01	2.2	0.46 ± 0.00	0.0
		29-Jul-04	3	1.33 ± 0.02	1.5	1.16 ± 0.01	0.9
		16-Aug-04	3	1.75 ± 0.02	1.1	1.83 ± 0.04	2.2
		2,3-Sep-04	9	0.91 ± 0.01	1.1	1.02 ± 0.01	1.0
		14-Sep-04	3	2.31 ± 0.03	1.3	2.32 ± 0.01	0.4
	TKN	16-Jul-03	3	0.99 ± 0.02	2.0	1.21 ± 0.06	5.0
		25-Aug-03	2	1.14 ± 0.00	0.0	1.24 ± 0.13	10.5
		04-Sep-03	2	1.02 ± 0.03	2.9	1.13 ± 0.01	0.9
		10-Sep-03	2	1.09 ± 0.01	0.9	1.15 ± 0.01	0.9
		16-Jul-04	3	1.18 ± 0.04	3.4	1.04 ± 0.05	4.8
		29-Jul-04	3	0.96 ± 0.03	3.1	1.13 ± 0.05	4.4
		16-Aug-04	3	0.96 ± 0.02	2.1	1.05 ± 0.04	3.8
		2,3-Sep-04	9	0.95 ± 0.03	3.2	0.95 ± 0.05	5.3
		14-Sep-04	3	1.47 ± 0.02	1.4	1.44 ± 0.04	2.8

Table 6. Percent nitrogen retention and associated standard error over a 24 hour period. Real water parcel pairing indicates that upstream (US) and downstream (DS) comparisons were made on the same parcel of water as it travelled through the reach (conducted only at Parkway). Instantaneous (Inst.) represents a US, DS pairing of samples collected at the same point in time (minutes to 1 – 2 hours apart). Diel refers to a single calculated retention value based on the average of US and DS samples collected over a 24 hr period. Duplicates refer to a single calculated retention value from one US, DS comparison with duplicate water samples collected in the afternoon. Pairs indicates 8 to 9 calculations of retention based on separate US, DS pairings over a 24 hour period i.e. a separate pairing every collection time (every 3 hours). Standard error calculated as standard error of the ratio (SE_R, eq. 3) or simply as the standard error (SE, st.dev./$\sqrt{n}$).

	Nutrient	Range	% Retention		St. Error		Upstream and Downstream pairing
Parkway							
Sept. 20-21, 2004	NO_3^-	0 – 3.6	0.4	±	0.4	SE	Real 9 pairs
		-16.0 – 14.3	-0.7	±	4.2	SE	Inst. 8 pairs
		N/A	0.4	±	3.9	SE_R	Real Diel
		N/A	0	±	N/A*	SE_R	Real Duplicates
	TKN	-2.1 – 17.3	7.7	±	2.2	SE	Real 9 pairs
		0 – 15.4	7.5	±	2.3	SE	Inst. 8 pairs
		N/A	8.8	±	2.3	SE_R	Real Diel
		N/A	16.3	±	2.6	SE_R	Real Duplicates
Plantagenet							
Sept. 2-3, 2004	NO_3^-	-13.3 – -8.6	-11.3	±	0.5	SE	Inst. 9 pairs
		N/A	-11.3	±	0.7	SE_R	Inst. Diel
		N/A	-12.1	±	1.1	SE_R	Inst. Duplicates
	TKN	-5.2 – 6.3	-0.1	±	1.3	SE	Inst. 9 pairs
		N/A	-0.1	±	1.9	SE_R	Inst. Diel
		N/A	-3.8	±	1.6	SE_R	Inst. Duplicates

* No standard error of the ratio due to identical US and DS chemistry

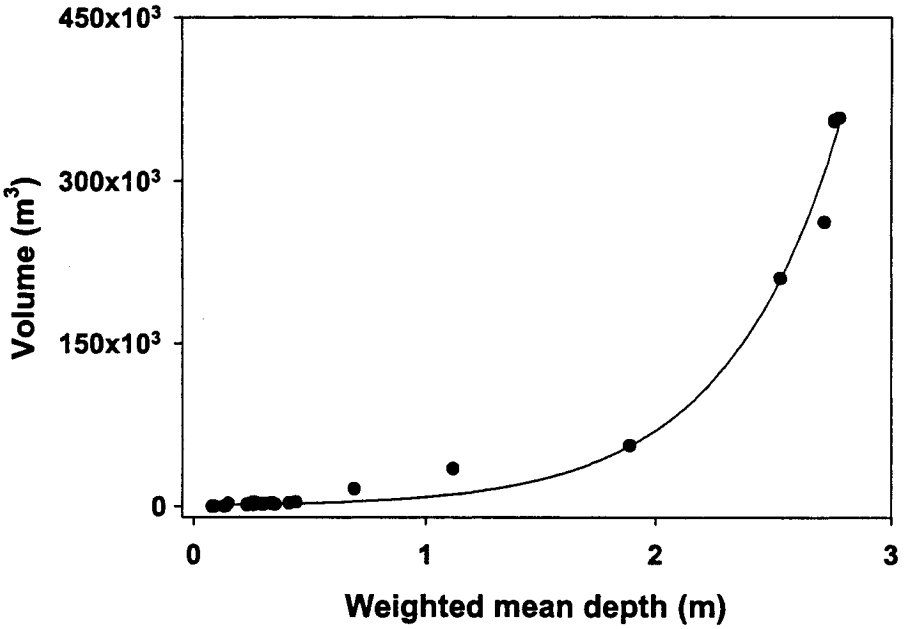


Figure 2. Water volume of reach as a function of stream size (depth) within the South Nation watershed ($y = 1113 \times 7.9^{X}$; $r^2 = 0.99$, $p = <0.0001$, $n = 31$). Different reach sizes were standardized by dividing total reach volume by total length of reach.

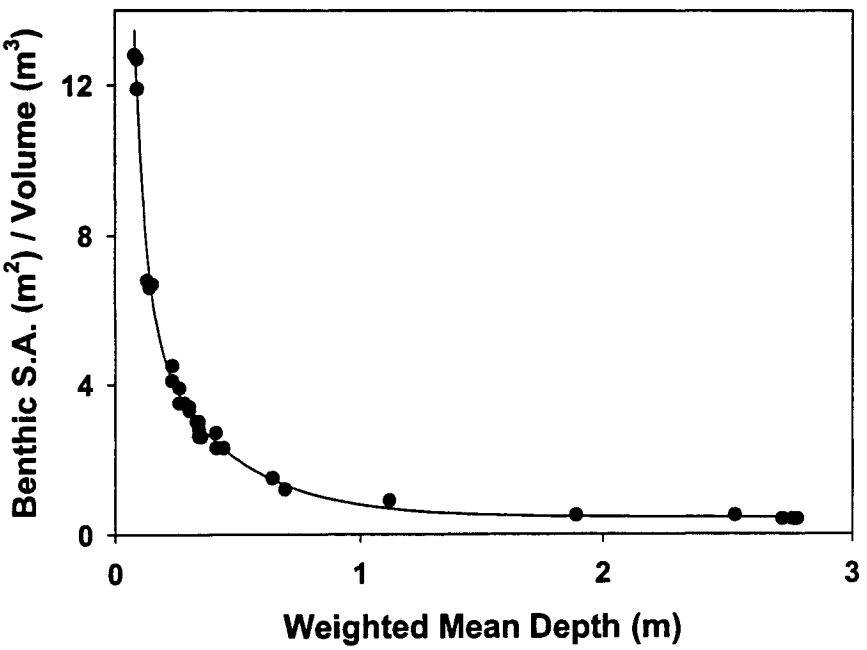


Figure 3. Ratio of benthic surface area to volume as river depth increases ($y = 0.45 + 47.31e^{-22.75*X} + 6.80e^{-2.99*X}$; $r^2 = 0.99$, $p = <0.0001$, $n = 31$).

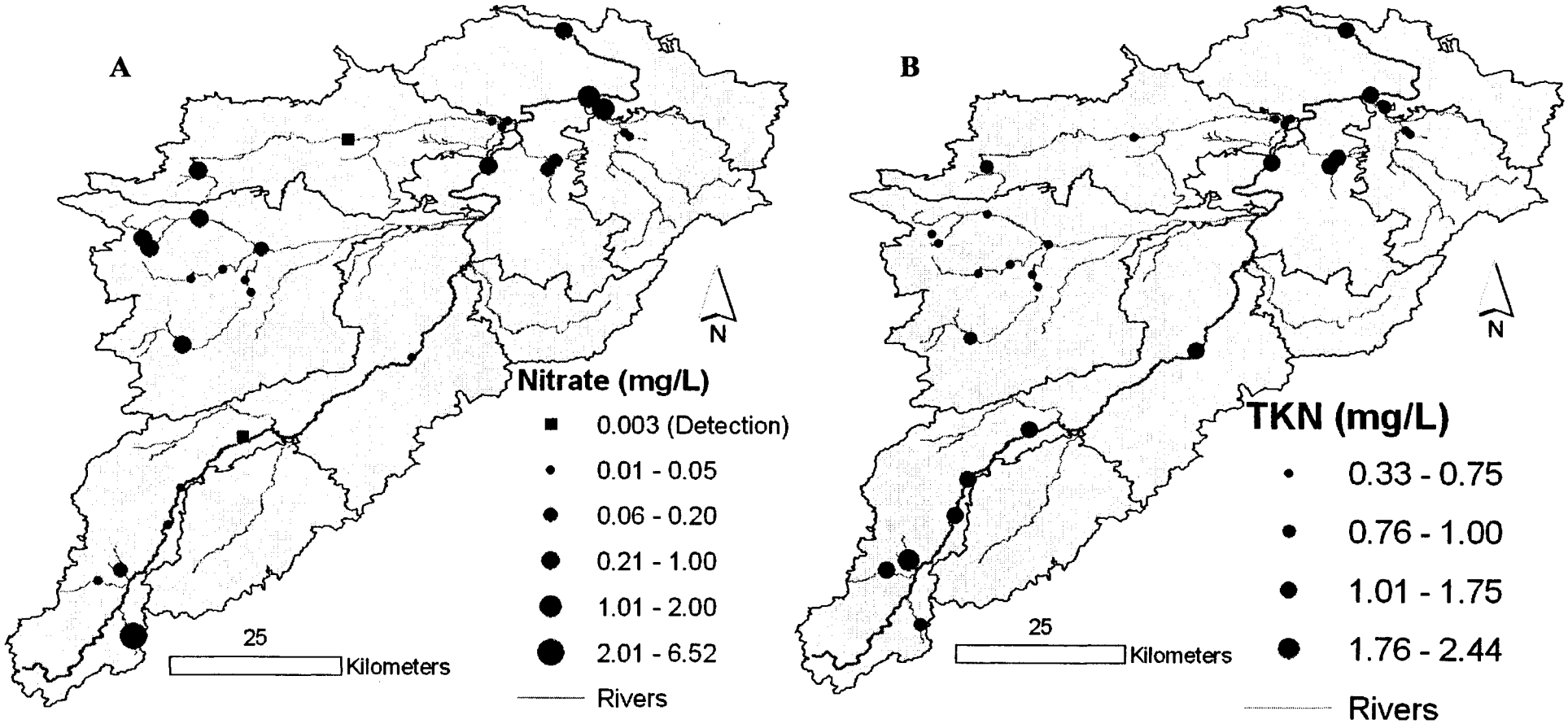


Figure 4. Map of (A) nitrate and (B) total Kjeldahl-N concentrations across the South Nation watershed in 2003. Watershed and sub-drainage basins map source Natural Resources Canada, GeoGratis.

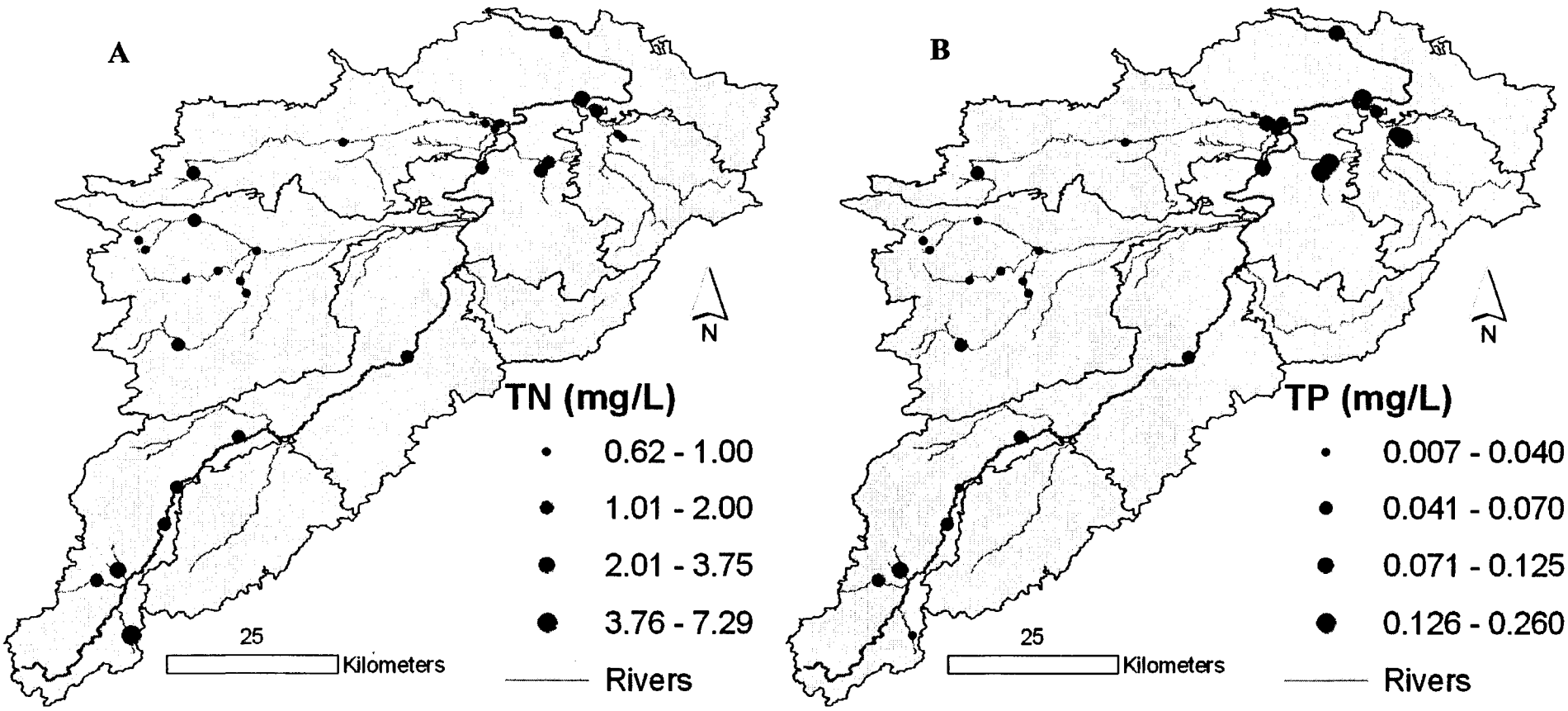


Figure 5. Map of (A) total nitrogen and (B) total phosphorous concentrations across the South Nation watershed in 2003. Watershed and sub-drainage basins map source Natural Resources Canada, GeoGratis.

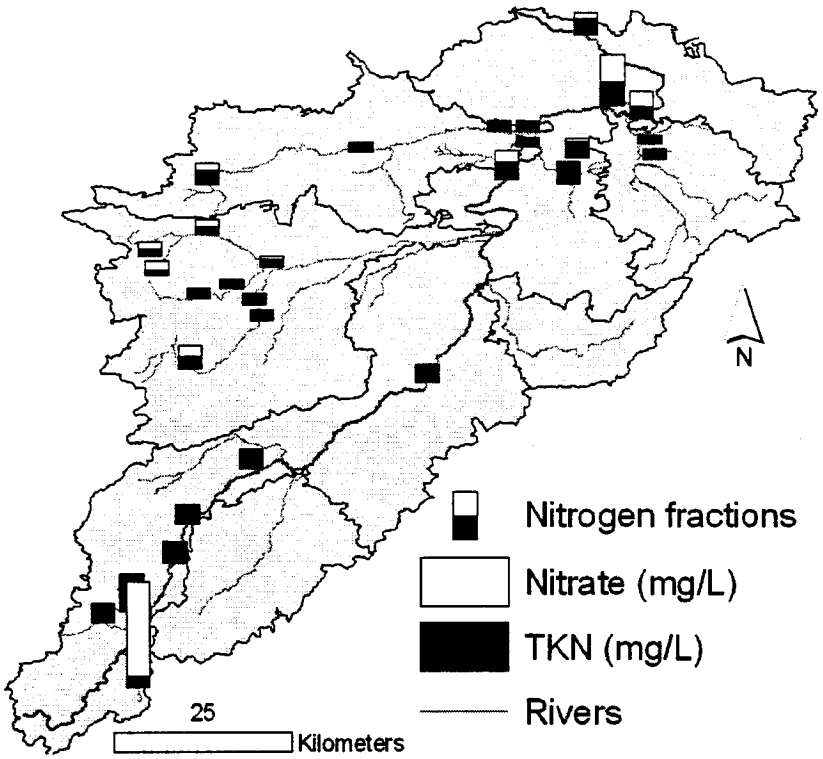


Figure 6. Map of nitrate and total Kjeldahl-N fractions across the South Nation watershed in 2003. Sites are displayed for which depth and water residence time measurements were made (n = 29 sites).

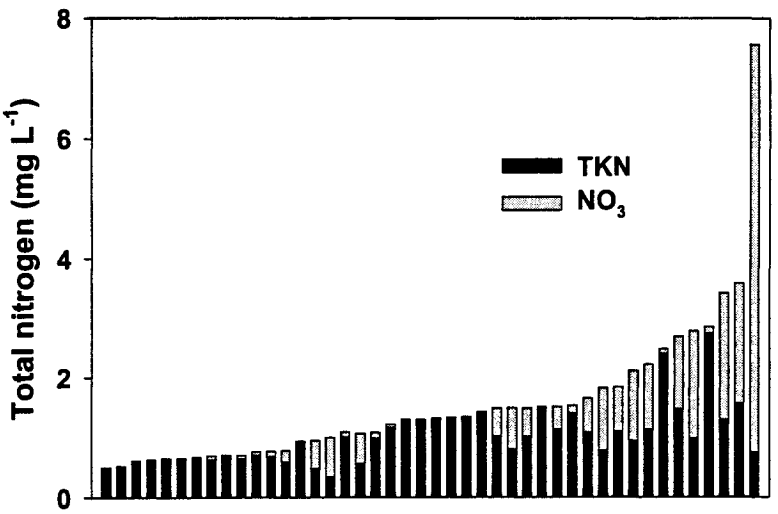


Figure 7. Changes in nitrate and total Kjeldahl-N fractions as total nitrogen concentration increases. A total of 42 sites are displayed including sites for which depth and water residence time measurements were not made.

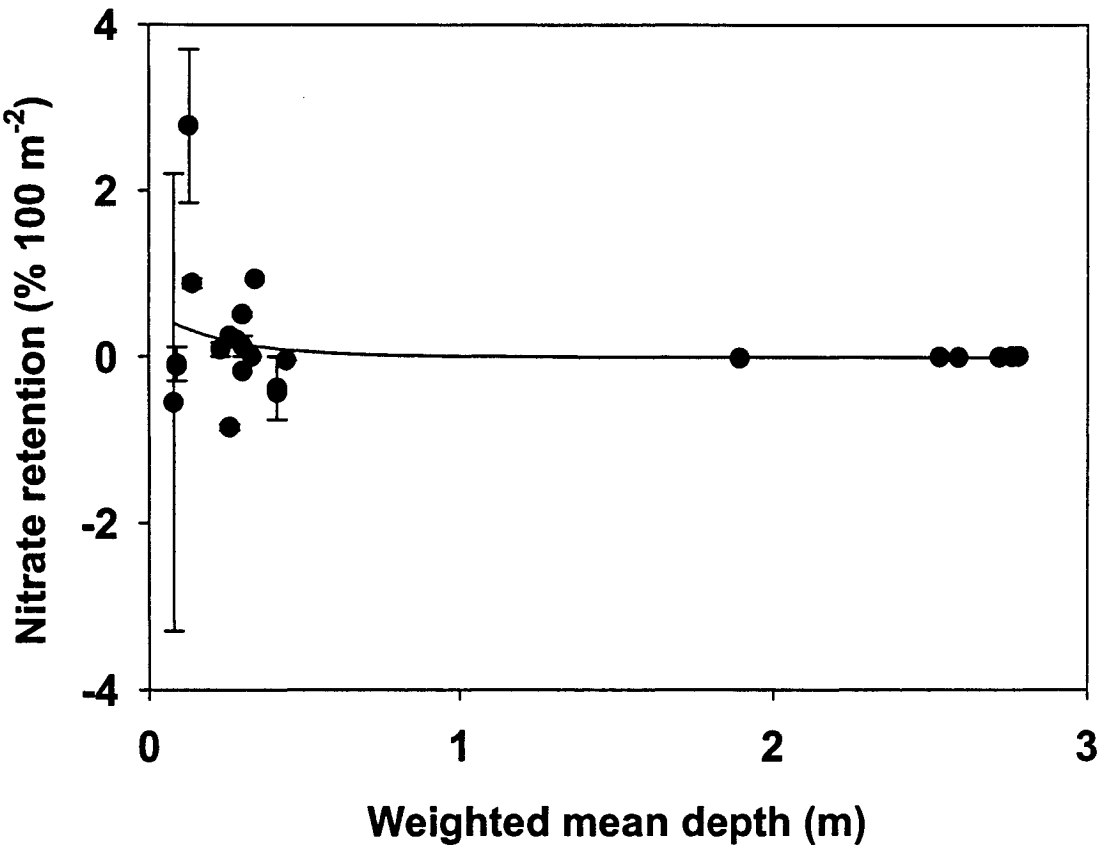


Figure 8. Percent nitrate retention versus stream depth. Retention is expressed per 100 m^2 of streambed. Vertical error bars represent the standard error of the ratio expressed per 100 m^2 of streambed. ($y= 0.57e^{-4.41*X}$; $r^2 = 0.05$, $p = 0.31$, $n = 24$). No error bars indicate that the error is smaller than the symbol.

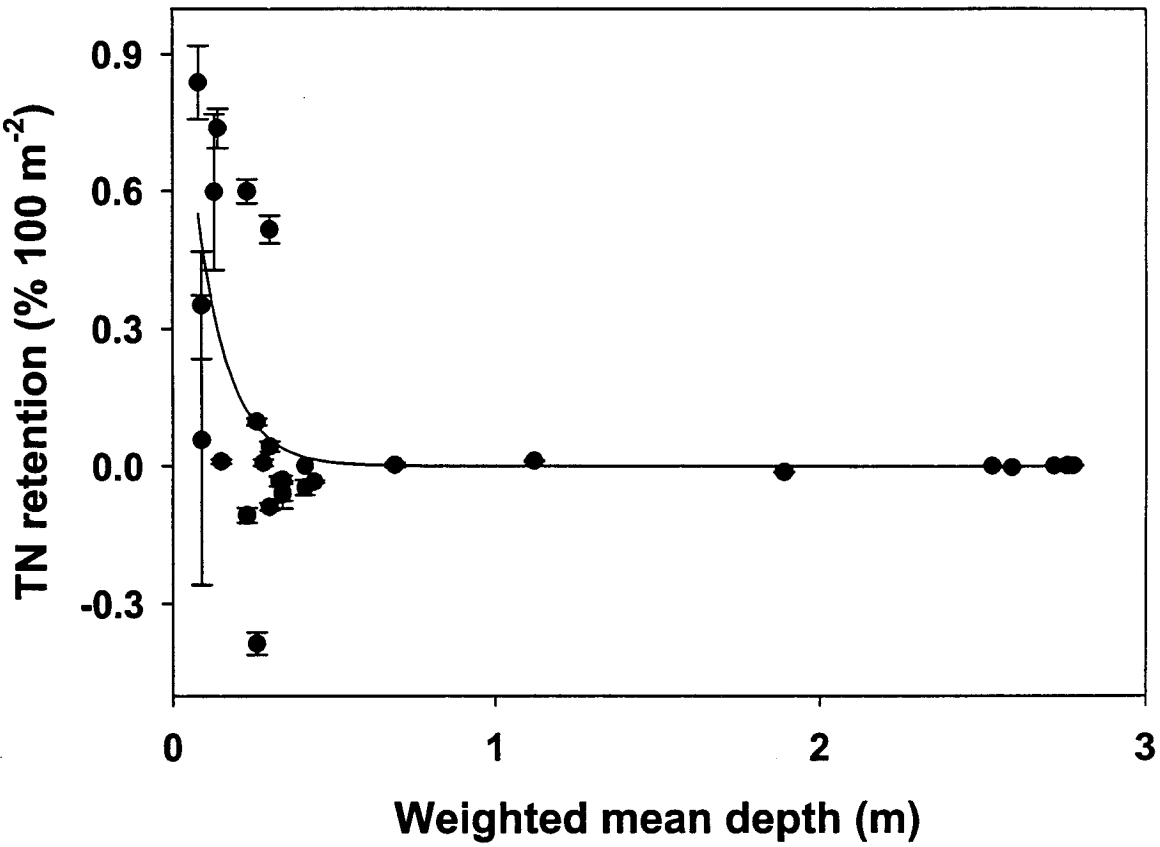


Figure 9. Percent total nitrogen retention versus stream depth. Retention is expressed per 100 m^2 of streambed. Vertical error bars represent the standard error of the ratio expressed per 100 m^2 of streambed. ($y = 1.24e^{-10.13*X}$; $r^2 = 0.37$, $p = 0.0003$, $n = 30$). No error bars indicate that the error is smaller than the symbol.

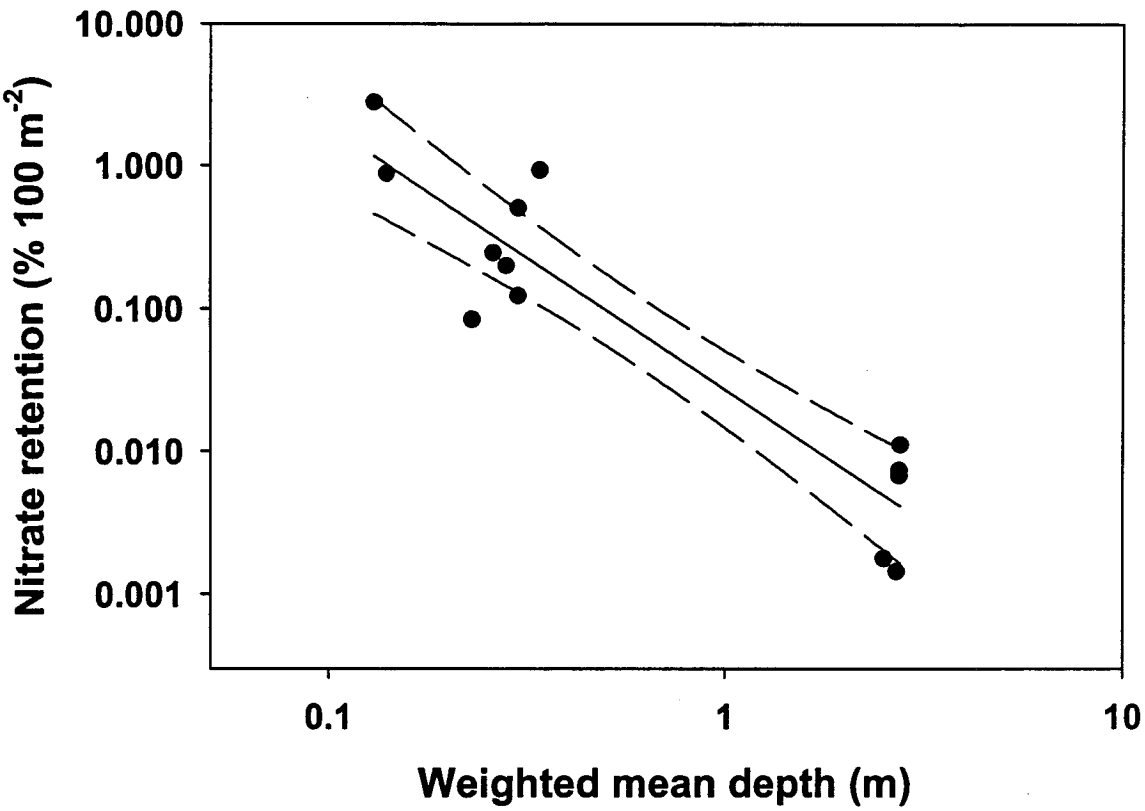


Figure 10. Percent nitrate retention versus stream depth on log scale. Retention is expressed per 100 m^2 of streambed. Regression (solid line) and 95% confidence intervals (dashed line) are given (log y = -1.84 (log x) – 1.57; $r^2 = 0.86$, $p < 0.0001$, n = 13). Note: only sites displaying retention were used.

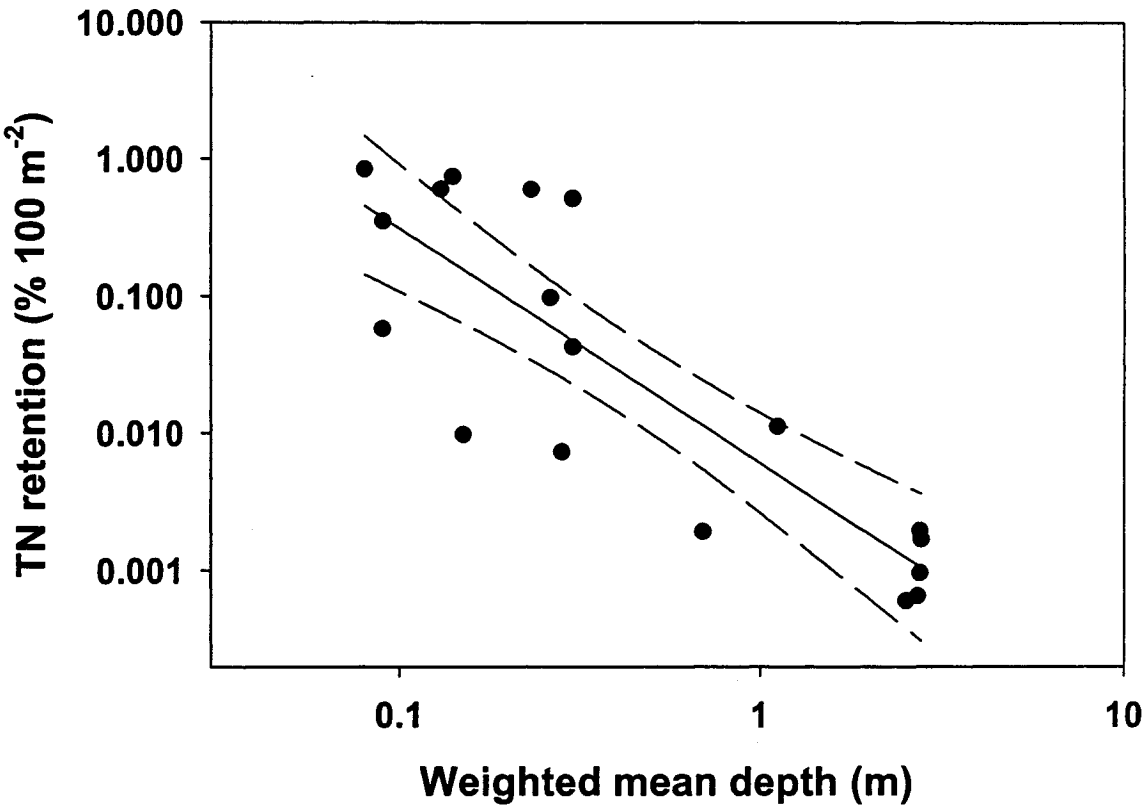
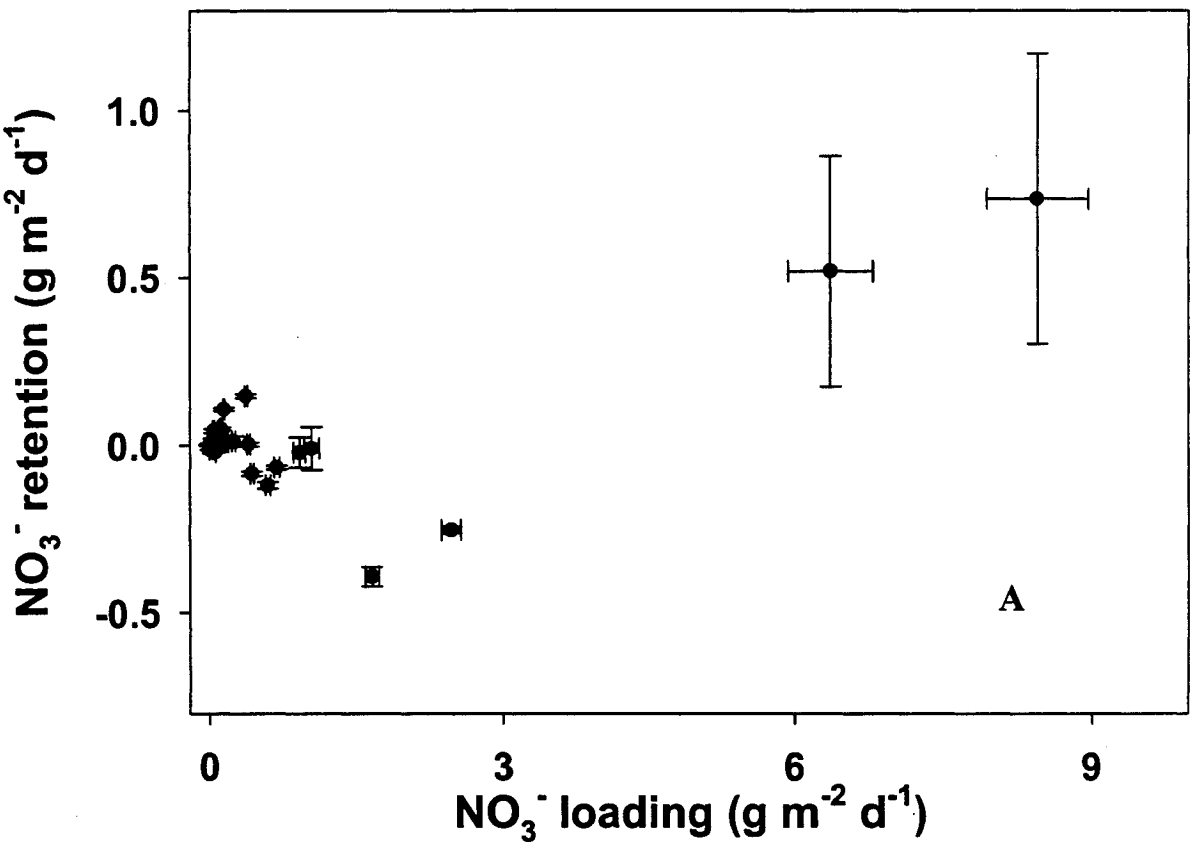
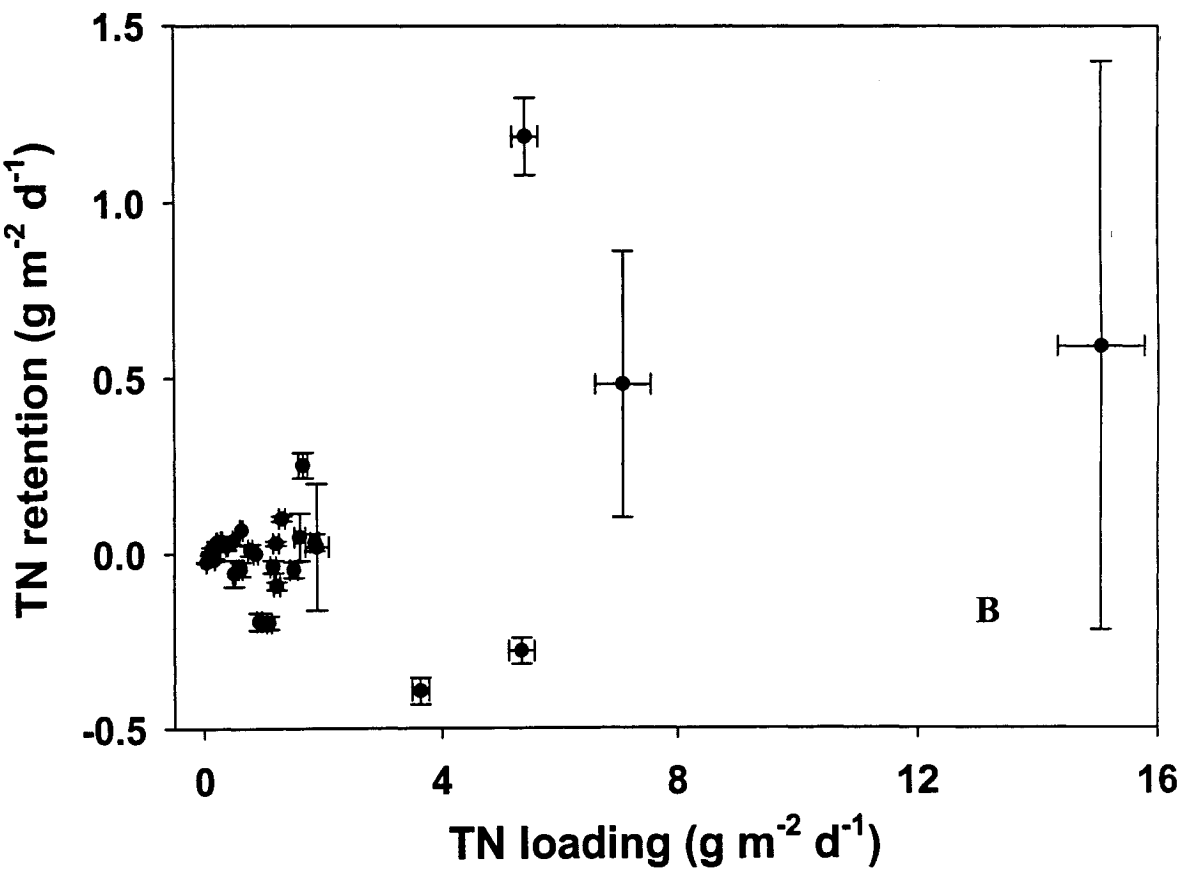


Figure 11. Percent total nitrogen retention versus stream depth on log scale. Retention is expressed per 100 m^2 of streambed. Regression (solid line) and 95% confidence intervals (dashed line) are given (log y = -1.71 (log X) – 2.22; $r^2 = 0.72$, $p < 0.0001$, n = 18). Note: only sites displaying retention were used.

Figure 12. Areal retention of (A) nitrate (n = 25) and (B) total nitrogen (n = 31) within a reach for various areal nitrogen loading levels to reaches across sites. Positive numbers on the y-axis represent retention of nitrogen and negative numbers indicate loading from the reach. Horizontal and vertical error bars represent the standard deviation.


1.0
0.5
0.0
-0.5
NO_3^- retention (g m^{-2} d^{-1})
A
0
3
6
9
NO_3^- loading (g m^{-2} d^{-1})


1.5
1.0
0.5
0.0
-0.5
TN retention (g m^{-2} d^{-1})
B
0
4
8
12
16
TN loading (g m^{-2} d^{-1})

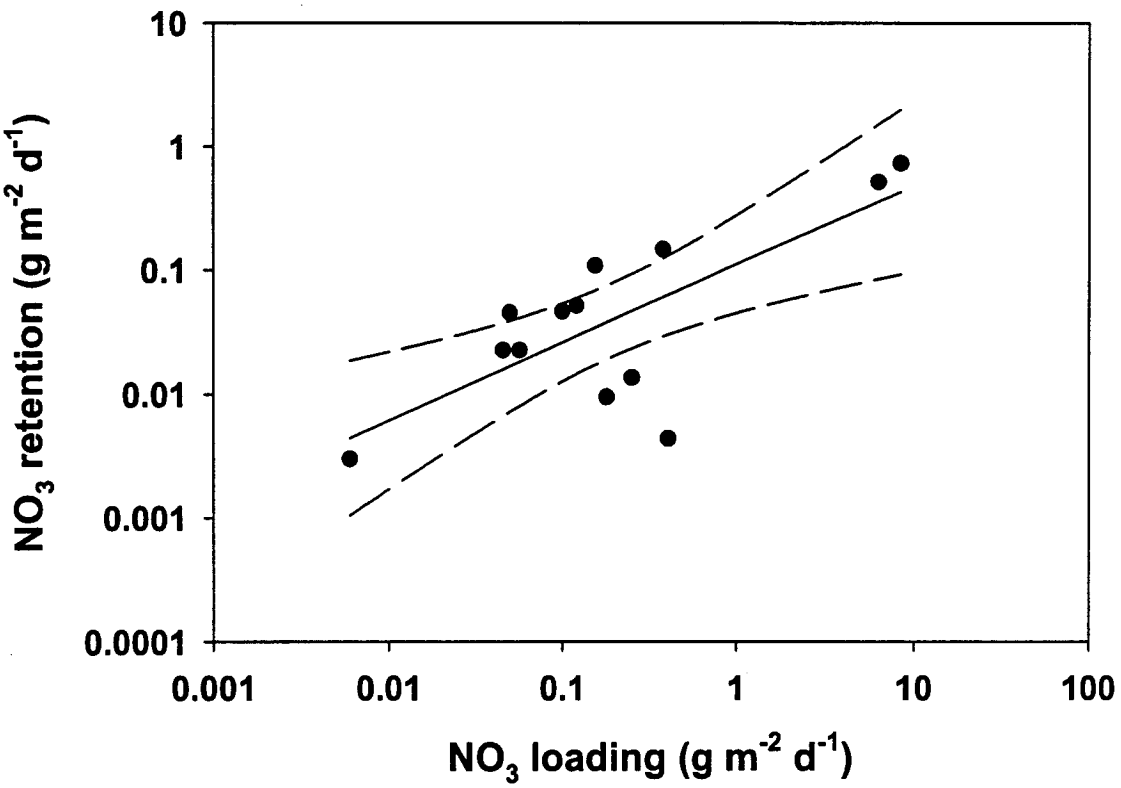


Figure 13. Areal nitrate retention within a reach for various levels of areal nitrate loading. Regression (solid line) and 95% confidence intervals (dashed line) are given (log y = 0.64 (log x) - 0.93; $r^2 = 0.57$, p = 0.003, n = 13). Note: only sites displaying retention were used.

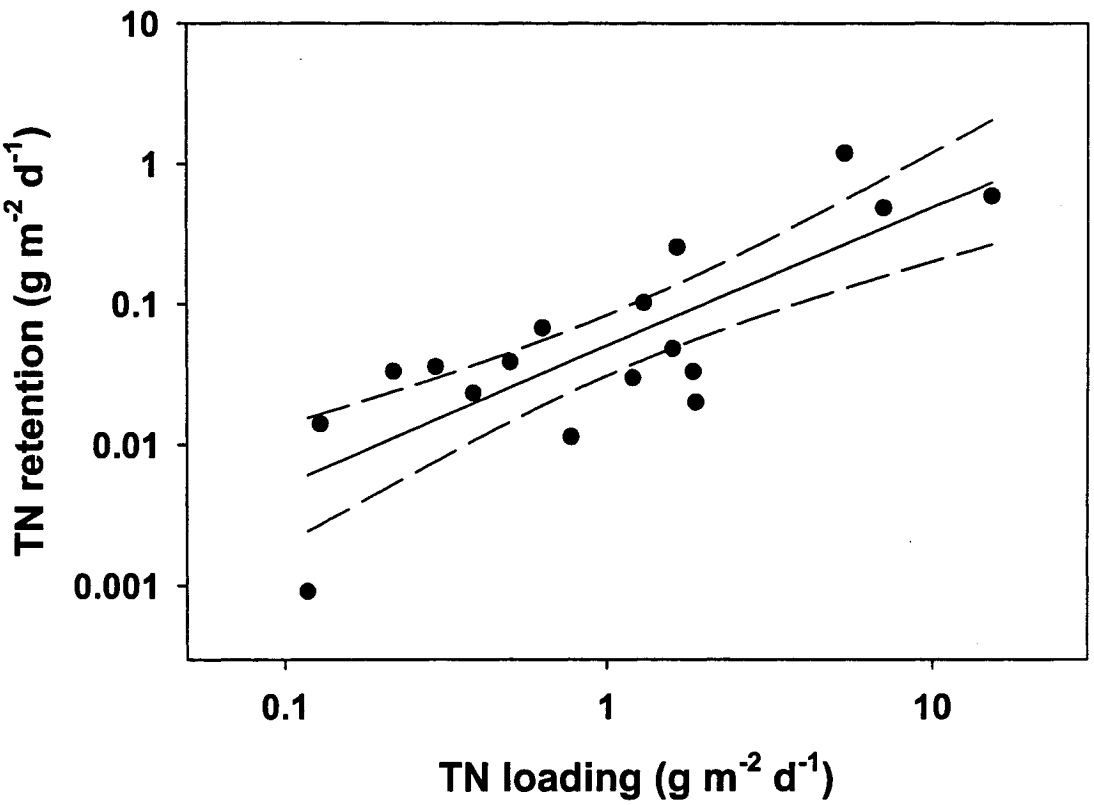


Figure 14. Areal total nitrogen retention within a reach for various levels of areal total nitrogen loading. Regression (solid line) and 95% confidence intervals (dashed line) are given (log y = 1.02 (log x) – 1.30; $r^2 = 0.65$, $p < 0.0001$, n = 18). Note: only sites displaying retention were used.

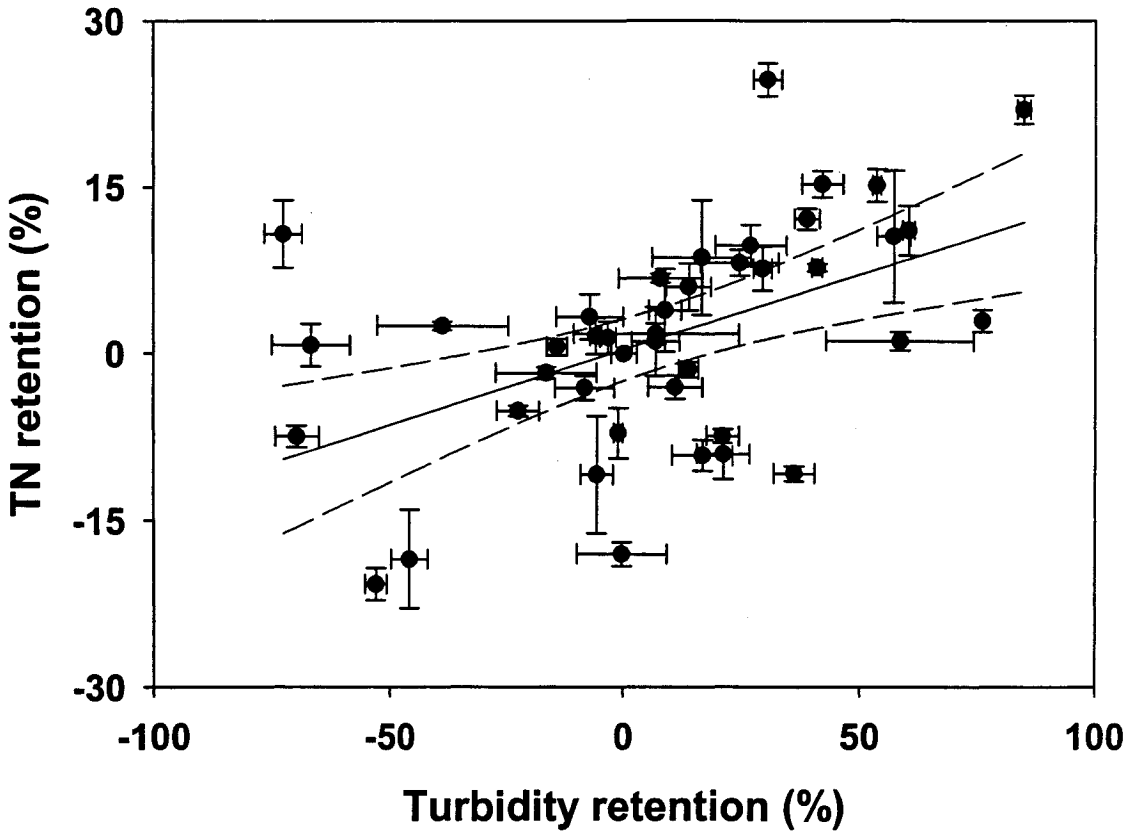


Figure 15. Percent total nitrogen retention versus percent retention in turbidity. Vertical and horizontal error bars represent the standard error of the ratio expressed as a percent. No error bars indicate that the error is smaller than the symbol. Regression (solid line) and 95% confidence intervals (dashed line) are given ($y = 0.14\ (x) + 0.32$; $r^2 = 0.25$, $p = 0.0007$, $n = 42$). Two cases with large leverage have been omitted from the analysis and graph.

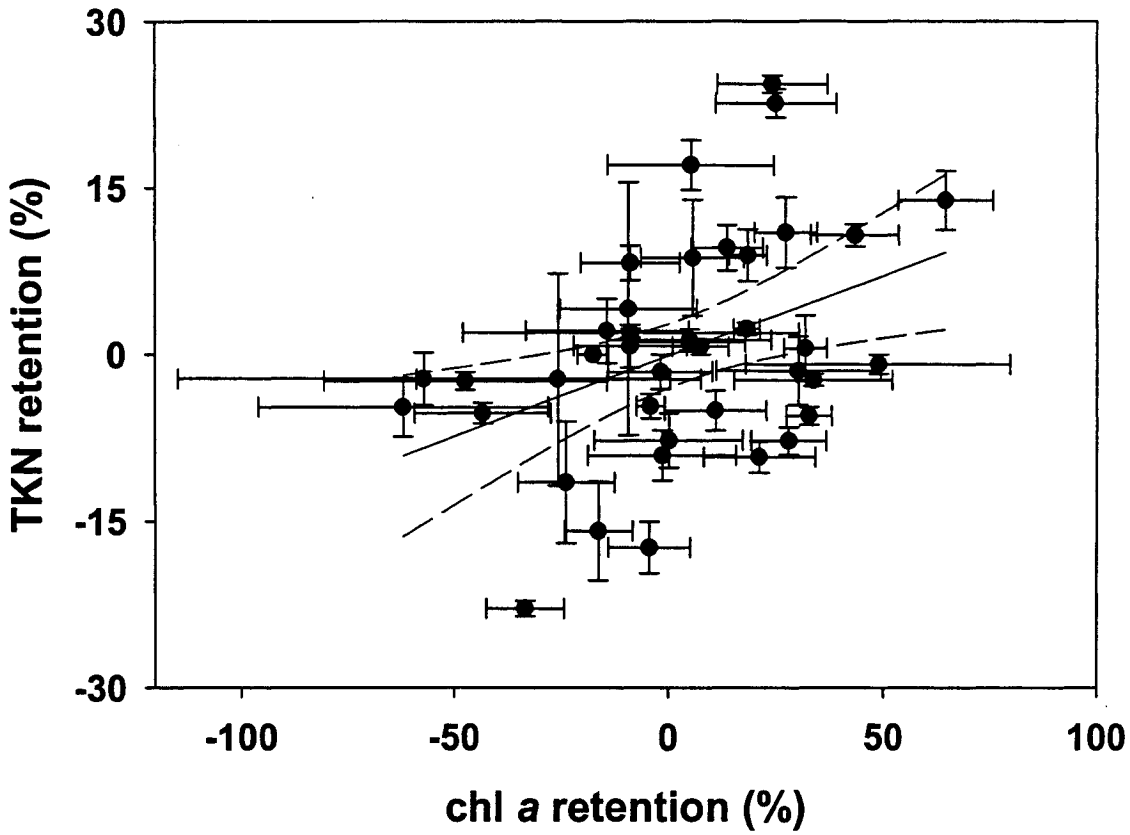


Figure 16. Percent total Kjeldahl-N retention versus percent retention in chlorophyll *a*. Vertical and horizontal error bars represent the standard error of the ratio expressed as a percent. No error bars indicate that the error is smaller than the symbol. Regression (solid line) and 95% confidence intervals (dashed line) are given ($y = 0.15\ (x) - 0.15$; $r^2 = 0.17$, $p = 0.008$, $n = 40$). Four cases with large leverage have been omitted from the analysis and graph.

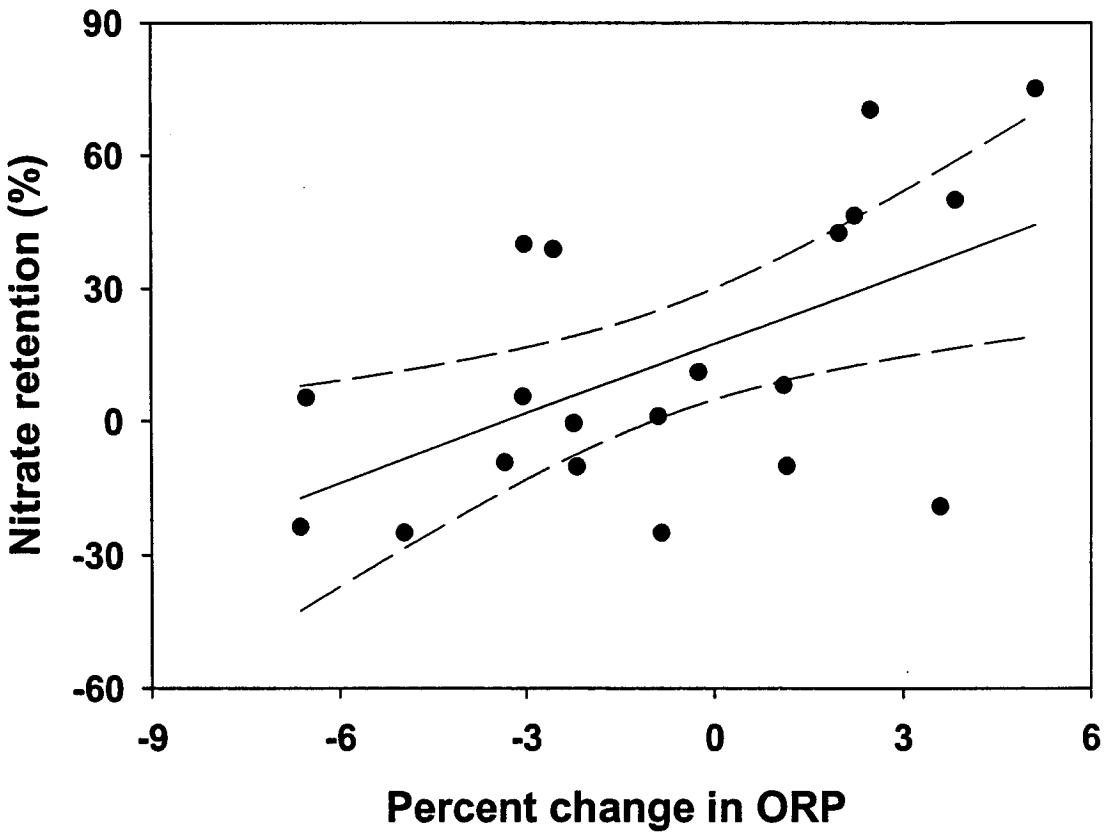


Figure 17. Percent nitrate retention versus percent change in reach ORP. Regression (solid line) and 95% confidence intervals (dashed line) are given ($y = 5.27\ (x) + 17.58$; $r^2 = 0.32$, $p = 0.01$, $n = 20$). Positive numbers on the x-axis represent a decrease in redox potential over the length of the reach (reach becoming more reducing) whereas negative values represent an increase in redox potential (reach becoming more oxidized).

Figure 18. Nitrate concentrations in relation to discharge at (A) Little Castor North Branch (B) Little Castor (Longtin Rd.) and (C) South Nation River at Plantagenet. Nitrate concentrations and discharge are for the downstream locations except at Plantagenet where the discharge value was obtained at the upstream end. Similar results were observed for upstream values of chemistry and flow. Linear regression (solid line) and the 95 % confidence interval (dashed line) are given. Open circles (○) at Plantagenet represent 2003 data, closed circles (●) 2004. Vertical error bars represent the standard deviation. No error bars indicate that the error is smaller than the symbol. Nitrate sample size for L. Castor N.Br. and Longtin is four, Plantagenet three in 2004 and two in 2003.

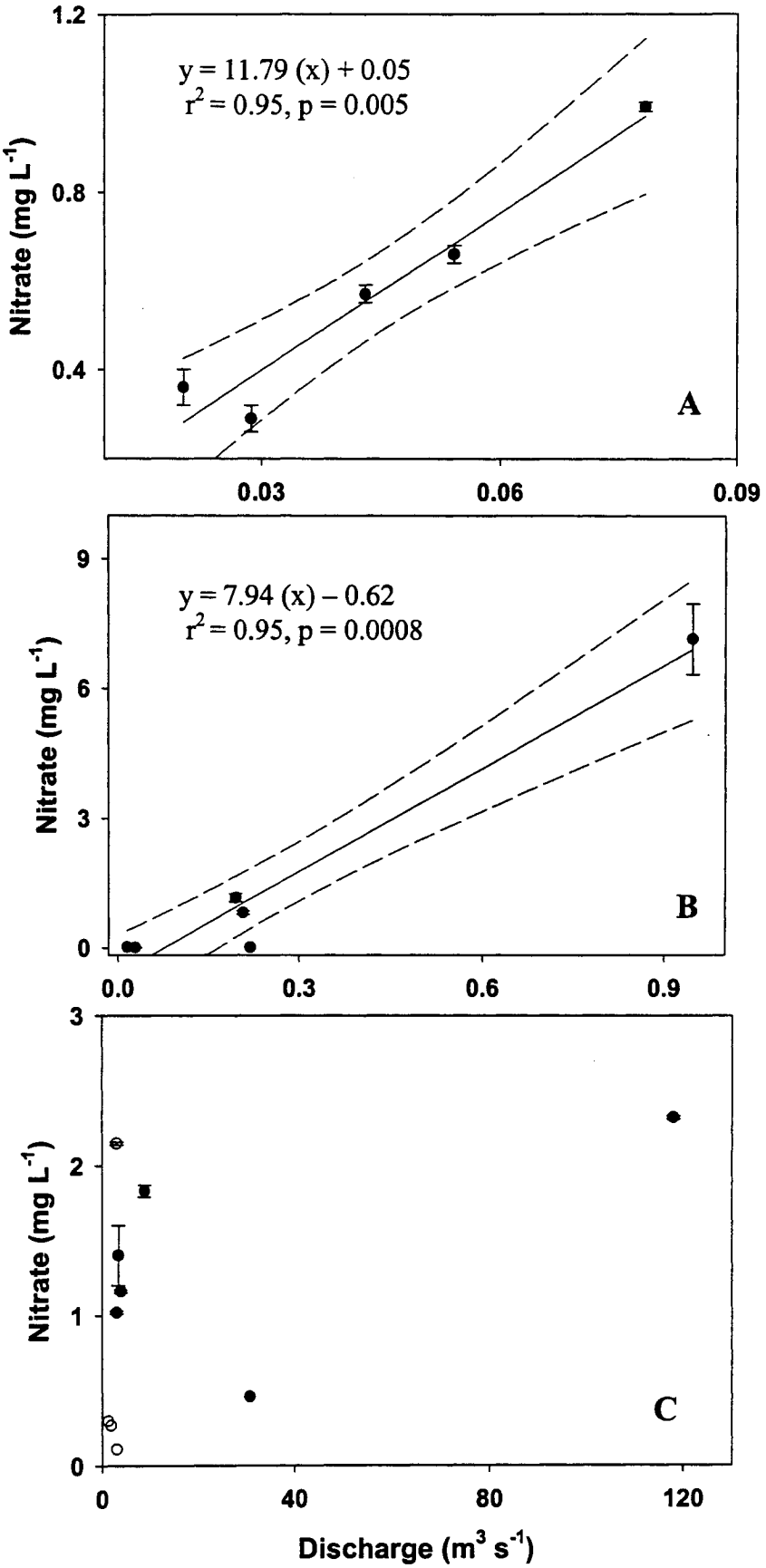

y = 11.79 (x) + 0.05
r² = 0.95, p = 0.005
Nitrate (mg L⁻¹)
A
y = 7.94 (x) – 0.62
r² = 0.95, p = 0.0008
Nitrate (mg L⁻¹)
B
Nitrate (mg L⁻¹)
C
Discharge (m³ s⁻¹)

Figure 19. Percent nitrate retention during summer 2004 at (A) Little Castor North Branch (B) Little Castor (Longtin Rd.) and (C) South Nation River at Plantagenet. Julian day 180 represents June 28th and Julian day 267, September 23rd. Horizontal line represents seasonal average; 18 ± 13 % (0.3 ± 0.2 % per 100 m^{-2}) graph A, -7 ± 48 % (-0.007 ± 0.2 % per 100 m^{-2}) graph B, -3 ± 9 % (-0.0005 ± 0.001 % per 100 m^{-2}) graph C. Vertical error bars represent the standard error of the ratio. No error bars indicate that the error is smaller than the symbol. Nitrate sample size at each location (US and DS) for L. Castor N. Br. and Longtin is four and Plantagenet three. Sampling date, July 13 at L. Castor N. Br. was not used due to numerous, large tributary inputs.

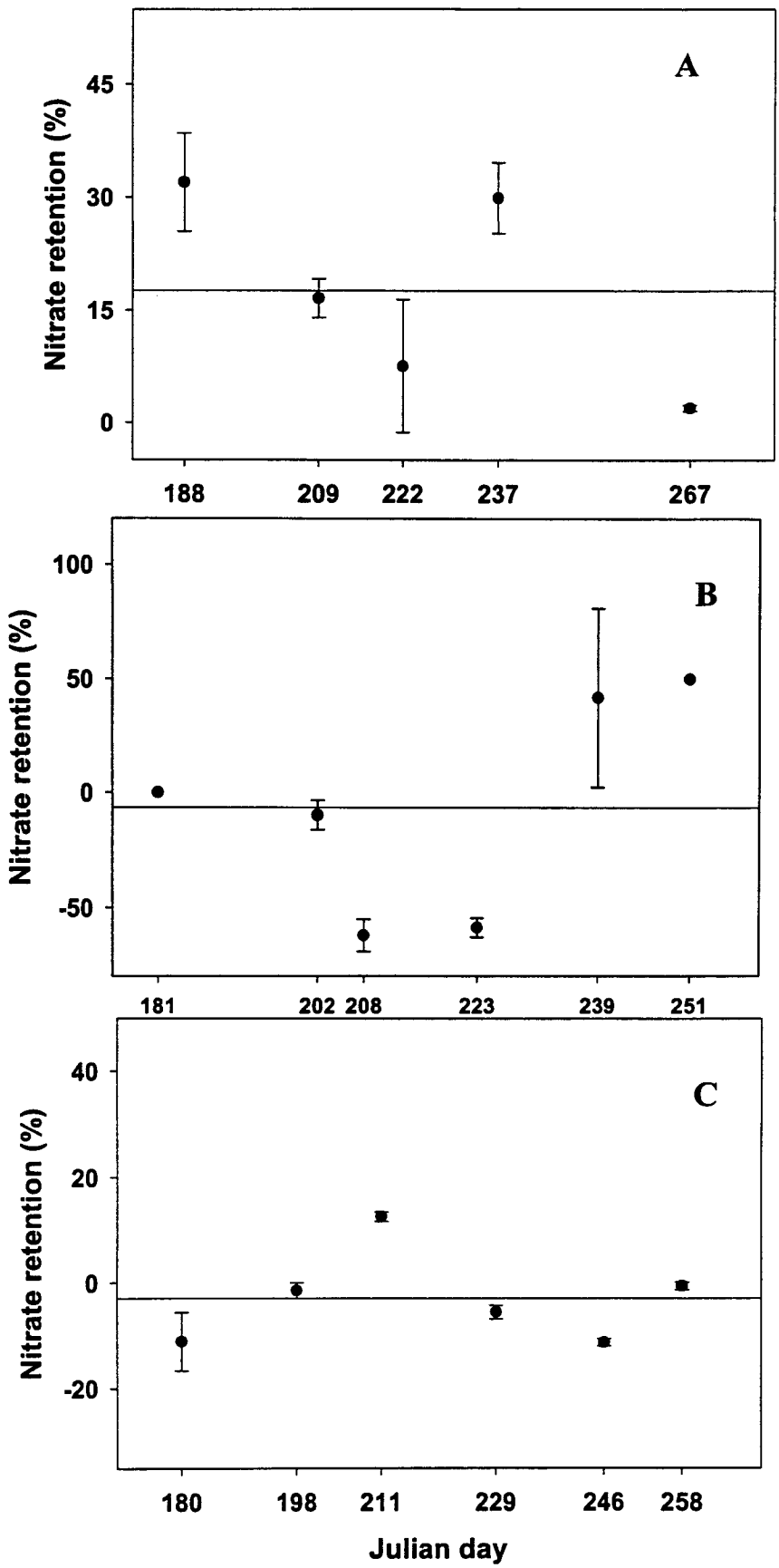
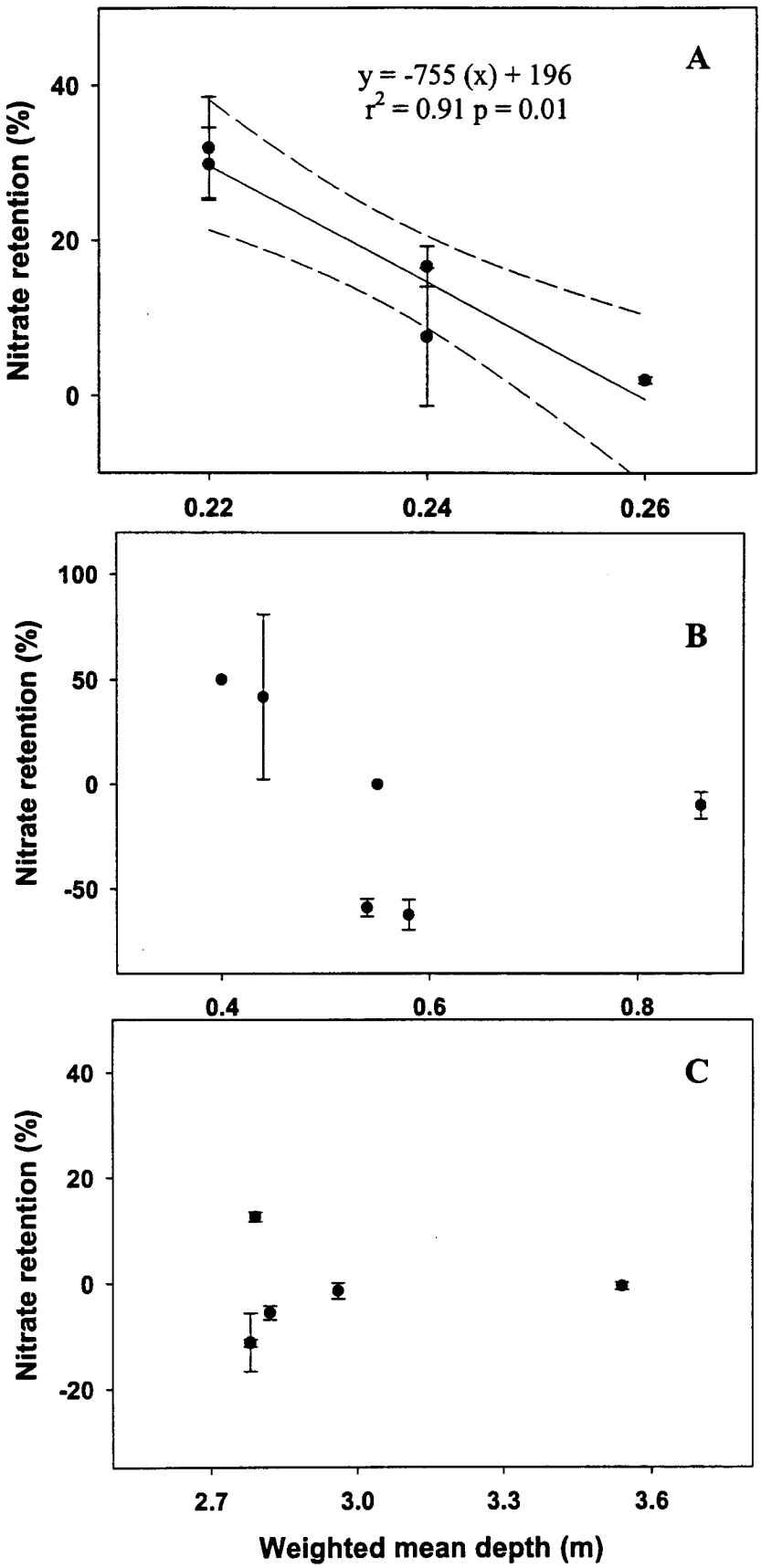

A
Nitrate retention (%)
45
30
15
0
188
209
222
237
267
B
Nitrate retention (%)
100
50
0
-50
181
202
208
223
239
251
C
Nitrate retention (%)
40
20
0
-20
180
198
211
229
246
258
Julian day

Figure 20. Percent nitrate retention as a function of depth at (A) Little Castor North Branch (B) Little Castor (Longtin Rd.) and (C) South Nation River at Plantagenet. Regression (solid line) and 95 % confidence intervals (dashed line) are given. Vertical error bars represent the standard error of the ratio. No error bars indicate that the error is smaller than the symbol. Nitrate sample size for L. Castor N. Br. and Longtin is four and Plantagenet three.


A
y = -755 (x) + 196
r² = 0.91 p = 0.01
Nitrate retention (%)
40
20
0
0.22
0.24
0.26
B
Nitrate retention (%)
100
50
0
-50
0.4
0.6
0.8
C
Nitrate retention (%)
40
20
0
-20
2.7
3.0
3.3
3.6
Weighted mean depth (m)

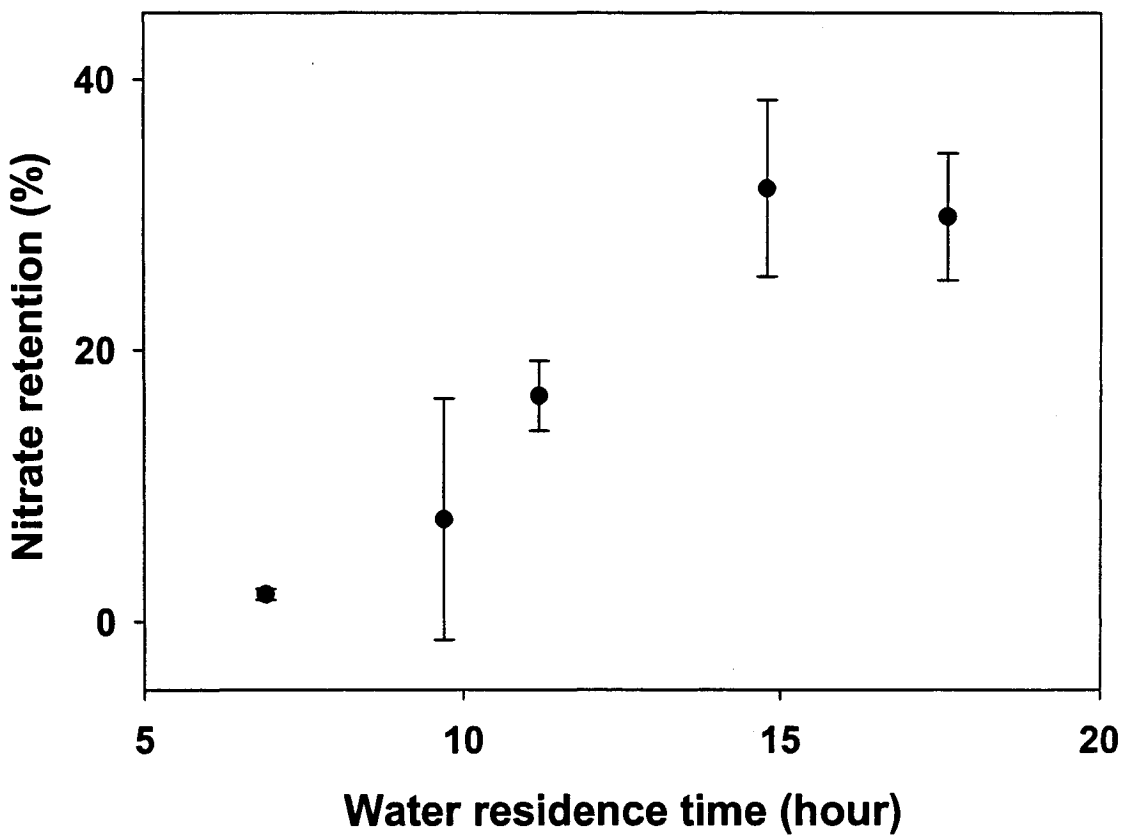


Figure 21. Changes in percent nitrate retention with increasing water residence times at Little Castor North Branch. Vertical error bars represent the standard error of the ratio. Sample size is four for each data point.

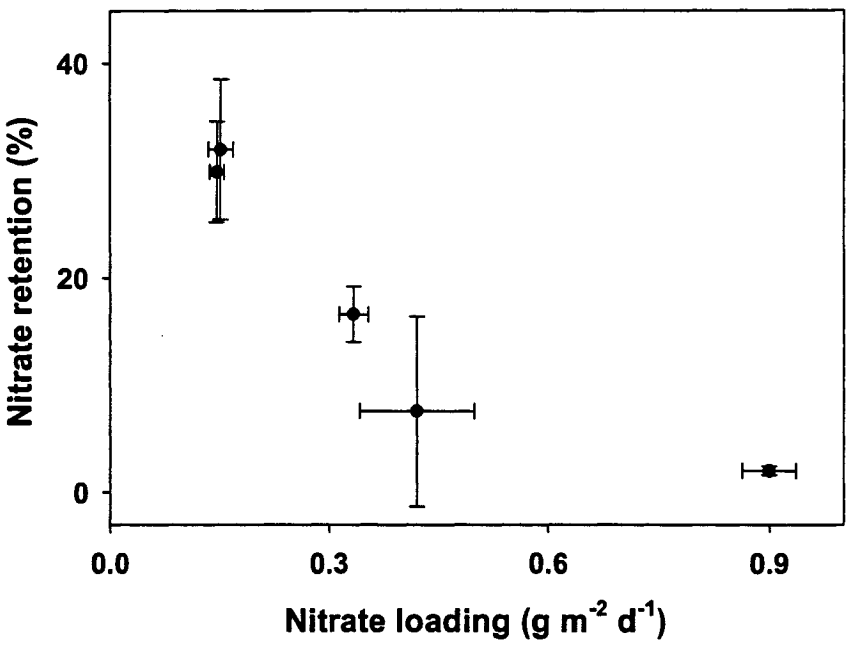


Figure 22. Percent nitrate retention with increasing areal nitrate loading at Little Castor North Branch. Vertical error bars represent the standard error of the ratio and horizontal error bars represent the standard deviation.

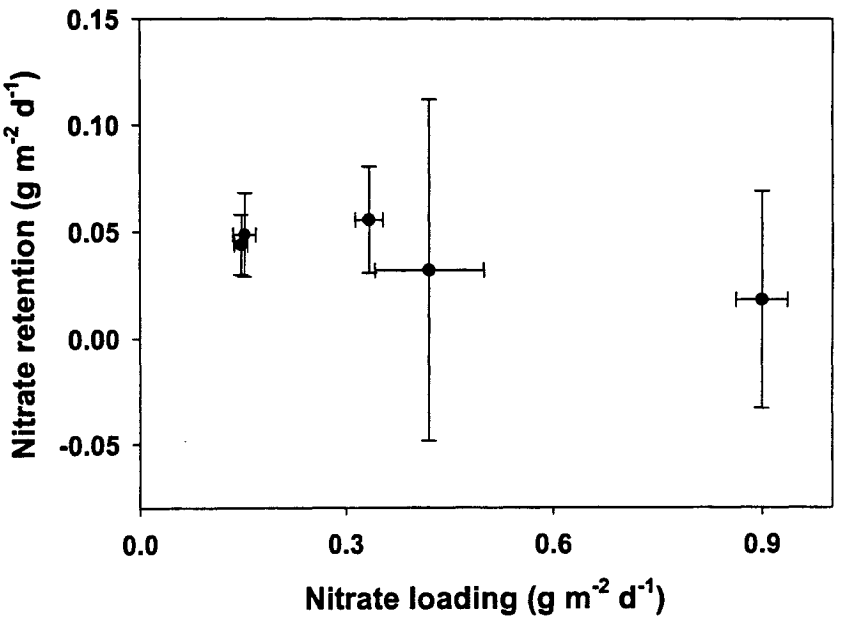


Figure 23. Areal nitrate retention versus areal nitrate loading at Little Castor North Branch. Vertical and Horizontal error bars represent the standard deviation.

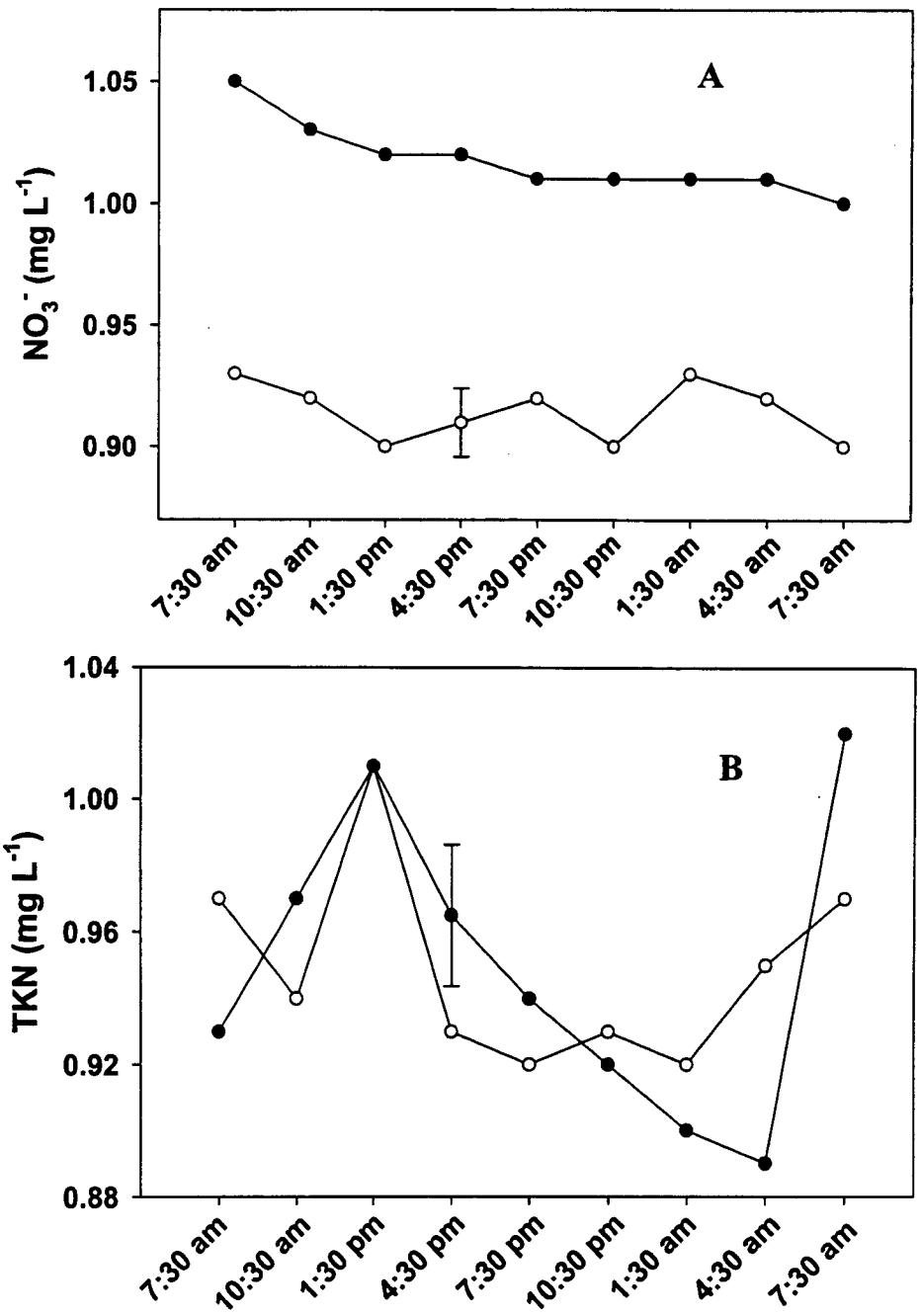


Figure 24. Diel change in (A) nitrate and (B) total Kjeldahl-N concentration at Plantagenet at upstream (○) and downstream (●) locations. Duplicate samples were collected at 4:30 pm at each location with error bars representing the standard deviation for that time. One sample was collected at each location at all other times.

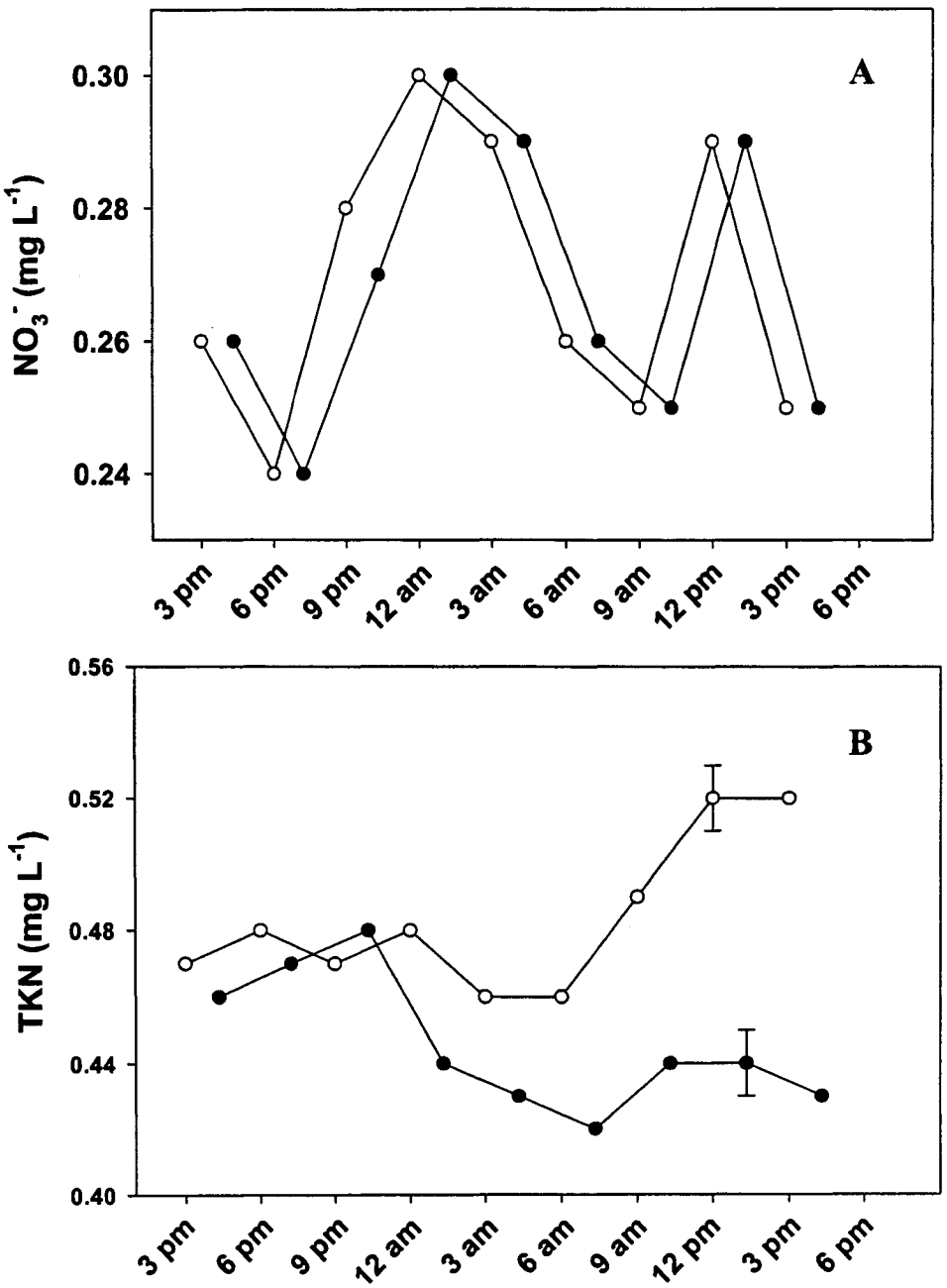


Figure 25. Diel change in (A) nitrate and (B) total Kjeldahl-N concentration at Parkway at upstream (○) and downstream (●) locations. Duplicate samples were collected upstream at 12 pm and downstream at 1:20 pm with error bars representing the standard deviation for that time. No error bars indicate that the error was smaller than the symbol. One sample was collected at each location at all other times.

Chapter 4

Discussion

The focus of this research was to test the hypothesis that river reaches of different sizes differ in their capacity to process nitrogen and that the differences are related to stream depth. In theory, the percent retention of nitrogen decreases with depth because deeper sites have a larger volume of water that must be processed by a relatively smaller benthic surface area (the main site for removal) than shallower sites, resulting in a diminished processing capacity. The null hypothesis is that rivers of all sizes have the same nitrogen retention efficiency. In addition, the influence of other reach characteristics on retention were also investigated.

The unique aspect of the present study was to estimate nitrogen removal at numerous sites across a single river network over a range in stream/river sizes. Most nitrogen mass balance studies are performed on a single, or few, reaches of river measured on several occasions or presented as a seasonal or annual average, which results in a narrow range in depths encountered relative to the range in depths experienced over an entire watershed. My intention was to increase the range in depths studied by sampling many different sites within a watershed from headwaters to the outflow.

4.1 Nitrogen retention across the South Nation watershed

Nitrogen retention on a percentage basis

In general, the percent retention (retention expressed as a percentage of inputs) of nitrate and total nitrogen varied by two orders of magnitude across the South Nation watershed from negative values suggesting an increase of N over the reach (loading) to the highest value representing nearly complete removal of nitrate. The range in retention experienced for TKN was narrower than that of nitrate. This possibly reflects the highly refractory nature of TKN versus the more labile nitrate fraction (Ruttner 1974).

This study measured the nitrogen concentration at an upstream and downstream location. A significant difference in upstream, downstream concentration was found in 54 % of the sites for nitrate and 43 % for TN. Post-hoc power analysis showed that the lack of significance for some sites was probably due to duplicates being an inadequate sample size for the t-test; a modest increase in sample size would likely have brought the total number of sites with significant differences in concentration to roughly 75 % for both nitrate and TN comparisons. Despite the lack of significant retention or loading at several sites, collectively the data show the expected pattern of exponential decline in percent retention with depth (Fig. 9 and Fig. 26) (Seitzinger *et al.* 2002, Howarth *et al.* 1996).

Shallow sites had the highest percent nitrate retention per square metre (Fig. 8), although the relationship between retention and depth was not significant probably due to numerous shallow sites that displayed nitrate loading. When the data were log transformed for sites showing retention, a significant relationship was observed (Fig. 10). Similarly, shallow reaches were more efficient at removing TN and it appears that the

ability of river reaches to process TN declines exponentially with depth (Fig. 9), or linearly with depth when sites showing retention were log transformed (Fig. 11).

An unexpected result in the present study was the number of sites where an increase in nitrate or TN was observed along the reach (loading) during the sampling period in the absence of any obvious surface inputs, although, it should be noted that only about half of these sites showed statistically significant nitrate or TN loading. During summer baseflow conditions the literature consistently reports retention of nitrate in streams, however, loading of organic-N or TKN within a reach has occasionally been reported (Cooper and Cooke 1984, Hill 1988). Nitrate loading has been reported during winter when discharge is high and the water temperature is low thereby prohibiting settling of particles or biological processing (Hill 1983). Net nitrate loading has been recorded in the summer but only during the rising phase of a storm event with nitrate retention resuming during the peak phase of the storm flow (House *et al.* 2001).

In the absence of any surface inflows, possible reasons for the observed nitrogen loading in the present study could include 1) the sampling limitations in methodology, 2) groundwater contributions to the reach, 3) in-stream production of nitrate through nitrification and finally 4) resuspension of sediments as a source of organic-N (Svendsen and Kronvang 1993). A discussion of these possible reasons for the observed N loading follows.

In terms of the sampling methodology, all tributaries to the study reaches were sampled and there was no observed overland flow during the course of sampling, however it is possible that runoff and associated N could have entered the reach prior to the sampling date. For example, a heavy rainfall might have produced a nutrient pulse

within the river upstream of the reach or between the reach boundaries as overland flow, tile drainage or from tributaries shortly prior to sample collection. Daily rain records from Ottawa and Russell available from Environment Canada (www.weatheroffice.ec.gc.ca) revealed that it rained in total between 0.6 mm to close to 60 mm (average between 15 – 25 mm) during the seven days prior to the sampling date for all but one of the sites that displayed loading and also for all but one of the sites that displayed retention. Most of the sites that displayed loading had short water residence times (WRT, 1 – 15 hours) and it is therefore reasonable to assume that no surface water would have entered the reach between the US and DS locations within the short hours of the WRT prior to sampling. However, it is possible that fluctuations in river chemistry due to rain events in the days before sampling could have produced some of the observed loading events. The effects of changing discharge at a particular site can be seen from sites that were sampled more than once in 2003, some of which displayed nitrate loading. These repeat sample sites provide a clue to the conditions under which loading may occur. It appears that as discharge increases, percent nitrate retention decreases possibly to the point where the reach begins to act as a source of nitrate. Four sites showed a general pattern of decreased retention with increased discharge, with one site showing nitrate retention at low discharge (40 ± 27 % and 11 ± 0 % retention at 15 and 20 L s^{-1}, respectively) and nitrate loading at the highest observed discharge (20 ± 1 % loading at 80 L s^{-1}). Summer nitrate loading has been observed under high discharge conditions elsewhere in the literature and is usually associated with a storm (Jansson *et al.* 1994b, House *et al.* 2001), however in one study nitrate loading was seen ten days after a large

storm had passed even though the discharge at the time of sampling had returned to baseflow (Cooper 1990).

In this study comparisons were not made on the same water parcel (except for the diel study at Parkway) as it travelled through the reach since this would have necessitated a prior knowledge of the water residence time and a lengthy sampling period. Instead, an assumption was made that the upstream chemistry was representative of downstream chemistry when the water parcel was originally at the upstream location. The assumption that the US chemistry remains unchanged over the duration of the water residence time is probably more valid for reaches with a short water residence time and is less likely to be correct over longer WRT. However, in contrast loading events occurred mostly at short water residence times for nitrate while TKN exhibited loading at both long and short water residence times. The magnitude of TKN loading events generally increased with longer WRT, possibly indicating greater algal growth in sections of the river with long water residence times.

Another explanation related to the sampling methods is the possible diel variation in retention. The standard error for estimating multiple values of retention over a 24 hour period is low (average S.E. from Table 6 = 1.8%), however individual estimates can vary considerably (Table 6).

Aside from sampling issues, groundwater could also be a source of N to the reach. It was not possible to effectively evaluate the influence of groundwater on nitrogen loading because groundwater nitrate samples were not collected and estimating groundwater discharge to a reach was difficult because of the error involved in discharge measurements associated with sampling at different locations. However, it is unlikely

that groundwater inputs would have produced the observed nitrate loading due to the lack of both a significant DS increase in discharge and nitrate loading (only one of ten loading events). Large groundwater inputs appear to be highly localized and infrequent within the watershed, at least along the main stem of the South Nation River (Kingsley 2004). In addition, several studies indicate that groundwater nitrate is largely removed before entering a stream by the riparian zone (Cooper 1990) and within the hyporheic zone (Burns 1998).

The third possible explanation for nitrate loading could be the process of nitrification. The surface water nitrate concentration of a nutrient poor desert stream was strongly correlated to the magnitude of upwelling of nitrogen-rich hyporheic water, however the origin of the hyporheic nitrate was not completely known but was attributed to floodwater stored in the hyporheic sediments and/or nitrification in the hyporheic zone (Valett *et al.* 1994). Nitrate production from nitrification (6986 t yr^{-1}) slightly exceeded removal due to denitrification (6939 t yr^{-1}) in a 37.5 km long, 82.1 km^2 section of the Mississippi River that included vast areas of impoundments and contiguous backwaters with the main and side channels (Richardson *et al.* 2004). Similarly, nitrification produced 300 t yr^{-1} of nitrate while denitrification removed 3600 t yr^{-1} over a 105 km section of the South Platte River, Colorado (Sjodin *et al.* 1997). Failure to estimate nitrate inputs from nitrification would have underestimated reach removal of nitrate in the Mississippi by 6 % and underestimated removal by denitrification in the South Platte River by 2 %. The possible role of nitrification in nitrate loading observed in the present study could not be properly assessed because nitrification rates in the South Nation watershed were not estimated, however, results from the literature indicate that

nitrification can act as a source of nitrate within stream reaches. Mass balance studies of nitrate and/or TN rarely estimate nitrate inputs due to nitrification.

Stream depth, discharge and changes in turbidity and chl *a* all failed to explain the observed pattern in nitrate retention. The only significant relationship found with percent nitrate retention was changes in ORP (Fig. 17). There was an observed pattern of nitrate retention as the redox potential decreased along the reach. The redox potential in the water column was generally too high to support denitrification (~280 - 350 mV), however, the decrease in water column redox potential might reflect increasingly reducing conditions in the sediments which may have been the true driver in the significant relationship between nitrate retention and water column redox potential.

Finally, loading of TKN over the length of a reach was perhaps due to resuspension of sediment, organic matter or sloughing of periphyton, while TKN retention was likely due to settling or filtration of particles or bacterial utilization of some forms of organic-N. At a single site, Plantagenet, higher TKN concentrations were observed at higher water column turbidity over a two year period (Appendix X), while across different sites in 2003 TKN concentration also increased with higher turbidity, however at low turbidity levels (generally < 10 NTU) a wide range in TKN concentrations was observed. The significant positive relationship between % TKN and % turbidity retention ($r^2 = 0.21$, $p = 0.002$) supports the possibility that sedimentation or filtering of particles leads to retention of TKN while increases in turbidity, either through resuspension of particles or growth of suspended algae, is associated with increases in TKN loads along the length of a reach. Svendsen and Kronvang (1993) found that mobilization of organic matter accounted for 15 – 20 % of the organic N export and 3 – 6

% of total N export during the fall for a Danish watershed. Loading of TKN within a reach may also be due to growth of suspended algae, or release of organic-N from living or decaying macrophytes. The significant positive relationship between % TKN and % chl *a* retention ($r^2 = 0.17$, $p = 0.008$) suggests that increasing TKN levels may be partially explained by growth of suspended algae. Cooper and Cooke (1984) reported that the main effect of grassed reaches (*Glyceria fluitans*) was to modify stream nitrogen chemistry, acting as a source of TKN and NH_4^+ while removing NO_3^- and TN in two headwater vegetated channels compared to a non-vegetated channel. In addition, it was observed that the plants may remove all or most of the nitrate and release it as an estimated 40% not amenable to mineralization (Cooper and Cooke 1984). Multiple regressions using both turbidity and chl *a* improved the ability to predict both TKN and TP retention ($r^2 = 0.38$, $p = 0.0002$ and $r^2 = 0.53$, $p < 0.0001$, respectively).

In summary, although all of the above mechanisms are possible sources of N to the water column, groundwater and nitrification are the least likely. The sampling method is the most likely explanation for most of the observed nitrate loading, but not necessarily as important a factor for TKN loading which is most likely due to resuspension of sediments or algal growth. Continuous sampling of both discharge (gauged) and water chemistry (autosamplers) over several water residence times would be necessary to properly compare all inputs and outputs within a reach.

Retention in the South Nation watershed can be compared to two models in the literature that predict stream/river N retention (Alexander *et al.* 2000, Seitzinger *et al.* 2002). Alexander *et al.* (2000) predicted that the in-stream loss rates of TN declines rapidly with channel depth within the Mississippi River basin. The TN decay coefficients

were a function of water travel time, streamflow and whether or not the channel was part of a reservoir. They divided streams into 4 discrete depth classes and predicted a 45 % loss of TN per day of travel time for streams between 0.5 m to 1.1 m deep, a 12 % d^{-1} loss for rivers between 1.1 m to 2.7 m deep, 5 % d^{-1} loss between 2.7 m to 4.1 m and 0.5 % d^{-1} from 4.1 to 12.6 m. When South Nation TN loss rates were expressed per day of travel time (WRT), they were considerably lower than that found in the Mississippi basin with overall loading occurring in the middle range of depths; 11 ± 54 % d^{-1} for depths below 1.1 m, -1.6 ± 4 % d^{-1} for depths between 1.1 to 2.7 m, and 2.6 ± 3 % d^{-1} for depths above 2.7 m. Overall, there was no significant difference in retention from the current study for the three different size classes due to the large variability in each class.

Another model, RivR-N, (Seitzinger *et al.* 2002) used literature estimates of N retention in 23 lake and 10 river studies to predict N retention (R; expressed as a percentage of N inputs) based on the ratio of stream depth (D; in m) to water travel time (T; in years) ($R = 88.45(D / T)^{-0.3677}$, $r^2 = 0.73$) (Fig. 26). The model explained less of the variability in N removal when only the literature river data were used ($r^2 = 0.43$). Higher D/T ratios reflect larger channel sizes because although depth and velocity both increase with larger channels, depth increases relatively faster (Seitzinger *et al.* 2002). The authors commented that the data and residuals displayed greater scatter for larger D/T ratio values, > 100, which included most of the river observations. The D/T ratios for the South Nation watershed (SNW) cover the range typically found for rivers. However nitrate retention within the SNW displayed a much wider range in values than the literature. Around a third of TN retention estimates from the SNW were considerably lower than the RivR-N model predictions (Fig. 26). RivR-N appears to be a poor

predictor of nitrate retention in the South Nation watershed with 9 estimates from the present study greater than the highest river N retention encountered in the model. Also, the model cannot predict negative retention and so cannot predict the several occurrences of nitrate and TN loading observed in the present study because no studies in the literature reported loading.

Nitrogen retention on an areal basis

Nitrate and TN retention on an areal basis increases with the magnitude of the areal loading (Fig. 13 and 14, respectively) across sites in the South Nation watershed. This relationship seen in the South Nation is consistent with the literature (Fig. 27). The individual stream reaches, tributaries and the South Nation River itself, exhibit areal N loading and retention values that span the entire range encountered in the literature from North America, Europe and New Zealand. For both the South Nation watershed and the literature data, there is a significant relationship between nitrate loading and nitrate retention on an areal basis but the slope of the relationship using the literature data appears to be higher (slope for literature nitrate data = 0.82) compared to the South Nation data (slope = 0.64).

Areal nitrate loading in the present study had less effect on areal nitrate retention (slope = 0.64, Fig. 13) than areal TN loading on areal TN retention (slope = 1.02, Fig. 14). The weaker effect of increased areal nitrate loading on areal nitrate retention may be due to saturation of the biological removal mechanisms of nitrate (plant uptake and denitrification) as loading increases. Schlesinger (1997, Fig. 12.7) reported a saturation of net primary productivity when the N load to terrestrial, aquatic and marine systems was roughly 10 g N m^{-2} yr^{-1} (0.03 g m^{-2} d^{-1}). This saturation point may be higher when

expressed over the summer season instead of annually. N loading in wetlands greater than 0.1 g m^{-2} d^{-1} can saturate N retention (Downing *et al.* 1999). Another reason for the decrease in areal nitrate retention is shorter water residence times generally associated with increased loading resulting in less time for nitrate to be processed. In contrast, the slope for TN retention suggests that the efficiency in areal TN retention does not decrease with higher areal TN loading levels.

Although it appears that nitrate retention is less efficient with increasing N loading compared to TN, overall reaches still retain a higher percentage of nitrate inputs compared to TN. It can be seen in Figure 27 that estimates of nitrate retention are closer to the to the 1:1 line (100 % retention), with a few reaches from the present study and the literature displaying nearly complete nitrate removal, while TN retention estimates are further from the 1:1 ratio. The lower TN retention possibly indicates the dominance of the TKN fraction in TN (Fig. 7) and the highly refractory nature of TKN compared to nitrate. The magnitude and efficiency in TN retention might be expected to increase if the TN is dominated by nitrate and the loading is occurring in a section of river where conditions are conducive to effective nitrate removal (i.e. headwaters and shallow sites).

Similar analysis performed on lakes, ponds, and wetlands show that there is a linear increase in areal N retention with areal N loading, but that the slopes are < 1 indicating that in general freshwater systems become less efficient at removing N as loading increases (Fleischer and Stibe 1991, Saunders and Kalff 2001).

This decrease in N retention efficiency at higher areal N loading is illustrated in Figure 28. A wide range in retention efficiencies (percent retention estimated from Fig. 27) are encountered at low loading while the percentage of N that is retained within a

reach declines sharply with increased loading. The large range in retention efficiency at low loading across different reaches/rivers may reflect differences in denitrification rates, primary productivity, water residence times, or location of the reach within the river i.e. for similar areal loading levels a deeper reach would be expected to have poorer retention than a shallow reach.

Higher loading to a reach is usually associated with both an increase in nitrogen concentrations and discharge which are highly correlated in temperate regions (Bernot and Dodds 2005). Higher discharge would decrease percent N retention due to a deepening of the water column, increased water velocity and scouring encountered at very high flows. Higher N concentrations may lead to saturation of plant uptake and denitrification (due to possible carbon limitation), which would also lead to lower retention efficiencies. It appears that across different sites, retention efficiency drops below 50 % with summer N loading greater than 2 g m^{-2} d^{-1} (dashed line).

In support of the findings presented in Figures 27 and 28 for rivers, Billen *et al.* (1991) showed a decline in percent N retention with increased annual areal loading to 11 lakes, mostly European. However, varying results have been seen with respect to lakes. Despite a wide range in annual areal nitrogen loading to 69 shallow Danish lakes, there was a comparatively narrow range in areal N retention and the percent N retention was fairly constant, averaging 43 % (Jensen, Kristensen, and Jeppesen 1990).

When Billen *et al.* (1991) expressed percent N retention as a function of watershed area, lake and river (11 rivers) percent N retention showed an increase with higher loading to the watershed. Seitzinger *et al.* (2002) showed a theoretical asymptotic increase in percent N retention for 16 north eastern U.S. rivers with an increasing size in

watershed area. A possible reason for the increased N retention with larger watersheds is that as a drainage basin increases in size, it tends to elongate resulting in longer main channel lengths (Leopold 1994).

The reason why areal N retention increases linearly with areal N loading is because denitrification rates also increase linearly with loading. Kalff (2002, fig. 18-4, pg. 276) used literature data to look at the relationship between nitrogen loading to lakes and the denitrification rate occurring in the sediments and found a positive linear relationship between the two variables with a slope roughly equal to one. Numerous river studies have shown that higher areal denitrification rates are obtained with higher nitrate concentrations (both ambient stream and laboratory amended) in the water overlying the sediments (Pattinson *et al.* 1998, Martin *et al.* 2001, Pind *et al.* 1997, Christensen *et al.* 1989, Cooper and Cooke 1984, Hill 1981).

One possible reason for the increase in denitrification activity with higher water column nitrate concentrations is that nitrate diffuses deeper into the sediments when at higher concentrations, thus extending the zone of denitrification. A ten fold increase in water nitrate concentrations led to a 3.5 fold increase in the rate of denitrification and a 5.5 fold increase in the depth of the denitrification zone in sediment cores from a Danish stream (Christensen *et al.* 1989). The difference in areal denitrification rates between the two nitrate levels was due to a larger zone of activity and not higher microbial activity at higher nitrate concentrations.

4.2 Seasonal nitrogen retention

Depth, and the closely related variable discharge, largely explained changes in N retention on a seasonal basis. Percent nitrate retention at L. Castor N. Br. displayed a significant negative relationship with depth (Fig. 19 A) and Longtin also showed a general pattern of decreasing retention with depth (Fig. 19 B). The reason for the increased retention is that as depth and discharge decrease, the water residence time within the reach increases (Fig. 20, Appendix XII) allowing more time for retention (plant uptake/denitrification) processes to occur. Sedimentation also increases with slower water velocities and longer water residence times, however this process is only expected to be an effective retention mechanism for particulate-N and not nitrate.

In agreement with the observed relationship between retention and discharge in the present study, Jansson *et al.* (1994b) reported a range in summer retention for a 7 km stretch of river from 4 % TN loading, during the period of highest observed discharge (0.788 $m^3 s^{-1}$) to 25 % TN retention which occurred during the period of lowest discharge (0.038 $m^3 s^{-1}$). They concluded that discharge was the major factor controlling N retention and that significant retention only occurred at or below normal summer low flows (~ 0.2 - 0.3 $m^3 s^{-1}$). Summer nitrate retention in two different reaches of the Neversink River, NY, varied from 10 % to 20 % for both reaches and displayed a clear negative relationship with discharge (Burns 1998).

The effects of discharge were not observed at Plantagenet presumably because the site is deep and overall retention is low. It was surprising that Longtin did not display greater retention considering the low volume and discharge for the size of the river. Longtin actually had a longer average water residence time than L. Castor N. Br. when

reach lengths were taken into account (7.5 hr km^{-1} and 6.4 hr km^{-1}, respectively). The ratio of benthic surface area available to process the volume of the water column is a potential indicator of a reaches capacity to process nitrogen, with a greater potential for N removal with high ratios. Longtin had a similar ratio of benthic surface area to reach water volume (1.9 ± 0.4 m^2 m^{-3}) as L. Castor N. Br. (4.3 ± 0.3 m^2 m^{-3}) over the season, although it performed more closely in N removal to Plantagenet which had the lowest ratio of any reach in the watershed (0.35 ± 0.03 m^2 m^{-3}). It must be noted that the two dates of high retention and low discharge had low nitrate concentrations (detection to 0.02 mg L^{-1}) with one retention event not significant (Appendix VIII). Possible reasons why Longtin did not display greater retention includes the long water residence time of the reach (12 -197 hours) and the assumption that the upstream N concentration remains unchanged over the period of the water residence time as discussed earlier.

In contrast to what was seen across reaches/rivers in different watersheds (Fig. 27), increased nitrate loading to a single site did not produce an increase in areal nitrate retention in the current study. The areal nitrate retention at L. Castor N. Br. ranged between 0.018 g m^{-2} d^{-1} to 0.056 g m^{-2} d^{-1} and actually showed a general, but non-significant linear decrease with increased loading (Fig. 23). The decline in areal retention at L. Castor N. Br. despite a higher nitrate loading to the reach was most likely due to an increase in discharge associated with the increased loading (Fig. 18 A) which would result in shorter water residence times (Appendix XII). The implications of static or declining areal retention with increased loading to a given reach is that the stream will remove proportionally less N compared to the inputs as loading increases resulting in lower retention efficiencies (Fig. 22).

Studies from the literature show a variety of responses in areal retention and retention efficiency to increasing N loads for a given reach during the summer. Faafeng and Roseth (1993) observed a dramatic increase in areal retention with nitrate loading in a single reach when the loading was driven by experimentally adding a nitrate solution, while the discharge remained relatively constant. The nitrate retention efficiency generally remained the same (20 – 35%) over the range in nitrate loading with a possible indication of increased efficiency at very high loading levels (levels that would not occur under natural conditions). Burns (1998) showed similar results to the present study of decreased nitrate retention efficiency with increased discharge for two reaches of the Neversink River, NY, on three separate dates, however in contrast to the present study the areal nitrate retention generally increased with higher nitrate loading to the reach. It appears that in the study by Burns (1998), higher discharge decreased the retention efficiency of the reach but did not completely off-set the expected increase in areal retention with a greater nitrate flux to the sediments (Fig. 27). Monthly summer nitrate budgets in a New Zealand headwater stream showed a general decline in nitrate retention efficiency with increasing discharge (Cooper 1990). Areal nitrate retention increased with increasing loading for three dates that displayed similar nitrate concentration and discharge values, presumably due to increasing percent plant cover, while subsequent areal retention at higher loading levels decreased probably due to high discharge for one of the dates and low percent plant cover for another date.

4.3 Nitrogen cycling at the watershed scale

Nitrogen in a stream or river is continuously removed from the water column by biotic and abiotic processes as it travels downstream. The present study and studies from the literature (Seitzinger *et al.* 2002, Alexander *et al.* 2000, Howarth *et al.* 1996) indicate that within a watershed, shallow reaches are more efficient at retaining N and that removal efficiency decreases as the channel size increases. As a result, a river network will remove a greater proportion of nitrogen if the loading is restricted to the headwaters; when loading is increased to the higher order reaches the overall river network retention efficiency declines. The implications of decreased retention efficiency with depth is that, on average, a particle of N will travel further before being removed in deep sections of a river compared to shallower sections. Alexander *et al.* (2000) estimated the proportion of N export from 742 watersheds within the Mississippi basin that is ultimately delivered to the Gulf of Mexico. Watersheds located on large rivers, even 2 500 km from the Gulf, exported 90 % of their N load while watersheds on small streams, even within a few hundred kilometres from the Gulf, delivered substantially less than 40 % of their N load (Alexander *et al.* 2000). Seitzinger *et al.* (2002) estimated that 60 – 70 % of inputs to 1 – 5 order streams, in three north eastern U.S. watersheds, were removed by the time the inputs reached the outlet, while only 5 – 10 % of inputs to 8th order rivers were removed (90 -95 % exported) due to the poor retention efficiency of large order rivers and the reduced travel distance to the outflow. Seitzinger *et al.* (2002) examined how different patterns in the distribution of N loading within a watershed affects N retention in five north eastern U.S. watersheds. When the two highest order reaches within the watersheds received 33 % of the total N load compared to < 10 % of the N load under a base case

scenario of uniform loading, the proportion of N removed decreased by 6 – 7 %. In terms of managing nitrogen export from watersheds, loading to smaller tributaries would be preferable, while loading to deeper sections of rivers should be avoided.

An important additional factor in reducing N transport is to increase the amount of time that it takes for water to travel through a watershed. Land conversion to urban and agricultural landscapes often "improves" drainage by directing precipitation that falls on the land towards a watercourse and moved downstream as quickly as possible. This is accomplished by placing tile drains underneath the soil in agricultural fields, draining wetlands and channelizing watercourses. Reintroducing meanders to channelized streams and re-establishing wetlands and ponds would increase the length and time that water would spend within a stream/river resulting in higher N retention. In addition, high nitrate concentrations in tile drainage that is discharged directly to a stream/river can act as a significant point source of N (David *et al.* 1997) which should be treated (i.e. in diked ditches or ponds) prior to export to the stream.

Since areal retention increases with areal loading (Fig. 27) ponds and wetlands used to remove riverine nutrients should be placed downstream within the watershed where the river N flux (kg s^{-1}) is higher and many small ponds/wetlands would be preferable in order to maximize areal loading, as long as they are still designed with a minimum favourable WRT for N removal (Jansson *et al.* 1994a).

However, any attempts to improve N retention within a river network, must take into consideration annual N export characteristics. Most of the annual nutrient transport in temperate rivers, including the South Nation, occurs in winter and especially spring when in-stream concentrations and flow are high and temperatures are low. Under these

conditions, stream removal mechanisms are not effective and only ponds with a large storage volume and long water residence time will be effective at removing N for loading that occurs at this time of year. In this case, additional strategies must be employed that reduce nutrient transport during spring runoff and this may include the timing and application method of fertilizers and physical barriers or sinks for N including vegetated buffer strips and floodplains.

Compared to other agricultural watersheds the N loads within the South Nation reaches were moderate. The loading rates of nitrogen to streams ranged from 0.0003 to 8.4 g N m^{-2} d^{-1} for nitrate and 0.04 to 15 g N m^{-2} d^{-1} for TN. For a few sites the areal loading is sufficient to alone result in low retention efficiency (Fig. 28). Although not the focus of the present study, phosphorous is likely the limiting nutrient in the South Nation river network. Total nitrogen to total phosphorous ratios (by atom) in the South Nation ranged from 11 to 295 with an average of 56 ± 106 and a median of 46 (n = 44). One site was likely N limited (N:P = 10), assuming no other limiting factors to algal growth, while 11 % of the sites may be N limited (N:P =< 20 > 10). Average N:P supply ratios (by atom) from agricultural catchments are roughly 44, with export from forested soils experiencing ratios of roughly 135, the Mississippi River 27, and feedlot runoff and sewage both around 14 (Kalff 2002, Table 8-2). Interestingly, total phosphorous areal retention displayed a similar significant linear relationship with areal loading as seen in with nitrate and TN (Appendix XVI) and correlation analysis revealed a significant linear relationship between percent TN and TP retention ($r = 0.57$, $p = 0.0001$).

Conclusion

The hypothesis for this research was that the ability of different sized river reaches to process N varies, and that these differences are largely attributed to the amount of water volume (column height) that is processed, primarily, by benthic processes (denitrification). The prediction was that shallower streams would be better at processing N because of a large benthic surface area relative to stream volume.

Across the South Nation watershed, shallow sites appear to be important to N retention, especially TN, and within a site discharge is an important determinant in N retention. Sites are most efficient at removing N when they are shallow, have low flow and they remove the largest amount (in mass) when loading is high.

For all sites that acted as a sink for nitrogen in the South Nation watershed, the absolute retention (areal) fit the expected relationship with loading seen in the literature for rivers, lakes and wetlands, indicating that the absolute retention values obtained in this study are valid measurements. The rare reporting of summer baseflow loading of TN and especially nitrate in the literature suggests that the observed loading in the present study might be due to limitations of the sampling methods and less so due to inputs from groundwater and/or nitrification. Assuming that all or most of the observed loading were due to the sampling methods, the high number of N loading events (~ 40 %) is an unacceptable cost for the benefit of reduced sampling times, effort and obtaining multiple sites.

The results from the literature and the seasonal study in the South Nation show that nitrate retention efficiency declines with increasing discharge to a particular reach. Areal nitrate retention may decline or show a less intense rise with increased nitrate

loading, when the loading is driven by discharge, possibly due to the shortened water residence time and disturbance to the reach substrate. It seems that when loading is driven by increases in nitrate concentration and not discharge, large increases in areal retention are observed, presumably due to higher denitrification, and with similar retention efficiencies at different loading levels.

Overall, the retention of N within the South Nation would appear low, but whether it is lower than for other river systems as suggested by Alexander *et al.* (2000) is difficult to determine. More river systems need to be studied with standard methods and units in order to make such comparisons.

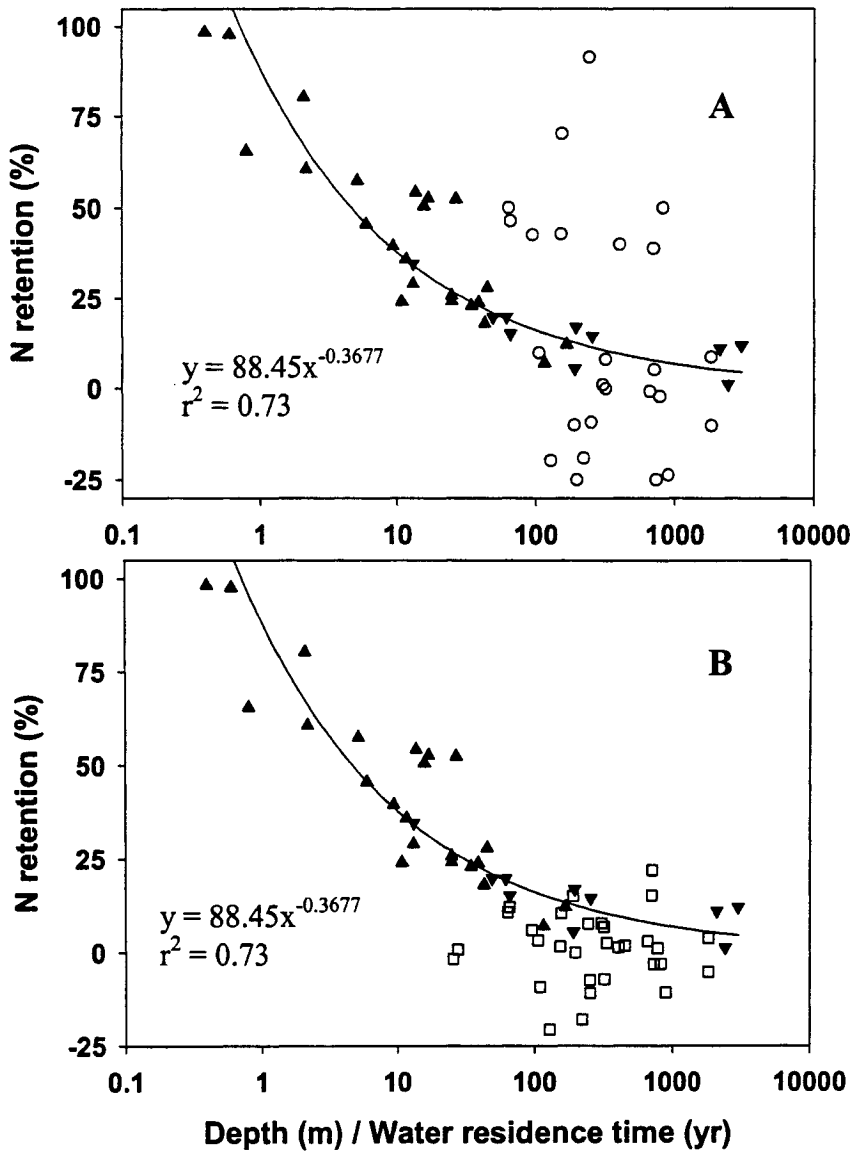


Figure 26. Relationship between percent N retention (including both nitrate and TN) in a study area and depth divided by water residence time from the literature superimposed with estimates of (A) percent nitrate retention (○) and (B) percent total nitrogen retention (□) from the South Nation. Solid symbols represent literature estimates of N retention for lakes (▲) and rivers (▼). Seven of the river N retention estimates were for nitrate and three for TN, while the particular N fraction studied in the lakes was not reported. Model (solid line), fit to literature data only, was developed in Seitzinger *et al.* (2002). All lake estimates of N retention were based on annual studies, while only three of the ten river data were annual studies.

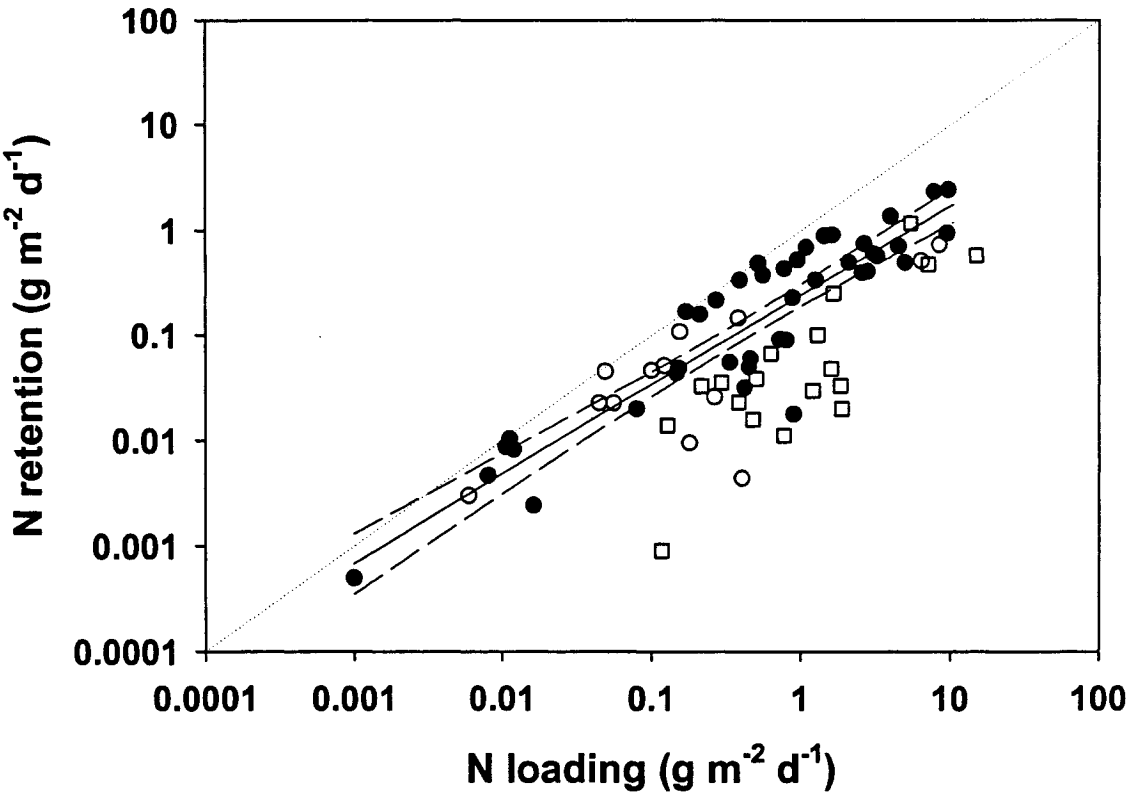


Figure 27. Relationship between log areal nitrogen retention in river reaches and log areal nitrogen loading during summer months in temperate climates. Solid symbols represent literature estimates for nitrate (•); open symbols represent estimates from the South Nation watershed for nitrate (○) and TN (□). Linear regression (solid line) and the 95 % confidence interval (dashed line) are for the literature data and nitrate data from the present study (log y = 0.82 (log x) – 0.59; $r^2 = 0.79$, p = < 0.0001, n = 47). Dashed line is 1:1 ratio. Total nitrogen data from the current study was not used in the model since literature estimates are for nitrate. The literature data represent 17 different sites, 12 of which are a single summer value, while 5 sites are presented between 3 – 6 times each representing individual sampling dates. Literature sources include: (Kalff 2002, Kaushik and Robinson 1976, Faafeng and Roseth 1993, Bachmann *et al.* 1993, Cooper 1990, Burns 1998, Hill 1988, Hill 1983, van Kessel 1977, Hoare 1979, Sjodin *et al.* 1997).

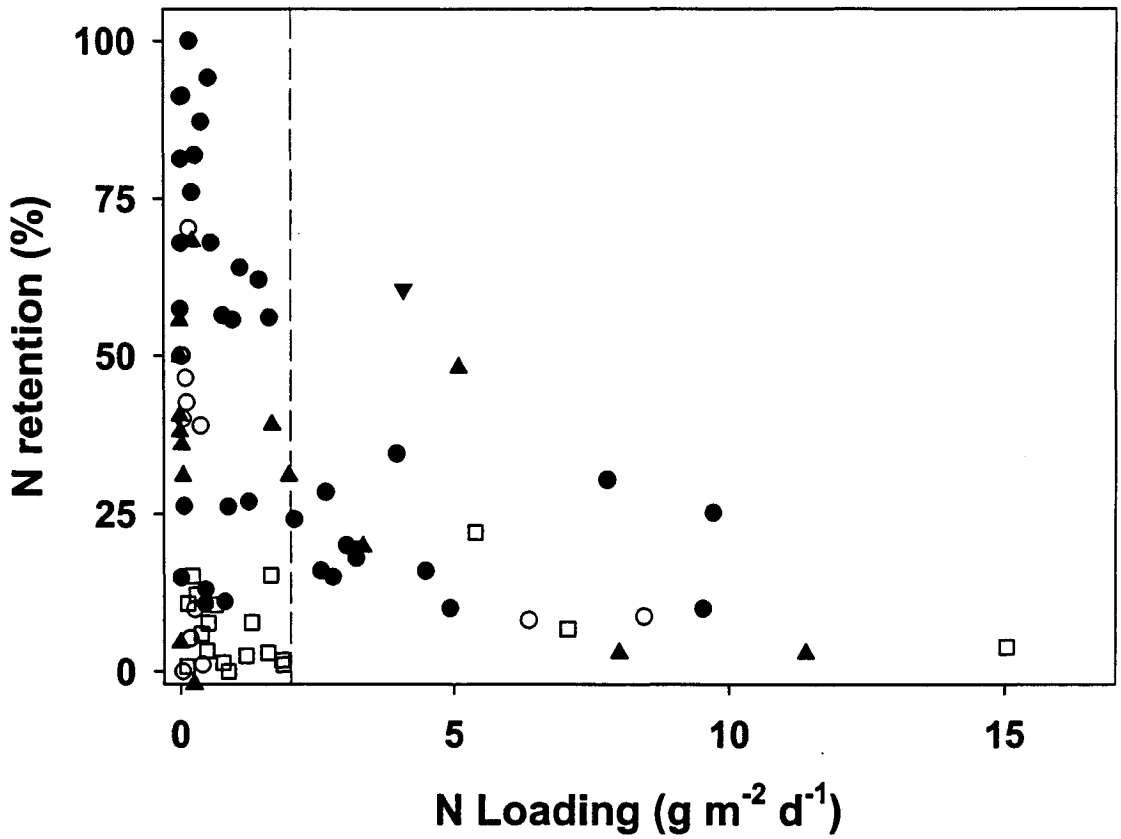


Figure 28. Relationship between percent nitrogen retention in river reaches and areal nitrogen loading. Solid symbols represent literature estimates for nitrate (●) in the summer and annual or winter for nitrate (▲) and TN (▼) estimates; open symbols represent summer estimates from the present study for nitrate (○) and TN (□). Dashed line represents possible point in N loading where there is a decrease in summer N retention (2 g m^{-2} d^{-1}). Literature sources for summer retention are the same as in figure 26, additional annual or winter estimates (some of which produced unexpectedly high retention) include: (Billen *et al.* 1985, Swank and Caskey 1982, Bachmann *et al.* 1993, Richardson *et al.* 2004, Robinson *et al.* 1979, Sjodin *et al.* 1997, Cooper 1990, Burns 1998).

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Appendix I Denitrification rates (mg NO_3-N m^{-2} hr^{-1}) in river/stream sediments during summer (May - September). Substrate: (org.) organic. Carbon content: (IG) loss on ignition, (OM) organic matter, (C) carbon. Method: (AI) acetylene inhibition, (ND) NO_3^- decrease in concentration, (N_2) N_2 flux method, (^{15}N) stable isotope method, (*) sediment slurry analyzed, rest of studies used intact cores.

River/Stream	Location	Substrate	Carbon content	Temp. (°C)	Nitrate (mg/L)	Denitrification (mg N m^{-2} hr^{-1})	Method	Reference
River Råån	Sweden	sandy, low org.	IG <1%	13		2.2 & 9.6	AI	Jansson *et al.* 1994
"	"	sandy, some org.	IG 1-3%	22-24		13 & 46	"	"
Bony Shin Hollow	New York	sand/gravel	400 mg/L	20	883	1	AI*	(Steinhart, Likens, and Groffman 2000)
"	"	organic debris	"	"	"	44		
Unnamed stream	New York	sand/gravel	400 mg/L	20	883	6.2	"	"
		organic debris	"	"	"	31		
Bear Brook	N. Hamp.	sand/gravel	400 mg/L	20	883	1 - 19	"	"
"	"	"	"	"	"	(6 ± 7)	"	"
"	"	organic debris	"	"	"	4 & 8		
East Bear Brook	Maine	sand/gravel	400 mg/L	20	883	1	"	"
"	"	organic debris	"	"	"	2		
West Bear Brook	Maine	sand/gravel	400 mg/L	20	883	.5	"	"
Swale-Ouse	England		0.31% C	7 - 16	0 - 0.50	0 - 0.2	AI	Pattinson *et al.* 1998
(Ravenseat)	"		"	(12 ± 3)	(0.18 ± 0.19)	(0.1 ± 0.1)	"	"
Swale-Ouse	"		0.42 % C	7 - 16	0.26 - 1.22	0.1 - 0.4	"	"
(Ivelet bridge)	"		"	(13 ± 3)	(0.63 ± 0.33)	(0.2 ± 0.1)	"	"
Swale-Ouse	"		0.62 % C	10 - 19	6 - 8.7	0.4 - 3.3	"	"
(Catterick Bridge)	"		"	(15 ± 4)	(6 ± 2)	(1.8 ± 1.1)	"	"
Swale-Ouse	"		0.11 % C	11 - 20	8.3 - 27	0.9 - 3.2	"	"
(Thornton Manor)	"		"	(16 ± 4)	(15 ± 6)	(2.3 ± 0.8)	"	"

Continued on next page

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Swale-Ouse	"		0.43 % C	11 - 22	10.6 - 22	0.5 - 9.2	"	"
(Naburn Weir)	"		"	(17 ± 4)	(15 ± 6)	(2.8 ± 2.9)	"	"
River Wiske	"		0.47 % C	11 - 17	9.8 - 57	3.6 - 12.3	"	"
"	"		"	(15 ± 3)	(28 ± 15)	(6 ± 3)	"	"
San Francisco Crk.	California					0.8	AI	Seitzinger 1988
Little Lost Man Crk.						0.0	AI	Seitzinger 1988
Swift Brook	Ontario			22	0.5 - 4	1.7 - 4.2	ND	Seitzinger 1988
Potomac River						2.9 - 3.3	N_2	Seitzinger 1988
Delaware River						2.3 - 4.8	*	Seitzinger 1988
Gudenå	Denmark		3-5% IG		34	13.9	AI	Christensen *et al.* 1989
Århus Å	Denmark		3-5% IG	22	7 - 77	4.8 - 17.4	AI	Christensen *et al.* 1989
"	"		"	"	(30 ± 41)	(9.9 ± 6.6)	"	"
Gelbæk	Denmark			10 - 15	3.2 - 21	1.2 - 9.9	^{15}N	Pind *et al.* 1997
"	"			(12 ± 2)	(11.7 ± 6.6)	(4.9 ± 3.3)	"	"
Gelbæk	Denmark	sand, some org.	up to 10% IG	9 - 13	16 - 25	1.7 - 8.7[a]	AI	Christensen *et al.* 1990
"	"	"	"	(11 ± 2)	(21 ± 4)	(5.2 ± 2.8)[a]	"	"
Gelbæk	"	sand, some org.	up to 10% IG	9 - 13	16 - 46	11.9 - 19.2[b]	"	"
"	"	"	"	(11± 2)	(25 ± 12)	(15.4 ± 3.2)[b]	"	"
Gelbæk	Denmark	Organic		16	9 - 31	1.9 - 5.3	AI	Christensen and Sørensen 1988
"	"	"		"	(17 ± 9)	(3.3 ± 1.3)	"	"
Rabis Bæk	Denmark	Sandy	<1% IG	13	6 - 9	0.5 - 2.2	"	"
"	"	"	"	"	"	(1.6 ± 0.5)	"	"
Rabis Bæk	Denmark	plants	25-50% IG	13	6 - 9	1.3 - 6.5	"	"
"	"	"	"	"	"	(3.9 ± 2.5)	"	
Scotsman Valley	N. Zealand	Coarse sand	22 µg RMC g^{-1}	18	0.05	B.D.	AI	Cooper 1990
"	"	detritus laden	125 µg RMC g^{-1}	18	0.06	0.05	"	"

* unknown method

[a] cores incubated under illuminated conditions

[b] cores incubated under dark conditions

Appendix II Name, sampling date and geographic location of reaches sampled in the South Nation watershed for (A) 2003 and (B) 2004. For rivers with multiple reaches, the sites are distinguished by either a town or road name found close by as indicated in parentheses. Abbreviations are as follows; trib.=tributary; Br.=Branch; Conc.=Concession; Rd.=Road; Rte.=Route; Hwy.= Highway; N.=North; M.=Middle; S.=South; L.=Little.

(A)

Site Name	Sampling Date(s)				Geographic Coordinates			
					Upstream		Downstream	
	Jun.	Jul.	Aug.	Sept.	Latitude	Longitude	Latitude	Longitude
N. Castor (Hwy. 31)			3		45°15'21"N	75°32'48"W	45°15'30"N	75°32'39"W
N. Castor (Sale Barn Rd.)			3		45°16'07"N	75°33'18"W	45°16'19"N	75°32'56"W
S. Nation (Ventnor)		14	26		44°53'10"N	75°31'27"W	44°53'21"N	75°31'12"W
Black Creek			28		45°24'59"N	75°05'15"W	45°25'07"N	75°05'16"W
Dump Creek		9		7	44°44'18"N	75°34'11"W	44°44'28"N	75°34'08"W
Scotch trib. (Conc. 16 Rd.)				9	45°24'12"N	74°55'14"W	45°24'31"N	74°55'33"W
Bearbrook (Hwy. 417)		18			45°21'31"N	75°29'00"W	45°21'39"N	75°29'05"W
Keeler's Creek	26		13		44°49'35"N	75°35'07"W	44°49'14"N	75°35'05"W
Bearbrook (Sanmure Rd.)				8	45°23'56"N	75°17'18"W	45°24'04"N	75°16'59"W
S. Castor (Belmeade Rd.)		30	26	17	45°07'40"N	75°30'16"W	45°07'32"N	75°29'57"W
Castor (Hwy. 41)		17		2	45°15'18"N	75°24'06"W	45°15'11"N	75°23'23"W
Scotch (Conc. 15 Rd.)				9	45°24'30"N	74°55'38"W	45°25'05"N	74°56'05"W
Moose Creek (trib. 1)			17		45°22'13"N	75°01'04"W	45°22'19"N	75°01'34"W
S. Castor (Springhill Rd.)			21		45°11'53"N	75°24'54"W	45°12'53"N	75°25'24"W
N. Castor (Parkway Rd.)		29			45°17'41"N	75°28'59"W	45°17'37"N	75°28'37"W
S. Castor (Kenmore)			21		45°12'53"N	75°25'24"W	45°13'33"N	75°24'53"W
Bearbrook (Hwy. 19)			28		45°25'25"N	75°06'00"W	45°25'06"N	75°05'18"W

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M. Castor (Hwy. 31)		30			45°12'56"N	75°29'39"W	45°13'19"N	75°29'36"W
Moose Creek (trib. 2)			17		45°21'32"N	75°01'40"W	45°21'56"N	75°01'48"W
M. Castor (Metcalfe)			4, 22	2	45°13'40"N	75°27'08"W	45°13'58"N	75°26'51"W
Scotch (River Rd.)			20		45°26'20"N	74°57'19"W	45°26'38"N	74°57'41"W
Indian Creek	30			7	44°48'42"N	75°36'52"W	44°48'31"N	75°36'28"W
Bearbrook (S. Nation)			14	1	45°25'26"N	75°04'47"W	45°25'13"N	75°04'17"W
S. Nation (Sandy Row Rd.)		3		18	45°00'12"N	75°25'39"W	45°00'51"N	75°23'41"W
S. Nation (Chesterville)		15			75°12'20"N	45°6'40"W	45°7'34.6"N	75°11'34"W
S. Nation (Hyndman)		23			44°56'10"N	75°30'28"W	44°56'28"N	75°30'13"W
S. Nation (Lemieux)		8		11, 16	45°21'51"N	75°06'20"W	45°23'20"N	75°04'25"W
S. Nation (Plantagenet)		16	25	4, 10	45°32'37"N	75°00'26"W	45°33'28"N	75°03'41"W
S. Nation (Hwy. 9)			7	23	45°27'19"N	74°58'26"W	45°27'09"N	74°54'49"W

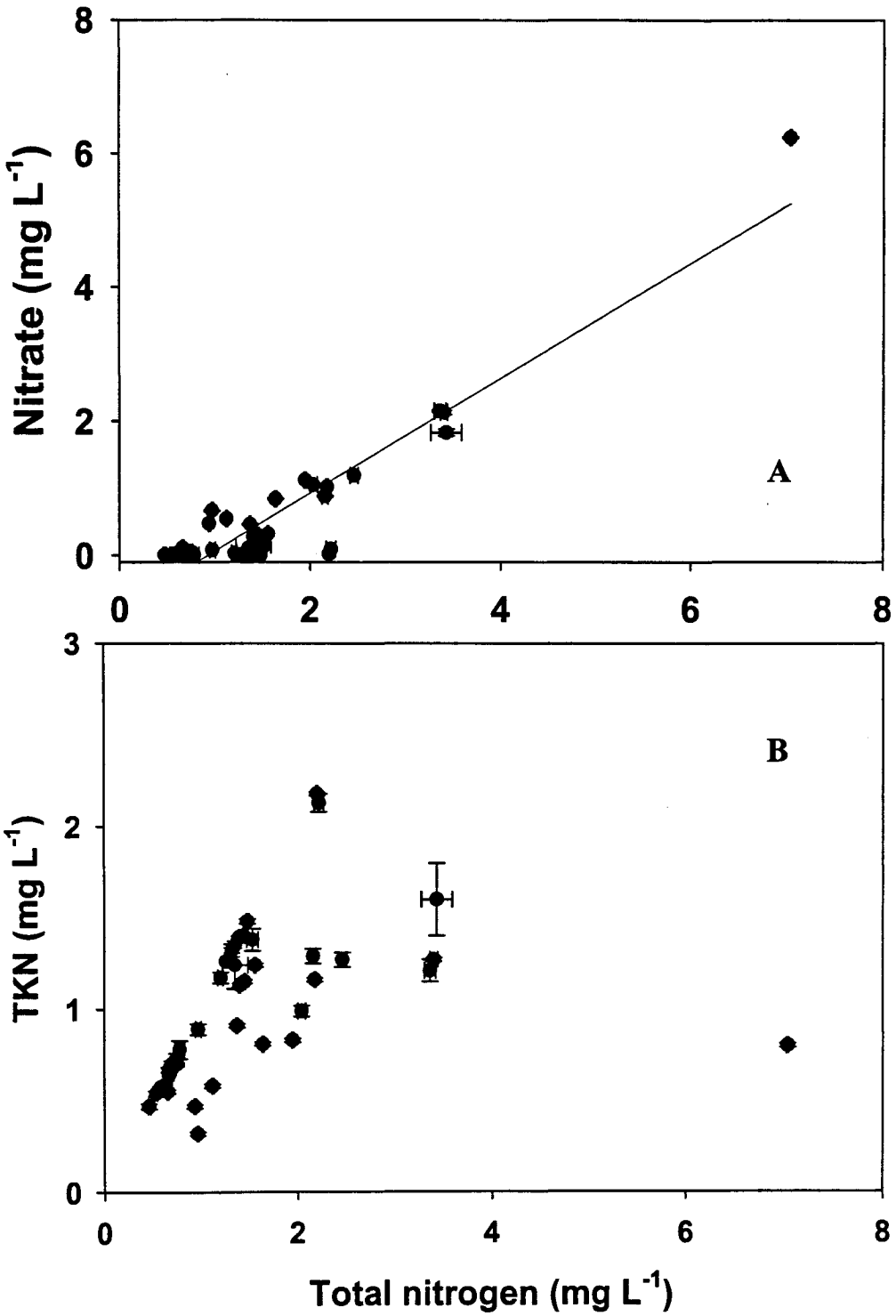
(B)

Site Name	Sampling Date(s)				Geographic Coordinates			
					Upstream		Downstream	
	Jun.	Jul.	Aug.	Sept.	Latitude	Longitude	Latitude	Longitude
L.Castor N. Br.		6, 13, 27	9, 24	23	45°12'25"N	75°17'19"W	45°13'18"N	75°17'12"W
L.Castor (Longtin Rd.)	29	20, 26	10, 26	7	45°16'48"N	75°11'33"W	45°17'06"N	75°09'49"W
S. Nation (Plantagenet)	28	16, 29	16,	2-3, 14	45°32'37"N	75°00'26"W	45°33'28"N	75°03'41"W
N.Castor (Parkway Rd.)				20-21	45°17'41"N	75°28'59"W	45°17'37"N	75°28'37"W

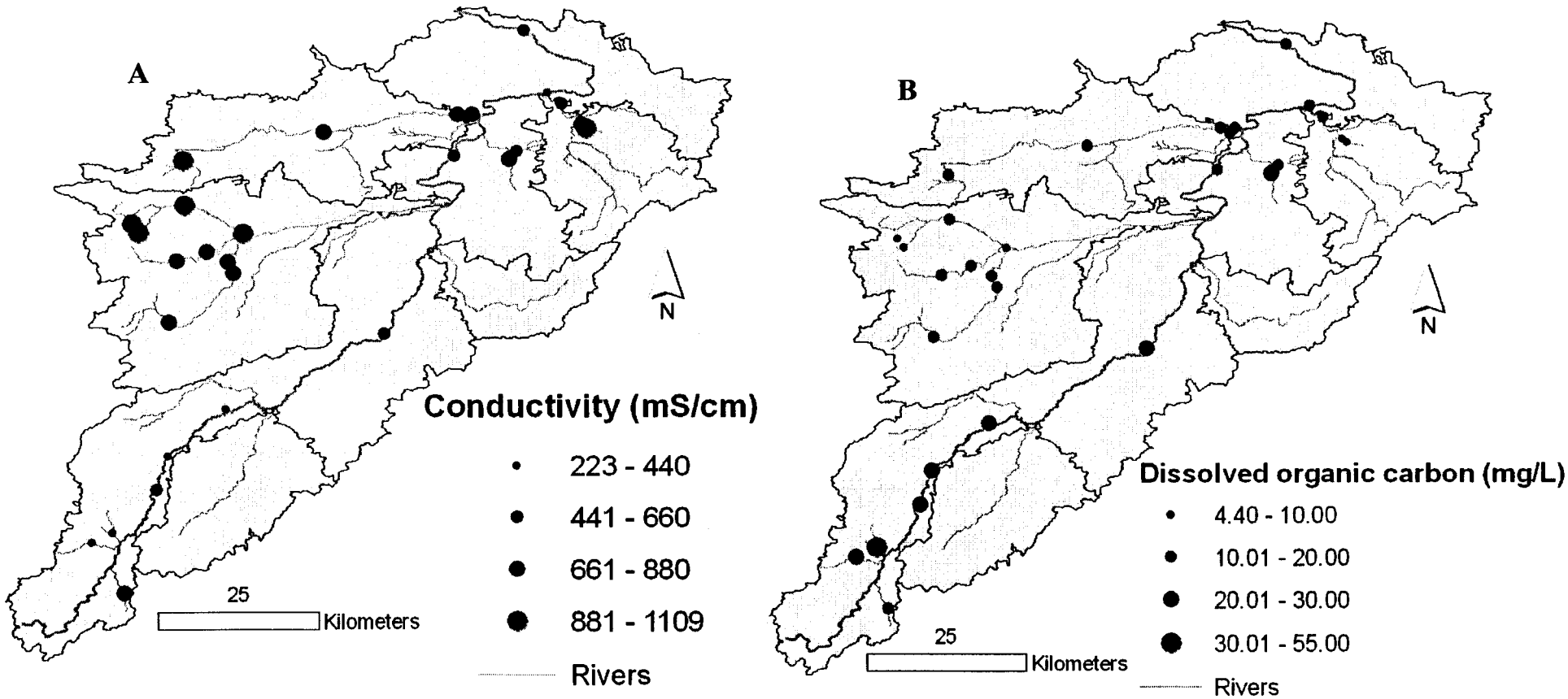
Appendix III Discharge measurement error. Average is three measurements taken at the same location and at the same vertical spacing.

Site	Sampling date	Location	Average discharge ($m^3 s^{-1}$)	Standard Deviation ($m^3 s^{-1}$)	C.V. %
L. Castor Longtin	26/08/2004	US	0.016	0.001	9.1
L. Castor N.Br.	24/08/2004	US	0.0226	0.0004	1.8
L. Castor N.Br.	27/07/2004	DS	0.043	0.001	2.6
Scotch (River Rd.)	20/08/2003	DS	0.183	0.003	1.5

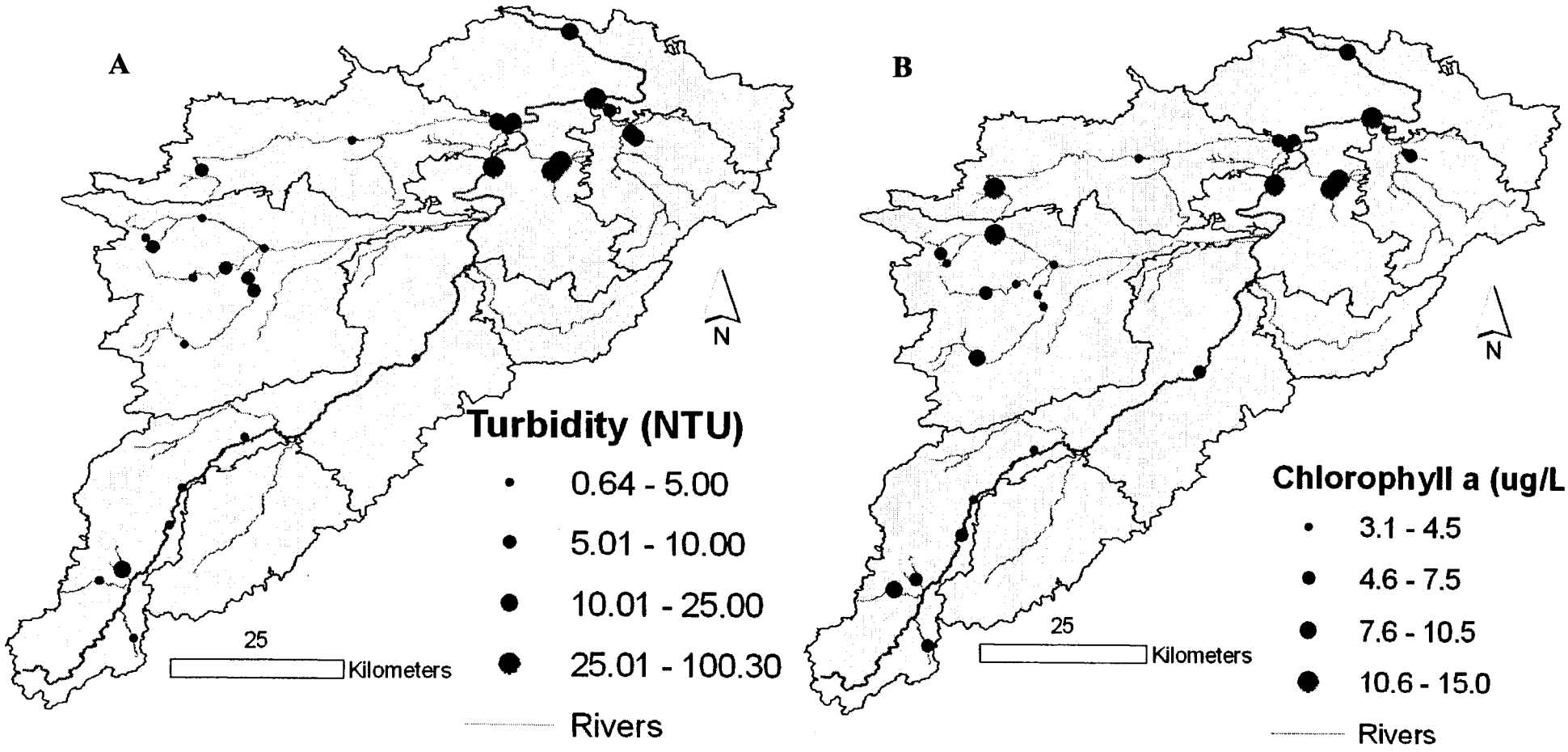
Appendix IV Relationship between (A) nitrate and (B) total Kjeldahl-N fractions with increasing concentrations of total nitrogen in 2003. Horizontal and vertical error bars are the standard deviation. All fractions were measured at the downstream end of the reach.



Appendix V Map of (A) conductivity and (B) dissolved organic carbon across the South Nation river network in 2003.



Appendix VI Map of (A) turbidity and (B) chlorophyll *a* across the South Nation river network in 2003.



Appendix VII Individual replicate chemical measurements (mg L^{-1}) for sites sampled in 2003. Sites appear in order of increasing depth. Fully shaded rows represent sites for which depth or water residence time could not be estimated (not used in nitrate, TKN or TN analysis). Partially shaded rows indicates that the upstream (US) and/or downstream (DS) nitrate were at detection (not used in nitrate analysis). Nitrate value of 0.003 mg L^{-1} was the detection limit. Percent columns refer to % retention (if positive) or loading (if negative). Italicized and bolded values indicate significant retention or loading (not performed for TP). Reach depth and length in metres.

Site	Date	Depth Length	US NO3	DS NO3	% NO3	US TKN	DS TKN	% TKN	US TN	DS TN	% TN	US TP	DS TP
N. Castor (Hwy 31)	03-Aug	0.09	0.64	0.65	-0.8	0.36	0.31	11.0	1.00	0.96	3.0	0.007	0.005
		460	0.66	0.66		0.34	0.32		1.00	0.98		0.008	0.006
N. Castor (Sale Barn)	03-Aug	0.09	0.46	0.47	-2.2	0.54	0.47	4.1	1.00	0.94	1.1	0.015	0.017
		735	0.46	0.47		0.43	0.46		0.89	0.93		0.016	0.018
Ventnor	14-Jul		0.003	0.003	0.0	1.34	1.31	1.1	1.34	1.31	1.1	0.043	0.042
		678	0.003	0.003		1.33	1.33		1.33	1.33		0.043	0.043
Ventnor	26-Aug	0.15	***0.01***	***0.003***	70.0	1.49	1.47	1.3	1.50	1.47	1.8	0.058	0.044
		899	***0.01***	***0.003***		1.51	1.49		1.52	1.49		0.058	0.046
Black Crk	28-Aug	0.13	0.03	0.02	50.0	0.60	0.56	8.9	0.63	0.58	10.8	0.046	0.04
		697	0.03	0.01		0.64	0.57		0.67	0.58		0.046	0.041
Dump Crk	07-Sep	0.14	***6.83***	***6.25***	8.2	***0.75***	***0.79***	-5.3	***7.58***	***7.04***	6.8	0.013	0.014
		354	***6.76***	***6.23***		***0.76***	***0.80***		***7.52***	***7.03***		0.013	0.013
Scotch trib (conc. 16)	09-Sep	0.08	0.05	0.08	-10.0	***0.71***	***0.57***	17.0	***0.76***	***0.65***	15.2	0.132	0.128
		920	0.05	0.03		***0.70***	***0.60***		***0.75***	***0.63***		0.137	0.118
Bearbrook (417)	18-Jul	0.23	0.46	0.45	1.1	***1.02***	***0.92***	10.8	***1.48***	***1.37***	7.8	0.066	0.047
		277	0.46	0.46		***1.02***	***0.90***		***1.48***	***1.36***		0.065	0.047
Keeler's	26-Jun		***0.08***	***0.02***	75.0	2.34	2.17	9.0	***2.42***	***2.19***	11.1	0.116	0.088
		942	***0.08***	***0.02***		2.45	2.19		***2.53***	***2.21***		0.118	0.09
Keeler's	13-Aug	0.30	0.10	0.09	5.3	***2.75***	***2.09***	22.6	***2.85***	***2.18***	22.0	0.15	0.077
		942	0.09	0.09		***2.74***	***2.16***		***2.83***	***2.25***		0.147	0.081
Bearbrook (Sanmure)	08-Sep	0.23	0.003	0.003	0.0	***0.62***	***0.68***	-9.2	***0.62***	***0.66***	-9.2	0.034	0.032
		927	0.003	0.003		***0.61***	***0.66***		***0.61***	***0.68***		0.033	0.032
			0.003			***0.61***			***0.61***			0.033	
S. Castor (Belmeade)	30-Jul	0.26	***0.67***	***0.84***	-23.7	0.81	0.81	0.0	***1.48***	***1.65***	-10.8	0.055	0.05
		539	***0.68***	***0.83***		0.80	0.80		***1.48***	***1.63***		0.056	0.05
S. Castor (Belmeade)	26-Aug		0.09	0.08	11.1	***0.99***	***0.88***	9.6	***1.08***	***0.96***	9.8	0.106	0.118
		539	0.09	0.08		***0.98***	***0.87***		***1.07***	***0.95***		0.107	0.116
				0.08			***0.92***			***1.00***			0.117
S. Castor (Belmeade)	17-Sep		0.03	0.01	40.0	***0.91***	***0.68***	24.3	***0.94***	***0.69***	24.7	0.108	0.087
		539	0.02	0.02		***0.90***	***0.69***		***0.92***	***0.71***		0.108	0.084
Castor (Hwy 41)	17-Jul	0.26	***0.18***	***0.11***	38.9	***0.59***	***0.56***	8.3	***0.77***	***0.67***	15.3	0.033	0.025
		1096	***0.18***	***0.11***		***0.62***	***0.55***		***0.80***	***0.66***		0.035	0.025
			0.18	***0.11***		***0.60***	***0.55***		***0.78***	***0.66***		0.033	0.025
Castor (Hwy 41)	02-Sep		0.003	0.003	0.0	0.50	0.55	-9.1	0.50	0.55	-9.0	0.026	0.025
		1096	0.003	0.003		0.49	0.53		0.49	0.53		0.026	0.024
Moose trib#1	17-Aug	0.35	0.08	0.32	-300.0	***1.00***	***1.24***	-22.9	***1.00***	***1.56***	-54.7	0.21	0.22
		810		0.32		***1.01***	***1.23***		***1.01***	***1.55***		0.22	0.22

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site	Date	Depth Length	US NO3	DS NO3	% NO3	US TKN	DS TKN	% TKN	US TN	DS TN	% TN	US TP	DS TP
S. Castor (Springhill)	21-Aug	0.30	***0.08***	***0.01***	91.3	0.67	0.68	-1.5	0.75	0.69	7.7	0.039	0.031
		2124	***0.07***	***0.003***		0.70	0.71		0.77	0.71		0.038	0.03
N. Castor (Parkway)	29-Jul	0.30	0.49	0.54	-10.2	0.57	0.57	-0.9	***1.06***	***1.11***	-5.2	0.026	0.031
		833	0.49	0.54		0.57	0.58		***1.06***	***1.12***		0.027	0.03
S. Castor (Kenmore)	21-Aug	0.34	0.01	0.003	53.8	0.68	0.74	-11.5	0.69	0.74	-10.9	0.031	0.028
		1968	0.003	0.003		0.71	0.81		0.71	0.81		0.03	0.03
Bearbrook (Hwy 19)	28-Aug	0.33	0.05	0.05	0.0	0.63	0.69	-7.8	0.68	0.74	-7.2	0.083	0.08
		2574	0.05	0.05		0.66	0.70		0.71	0.75		0.086	0.08
M.Castor (Hwy 31)	30-Jul	0.34	***0.02***	***0.01***	50.0	0.65	0.67	-4.7	0.67	0.68	-3.0	0.022	0.023
		839	***0.02***	***0.01***		0.64	0.68		0.66	0.69		0.022	0.022
Moose trib#2	17-Aug	0.41	***0.12***	***0.15***	-25.0	1.42	1.34	2.1	1.54	1.49	0.0	0.2	0.192
		836	***0.12***	***0.15***		1.40	1.42		1.52	1.57		0.2	0.195
M. Castor (Metcalfe)	04-Aug	0.41	0.02	0.02	-25.0	0.62	0.64	-2.4	0.64	0.66	-3.1	0.032	0.03
		724	0.02	0.03		0.63	0.64		0.65	0.67		0.032	0.032
M. Castor (Metcalfe)	22-Aug		***0.003***	***0.02***	-566.7	0.65	0.71	-15.9	0.65	0.73	-18.5	0.026	0.037
		724	***0.003***	***0.02***		0.61	0.75		0.61	0.77		0.026	0.035
M. Castor (Metcalfe)	02-Sep		0.003	0.003	0.0	0.49	0.46	8.7	0.49	0.46	8.7	0.021	0.021
		724	0.003	0.003		0.54	0.48		0.54	0.48		0.026	0.022
Scotch (River Rd.)	20-Aug	0.44	***1.02***	***1.12***	-9.3	0.80	0.82	-5.1	***1.82***	***1.94***	-7.4	0.062	0.066
		2334	***1.03***	***1.12***		0.78	0.84		***1.81***	***1.96***		0.06	0.064
Indian Crk	07-Sep	0.34	***0.01***	***0.003***	70.0	1.31	1.34	-2.3	1.32	1.34	-1.7	0.037	0.058
		806	***0.01***	***0.003***		1.30	1.33		1.31	1.33		0.036	0.053
Indian Crk	30-Jun		0.01	0.003	53.8	***1.27***	***1.38***	-7.8	***1.28***	***1.38***	-7.5	0.034	0.05
		806	0.003	0.003		***1.30***	***1.39***		***1.30***	***1.39***		0.034	0.051
Bearbrook (outflow)	14-Aug		***1.07***	***1.02***	5.6	1.11	1.15	-2.2	2.18	2.17	1.6	0.111	0.115
		2200	***1.09***	***1.02***		1.16	1.17		2.25	2.19		0.114	0.114
Bearbrook (outflow)	01-Sep	0.28	***0.05***	***0.03***	40.0	0.65	0.65	-1.6	0.70	0.68	1.4	0.067	0.067
		2085	***0.05***	***0.03***		0.63	0.65		0.68	0.68		0.068	0.066
Sandy Row-Baldwin's	03-Jul		***0.01***	***0.04***	-300.0	1.41	1.41	0.7	1.42	1.45	-1.4	0.072	0.076
		1665	***0.01***	***0.04***		1.41	1.39		1.42	1.43		0.074	0.074
Sandy Row-Baldwin's	18-Sep	0.69	0.003	0.003	0.0	1.33	1.29	0.8	1.33	1.29	0.8	0.038	0.044
		1998	0.003	0.003		1.32	1.34		1.32	1.34		0.04	0.046
Hyndman	23-Jul	1.12	***0.01***	***0.003***	70.0	***1.28***	***1.26***	1.9	***1.29***	***1.26***	2.5	0.036	0.037
		725	***0.01***	***0.003***		***1.29***	***1.26***		***1.30***	***1.26***		0.038	0.036
Lemieux-Martel's	08-Jul		2.11	2.15	-0.5	1.30	1.27	2.3	3.41	3.42	0.6	0.09	0.083
		4559	2.13	2.11		1.29	1.26		3.42	3.37		0.086	0.081
Lemieux-Martel's	11-Sep		1.19	1.19	1.2	***1.50***	***1.30***	13.9	***2.69***	***2.49***	8.2	0.138	0.082
		4559	1.22	1.19		***1.45***	***1.24***		***2.67***	***2.43***		0.136	0.085
Lemieux-Martel's	16-Sep	1.89	***0.74***	***0.87***	-19.0	***1.09***	***1.31***	-17.4	***1.83***	***2.18***	-18.0	0.106	0.116
		4559	***0.73***	***0.88***		***1.10***	***1.26***		***1.83***	***2.14***		0.103	0.12
Jessup-Plantagenet	16-Jul	2.59	***1.82***	***2.15***	-19.7	***1.01***	***1.18***	-22.6	***2.83***	***3.33***	-20.7	0.053	0.052
		5546	***1.77***	***2.14***		***0.98***	***1.28***		***2.75***	***3.42***		0.053	0.058
			1.79	***2.15***		***0.97***	***1.17***		***2.76***	***3.32***		0.052	0.052
Jessup-Plantagenet	25-Aug	2.78	***0.37***	***0.11***	70.3	1.14	1.15	-8.8	1.51	1.26	10.6	0.109	0.088
		4819	***0.37***	***0.11***		1.14	1.33		1.51	1.44		0.113	0.126
Jessup-Plantagenet	04-Sep	2.76	***0.48***	***0.27***	42.6	***1.04***	***1.12***	-10.8	1.52	1.39	6.0	0.087	0.089
		4819	***0.46***	***0.27***		***1.00***	***1.14***		1.46	1.41		0.086	0.1
Jessup-Plantagenet	10-Sep	2.76	***0.57***	***0.30***	46.4	***1.09***	***1.15***	-5.5	***1.66***	***1.45***	12.2	0.088	0.089
		4819	***0.55***	***0.30***		***1.08***	***1.14***		***1.63***	***1.44***		0.088	0.082
Scotch-Paxton	07-Aug	2.72	1.94	1.88	8.7	1.56	1.46	5.0	3.50	3.34	6.6	0.229	0.227
		5244	2.07	1.82		1.57	1.51		3.64	3.33		0.233	0.226
Scotch-Paxton	23-Sep	2.53	1.11	1.05	9.9	0.96	1.01	-4.8	2.07	2.06	3.3	0.078	0.08
		5244	1.21	1.04		0.93	0.97		2.07	2.06	3.3	0.078	0.08

Appendix VIII Individual replicate chemical measurements (mg L^{-1}) for sites sampled in 2004. Sites appear in order of increasing depth. Nitrate value of 0.002 mg L^{-1} indicates sample was at detection. Percent column refers to % retention (if positive) or loading (if negative). Nitrate values italicized and bolded indicate significant retention or loading (significance testing not performed for other chemical parameters). Highlighted values indicates suspect value, not used in analysis. RP = reactive phosphorous.

Site	Date	Depth (m)	US NO_3^-	DS NO_3^-	% NO_3^-	US NH_4^+	DS NH_4^+	US TKN	DS TKN	US TN	DS TN	US TP	DS TP	US RP	DS RP
L.Castor	06-Jul	0.22	0.75	***0.34***	40.0										
N.Br.			***0.41***	***0.29***											
			0.40	***0.28***											
			0.48	***0.26***											
L.Castor	13-Jul	0.25	0.75	3.36	N/A	0.06	0.03								
N.Br.			0.61	3.34		0.04	0.05								
			0.52			0.04									
			0.49	3.44		0.04	0.04								
L.Castor	27-Jul	0.24	***0.72***	***0.59***	16.6	0.03	0.04								
N.Br.			***0.68***	***0.56***		0.00	0.03								
			0.65	***0.56***		0.00	0.01								
			0.66	***0.55***		0.01	0.00								
L.Castor	09-Aug	0.24	0.84	0.64	7.6	0.00	0.00								
N.Br.			0.73	0.66		0.01	0.00								
			0.58	0.68		0.00	0.00								
			2.86	0.67		0.00	0.01								
L.Castor	24-Aug	0.22	***0.55***	***0.39***	29.9	0.02	0.01								
N.Br.			***0.51***	***0.37***		0.01	0.01								
			0.49	***0.30***		0.01	0.01								
			0.49	***0.37***		0.00	0.00								
L.Castor	23-Sep	0.26	***1.00***	***0.99***	2										
N.Br.			***1.00***	***0.98***											
			1.01	***0.98***											
			1.01	***0.99***											
L.Castor	29-Jun	0.55	0.01	0.01	0										
Longtin			0.01	0.01											
			0.01	0.01											
			0.01	0.05											
L.Castor	20-Jul	0.86	6.52	7.10	-9.9	0.03	0.02								
Longtin			6.70	6.66		0.01	0.01								
			6.48	6.52		0.01	0.02								
			6.33	8.32		0.01	0.03								
L.Castor	26-Jul	0.58	***0.79***	***1.11***	-62.2	0.10	0.01								
Longtin			***0.69***	***1.30***		0.01	0.01								
			0.70	***1.12***		0.02	0.00								
			0.68	***1.11***		0.00	0.00								

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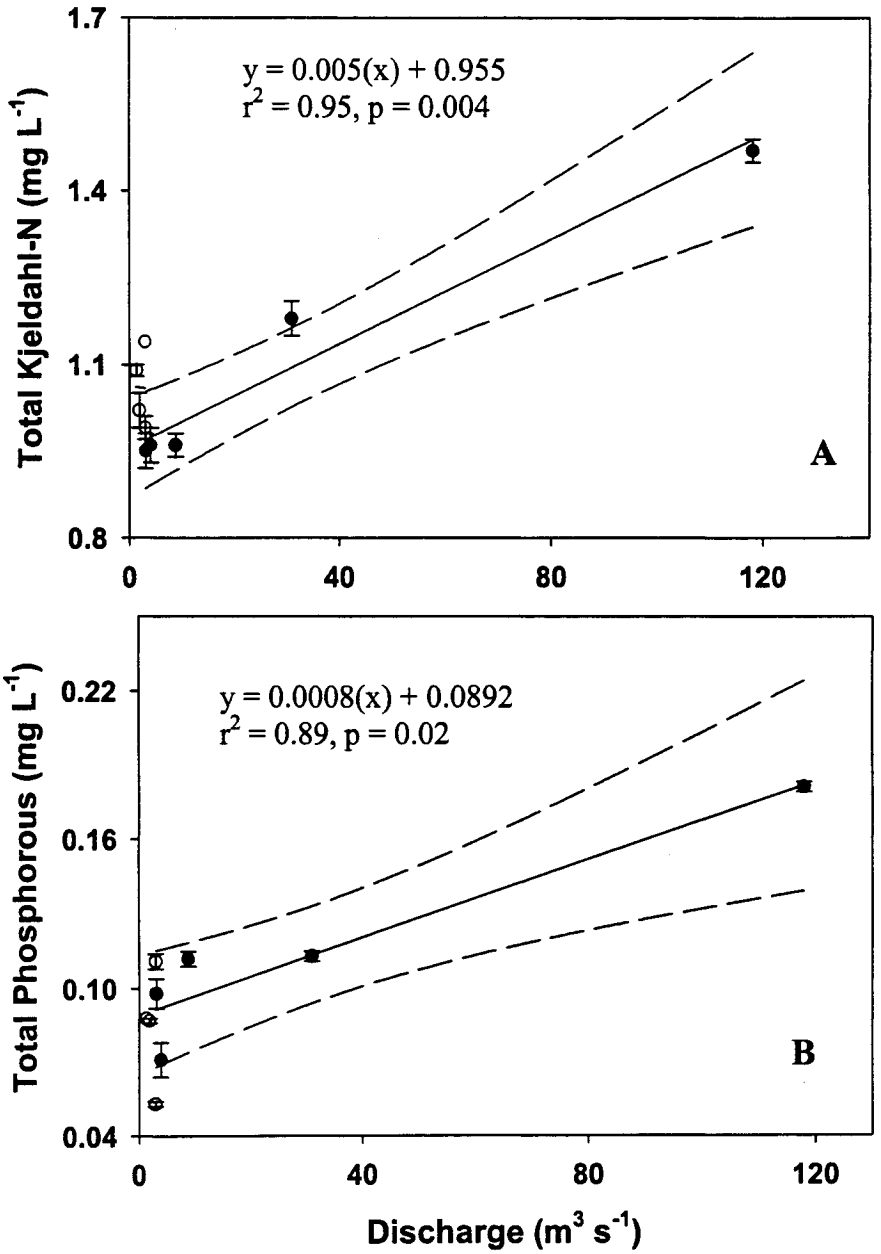
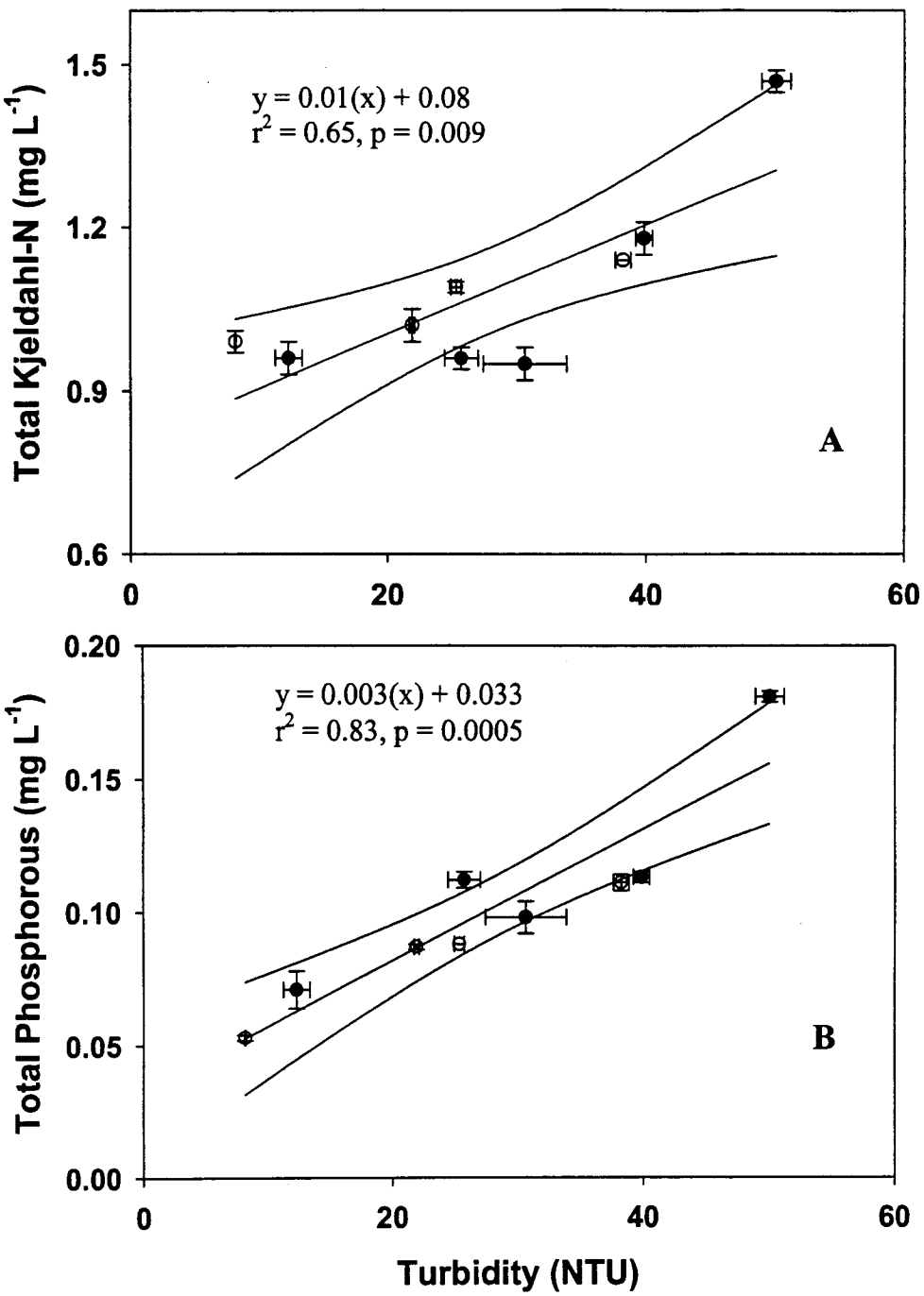
Site	Date	Depth (m)	US NO_3^-	DS NO_3^-	% NO_3^-	US NH_4^+	DS NH_4^+	US TKN	DS TKN	US TN	DS TN	US TP	DS TP	US RP	DS RP
L.Castor	10-Aug	0.54	***0.52***	***0.84***	-58.8	0.02	0.01								
Longtin			0.88	***0.77***		0.01	0.00								
			0.50	***0.84***		0.01	0.01								
			0.51	***0.79***		0.00	0.00								
L.Castor	26-Aug	0.44	0.01		41.7	0.02	0.01								
Longtin			0.002	0.002		0.02	0.01								
			0.01	0.01		0.02	0.02								
			0.01	0.002		0.01	0.00								
L.Castor	07-Sep	0.40	***0.02***	***0.01***	50	0.02	0.00								
Longtin			***0.02***	***0.01***		0.03	0.00								
			0.02	***0.01***		0.04	0.00								
			0.02	***0.01***		0.04	0.00								
Plant.	28-Jun	2.78	1.23	1.29	-11.1										
			1.19	1.57											
			1.29	1.32											
			1.32	1.41											
Plant.	16-Jul	2.96	0.46	0.46	-1.5	0.152	0.136	1.20	1.09	1.66	1.55	0.114	0.079	0.076	0.055
			0.46	0.46		0.154	0.129	1.14	1.02	1.60	1.48	0.114	0.079	0.075	0.057
			0.44	0.46		0.160	0.130	1.20	1.00	1.64	1.46	0.110	0.079	0.074	0.055
Plant.	29-Jul	2.79	***1.34***	***1.17***	12.5	0.070	0.015	0.99	1.08	2.33	2.25	0.072	0.057	0.065	0.031
			1.34	***1.17***		0.066	0.012	0.93	1.14	2.27	2.31	0.077	0.063	0.065	0.030
			1.31	***1.15***		0.055	0.011	0.95	1.18	2.26	2.33	0.064	0.070	0.053	0.029
Plant.	16-Aug	2.82	***1.72***	***1.87***	-5.6	0.065	0.061	0.96	1.03	2.68	2.90	0.115	0.107	0.108	0.093
			1.75	***1.83***		0.065	0.071	0.95	1.02	2.70	2.85	0.112	0.106	0.104	0.095
			1.74	***1.80***		0.070	0.079	0.98	1.09	2.72	2.89	0.110	0.107	0.102	0.094
Plant.	2-Sept	2.78	***0.93***	***1.05***	-11.3	0.047	0.049	0.97	0.93	1.90	1.98	0.103	0.088	0.073	0.077
			0.92	***1.03***		0.034	0.055	0.94	0.97	1.86	2.00	0.101	0.093	0.073	0.082
			0.9	***1.02***		0.027	0.040	1.01	1.01	1.91	2.03	0.109	0.098	0.067	0.081
			0.91	***1.02***		0.033	0.032	0.93	0.97	1.84	1.99	0.097	0.094	0.076	0.080
			0.92	***1.01***		0.038	0.023	0.92	0.94	1.84	1.95	0.093	0.094	0.077	0.076
			0.9	***1.01***		0.036	0.037	0.93	0.92	1.83	1.93	0.097	0.090	0.075	0.077
			0.93	***1.01***		0.048	0.025	0.92	0.90	1.85	1.91	0.090	0.087	0.079	0.074
			0.92	***1.01***		0.041	0.033	0.95	0.89	1.87	1.90	0.093	0.090	0.075	0.078
			0.9	***1.00***		0.036	0.052	0.97	1.02	1.87	2.02	0.102	0.098	0.071	0.084
Plant.	14-Sep	3.54	2.33	2.32	-0.6	0.081	0.088	1.45	1.45	3.78	3.77	0.180	0.175	0.121	0.120
			2.28	2.31		0.078	0.083	1.48	1.40	3.76	3.71	0.181	0.171	0.119	0.118
			2.31	2.33		0.084	0.087	1.49	1.48	3.80	3.81	0.183	0.179	0.122	0.123

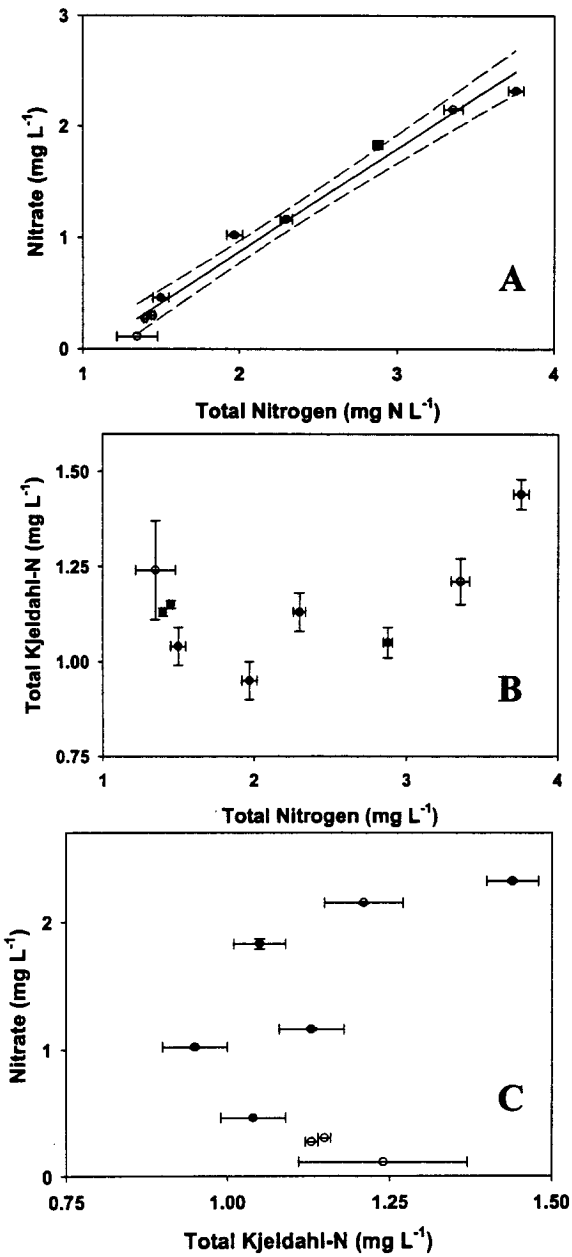
Appendix IX Relationship between (A) Total Kjeldahl-N and (B) Total Phosphorous with discharge at Plantagenet in 2003 (○) and 2004 (●). Chemistry from the upstream location. Regression line (solid) and 95 % confidence intervals (dashed) are for 2004 data. Vertical error bars represent the standard deviation.



Appendix X Relationship between (A) Total Kjeldahl-N and (B) Total Phosphorous concentration and turbidity at Plantagenet in 2003 (○) and 2004 (●). All values are for the upstream location. Vertical and horizontal error bars represent the standard deviation.



Appendix XI Relationship between nitrogen fractions at Plantagenet in 2003 (○) and 2004 (●) (A) nitrate vs. TN ($y = 0.92\ (x) - 0.98$; $r^2 = 0.98$, $p < 0.0001$) (B) TKN vs. TN (C) nitrate vs. TKN. All concentrations were measured at the downstream location. Vertical and horizontal error bars represent the standard deviation. No error bars indicates that the error was smaller than the symbol.



Appendix XII Pearson correlation matrix of Little Castor North Branch variables. Discharge is the average of the upstream and downstream location, in $m^3 s^{-1}$. Water residence time (WRT) in hours, weighted mean depth (WMD) in metres, nitrate concentration in mg L^{-1}. Due to the low sample size (n=5) and multiple comparisons, individual significance tests (Bonferroni) were considered suspect and thus not reported.

	Nitrate retention (%)	Nitrate retention ($g\ m^{-2}\ d^{-1}$)	Nitrate loading ($g\ m^{-2}\ d^{-1}$)
Discharge	-0.924	-0.821	0.992
Water residence time	0.951	0.656	-0.896
Weighted mean depth	-0.953	-0.703	0.962
Nitrate concentration	-0.944	-0.782	0.978

	Discharge	WRT	WMD	Nitrate conc.
Discharge	1.000			
WRT	-0.942	1.000		
WMD	0.972	-0.954	1.000	
Nitrate conc.	0.971	-0.905	0.985	1.000

Appendix XIII Diel data collected at upstream (A) and downstream (B) locations on the South Nation River (Plantagenet), September 2-3, 2004. SpC, pH, ORP, temperature and dissolved oxygen measured at two depths for each sampling period, surface (0.5 m) and close to the bottom (2.5 m). Nutrient, turbidity and chl a collected over the depth of the water column using an integrated tube sampler. Duplicate samples were collected at 4:30 pm at both locations. SpC = Conductivity (mS cm^{-1}), ORP = oxidation reduction potential (mVolts), Temp. (°C), DO = dissolved oxygen (mg L^{-1}). Distance between upstream and downstream site is 4.8 km. Blank space in row represents time period where duplicate water chemistry samples were taken (other measurements were recorded once).

A) Upstream

Time	SpC (0.5m)	SpC (2.5m)	pH (0.5m)	pH (2.5m)	ORP (0.5m)	ORP (2.5m)	Temp. (0.5m)	Temp. (2.5m)	DO (0.5m)	DO (2.5m)	chl a (µg/L)	turb. (NTU)	NO_3^- (mg/L)	NH_4^+ (mg/L)	TKN (mg/L)	TN (mg/L)	RP (mg/L)	TP (mg/L)
7:30 AM	571.1	571.2	8.29	8.09	524	534	20.37	19.92	7.42	6.41	18.6	31.5	0.93	0.047	0.97	1.9	0.073	0.103
10:30 AM	568.2	570.3	8.32	8.04	458	475	20.95	19.69	7.69	5.98	12.7	33.7	0.92	0.034	0.94	1.86	0.073	0.101
1:30 PM	566.6	570.0	8.53	7.88	451	491	22.61	19.61	9.94	5.31	21.5	33.2	0.90	0.027	1.01	1.91	0.067	0.109
4:30 PM	566.6	571.1	8.61	7.94	476	510	23.56	19.58	9.51	5.52	8.9	35.0	0.92	0.036	0.93	1.85	0.077	0.098
4:30 PM													0.90	0.030	0.93	1.83	0.074	0.095
7:30 PM	565.5	570.2	8.88	8.18	471	506	22.75	19.60	11.75	7.00	12.5	31.3	0.92	0.038	0.92	1.84	0.077	0.093
10:30 PM	569.6	571.5	8.65	8.03	494	522	21.30	19.53	9.95	5.88	6.8	27.8	0.90	0.036	0.93	1.83	0.075	0.097
1:30 AM	572.6	572.0	8.45	8.03	510	530	20.31	19.60	8.41	5.31	6.5	28.6	0.93	0.048	0.92	1.85	0.079	0.090
4:30 AM	575.3	573.6	8.42	7.99	511	530	19.63	19.37	8.08	5.03	11.4	25.0	0.92	0.041	0.95	1.87	0.075	0.093
7:30 AM	575.5	572.9	8.37	8.10	496	510	19.28	19.33	7.78	6.17	16.1	29.0	0.90	0.036	0.97	1.87	0.071	0.102

B) Downstream

Time	SpC (0.5m)	SpC (2.5m)	pH (0.5m)	pH (2.5m)	ORP (0.5m)	ORP (2.5m)	Temp. (0.5m)	Temp. (2.5m)	DO (0.5m)	DO (2.5m)	chl a (µg/L)	turb. (NTU)	NO_3^- (mg/L)	NH_4^+ (mg/L)	TKN (mg/L)	TN (mg/L)	RP (mg/L)	TP (mg/L)
7:36 AM	565.8	565.8	8.07	8.07	449	450	20.98	20.96	5.55	5.46	5.08	18.9	1.05	0.049	0.93	1.98	0.077	0.088
10:38 AM	566.6	566.2	8.07	8.05	460	465	21.03	20.97	5.47	5.28	5.28	22.2	1.03	0.055	0.97	2.00	0.082	0.093
1:38 PM	567.5	566.4	8.16	8.02	459	466	21.67	21.00	6.21	5.28	14.23	22.1	1.02	0.040	1.01	2.03	0.081	0.098
4:36 PM	567.2	566.1	8.24	7.97	497	504	23.29	20.99	6.92	5.15	16.87	22.3	1.02	0.031	0.98	2.00	0.080	0.097
4:36 PM													1.02	0.033	0.95	1.97	0.079	0.091
7:36 PM	566.2	565.5	8.41	7.92	474	484	23.38	20.84	7.84	4.73	14.45	23.3	1.01	0.023	0.94	1.95	0.076	0.094
10:39 PM	567.0	566.3	8.25	7.98	511	516	22.20	20.83	6.98	4.83	9.49	21.3	1.01	0.037	0.92	1.93	0.077	0.090
1:40 AM	566.8	566.4	8.29	7.98	524	529	21.40	20.84	6.80	4.60	8.78	21.8	1.01	0.025	0.90	1.91	0.074	0.087
4:38 AM	567.5	566.8	8.20	7.98	537	540	20.84	20.82	6.28	4.32	7.50	20.7	1.01	0.033	0.89	1.90	0.078	0.090
7:45 AM	567.2	566.7	8.12	8.12	544	543	20.61	20.67	5.68	5.61	9.01	20.8	1.00	0.052	1.02	2.02	0.084	0.098

Appendix XIV Diel data collected at upstream (A) and downstream (B) locations at North Castor (Parkway Rd.), September 20-21, 2004. Duplicate samples were collected at 12 pm at the upstream location and 1:20 pm at the downstream location. ORP = oxidation reduction potential, DO = dissolved oxygen. The distance between upstream and downstream locations was 0.8 km. Blank space in row represents time period where duplicate water chemistry samples were taken (other measurements were recorded once).

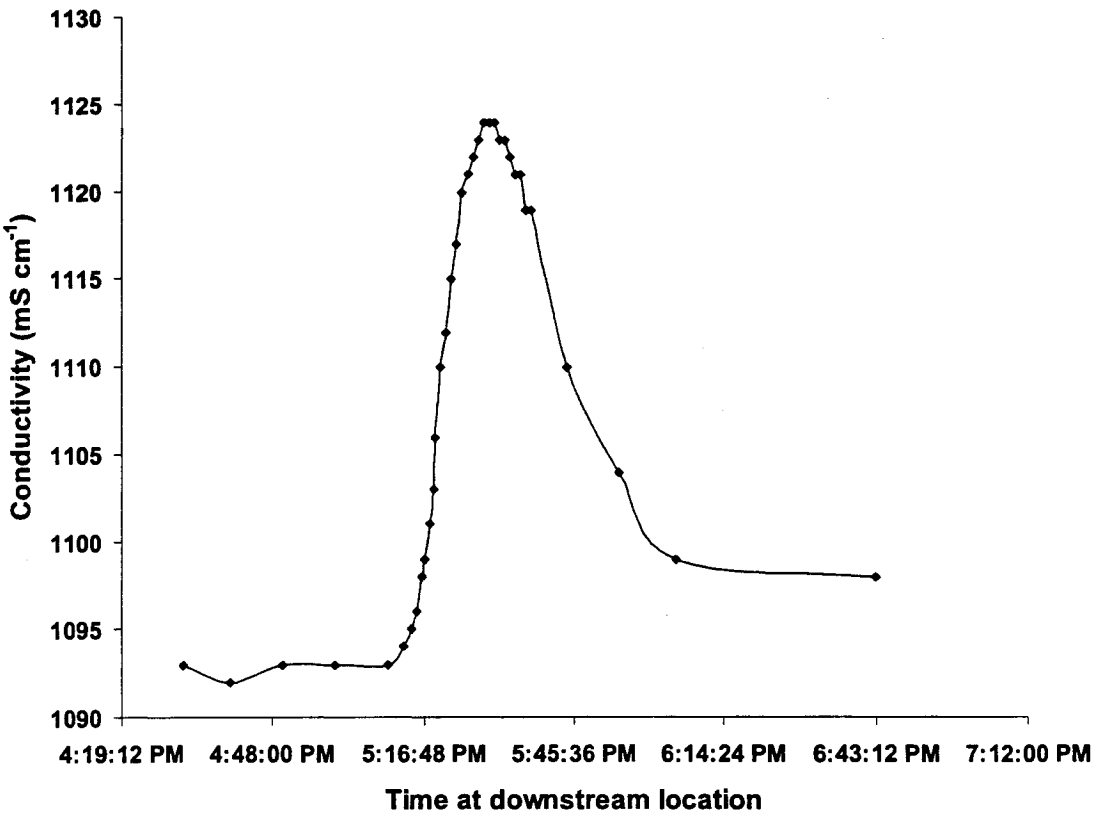
A) Upstream

time	Conductivity (mS cm^{-1})	pH	ORP (mVolts)	Temp. (°C)	DO (mg/L)	chl a (µg/L)	turbidity (NTU)	NO_3^- (mg/L)	NH_4^+ (mg/L)	TKN (mg/L)	TN (mg/L)	RP (mg/L)	TP (mg/L)
3:00 PM	1120.0	8.28	462	11.91	10.50	2.6	7.11	0.26	0.015	0.47	0.73	0.017	0.023
6:00 PM	1107.0	8.24	468	12.26	10.29	3.1	7.11	0.24	0.014	0.48	0.72	0.017	0.028
9:00 PM	1108.0	8.32	489	11.99	9.67	2.6	7.63	0.28	0.014	0.47	0.75	0.017	0.023
12:00 AM	1124.0	8.34	503	11.76	9.30	2.8	8.54	0.30	0.023	0.48	0.78	0.016	0.025
3:00 AM	1141.0	8.39	504	11.91	8.94	1.6	8.54	0.29	0.019	0.46	0.75	0.017	0.025
6:00 AM	1147.0	8.39	509	12.28	8.75	3.5	10.57	0.26	0.021	0.46	0.72	0.018	0.028
9:00 AM	1149.0	8.37	518	12.44	8.72	3.4	10.84	0.25	0.018	0.49	0.74	0.018	0.030
12:00 PM	1148.0	8.37	513	13.09	9.50	3.3	9.95	0.29	0.014	0.51	0.80	0.018	0.027
12:00 PM							10.60	0.29	0.021	0.53	0.82	0.023	0.031
3:00 PM	1143.0	8.39	466	14.13	10.32	1.9	9.46	0.25	0.018	0.52	0.77	0.018	0.025

B) Downstream

time	Conductivity (mS cm^{-1})	pH	ORP (mVolts)	Temp. (°C)	DO (mg/L)	chl a (µg/L)	turbidity (NTU)	NO_3^- (mg/L)	NH_4^+ (mg/L)	TKN (mg/L)	TN (mg/L)	RP (mg/L)	TP (mg/L)
4:20 PM	1118.7	8.32	505	12.30	10.39	2.5	7.10	0.26	0.015	0.46	0.72	0.018	0.024
7:15 PM	1108.2	8.36	506	12.34	10.38	2.3	7.22	0.24	0.014	0.47	0.71	0.018	0.024
10:20 PM	1108.2	8.35	506	12.06	9.61	2.4	9.99	0.27	0.021	0.48	0.75	0.020	0.031
1:20 AM	1122.9	8.36	508	11.74	9.25	3.3	9.30	0.30	0.014	0.44	0.74	0.017	0.026
4:20 AM	1140.7	8.39	510	11.92	9.09	3.0	9.98	0.29	0.013	0.43	0.72	0.016	0.028
7:20 AM	1146.9	8.39	510	12.20	8.91	3.0	11.2	0.26	0.017	0.42	0.68	0.020	0.030
10:20 AM	1149.0	8.39	487	12.70	9.18	2.8	8.80	0.25	0.014	0.44	0.69	0.018	0.026
1:20 PM	1144.8	8.38	470	13.74	9.85	2.9	8.91	0.29	0.015	0.43	0.72	0.023	0.027
1:20 PM							9.69	0.29	0.015	0.44	0.73	0.020	0.027
4:20 PM	1142.7	8.43	487	14.44	10.11	2.5	8.63	0.25	0.022	0.43	0.68	0.018	0.025

Appendix XV Water residence time determination by salt addition at North Castor (Parkway Rd.) Sept. 21, 2004. The estimated water residence time during the diel was 1 hour and 20 minutes which corresponds to a conductivity of 1110 mS cm^{-1} on the figure below. Verification of the true water residence time was done by adding salt to the upstream location after the diel experiment at 4 pm.



Appendix XVI Areal total phosphorous retention for various levels of areal total phosphorous loading across sites in 2003. Regression (solid line) and 95% confidence intervals (dashed line) are given (log y = 0.94 (log x) – 1.21; $r^2 = 0.50$, p = 0.0005, n = 20). Note: only sites displaying retention were used.