LONG-TERM NITROGEN AND PHOSPHORUS TRENDS IN THE GROUNDWATERS OF THE CORNELL TEACHING AND RESEARCH FARM IN HARFORD, NY: 1974-2016

A Thesis

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by

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ABSTRACT

Nitrogen (N) and phosphorus (P) concentrations at the Cornell University Ruminant Center (CURC) in Harford, NY, have been measured in ground and surface waters periodically since 1974. Here, I evaluate the effect of agriculture on groundwater from a farm located within two small catchments with two markedly different land use distributions. Groundwater nitrate (NO_3^-) concentrations are significantly higher in the more intensively farmed south catchment. There, mean monthly groundwater concentrations of NO_3^- have increased from 0.23 ± 12 mM-L^{-1} in 1974 to 0.94 ± 23 mM-L^{-1} in 2016. Groundwater NO_3^- concentrations in the smaller, less intensively farmed north increased from 0.27 ± 0.8 mM-L^{-1} in 1974 to 0.72 ± 0.12 mM-$^{-1}$ in 2016. Total Dissolved P was also measured, but has not significantly increased in either catchment over time, indicating that high soil sorption capacity continues to ensure applied P is retained in soils.

BIOGRAPHICAL SKETCH

Charles was born to Gregory and Roberta (nee Roblin) Ouellette on January 14, 1984 and grew up with his sister Alexis, in Rochester Hills, Michigan. They spent their childhood exploring wild places with friends, and just as often their dad, with an urgency that belied the transformation of the land during the urban sprawl of the late 1980s and 90s from old growth hardwood forests to landscaped lawns with Japanese Maples and lilacs, as wild brooks were tamed to ditches, and at least one menacing swamp became a blue hued ornamental pond with a fountain at the entrance to a subdivision. At least once, he came home with a goat he found wandering their neighborhood. They spent summers in the waters of Lake Michigan and exploring the hidden places along its coast, canoeing on the Pere Marquette River with cousins, aunts and uncles. Winters passed quickly, too, ice skating on the pond behind their home, building igloos, and sledding; ever outdoors enjoying the wealth of nature.

Though raised in a working-class family, Charles' parents made their children's education their highest priority. He and his sister were educated in Catholic schools. In high school, Charles was educated by the Marist Fathers, whose appeal to Our Lady, Seat of Wisdom and the school's motto: "to form good, Christian people, upright citizens, and academic scholars" has remained an important calling throughout his subsequent endeavors. Here, also, Charles was heavily influenced by high school courses in economics, rhetoric and history, and pursued a synthesis of these fields in undergraduate studies.

Charles' grandfather, a veteran of World War II and Korea, prolific reader, gentleman gardener, and financial wizard was quite influential in many aspects of Charles' life. Charles decided to follow in his grandfather's footsteps, attending Michigan State University and subsequently enlisted in the U.S. Army Reserve as an undergraduate on his grandfather's advice, drilling in a Combat Support Hospital. After graduation, Charles was selected by a board of officers to attend Officer Candidate School and transitioned to active duty where he earned his commission as a Second Lieutenant in the Engineer Regiment on Pearl Harbor Day, 2006. Thereafter, he served as a platoon leader and company executive officer in the 37th Engineer Battalion (Combat)(Airborne) on "Fortress Bragg" and commanded a company of paratroopers in the 4th Brigade Combat Team (Airborne), 25th Infantry Division on Fort Richardson, Alaska, jumping out of perfectly good airplanes (and helicopters). Between assignments, Charles earned an M.S. in Geological Engineering from the University of Missouri Science and Technology in Rolla, Missouri. Charles is a combat veteran of both Iraq and Afghanistan. His military awards and decorations include the Bronze Star Medal (two awards), the Purple Heart, the Meritorious Service Medal, the Army Commendation Medal (two awards) and the Army Achievement Medal.

Charles is married to his wife, Dana, whom he met in college one spring evening when she called up to his window and invited him to dance in the rain. A decade, four states and two wars later, they remain madly in love and are teaching their children to dance in the rain, too.

"The use of manure for its crop-producing potential has had its ups and downs, from the time when the size of a man's manure pile was a measure of his wealth to the present time, when the same pile might be the basis for a lawsuit."

L.F. Marriott *et al.* (1977)

ACKNOWLEDGEMENTS

To my bride, Dana, and our children, my parents and grandparents, mentors, dear friends, and educators who have believed in me: I have not done anything but for your love and support, and the energy you invested to my continuing formation. Thank you from the depths of my soul.

As I finish this work and my time at Cornell, I'm more convinced than ever that what I do not yet know vastly exceeds what I do know and that I'm only just starting out on this journey of scientific discovery.

I am especially grateful to Professors Bob Howarth and Todd Walter for generously funding this project. Bob was so open to having an Army Paratrooper and a semi-reformed economist as a member of his lab group in the spirit of Ezra Cornell, who famously said he would found an institution where a person from any background could seek an education in any field. From the outset, Bob was generously open to mentoring someone with a very different life experience than many students who pass through these halls. I am grateful that he was so open to me and for his sound advice and honest feedback which set me out on what I hope will be a lifelong endeavor. Todd's passion for his work and for teaching and mentoring students is both inspiring and infectious.

My sincere thanks Roxanne Marino for the many times she so selflessly gave of her time to help me plan field and lab work, and for the occasional nudge in the right direction to move me along in my quest for data. Roxanne helped me think through many difficult problems with an analytical clarity to which I greatly aspire. Without her advice and support, I could not have completed this work.

Big thanks Dennis Swaney for his sage advice, encouragement and friendship. Dennis helped me to think in new ways about my data and analyses. And after the birth of my daughter when Dana and I were living at the Ronald McDonald House in Syracuse, Dennis and his wife Karin Limburg were incredibly generous and supportive.

Thanks to Tom Butler for showing me the ropes with my first trip to the field to collect samples; to Bongghi Hong for his advice and help learning to use R; and to my lab mates Liz Duskey and Michelle Wong for their camaraderie and advice.

Sincere thanks to Karl Czymmek and Dave Bouldin for allowing me to use their archived samples and unpublished data, and for the time and energy each invested in my success.

There are many others who I would like to publicly thank, including my good friend and mentor, Army Major Jason Toole, who set me on this path. The day I started my week-long journey home from Afghanistan to Alaska to comfort my family and put our lives back together after we lost all of our material possessions in a house fire, I was feeling completely overwhelmed. Just before I flew out of the small, dusty flight terminal on Forward Operating Base Salerno, he returned to tell me that in the coming days I would feel the urge to tell myself I had too much going on to study for the GRE (then just 60 days away) and apply to be an instructor at West Point. I had already had both of those thoughts. He told me to force myself to make the time because I would regret it deeply if I let this experience fall by the wayside. I know that certainly would have regretted it, having had the chance to work with all of these talented and wonderfully generous people, and imagine I will feel that so much more strongly after my time at West Point.

My heartfelt and continued thanks to you all.

DEDICATION

For Dana.

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LIST OF ABBREVIATIONS

AFO - Animal Feeding Operation
ANOVA - Analysis of Variance
AU - Animal Unit
CBW - Chesapeake Bay Watershed
CI - Confidence Interval
CNAL - Cornell Nutrient Analysis Laboratory
CURC (N,S) - Cornell University Ruminant Center (N - North, S - South Catchment)
DIW - Deionized Water
EBOC - East Branch Owego Creek Sub-Basin
FC - Fall Creek Sub-Basin
FG - Farmed groundwater
FS - Farmed surface water
HCl - Hydrochloric Acid
HSD - (Tukey's) Honest Significant Differences
L - Liter
mM - Millimolar
MSS - Months since start, i.e. months since sampling began in May 1974
N - Nitrogen
NH_4^+ - Ammonium
NO_3^- - Nitrate
NOAA - National Oceanographic and Atmospheric Administration
NPS - Nonpoint source
NYS - New York State
OR/FL - Oswego River/Finger Lakes Basin
P - Phosphorus
PVC - Polyvinyl chloride
SE - Standard error
SOM - Soil organic matter
SRB - Susquehanna River Basin
SRP - Soluble reactive phosphorus
TDN - Total dissolved nitrogen
TDP - Total dissolved phosphorus
UG - Upland groundwater
US - Upland surface water
USDA - United States Department of Agriculture
US-EPA - United States Environmental Protection Agency

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ABSTRACT

Nitrogen (N) and phosphorus (P) concentrations at the Cornell University Ruminant Center (CURC) in Harford, NY, USA have been measured in ground and surface waters periodically since 1974. Here, I extend these previous measurements to evaluate the effect of agriculture on groundwater on this farm located in two small catchments with two markedly different land use distributions. I estimate the herd of 790 cattle, which has grown in size from 728 cattle in 1979, now produces approximately 11 million L manure per year which are presumably spread on the 526 ha farm. I use analysis of variance to determine significant differences between nutrient concentrations in each catchment according to land use and seasonally. Furthermore, I determine long-term trends of nitrate (NO_3^-), ammonium (NH_4^+), and total dissolved phosphorus (TDP) in each catchment. Concentrations are typically significantly greater and have higher seasonal variance in the more intensively farmed, 2.5 km^2 south catchment, termed CURC-South, where about 50 percent of land is dedicated to growing corn and where most of the dairy barns and a manure lagoon are located. Here, mean monthly groundwater concentrations of NO_3^- have increased from 0.23 ± 0.12 mM in 1974 to 0.94 ± 0.23 mM in 2016. Alternatively, the north catchment, though 1.5 times smaller in area, is almost two-thirds forest and grassland with very little land dedicated to support the feedlot. Groundwater NO_3^- concentrations in the smaller, less intensively farmed north increased from 0.27 ± 0.08 mM in 1974 to 0.72 ± 0.12 mM in 2016. NH_4^+ concentrations also vary according to land use and

season in each catchment, yet long-term NH_4^+ concentrations in the less intensively farmed catchment may be in decline. TDP concentrations average nearly twice as high in the more intensively farmed CURC-South catchment, but have not varied significantly in either catchment over time, indicating that soil sorption capacity may remain unaffected.

INTRODUCTION

Human activities have greatly increased the natural fluxes of nitrogen (N) and phosphorus (P) from inland watersheds to surface and coastal water bodies (Vitousek *et al.* 1997a; NRC 2000; Howarth *et al*. 2002; Howarth and Marino 2006). When delivered in excessive quantities these life essential nutrients over-fertilize receiving waters becoming eutrophying pollutants which cause nuisance or toxic algal blooms, oxygen depletion, declining biodiversity, loss of beneficial services to society and whole scale transformation of ecosystems (Vitousek *et al.* 1997a and b; Carpenter *et al.* 1998; US-EPA 2012). In the United States, as much as 60 percent of N-limited coastal waters and about 50 percent of P-limited lakes are classified as moderately to severely degraded by nutrient pollution (Schindler 1974; Carpenter *et al.* 1998; Howarth *et al.* 2002, Howarth and Marino 2006).

While crops grown with fixed Haber-Bosch N now sustain as much as 80 percent of the 7 billion inhabitants of our planet, the intensive practices which have characterized post-World War II agriculture have overwhelmed natural nutrient cycles and are a leading cause of environmental degradation (Carpenter *et al.* 1998; Hooda *et al*. 2000; Galloway *et al.* 2003; Howarth 2008). The quality of runoff and groundwater linked to surface waters may be changed by the application of manure fertilizer, in particular, and manure management is increasingly problematic as feedlots trend toward higher animal density and the role manure has been supplanted by chemical fertilizers and decoupled from many farms' nutrient cycles (Gilbertson 1979; Ribaudo *et al.* 2003). These practices result in situations where the average feedlot requires a cropped area about 1000 times greater than what is available to distribute nutrients at a rate commensurate with demand by crops, where the top 6 percent of animal feeding operations (AFOs) with more than 1,000 animal units (AUs) generate an estimated 65 percent of N and 68 percent of P pollution in the United States and where the top 2 percent of AFOs produce 43 percent of all animal waste (Carpenter *et al.* 1998; Ribaudo *et al.* 2003). Indeed, Henry and Seagraves (1960) and Roka and Hoag (1996) found that manure is commonly viewed as a problem, rather than a resource, and dispose of it on land closest to the facility, regardless of that land's ability to use applied nutrients.

Yet, when applied judiciously, manure can be of great benefit, improving both the chemical and physical properties of nearly all soil types, particularly shallow, coarse, or low organic matter (OM) soils (NRC 1993). Manure can also increase the soil's ability to hold water and resist compaction which will be of increasing value to farmers as certain regions become drier due to global change (Madison *et al.* 1986). Moreover, manure is a renewable resource which completes the nutrient cycle of a farm as manure fertilizes the soil used to grow crops, which in turn nourish livestock who will produce manure to repeat the cycle *ad infinitum*.

At the outset of WWII manure was considered a precious resource: "the measure of a man's wealth," and far more cost effective for improving soil fertility than purchasing chemical fertilizer (Marriott *et al.* 1977; NRC 1993; Ribaudo *et al.* 2003). Indeed, in the late 1930s a farmer could pay as much as 6 times the price of manure for chemical fertilizer, and the estimated gross value of manure in terms of crop production in the U.S. was $440 per farm, a staggering \$3 billion in 1938 dollars; more than \$46 billion and nearly 10 times the Federal government's ethanol subsidy payments in 2010 (NRC 1993). However, wartime demand for industrially fixed N to produce munitions resulted in a torrent of government contract money to producers for capital investment, which created the economies of scale which drove down costs and made chemical fertilizer, with the promise of greater yields, a highly attractive alternative to manure (Smil 2004). Storing and handling manure soon became a costly nuisance to farmers, particularly as the number of farms declined and less land was locally available for spreading (NRC 1993; USDA-EPA 1999).

Although the cost of energy used to industrially fix N has increased since the energy shock of the 1970s, chemical fertilizer remains a strongly attractive alternative, particularly in the Chesapeake Bay Watershed where total cost of manure land application can be as high as 50 percent of total net returns to animal production (Ribaudo *et al.* 2003). Howland and Karszes (2014) estimate the cost of spreading manure in NYS at \$2.98 per 1,000 L of manure or just over \$100,000 to spread the average volume of 36.5 million L-year^{-1} of manure produced by the 27 farms included in their study. Operating costs, including labor, fuel and utilities, and repairs account half of total costs associated with spreading. Labor alone is 16 percent of total costs. Fuel to transport manure to neighboring farms at an average distance of 5 km from the source-farm account for nearly 20 percent of total costs. And capital costs of spreading equipment, including insurance, depreciation and interest and repairs account for 26 percent of total costs. Still, land application remains the predominant method for disposing of manure and recycling its nutrient and organic content (USDA-EPA 1999).

It can be difficult to quantify the contribution of individual farms over widespread areas to regional nutrient imbalances, although Howarth *et al.* (2011) evaluated watersheds at scales as fine as 16 km^2. The 526 ha Cornell University Ruminant Center (CURC) located in the Southern Tier of New York State, USA, offers the ideal setting to study the effect of an intensive dairy farming for several reasons, not least of which include the thirty-eight ground and surface water monitoring sites which have been in operation and sampled periodically to determine N and P concentrations since 1974. The CURC is located along the drainage divide with no other anthropogenic nutrient inputs above it in the landscape. These activities include dairy production, from a herd which has grown from 728 cattle in 1974 to790 in 1994, pasturing of other ruminants, and crops, primarily corn (*Zea mays L.*) and alfalfa (*Medicago sativa L.*) grown in rotation to support husbandry there (Wang *et al.* 1999). All of these activities occur on the valley floor, *Figure 1*.

Figure 1. Land use at the CURC on either side of the drainage divide. Produced with ArcGIS web-based platform.

Farming is more intensive south of the drainage divide. The south catchment has almost twice the area of cropped land and is the location of most dairy barns and the manure lagoon. Alternatively, the north catchment, though 1.5 times smaller in area, is almost two-thirds forest and grassland with very little land dedicated to support the feedlot. Several monitoring sites are located above the farm, enabling the contrast of "natural" and agriculturally influenced nutrient levels. Finally, land use is significantly different on each side of the drainage divide allowing for a contrast in nutrient levels according to land use, which can affect nutrient cycling significantly.

Wang *et al.* (1999) observed significant increases in both N and P between 1974 and 1994 in groundwater at the Harford site. Here I analyze data collected over four decades, including this 1974 to 1994 period, at farmed and unfarmed sites in both small catchments including published and unpublished data, archived frozen samples, and samples collected during 2015-2016 for this study.

I hypothesized that the continued spreading of manure, which during this study was ongoing throughout the year whenever the ground was snow-free, and slow mineralization of organic N has resulted in increasing groundwater concentrations of the dominant forms of dissolved inorganic nitrogen (DIN), NO_3^- and NH_4^+. I further explored whether long-term manure application might saturate sorption sites resulting in the export of other than eroded particulate-P from the farm. The amount of P lost to surface waters increases with soil P content (Carpenter *et al.* 1998). Domagalski and Johnson (2012) show that intensive farming in the State of Washington can saturate phosphate-sorption sites in soils, resulting in mobilization to groundwater.

Soils in the Harford Valley floor are strongly acid Valois-Howard-Langford and Howard Association with high P sorption capacity (Wang *et al.* 1999, Seay 1961). I hypothesized that saturation of P-sorption sites may be indicated by increasing dissolved P in soil water. Land use is dramatically different in each of the CURC's small catchments. I hypothesized that nutrient concentrations vary within each catchment according to their respective distribution of land use, such that higher levels will be observed where a higher ratio of land is dedicated to agricultural activity. Finally, I hypothesized that nutrient concentrations would reflect seasonality, with the highest concentrations occurring during the spring and fall during periods of intensive manuring dispose accumulated quantities, and with concentrations higher in winter when uptake and assimilation by plants are lowest and lower in summer when fields are cropped and uptake and assimilation are greatest.

MATERIALS AND METHODS

Study Site

The 526 ha Cornell University Ruminant Center (CURC) is located approximately 2 km north of the Village of Harford, NY in the Harford Valley. The Harford Valley is one of 29 "through valleys" in the headwaters of the Susquehanna River Basin (SRB) and those of the Oswego River/Finger Lakes Basin (OR/FLW) in the Southern Tier of New York State (NYS). A through valley is defined by Randall *et al.* (1988) by its anomalous hydrology whereby the regional watershed divide does not follow the crest of ridges, but rather crosses the valley floor. The valley most likely formed during the last glaciation when advancing glaciers blocked north-draining valleys forming lakes from their meltwater. Eventually water from these lakes cut gorges through saddles along the divide. Advancing glaciers then deepened and widened those gorges and obliterated the pre-glacial saddles so that meltwater flowed unimpeded south to the SRB (Randall *et al.* 1988).

Soils in the valley floor where farming is intensive are well drained and highly permeable, strongly acid Valois-Howard-Langford and Howard Association, with high P sorption capacity (Seay 1961; Wang *et al.* 1999). The valley walls rise approximately 200 m above the floor and are composed of bedrock slopes mantled with a mixture of unstratified silt and clay, which is poorly permeable, however surficial layers are relatively loose and permeable soil due to weathering (Randall *et al*. 1988). As a result, most of the precipitation that falls on the uplands either evaporates and is returned to the atmosphere or runs off into streams on the surface or upper soil horizons (Randall *et al.* 1988). Ninety-five percent of drainage on the farm is as groundwater and 60 percent of groundwater drainage comes from permanent grassland above the farm with only 40 percent of groundwater the result of drainage from the intensively farmed valley floor (Wang *et al.* 1999).

The CURC is located along the drainage divide in the headwaters of both the 13,217.38 km^2 OR/FLW Basin to the north and the 71,222.80 km^2 SRB to the south, *Figure 2*. Locally, the CURC's hydrologic setting places it within the Fall Creek (FC) Sub-Basin to the north and the East Branch Owego Creek (EBOC) Sub-Basin to the south. The FC Sub-Basin drains an area of to 329 km^2 of Tompkins, Cayuga and Cortland Counties into Cayuga Lake. The EBOC Sub-Basin drains an area of 261 km^2 of Tioga and Cortland Counties into the main stem of the Owego Creek, approximately 3.5 river km upstream from its outlet to the Susquehanna River. Two small catchments in the headwaters of the FC and EBOC Sub-Basins drain the CURC. Approximately 1 km^2 of the CURC, termed CURC-North, is located with a small, 14.30 km^2

catchment of the FC Sub-Basin. It drains the north portion of the CURC to Dryden Lake and contains several barns and animal feed and part of the waste storage site. Approximately 2.5 km² of the CURC is located with a second small, 19 km² sub-watershed of the EBOC Sub-Basin, termed CURC-South. CURC-South drains the southern portion of the farm via an unnamed creek into the EBOC. CURC-South contains the main dairy barn and most of the waste storage site, several small outbuildings and several corn fields.

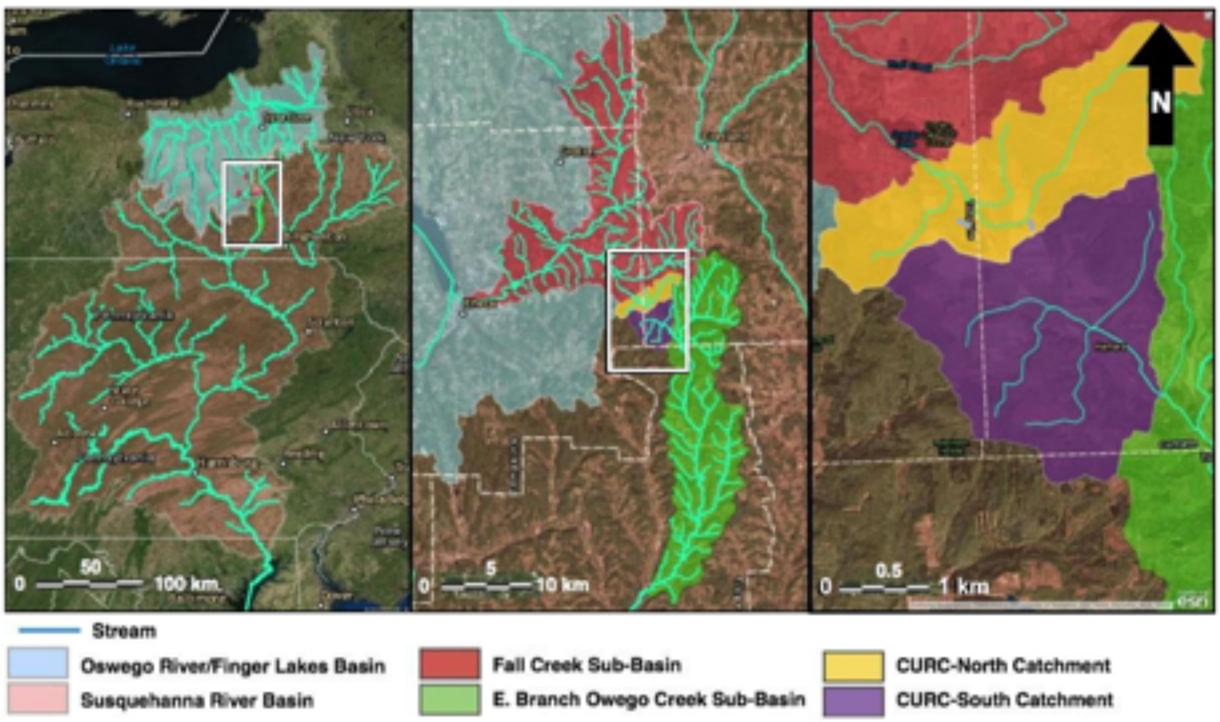

Figure 2. Nested views of the regional, local, and farm scale watersheds linked to the CURC, produced with web-based ArcGIS. From left to right: The Oswego River/Finger Lakes & Susquehanna River Regional Basins; The Fall Creek and E. Branch Owego Creek Sub-Basins; and local catchments draining the CURC, termed CURC-North and CURC-South.

The CURC has been operated by the NYS College of Agriculture and Life Sciences since the 1960s. Activities at the CURC support a herd of cattle which grew from 728 cattle in 1974 to 790 in 1994 (Wang et al. 1999). Crops, primarily corn (*Zea mays L.*) and alfalfa (*Medicago* *sativa L.*), are grown in rotation (Wang *et al.* 1999). Land use on the CURC varies significantly on either side of the drainage divide, *Table 1*. Land use was determined by site observation over the sample period, 2015-2016, and then measured using ArcGIS. The approximately 1 km^2 of the farm located in CURC-North is about 50 percent grassland, 27 percent forest, 18 percent corn field, and 5 percent impermeable surfaces including roads, administrative buildings and barns and an approximately 20,000 m^2 silage storage site. The approximately 2.5 km^2 of farm located in CURC-South is approximately 47 percent corn field, 40 percent grassland, 9 percent forest, and 4 percent impermeable surfaces including an approximately 12,000 m^2 manure lagoon and dairy barn where the herd is housed.

Table 1. Estimated percent of land on the CURC in its principal use by each small catchment in 2016. Uses were determined by site observation and measured in ArcGIS.

	% land in each usage class	
	CURC-North	***CURC-South***
Corn field	18	47
Forest	27	9
Grassland	50	40
Impermeable surface	5	4

From 2015-2016 manure spreading was observed to occur on the CURC in each season. For example, evidence of very recent spreading was observed during sampling after harvest between September and December 2015, when temperatures were above freezing, and again in early February 2016 following near complete snow melt. Evidence of recent manure spreading was noted when groundwater samples were collected in February 2016. *Figure 3* shows ponding from manure spreading in a corn field near one of the wells I resampled for this study.

Groundwater samples collected from a corn field in winter indicated a concentration of 1.16 mM NO_3^- (13.92 mg-L^{-1} NO_3—N) in groundwater, well above the 10 mg-L^{-1} US-EPA limit for safe drinking water.

***Figure 3*.** Evidence of recent manure spreading near a sampling well (*left*) at the edge of a corn field in CURC-South (*pictured right*) following an atypical warming event in late-January 2016.

Sample Collection

At various times there have been as many as thirty-eight ground and surface water monitoring wells in operation at the CURC since the 1970s and were numbered by Prof. David Bouldin when sampling began in 1974, *Figure 4*. Wells were dug with excavating equipment into shallow ground aquifers 1-2 meters to nearly 20 meters below ground (Bouldin 2015). Well casings are typically polyvinyl chloride (PVC) pipe, although several are cast iron. Because groundwater is not recharged from off-site nutrient sources, nutrient concentrations in groundwater at the farm are presumed to be a reliable indicator of the influence of this farm's activities on nutrient loading. Several wells, however, have since collapsed or have been destroyed by farm equipment and were not redeveloped since sampling last occurred in the early 2000s, and could not be resampled or accurately mapped. Currently, 30 monitoring sites are in operation at CURC.

The wells are distributed between both small catchments. Eleven are located in CURC-North and 35 are located in CURC-South. Despite large differences in the number of sites, both catchments have been sampled relatively evenly since 1974. Sites are also distributed between ground and surface water monitoring sites, located in the intensely farmed valley and on the steep valley sides which tend to be poorly drained, fallow grassland. For this study, I have classified actively farmed sites in each catchment as farmed groundwater (FG) and farmed surface water (FS); sites on the valley sides are termed upland groundwater (UG) and upland surface water (US).

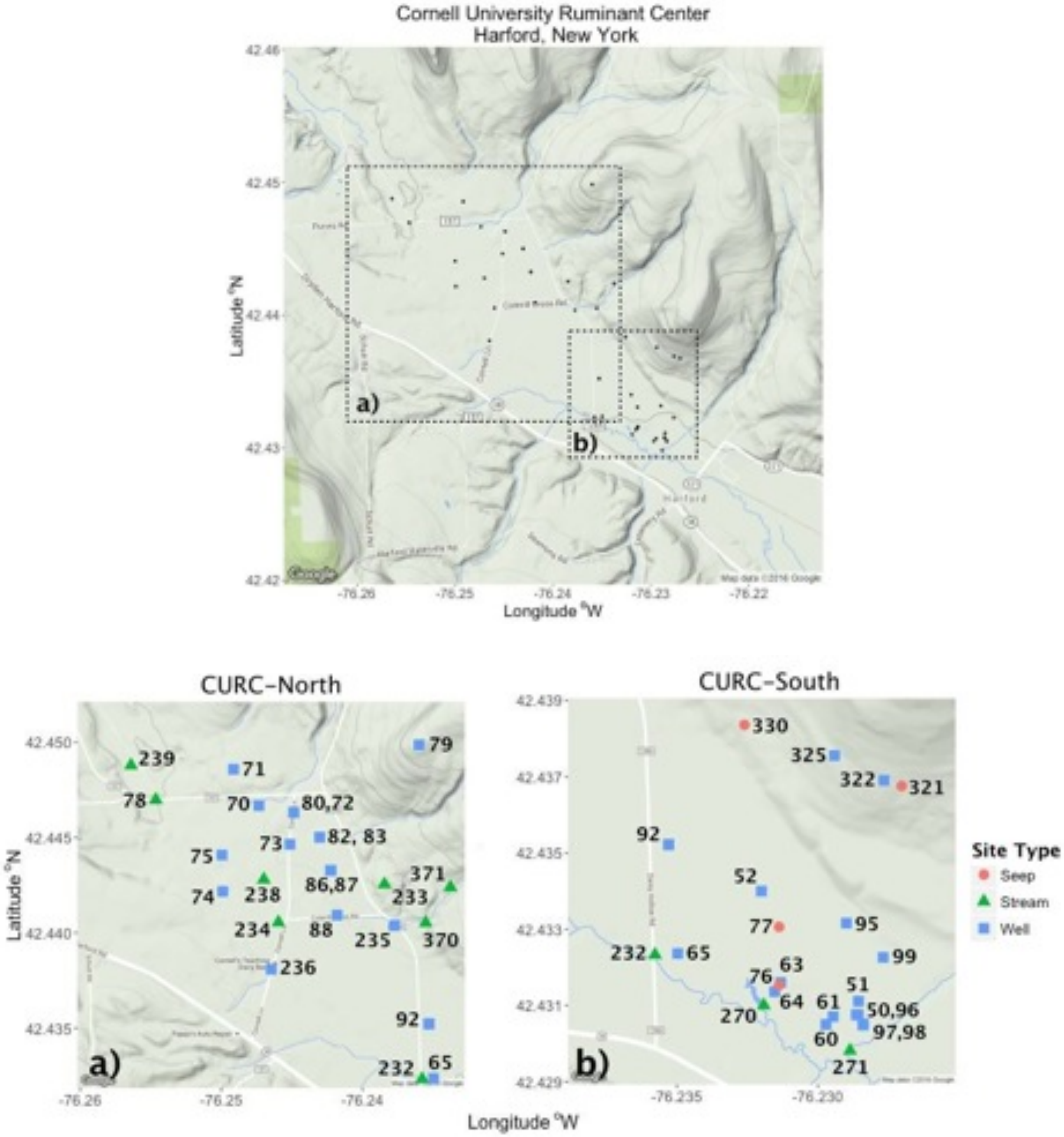

Figure 4. Water monitoring sites at the Cornell University Ruminant Center (CURC).

Selection of wells for resampling during this study was made on the basis of sampling viability, i.e. the site remains in operation, and by the quality of unpublished data sets made available, i.e., number and period covered by frozen, archived samples. Groundwater wells selected for resampling are located in the intensively farmed valley floor on both sides of the drainage divide, *Figure* 4. W63 is located in CURC-South along the edge of a corn field which was row-cropped with corn during the growing season and was frequently manured during the 2015-2016 sampling period. W74 is located in CURC-North near the dairy barn and animal waste storage lagoon, near the center of the farm. W96 and W98 are also located in CURC-South, about 20 meters outside the cropped areas downslope from Field 10 in the riparian buffer of the headwaters of the EBOC Sub-Basin, near the CURC-South outlet. W96 and W98 may be an accurate representation of the N and P entering the EBOC Sub-Basin from the farm.

Wang *et al.* (1999) sampled groundwater at the CURC throughout the year, although they weighted sampling effort to periods of aquifer recharge by heavy rain and snowpack melt in the spring. Wang *et al.* (1999) reports the concentration of nitrate (NO_3^-) in five wells: W73, W95, W96, W97 and W98 in corn fields and three unfarmed hillside locations W322, W325 and W330 between periods 1979-1981 and 1992-1994.

Resampling during 2015-2016 for this study was conducted each month from July 2015 to April 2016 at W63, W74, W96 and W96, *Table 2*. Below freezing temperatures from late-December 2015 through January 2016 prevented sampling in January, however atypical late-January warming event in which daily high temperatures exceeded 13°C for more than one week allowed sampling to resume. Thus winter 2016 sampling was not conducted until the first week of February.

Table 2. Sampling dates for 2015-2016 resampling of W63, 74, 96 and 98.

	Estimated depth to groundwater (m)								
Well	**10 Jul 2015**	**06 Aug 2015**	**11 Sep 2015**	**23 Oct 2015**	**11 Nov 2015**	**07 Dec 2015**	**02 Feb 2016**	**10 Mar 2016**	**13 Apr 2016**
63	0.25	0.51	*Dry**	*Dry**	*Dry**	*Dry**	*0.76*	*0.51*	*0.30*
74	5.03	5.79	*Dry*	*Dry*	*Dry*	*Dry*	*6*	*5.50*	*5.48*
96	0.58	1.04	1.35	1.35	1.80	1.02	1.62	1.52	*0.15*
98	0.38	0.74	1.37	*Dry**	*Dry**	*Dry**	*0.89*	*0.76*	*0.21*

*Blockages in Wells 63 and 98 were discovered during sampling on 02 Feb 16 and removed. "Dry" readings may be the result of these blockages.

Samples were collected using a self-priming Black and Decker "Jack Rabbit" hand crank pump fitted with a one-way valve on the inlet hose. The pump is rated for between 4-8 L min^{-1}. Prior to collection, each well was pumped for two-three minutes to clear stale water and allow for the collection of a representative groundwater sample from the well. Samples were collected in two 250 ml bottles from each producing well. One 250 ml sample was then filtered within 4 hours of collection in the lab through a Whatman GF/f glass microfiber filter to remove suspended particulate matter and then frozen. One sample from each date was frozen without filtering in order to determine whether filtration is significant, and frozen samples archived from the Wang *et al.* (1999) study were not filtered prior to freezing. Samples were frozen immediately. Samples collected on 2 February 2016 included the filtered/unfiltered subsample, as well as a frozen/unfrozen subsample to determine the effect of freezing on potential P co-precipitation with calcium carbonate in groundwater.

Laboratory Analyses

Samples collected by Wang *et al.* (1999) were analyzed for total N (TN) at the Cornell Nutrient Analysis Laboratory (CNAL) by the Kjeldahl method using a model 1030 Kjeltec AutoAnalyzer with cupric sulfate and potassium sulfate as the catalyst; NO_3^--N (mg-kg^{-1}) was then determined colorimetrically. Wang *et al.* (1999) determined the accumulation of total P (TP) by collecting soil samples in the spring from the plow layer (0 to 25 cm depth). Wang *et al.* (1999) extracted P with pH 4.8 Morgan's solution and determined concentration by inductively coupled plasma emission spectrophotometry. P was rarely detected in samples taken after 1976. Mean NO_3^- and P (mg-kg^{-1}) for the two periods were compared using a Student's t-test using MINITAB v.11.21, with $p < 0.05$ considered significant. Samples collected for this study and archived samples from 2003-2004 taken from W63, 74, 75, 96 and 98 were analyzed for NH_4^+-N, NO_3^--N (mg/L), and TDP as P (mg-L^{-1}) by the CNAL and converted to their respective molar concentration.

Prior to analysis in the CNAL, 60 mL bottles were acid washed in a 10 percent HCl solution for approximately 24 hours. Archived samples from 1992-2004 were then thawed over a 24 hour period. The same filtration protocol was used for archived and 2015-2016 samples. Working in random batches of 10 samples, I loaded plastic Swinnex filter holders with 47 mm, Whatman GF/f filters, making sure both the top and bottom o-rings were properly seated. I then wetted the surface of each holder with Nanopure deionized water (DIW) to hold filter in place prior to adding a filter on the holder base and seating it by gently pushing down the filter edges with forceps. Then I carefully screwed the top onto the base. I then removed the fully thawed samples from the refrigerator to be filtered and swirled each bottle to mix its contents well and let the sample settle while I set up the one 15 mL centrifuge tube, two 20 mL vials, and one 60 mL bottle. Subsampling was accomplished using a 60 cc plastic syringe. Prior to each use, the syringe was rinsed inside and outside with Nanopure DIW. To subsample I inserted the syringe into the sample bottle and removed 60 mL of sample, being careful to remove any air bubbles prior to filtering. I then pushed a small amount of sample (approximately 1 ml) through the filter directly into the 15 mL centrifuge tube, swirling it to rinse tube, then discarding the rinse fluid. Then, I pushed 10 mL of sample into centrifuge tube for P analysis. I then pushed approximately 15 mL into a 20 mL for N analysis and the remaining 30 mL in the syringe into a 60 mL bottle. Finally, I pulled 20 mL of additional fluid from the sample bottle and pushed it into a second 20 mL vial for duplicate N analysis. After filtering each sample, I stored it in a refrigerator until analysis at the CNAL, typically 48 hours after filtering. Archived samples were annotated to note the extraction of 80 mL fluid prior to refreezing. The 60 mL bottles for future analysis were labeled and refrozen along with original 250 mL bottles. This procedure was repeated over a period of three days for each of the 111 samples selected for analysis.

Archived and newly acquired samples were then taken to the CNAL for analysis. Samples were removed from refrigeration and allowed to heat to room temperature for approximately two hours before analysis. Samples were analyzed at the CNAL for NH_4^+-N and NO_3^--N and TP. NH_4^+ and NO_3^- were determined colorimetrically using a Bran+Lubbe Seal AutoAnalyzer, Standard Method No. G-145-94 Rev. 6 for Nitrate and Nitrite in Water, Waste Water and Soil Extracts, and Standard Method No. G-145-95 Rev. 2 for Ammonia in Water and Waste Water. Initial samples were analyzed for N in duplicate in order to determine the accuracy of equipment. AutoAnalyzer detection limits were 0.018 mg-L^{-1} NH_4^+-N and 0.032 mg-L^{-1}

NO_3^--N , respectively. TDP was determined in the CNAL by inductively coupled plasma (ICP) mass spectrometry using EPA Method 1060b. The ICP procedure had a detection limit from 5 µg-L^{-1} P to 300 mg-L^{-1} P. Results determined by both procedures were subsequently converted to a molar concentration by dividing NH_4^+-N and NO_3^--N by the atomic weight of N and TP by the atomic weight of P.

Statistical Analysis

I first examined whether or not there are any differences in nutrient concentrations at ground and surface water sites within each small CURC catchment. I used the web-based version of ArcGIS powered by ESRI to delineate each of the regional basins, local sub-basins and small catchments, which drain the CURC, and measured their area and determined major flow paths. I then used Analysis of Variance (ANOVA) and Tukey's Honest Significant Difference (HSD) testing using RStudio Version 0.98.1049 to determine whether or not presumed upland "natural" sites were significantly different from those in the actively farmed valley. Next, I compared ground and surface waters and between within each small catchment as differences may indicate leaching (NO_3^-) and sorption site saturation (P). I then compared ground and surface waters between CURC-North and CURC-South in order to better understand potential differences in groundwater nutrients in each watershed. To make comparisons between catchments I used an F test to compare sample variance and a Welch's Two Sample t-test with significance level, $\alpha = 0.05$ given either equal or unequal variance to compare sample means.

For statistical testing when sample size was less than 30, I used Bootstrap resampling with replacement to calculate two sample 95% confidence intervals and p-values. This was the case when NO_3^- concentrations in surface and groundwater samples (n=20) at upland sites in the EBOC Sub-Basin and confirmed previous t-test results.

Wang *et al.* (1999) compared periods 1979-1981 and 1992-1994 using a Student's t-test with significance level, $\alpha = 0.05$. Wang *et al.* (1999) data were reported in mg/kg as N and P respectively. For this study, I converted all data to the molar concentration (mM or µM). To examine time trends, I first compared mean concentration of all sites within a given among five multi-year periods following the basic framework used by Wang *et al.* (1999) using ANOVA testing. For a more direct examination of temporal trends, I used ANOVA of the mean monthly concentration of NO_3^-, NH_4^+ and TDP within each site type (FG, FS, UG, US) of CURC-North and CURC-South with the number of months (from 1 to 504) since sampling began in 1974, and seasons as factors. I used linear regression models to quantify significant results.

Nested linear models were compared for significance using an F-test:

$$F = \frac{\frac{SST-SSE}{df_t - df_e}}{\frac{SSE}{df_E}} = \frac{\frac{SSR}{df_R}}{\frac{SSE}{df_E}} = \frac{MSR}{MSE}$$

eqn. 1

Non-nested models were evaluated using Akaike information criteria (AIC):

$$AIC = 2k - 2 \cdot ln(L)$$

eqn. 2

where k is the number of estimated parameters and L is the maximum value of the likelihood function. Significant differences in models are indicated by a difference ≥ 2 AIC units, and the preferred model is indicated by the smallest AIC value when all compared models are calculated, Akaike (1974).

Although groundwater sites in the farmed valley were consistently sampled throughout the entire record in both catchments, upland site were sampled sparsely over different periods. I was concerned about sampling bias in making comparisons, and so performed dual analyses where sample periods differed: one comparing the full sets and one comparing only data from like time scales. Results of both analyses did not differ, and here I report results based on comparison of whole data sets.

RESULTS

Spatial Differences

From 1974 to 2016, NO_3^- concentrations are on average greater in the farmed valley than at unfarmed upland sites, *Table 3, Figure 5*. Furthermore, NO_3^- concentrations are significantly higher in both the ground and surface waters of the larger, more intensively farmed CURC-South catchment than the CURC-North. In both catchments, concentrations are higher in farmed groundwater sites than at farmed surface water sites. Above the farm, upland groundwater concentrations are lower than in surface waters.

Table 3. Comparison of mean molar concentrations of NO_3^- (mM) in surface and groundwaters in the two small catchments which drain the CURC from 1974-2016.

	CURC-North			***CURC-South***		
	Mean	*SE*	*n*	*Mean*	*SE*	*n*
FG	0.41	0.013	783	0.51	0.014	910
FS	0.09	0.011	90	0.23	0.018	200
UG	*NA*	*NA*	0	0.05	0.009	48
US	*NA*	*NA*	0	0.11	0.014	86

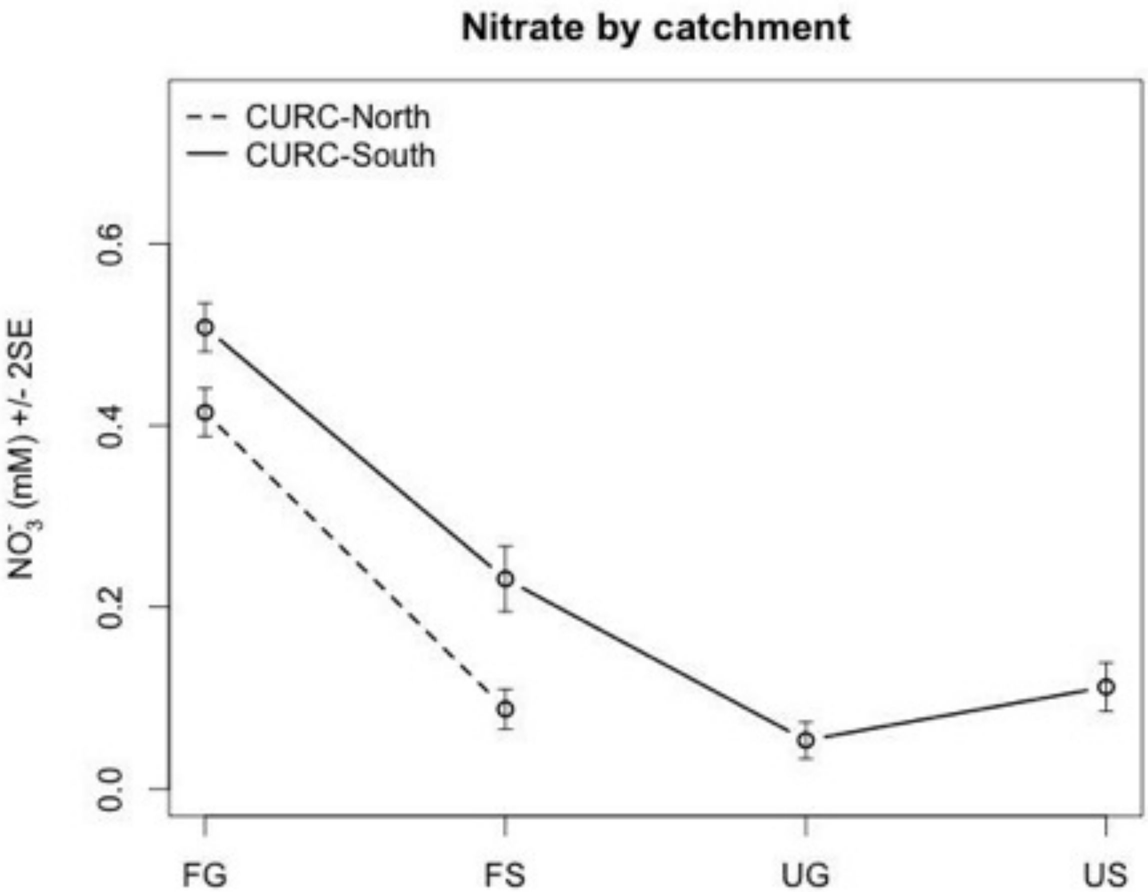

Figure 5. Comparison of mean molar concentration of NO_3^- (mM) with 95% Confidence Intervals (CI) by site type in each small catchment of the CURC, 1974-2016.

NH_4^+ concentrations are significantly higher in the groundwaters of each catchment, and overall higher in the groundwaters of CURC-North, however differences in the surface waters of the two small catchments are not significant, *Figure 6*. As such, surface water results were combined to farm-scale surface water concentrations, *Table 4*.

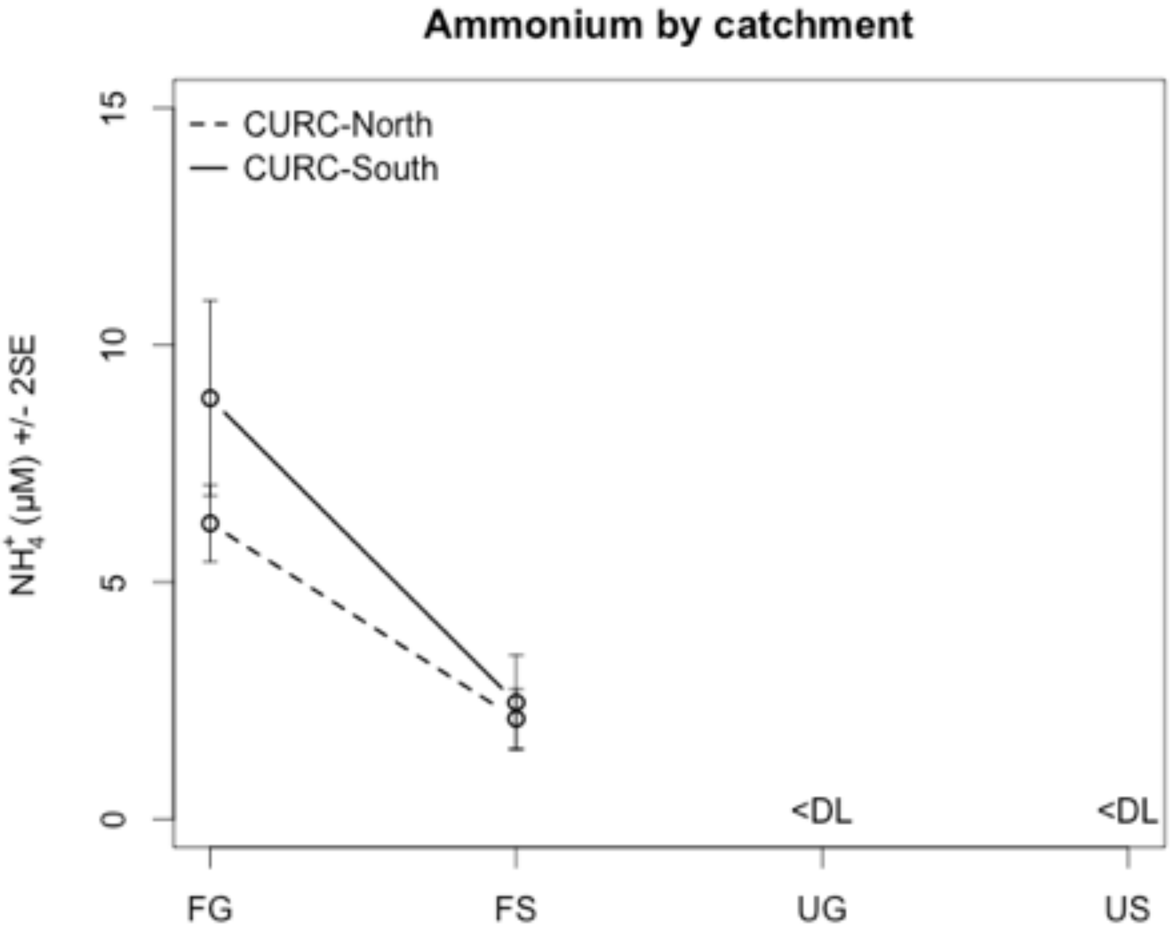

Figure 6. Comparison of mean molar concentration of NH_4^+ (µM) with 95% CIs by site type in each small catchment of the CURC, 1974-2016.

Table 4. Comparison of long-term mean molar concentrations of NH_4^+ (µM) from 1974-2016 in surface and groundwaters where farming occurs in the two small catchments which drain the CURC. Surface water concentrations were combined as "CURC" where test results lacked significance.

	CURC-North			***CURC-South***			***CURC***		
	Mean	*SE*	*n*	*Mean*	*SE*	*n*	*Mean*	*SE*	*n*
FG	6.25	0.41	414	8.90	1.05	246	*NA*	*NA*	*NA*
FS	2.12	0.30	24	2.45	0.50	75	2.37	0.39	99

Total dissolved nitrogen (TDN), the sum of NO_3^- and NH_4^+ is strongly influenced by NO_3^-, the dominant form of inorganic N on the farm. As such, TDN is significantly different among both ground and surface waters of each catchment. In the less intensively farmed CURC-North, TDN is significantly about 4.5 times higher in groundwater than surface water. In CURC-South, TDN is highest in farmed groundwater, about twice as high as in farmed surface water, *Table 5*. A bootstrap t-test shows that upland site types are significantly different from each other as well as from farmed sites. Upland water concentrations are significantly higher in surface waters than in confined groundwater aquifers. These significant differences indicate the overarching influence of farming, as concentrations are higher where farming occurs, but also the influence of site geology, as the relationship between ground and surface water concentrations are reversed depending on whether or not soils are well or poorly drained.

Table 5. Comparison of mean molar concentrations (mM) of TDN, 1974-2016, in surface and groundwaters in the two small catchments which drain the CURC.

	CURC-North			***CURC-South***		
	Mean	*SE*	*n*	*Mean*	*SE*	*n*
FG	0.38	0.01	858	0.50	0.01	933
FS	0.08	0.01	96	0.23	0.02	202
UG	*NA*	*NA*	0	0.04	0.01	61
US	*NA*	*NA*	0	0.11	0.01	87

Phosphorus in the groundwaters of both catchments is frequently below the minimum ICP detection limit. For instance, of the 111 samples analyzed in February 2016, ICP testing failed to detect P in 64 percent of samples. P was detected only in the groundwater of each catchment, and is significantly different in each, *Table 6*. Where TDP was reported below the minimum detection limit, data were omitted entirely; this may bias reported means upward. TDP is on average as much as twice as high in the intensively farmed CURC-South than it is in CURC-North ($p=0.007$).

Table 6. Comparison of long-term mean molar concentrations of TDP (µM) from 1974-2016 in groundwaters where farming occurs in the two small catchments which drain the CURC.

	CURC-North			***CURC-South***		
	Mean	*SE*	*n*	*Mean*	*SE*	*n*
FG	0.75	0.07	175	1.39	0.47	38

Temporal Trends

Over time, groundwater concentrations of NO_3^- have increased significantly in both catchments of the CURC. *Table 7* summarizes results of linear regression models of the change in mean monthly NO_3^- concentration from 1974 to 2016. Time is measured in a continuous count of 504 months since the first sampling in May 1974, "MSS."

Table 7. Linear regression model results of NO_3^- (mM) over time, expressed as a count of 504 months since sampling began in May 1974, "MSS."

	CURC-North				***CURC-South***			
	Estimate	*Std. Error*	*t-value*	*P-value*	*Estimate*	*Std. Error*	*t*	*P-value*
Intercept	2.719E-01	2.070E-02	13.136	<2e-16	0.229569	0.030468	7.535	1.73E-11
MSS	8.848E-04	8.905E-05	9.936	<2e-16	0.0014	0.000155	9.092	6.19E-15

In the less intensively farmed CURC-North, monthly mean concentrations NO_3^- have risen from 0.27 ± 0.08 mM in 1974 to 0.72 ± 0.12 mM in 2016, *Figure 7*. Residuals are normally distributed with no apparent change in variance from the mean. The overall trend explains 49 percent of the monthly variation in CURC-North NO_3^- concentrations. A polynomial model was tested, using time^2 as a term, however the coefficient was not significant.

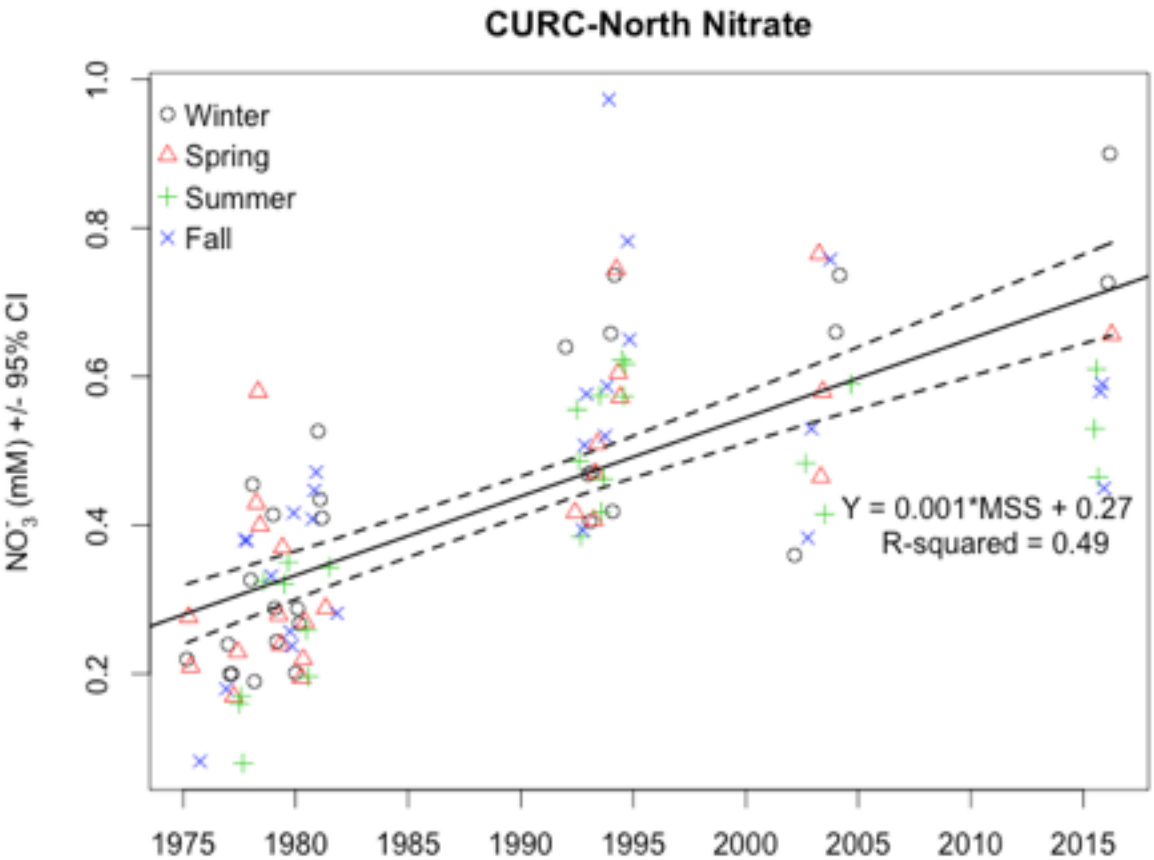

Figure 7. Mean monthly concentration of NO_3^- (mM) in CURC-North and 95% CI.

Alternatively, in the more intensively farmed CURC-South mean monthly NO_3^- concentrations have increased from 0.23 ± 0.12 mM in 1974 to 0.94 ± 0.23 mM in 2016, *Figure 8*. Residuals demonstrate no apparent change in variance from the mean, however a normal Q-Q plot indicates a left-tail. Logarithmic transformation removes skewness, however the model of log-transformed NO_3^- does not significantly improve in terms of prediction and was discarded in favor of the more parsimonious untransformed model; still it only explains about 43 percent of the NO_3^- time trend.

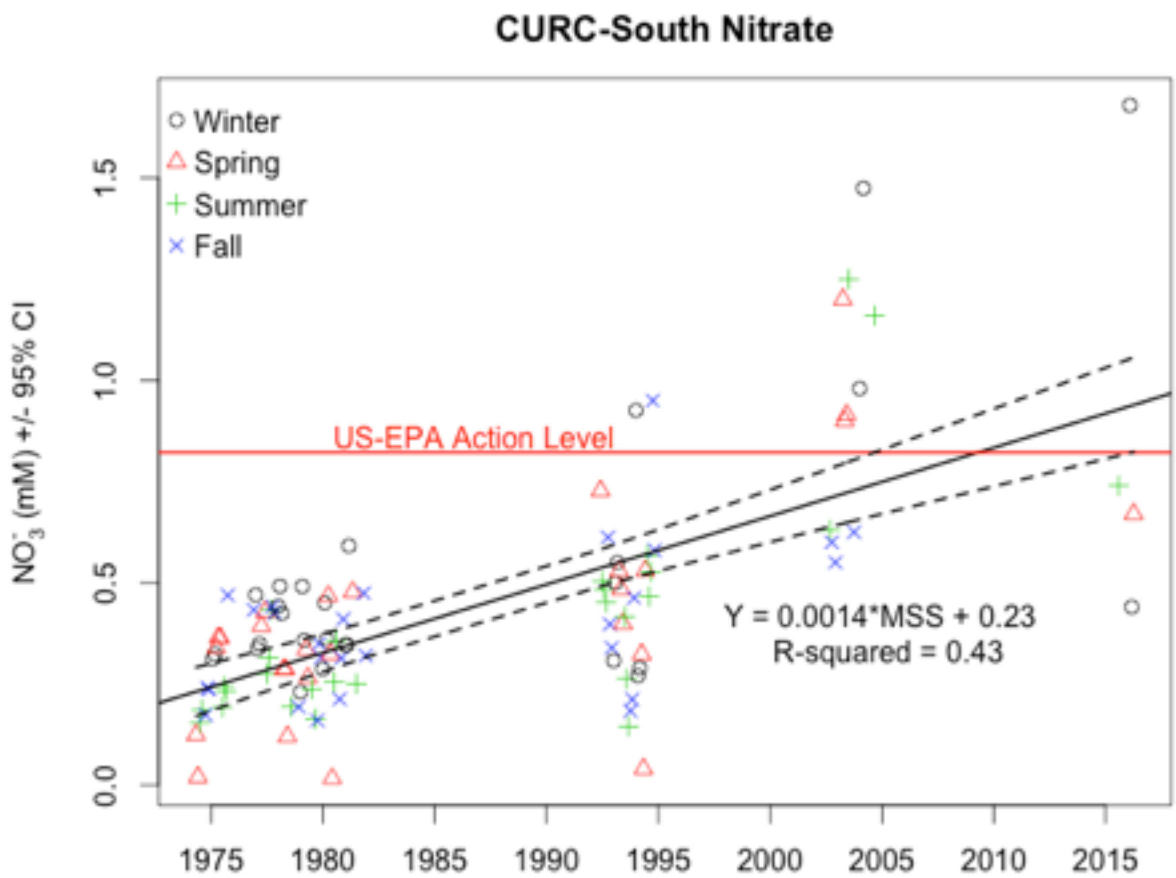

Figure 8. Mean monthly concentration of NO_3^- (mM) in CURC-South with trend line and 95% CI.

Table 8. Linear regression model results of NH_4^+ (µM) over time, expressed as a count of 504 months since sampling began in May 1974, "MSS."

	CURC-North				*CURC-South*			
	Estimate	*Std. Error*	*t-value*	*P-value*	*Estimate*	*Std. Error*	*t*	*P-value*
Intercept	5.328337	0.806667	6.605	2.11E-08	6.294413	0.480478	13.100	< 2e-16
MSS	-0.004324	0.003278	-1.319	0.193	-0.013569	0.002593	-5.233	2.24E-06

The other form of inorganic nitrogen, NH_4^+, was also examined for temporal trends. Results of linear regression modeling are summarized in Table 8. At sites throughout the farm NH_4^+ concentrations reach minimum detection limits in groundwater in just 27 percent of collected samples, and in surface waters only 4 percent of during a two-year period in the late 1970s and may indicate sample contamination during analysis.

NH_4^+ concentrations in CURC-North are quite low throughout the record of data and over time do not vary significantly, *Figure 9*.

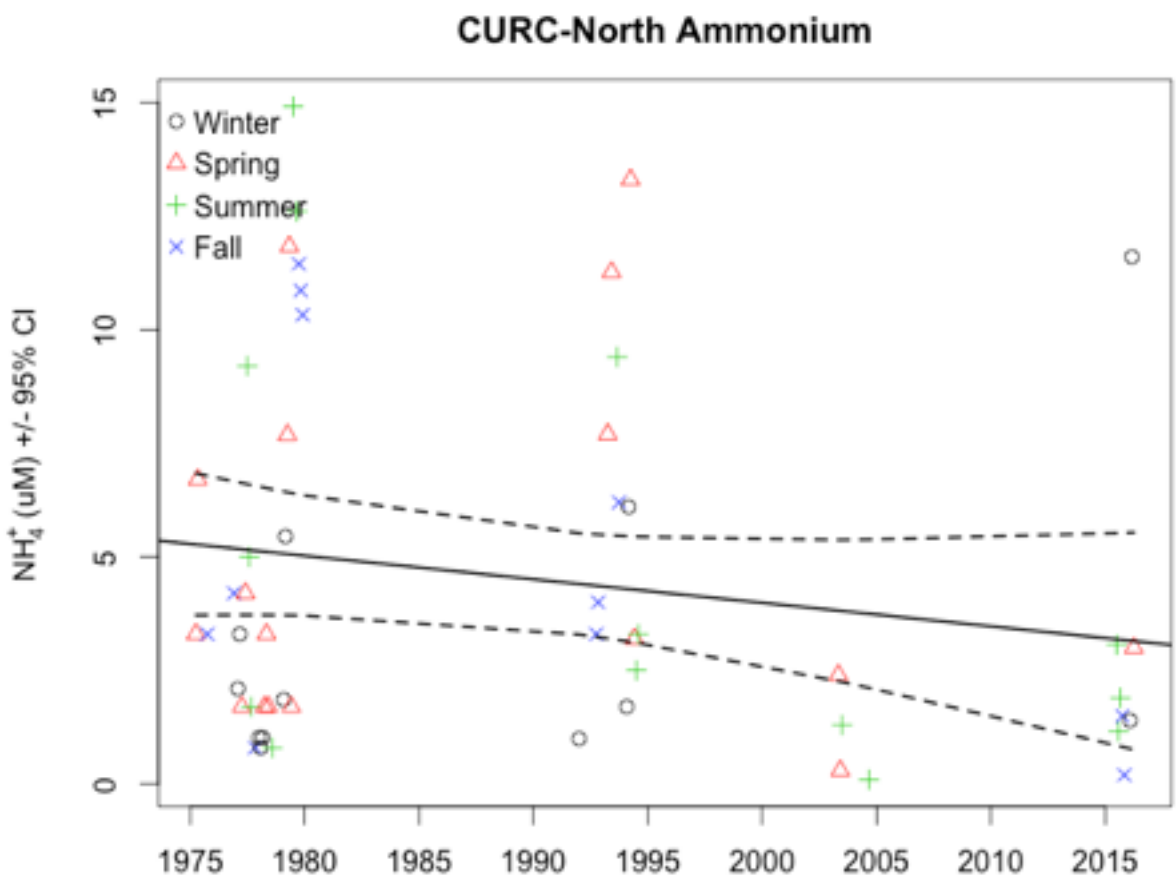

Figure 9. Mean monthly concentration of NH_4^+ (µM) in CURC-North with trend line and 95% Confidence Interval.

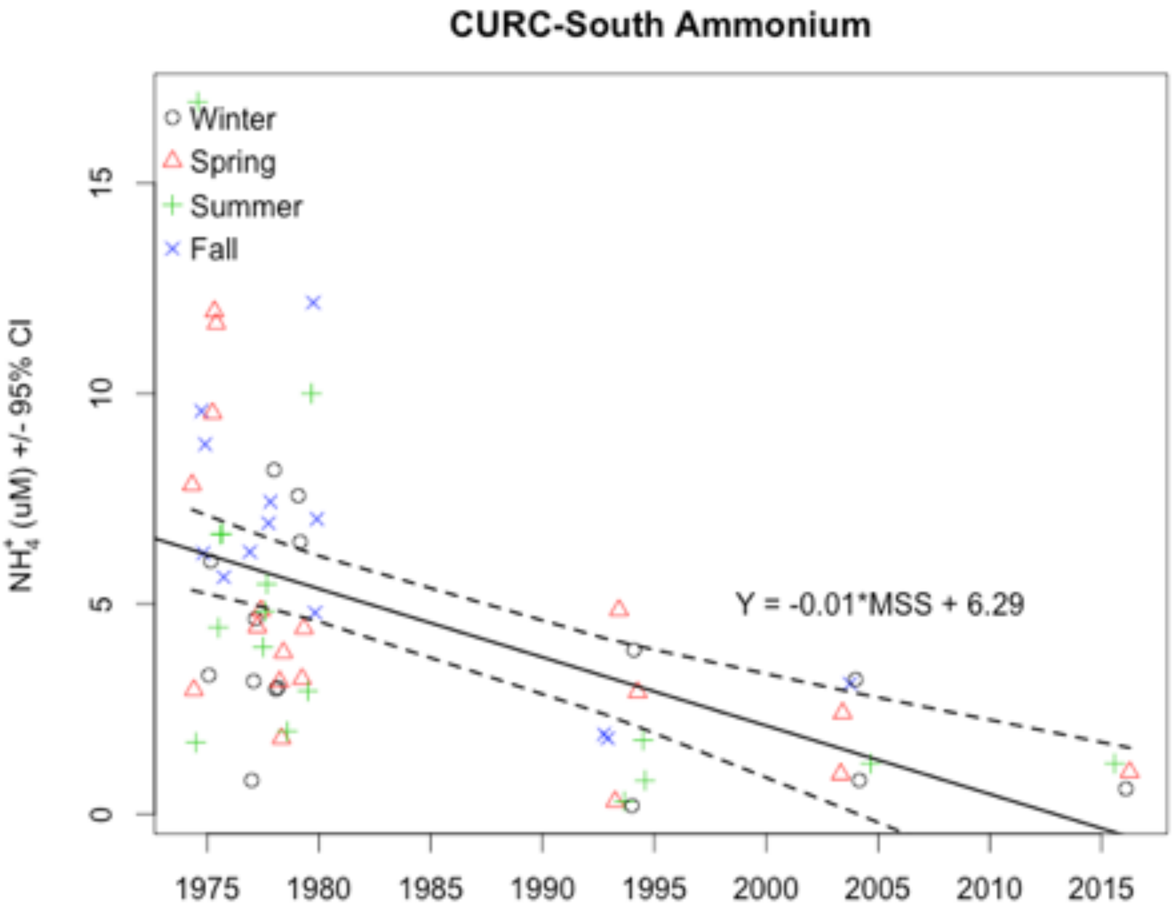

Figure 10. Mean monthly concentration of NH_4^+ (μM) in CURC-South with trend line and 95% Confidence Interval.

In CURC-South, however, although NH_4^+ concentrations are still very low, they have decreased significantly over time, from 6.29 ± 1.9 μM in 1974 at a rate of -0.01 μM-month^{-1} to effectively 0 in 2016, *Figure 10*. The model explains 30 percent of variation from the mean.

TDP was determined colorimetrically by ICP at the CNAL and only detected in groundwater where farming occurs. Surprisingly, P was never detected in surface water sites or at sites not actively farmed. Like NH_4^+, TDP data had a large variance and did not vary between catchments. I examine TDP at the farm-scale by re-aggregating data from both catchments and taking their monthly mean as with DIN, with time expressed as a count of 504 months since sampling began in May 1974, "MSS." Results of the linear regression model are shown in Table 9 and do not indicate a significant trend over time, *Figure 11*.

Table 9. Linear regression model results of NH_4^+ (µM) over time, expressed as a count of 504 months since sampling began in May 1974, "MSS."

	CURC-North			
	Estimate	*Std. Error*	*t-value*	*P-value*
Intercept	0.476887	0.431736	1.105	0.278
MSS	0.001599	0.001511	1.059	0.298

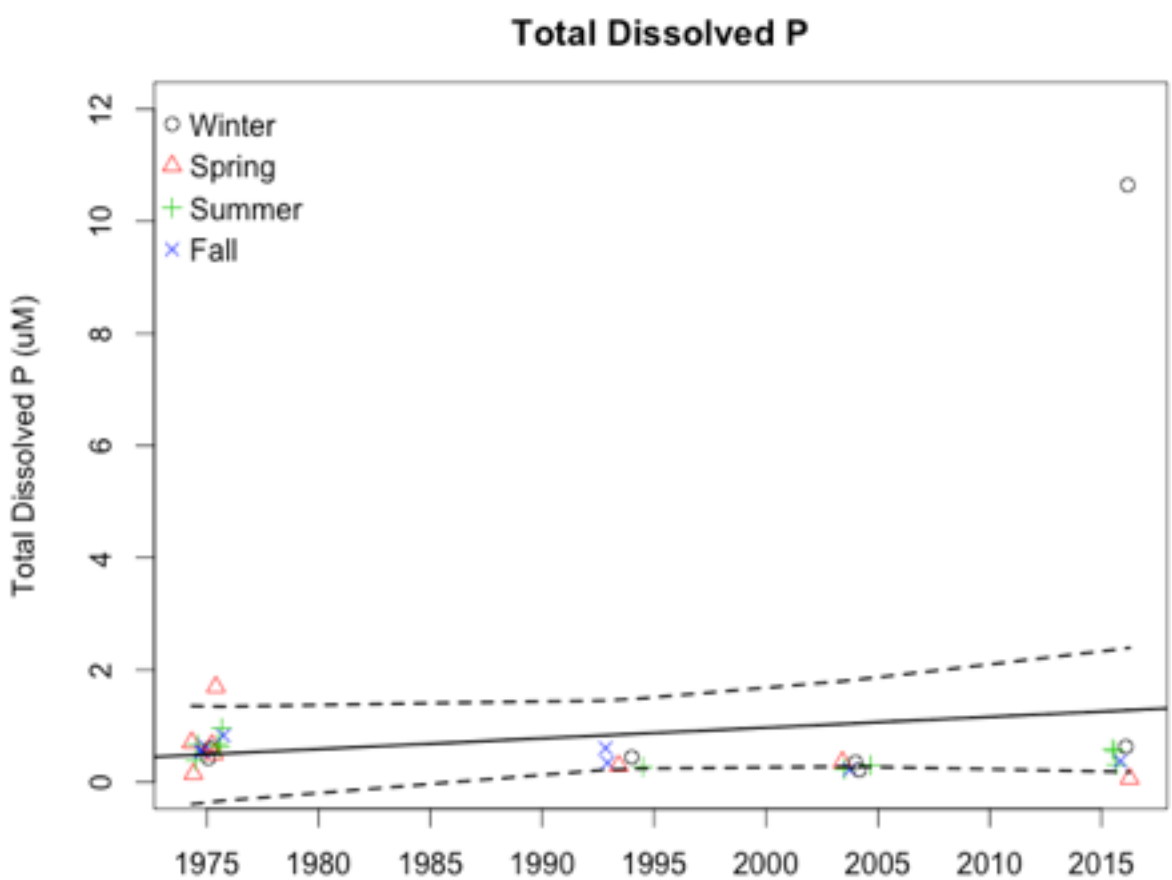

Figure 11. Mean monthly concentration of TDP (µM) at the CURC +/- 95% CI.

Seasonality

A visual inspection of the data plotted by concentration magnitude by site seems to indicate at least some seasonal differences in NO_3^- concentrations, *Figure 12*. I use ANOVA testing of NO_3^- concentrations with catchment, site type and season as factors. However, seasonal differences in the NO_3^- concentrations by ground and surface waters are not significant, *Table 10* and *Figure 13*.

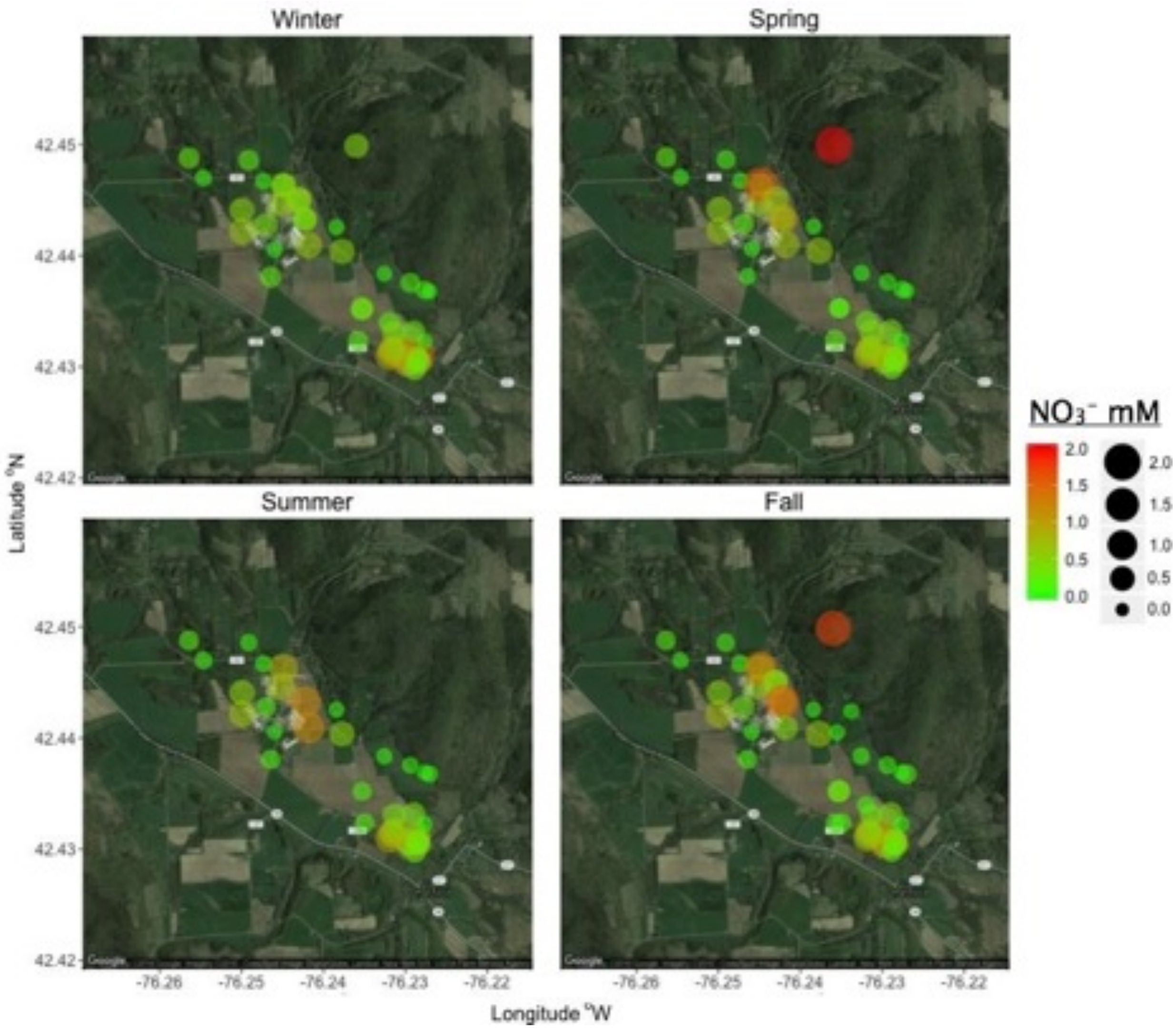

Figure 12. Bubble plots of mean seasonal NO_3^- concentration (mM) at all farmed and upland ground and surface water sites on satellite imagery of the CURC by season produced with R package "ggmap."

Table 10. ANOVA Table of NO_3^- concentrations contrasted by catchment by site type and season.

Source of Variation	**df**	**Sum of Squares.**	**Mean Square**	***f***	**Pr (>F)**
Catchment	1	0.73	0.73	5.556	0.0185
Site Type	3	37.21	12.404	94.421	<2e-16
Season	3	0.20	0.068	0.516	0.6712
Catchment and Site Type	1	0.15	0.148	1.125	0.2890
Catchment and Season	3	0.81	0.268	2.044	0.1057
Site Type and Season	9	0.95	0.105	0.801	0.6151
Catchment, Site Type and Season	3	0.39	0.130	0.989	0.3970
Residuals	2089	274.42	0.131		

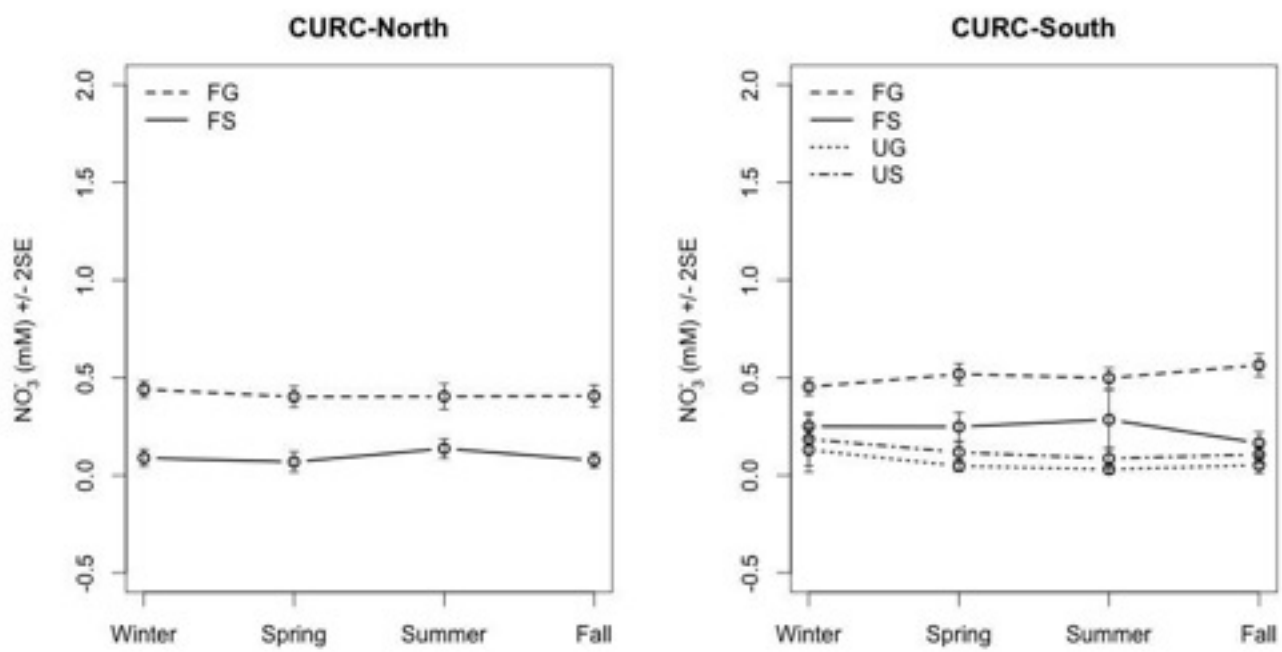

Figure 13. Comparison of NO_3^- concentrations (mM) +/- 95% CIs by site type and season in each small catchment of the CURC, 1974-2016. Concentrations vary between catchments according to ground and surface water, however they do not significantly vary by season.

Since the seasonal comparisons of ground and surface waters in farmed and unfarmed setting in both catchments were not statistically significant, I investigated whether the seasonal variations observed in *Figure 12* might be significance with different units more closely associated with a specific land use activity rather than coarse units "farmed" or "unfarmed."

Thus, I substituted the factor, "Site Type" with "Use", a factor with four levels: Animals, Corn, Grassland and Forest, and re-tested. The results indicate that season and use are significant factors in NO_3^- in both catchments, *Table 11*.

Table 11. ANOVA Table of NO_3^- concentrations (mM) contrasted by catchment by primary land use activity and season.

Source of Variation	**df**	**Sum of Squares.**	**Mean Square**	***f***	**Pr (>F)**
Catchment	1	0.74	0.741	6.113	0.013500
Use	3	32.41	10.805	89.189	< 2e-16
Season	3	0.37	0.124	1.024	0.380889
Catchment and Use	3	21.13	7.043	58.140	< 2e-16
Catchment and Season	3	0.20	0.068	0.561	0.640732
Use and Season	9	4.19	0.465	3.840	7.82e-05
Catchment, Use and Season	9	3.88	0.431	3.561	0.000211
Residuals	2085	252.58	0.121		

In CURC-North, Tukey HSD comparisons indicate the dominance of agricultural activity on NO_3^- concentrations, *Table 12*. I observed seasonal divergence of concentrations at sites associated with the production and distribution of manure while sites not associated with agricultural uses remain stable, with low concentrations throughout the year, *Figure 14*.

Table 12. Comparison of mean NO_3^- concentrations (mM) at ground and surface water sites in the farmed valley according to land use in CURC-North, 1974-2016.

CURC-North												
	Animals			***Corn***			***Forest***			***Grassland***		
Season	*mean*	*SE*	*n*	*mean*	*SE*	*n*	*mean*	*SE*	*n*	*mean*	*SE*	*n*
Winter	0.60	0.04	77	0.46	0.04	54	0.07	0.01	44	0.38	0.02	77
Spring	0.61	0.05	70	0.47	0.08	31	0.05	0.01	53	0.34	0.03	75
Summer	0.72	0.07	42	0.88	0.27	4	0.08	0.01	43	0.33	0.03	70
Fall	0.67	0.07	50	0.61	0.08	31	0.08	0.01	67	0.32	0.03	85

Irrespective of season, NO_3^- concentrations are on average greater at sites associated with animal husbandry than sites in either forested or grasslands, yet concentrations at animal sites remain stable across the seasons. Both ground and surface water sites in forested areas are consistently lower than sites in all other land uses, indicating that water-soluble NO_3^- is either immobilized before reaching forested areas or have a high N use efficiency. Ground and surface water sites located in corn fields are typically quite elevated at levels consistent with sites near animal barns, irrespective of season. However, ground and surface water sites located in corn fields and near barns have seasonally greater concentrations than do grasslands. During the summer and fall months, NO_3^- concentrations at ground and surface water sites in animal feed lots are greater than in sites located in grassland. Summer NO_3^- concentrations are low in sample size and have a very large α=0.05 CI and so is marginally insignificant from average summer grassland NO_3^- concentrations. Still, fall concentrations of NO_3^- at both ground and surface water sites in corn fields are significantly higher than at either site type located in grasslands.

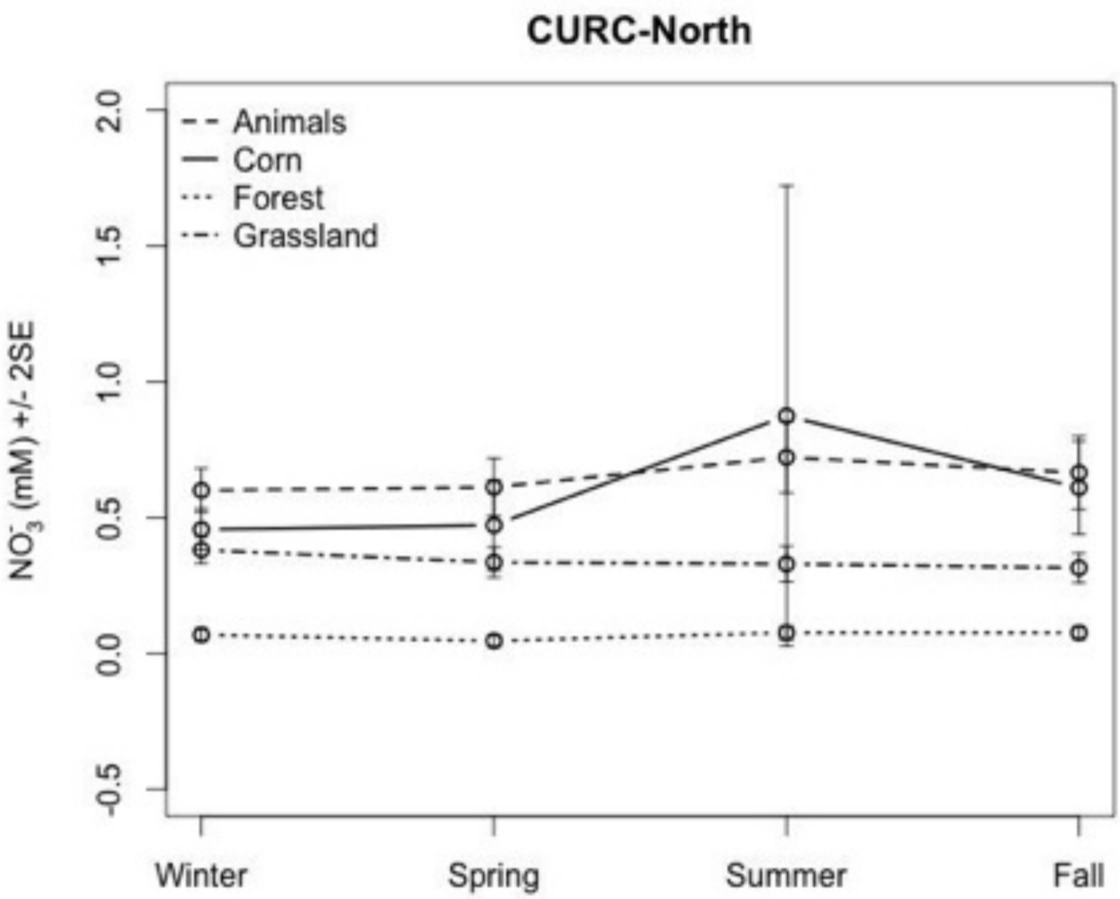

Figure 14. Comparison of NO_3^- concentrations (mM) +/- 95% CI in CURC-North by land use and season, 1974-2016. There is seasonal divergence of concentrations at sites associated with the production and distribution of manure. Sites not associated with agricultural uses remain stable, with low concentrations throughout the year.

Alternatively, in the CURC-South, where significantly more land is dedicated to agricultural uses, there is a year-round convergence of NO_3^- concentrations at elevated levels in both ground and surface water sites of all four land use categories. Only those ground and surface water sites in close proximity to animal feedlots vary seasonally. Concentrations at sites near feedlots are significantly greater during the summer months when manure may be stored in the lagoon until fields are harvested, *Figure 15*.

Table 13. Comparison of mean NO_3^- (mM) concentrations at sites according to land use in CURC-South, 1974-2016.

CURC-South

	Animals			***Corn***			***Forest***			***Grassland***		
Season	*mean*	*SE*	*n*	*mean*	*SE*	*n*	*mean*	*SE*	*n*	*mean*	*SE*	*n*
Winter	0.44	0.05	41	0.39	0.03	151	0.44	0.04	74	0.38	0.06	52
Spring	0.65	0.10	11	0.42	0.03	113	0.47	0.03	85	0.38	0.06	48
Summer	1.21	0.08	14	0.40	0.03	93	0.50	0.03	56	0.36	0.06	40
Fall	0.74	0.10	31	0.46	0.04	130	0.47	0.05	88	0.40	0.05	59

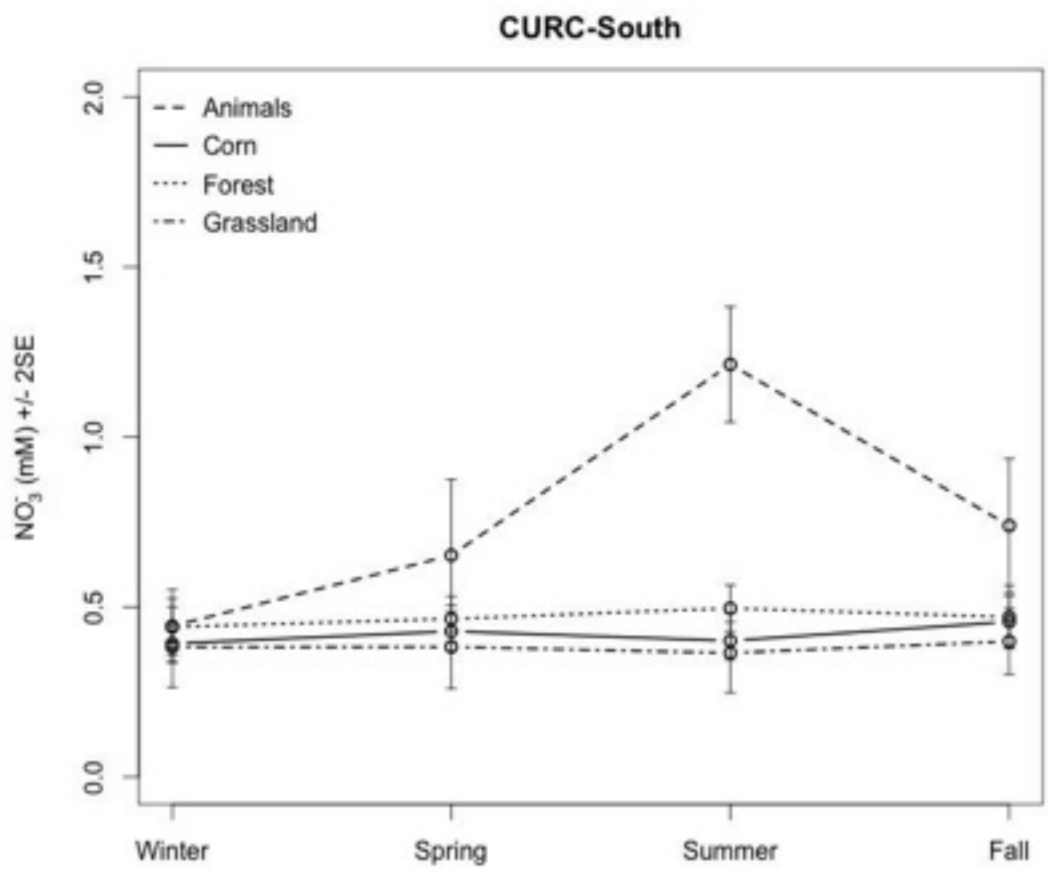

Figure 15. Comparison of NO_3^- concentrations (mM) +/- 95% CI in CURC-South by land use and season, 1974-2016. There is a strong year-round convergence of concentrations at elevated levels at sites irrespective of their association with agricultural activity. Only sites in close proximity to animal feedlots vary seasonally.

Ammonium data also appear to exhibit seasonal variation, *Figure 16*. I use ANOVA testing to show the seasonal variations NH_4^+ concentration observed in *Figure 16* are significant. ANOVA testing produces strong support that NH_4^+ concentrations vary significantly by land use activity and season across the two small catchments, *Table 14*.

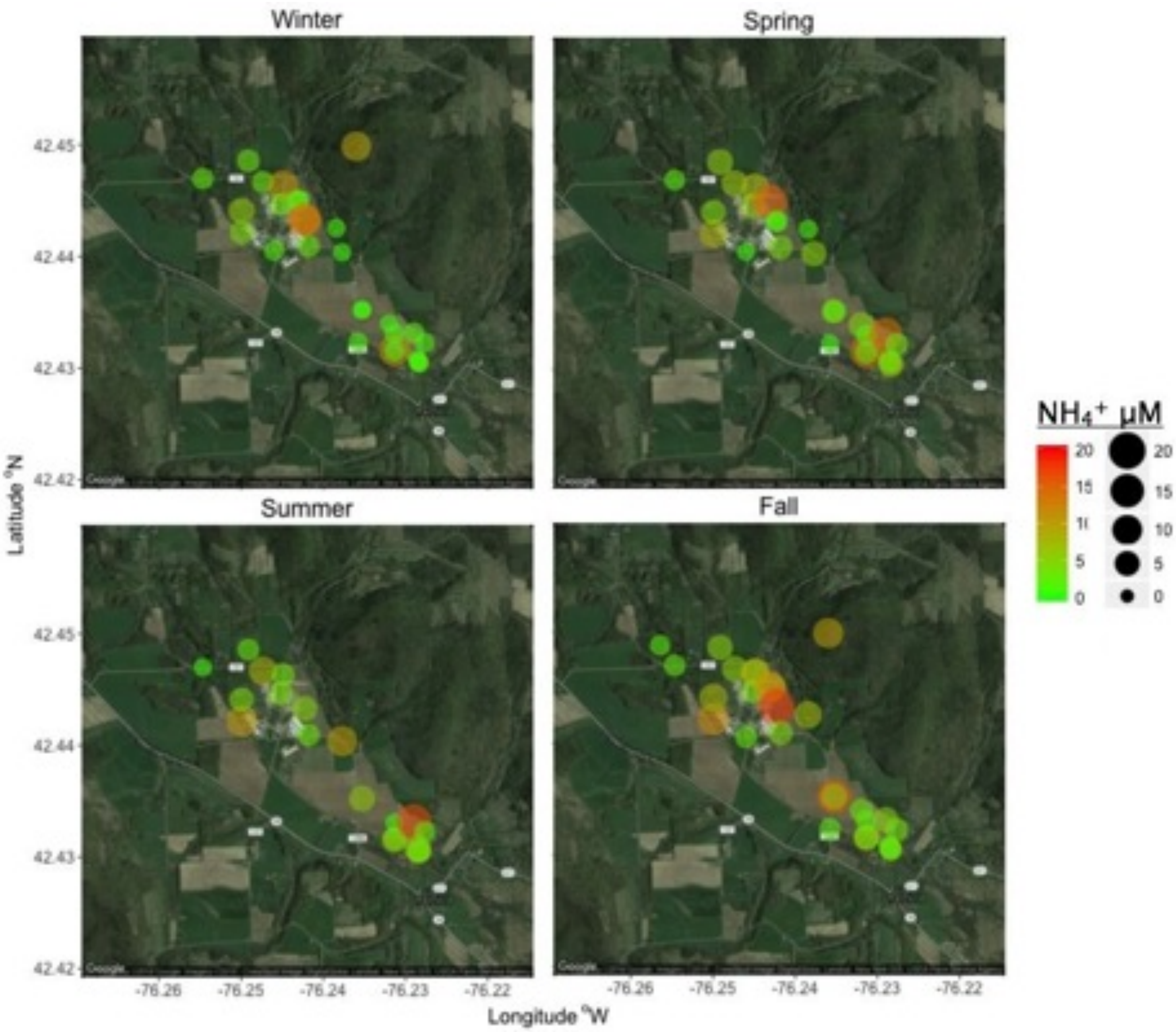

Figure 16. Bubble plots of mean seasonal NH_4^+ concentration (µM) at sites on the CURC, 1974-2016.

Table 14. ANOVA Table of NH_4^+ concentrations contrasted by catchment by primary land use activity and season.

Source of Variation	**df**	**Sum of Squares.**	**Mean Square**	***f***	**Pr (>F)**
Catchment	1	346	346	3.252	0.07175
Use	3	3258	1086	10.209	1.37e-06
Season	3	981	327	3.073	0.02714
Catchment and Use	3	14219	4740	44.552	< 2e-16
Catchment and Season	3	195	65	0.611	0.60822
Use and Season	9	424	47	0.443	0.91161
Catchment, Use and Season	9	2454	273	2.563	0.00661
Residuals	727	77342	106		

In CURC-North, NH_4^+ concentrations at monitoring sites do not significantly vary seasonally within each land use class, *Figure 17*. Indeed, not only are concentrations typically stable across seasons, but there is broad lack of statistical difference of NH_4^+ concentrations irrespective of use due to high variance of the data, *Table 15*.

Table 15. Comparison of mean NH_4^+ concentrations (µM) at sites according to land use in CURC-North, 1974-2016.

CURC-North

	Animals			***Corn***			***Forest***			***Grassland***		
Season	*mean*	*SE*	*n*	*mean*	*SE*	*n*	*mean*	*SE*	*n*	*mean*	*SE*	*n*
Winter	3.47	0.63	39	10.7	3.28	33	2.58	0.73	17	4.76	1.25	41
Spring	7.08	0.95	37	8.37	1.38	21	5.51	1.84	21	5.08	0.82	43
Summer	5.46	1.98	10	3.30	*NA*	1	7.21	2.54	15	3.68	0.59	26
Fall	7.55	1.25	30	9.63	1.76	16	4.39	0.76	37	6.54	1.12	50

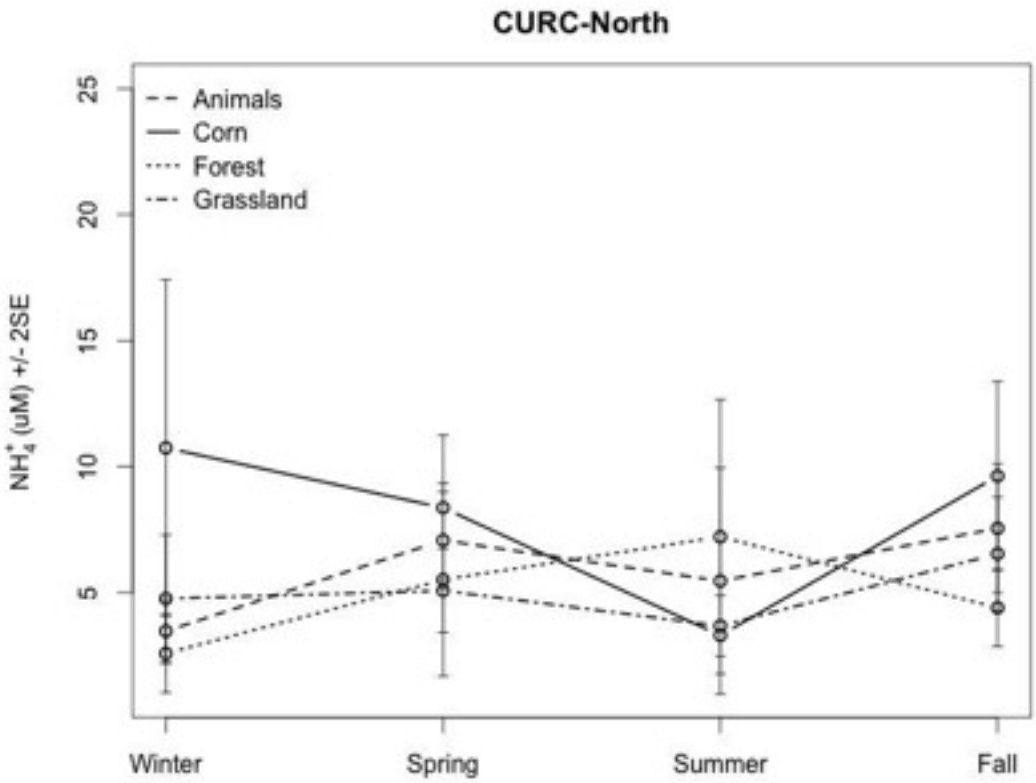

Figure 17. Comparison of NH_4^+ concentrations (µM) +/- 95% CI in CURC-North by land use and season, 1974-2016. There is typically a strong year-round convergence of concentrations irrespective of their association with agricultural activity.

In CURC-South there are a number of significant seasonal differences between various land uses, *Table 16*. Winter NH_4^+ concentrations near the dairy feedlot are not significantly different from those in grasslands during the same season, however concentrations at grassland sites are significantly higher than at feedlot sites in the spring when mineralization of organic N in crop residues may be stimulated by freeze-thaw and wet-dry cycles (Bartholomew 1965). Grassland concentrations are significantly higher than sites in corn fields in each season, and differences are greatest in the summer months; when corn fields are cropped concentrations at grassland sites are 37 µM greater. Grassland concentrations of NH_4^+ are also significantly higher than in forested sites during all seasons with differences here greatest in summer and smallest in winter. Finally, when compared to sites close to the dairy barns, grassland sites are only significantly different from feedlot sites during summer when grasslands sites may be as much as 38 µM higher than at sites near the feedlot.

Table 16. Comparison of mean NH_4^+ concentrations (µM) at sites according to land use in CURC-South, 1974-2016.

CURC-South

	Animals			***Corn***			***Forest***			***Grassland***		
Season	*mean*	*SE*	*n*	*mean*	*SE*	*n*	*mean*	*SE*	*n*	*mean*	*SE*	*n*
Winter	9.16	2.83	20	1.44	0.22	61	3.26	1.88	34	20.83	9.52	8
Spring	3.18	0.97	6	4.57	1.11	32	8.12	3.91	17	32.13	14.05	7
Summer	3.60	0.74	3	5.07	*1.21*	18	3.49	1.08	12	42.28	18.48	4
Fall	13.14	4.06	17	5.45	1.84	35	4.99	1.31	29	23.33	5.62	18

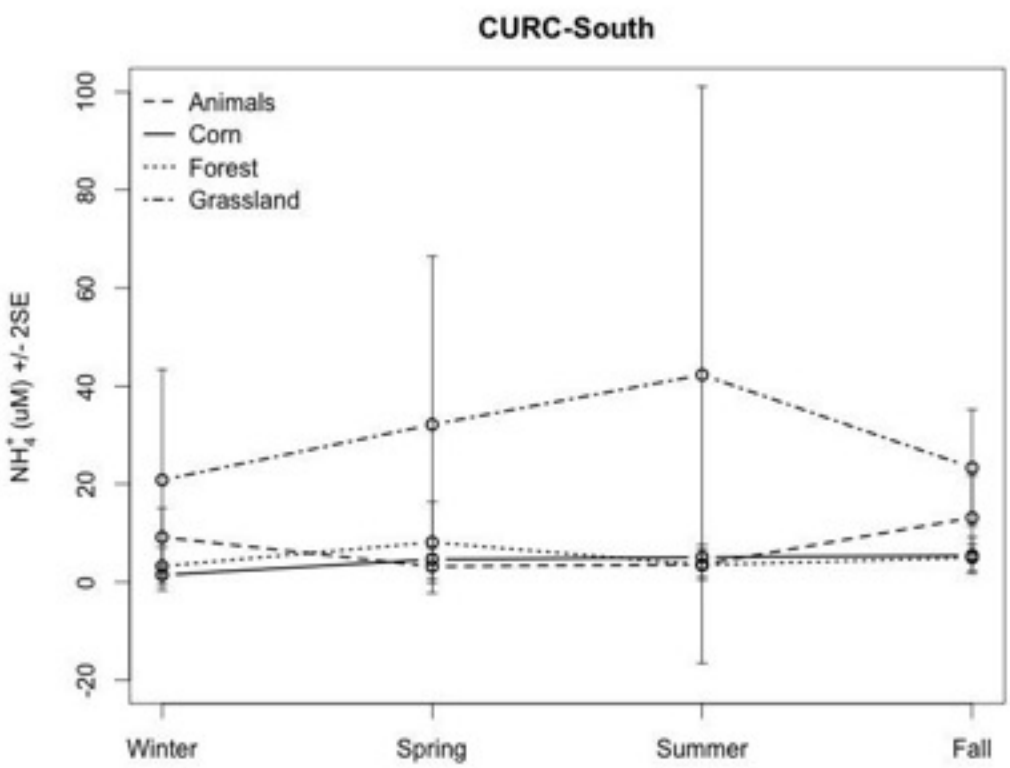

Figure 18. Comparison of NH_4^+ concentrations (µM) +/- 95% CI in CURC-South by land use and season, 1974-2016. There is typically a strong year-round convergence of concentrations irrespective of their association with agricultural activity.

With few exceptions at sites in corn fields, TDP does not appear to vary by seasons when viewed as a concentration plot by site on satellite imagery of the farm, *Figure 19*.

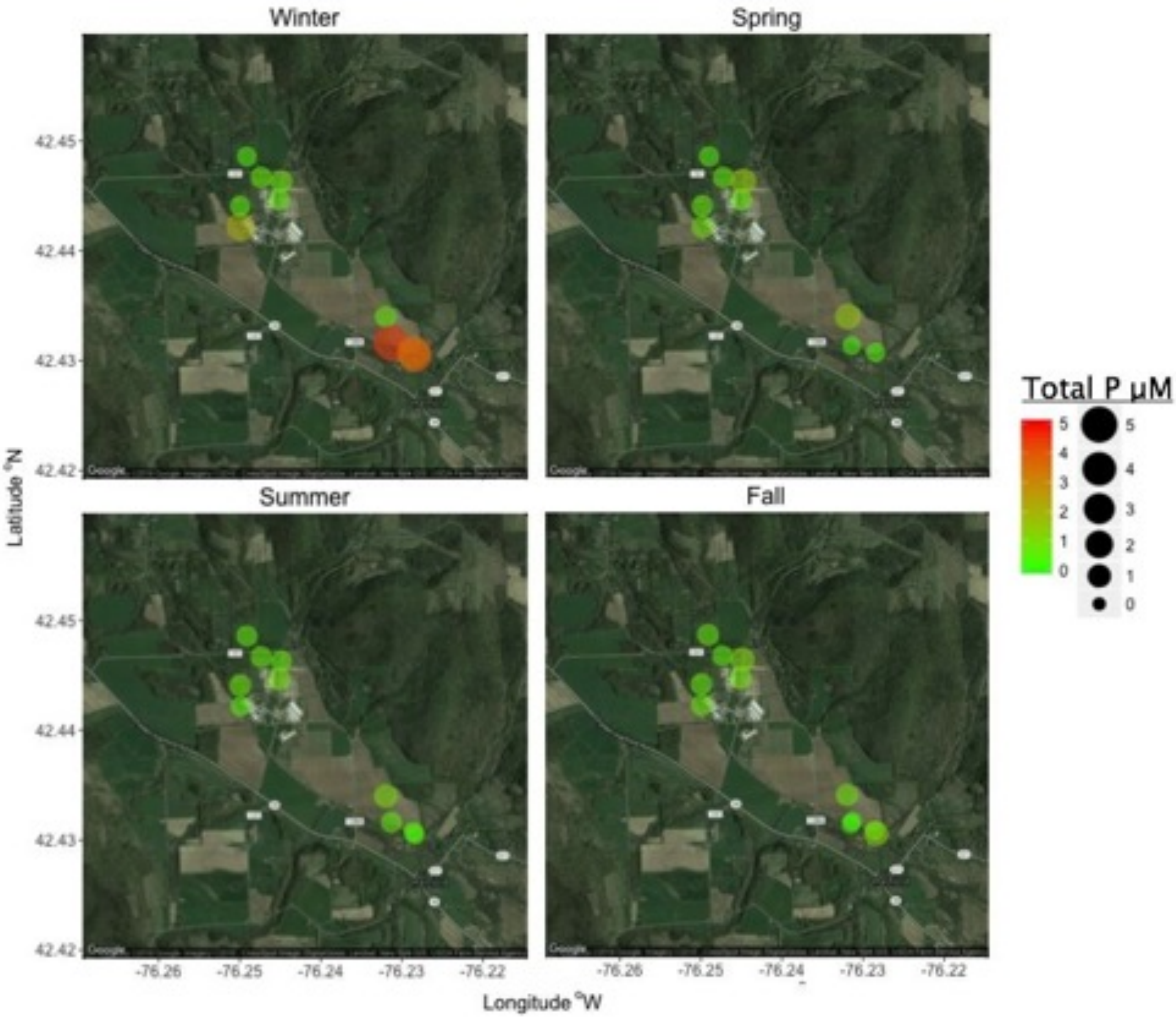

Figure 19. Bubble plots of mean seasonal TDP concentration (µM) at sites on the CURC, 1974-2016.

Table 17 ANOVA Table of TDP concentrations (μM) contrasted by catchment by primary land use activity and season

Source of Variation	**df**	**Sum of Squares.**	**Mean Square**	***f***	**Pr (>F)**
Catchment	1	12.6	12.578	6.117	0.014284
Use	3	5.5	1.834	0.892	0.446461
Season	3	27.2	9.057	4.404	0.005087
Catchment and Use	2	2.8	1.403	0.682	0.506684
Catchment and Season	3	39.8	13.253	6.445	0.000356
Use and Season	9	6.4	0.716	0.348	0.957398
Catchment, Use and Season	4	1.1	0.277	0.134	0.969489
Residuals	187	384.5	2.056		

I use ANOVA testing to determine significant sources of variance among TDP concentrations, *Table 17*. Here, unlike both species of N, P is seasonally significant independent of land use. Indeed, land use here is not a significant factor, though there remain significant differences between the two small catchments, with TDP in CURC-South 0.75 uM greater than CURC-North. Rather than assume the effect of agriculture is null given a lack of variation among land uses, these data strongly demonstrate the influence of agricultural activity and the distribution of land use on nutrient concentrations.

In both catchments, TDP concentration data show large variation due to low sample size of certain land use categories in certain seasons. In the less intensively farmed CURC-North, TDP concentrations at surface and groundwater sites associated with growing corn or the animal feedlot vary throughout the year, while concentrations at grassland and forest ground and surface water sites remain quite stable throughout the year, *Table 18, Figure 20*.

Table 18. Comparison of mean TDP concentrations (μM) at sites according to land use in CURC-North, 1974-2016.

CURC-North												
	Animals			***Corn***			***Forest***			***Grassland***		
Season	*mean*	*SE*	*n*	*mean*	*SE*	*n*	*mean*	*SE*	*n*	*mean*	*SE*	*n*
Winter	1.55	1.04	9	0.74	0.04	3	0.64	0.14	3	0.42	0.04	6
Spring	0.73	0.10	25	1.41	0.70	11	0.63	0.14	11	0.54	0.06	22
Summer	0.81	0.11	7	0.55	NA	1	0.65	0.09	7	0.66	0.09	13
Fall	0.78	0.09	15	1.14	0.21	3	0.52	0.06	13	0.67	0.04	26

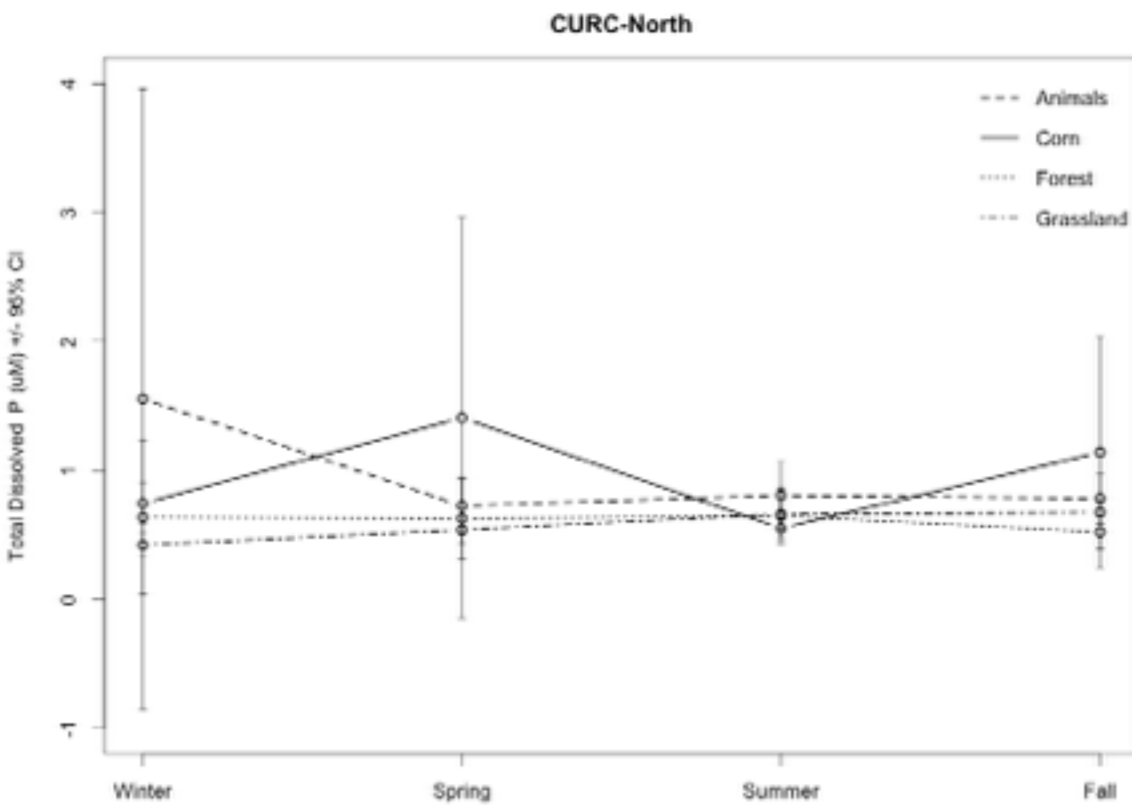

Figure 20. Comparison of TDP concentrations (μM) +/- 95% CI in CURC-North by land use and season, 1974-2016.

Alternatively, in the more intensively farmed CURC-South catchment TDP concentrations in forested and cornfield ground and surface water sites are quite high in winter, when there is no crop on the fields, and are quite low throughout the rest of the year, *Table 19, Figure 21*.

Table 19. Comparison of mean TDP concentrations (µM) at sites according to land use in CURC-South, 1974-2016.

CURC-South

	Animals			***Corn***			***Forest***			***Grassland***		
Season	*mean*	*SE*	*n*	*mean*	*SE*	*n*	*mean*	*SE*	*n*	*mean*	*SE*	*n*
Winter	*NA*	*NA*	0	3.54	1.98	7	3.76	3.33	3	*NA*	*NA*	0
Spring	*NA*	*NA*	0	0.90	0.29	7	0.01	*NA*	1	0.26	*NA*	1
Summer	*NA*	*NA*	0	0.55	0.11	7	0.32	0.05	3	*NA*	*NA*	0
Fall	*NA*	*NA*	0	0.54	0.14	7	1.25	*NA*	1	0.29	*NA*	1

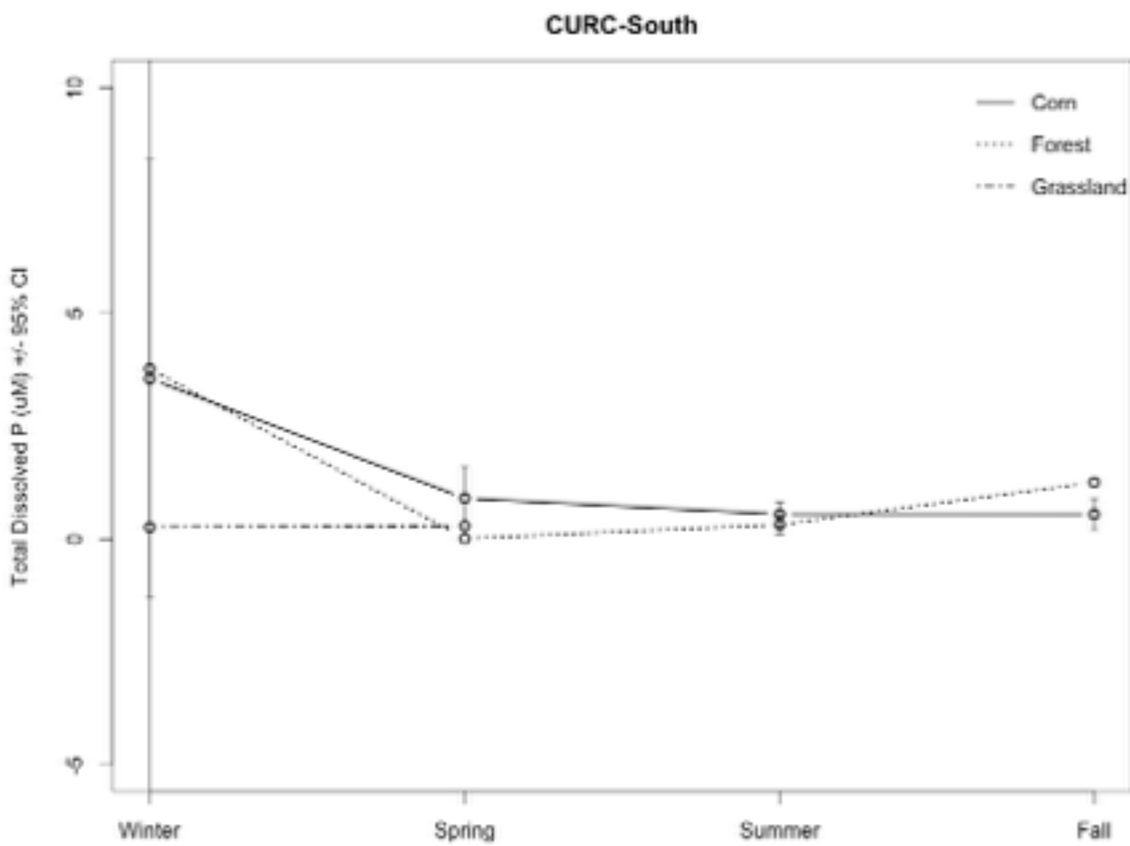

Figure 21. Comparison of TDP concentrations (µM) +/- 95% CI in CURC-South by land use and season, 1974-2016.

DISCUSSION

Application of manure may be beneficial when applied at rates commensurate with crop demand. Manure has been shown to improve both the chemical and physical properties of nearly all soil types, but particularly shallow, coarse, or low organic matter (OM) soils (NRC 1993). Manure can also increase the soil's ability to hold water and resist compaction (Madison *et al.* 1986). Yet when crop demand, timing and method of application, soil type, and climate are not considered, the quality of runoff or groundwater may be affected (Gilbertson 1979). The present reality in many situations in U.S. dairy farming is that animal density is sufficiently high that more manure is produced than can be used as fertilizer on locally available cropland (NRC 1993; Carpenter *et al.* 1998; Gollehon *et al.* 2001; Galloway *et al.* 2003; Cole *et al.* 2006; Cela *et al.* 2014).

An additional management problem exacerbating the excess supply of manure is that both P and N can accumulate in soils after repeated application so that in each succeeding year less manure need be applied to achieve the same amount of N for crops. NRC (1993) shows that when manure is applied to soil with only 1 percent dry mass N, about 22 metric tons of manure must be applied to supply 112 kg of N per ha during the first year. Because it may take up to 3 years before organic N in manure is mineralized and becomes available to plants, only 5.1 metric tons need be applied in the 20th year to supply the same amount. Sharpley (1984) found that 8 successive years of manuring at constant rates resulted in large accumulations in available soil P.

Manure application frequency and quantity at the CURC is not known or whether manure is the only source of fertilizer applied. However herd population is known to be ~800 cattle and has varied by less than 10 percent since 1974 (Wang *et al.* 1999). Gilbertson (1979) estimates one dairy cow produces about 13,700 L manure per year. Using this estimate, a herd of 800 cattle produces about 11 million L-year^{-1} and is presumably all spread on the farm. This equates to approximately 81,000 L-ha^{-1}-year^{-1} if manure is spread only on land dedicated to growing corn or about 38,000 L-ha^{-1}-year^{-1} if manure is also spread on grassland as well. Since each dairy cow is estimated by Gilbertson (1979) to produce the equivalent of 55.8 kg N and 9.5 kg P in waste per year, the CURC may add a much as 330 kg-ha^{-1}-year^{-1} N and 56 kg-ha^{-1}-year^{-1} P on cornfields from manure alone, although as much as 27 percent in N volatilization losses are expected from broadcast surface application.

Dissolved Inorganic Nitrogen

The relative balance of N, in its various forms, in the soil-water matrix of an agricultural setting is the result of several factors which influence biological and chemical processes. These include physical factors such as soil type, soil organic matter (SOM) content and quality, i.e. C:N ratios, and aeration status, as well as climatic factors are also important and include soil moisture, pH and temperature (Keeney 1982; Howarth *et al.* 2002). The main biological processes they influence are the opposing processes of immobilization and mineralization, and that of denitrification.

Immobilization is the transformation of inorganic to organic N by plants and microorganisms, whereas mineralization (or ammonification) is the breakdown of organic N to NH_4^+. The relative magnitude of these processes determines the amount of inorganic NH_4^+ in the soil-water matrix. Proteinaceous soils with C:N ratios less than 22, for example, tend to favor early rapid net mineralization and eventually equilibrate with the bulk of soils (Bartholomew 1965). Both freeze-thaw and wet-dry cycles promote mineralization

(Bartholomew 1965). Alternatively temperature, pH and soil moisture content affect turnover rates, with moist, still aerobic soils favoring immobilization and there is evidence that NH_4^+ can be preferentially immobilized to NO_3^- (Broadbent 1968).

Nitrification is the two-step microbial oxidation of NH_4^+ via NO_2^- to NO_3^-. NO_3^- which is far more mobile than NH_4^+ and thus able to leach into groundwater as a polluting nutrient in sufficient concentrations. In the warm summer months, under aerobic conditions and pH between 6 and 8, complete conversion of NH_4^+ to NO_3^- by nitrifying bacteria can be expected (Keeney 1982). Chemical processes affecting the availability of NH_4^+ are NH_4^+ exchange between cation exchange sites and soil solution, NH_4^+ fixation in the interlayers of non-expanding 2:1 clay minerals so that it is slowly released and made available for cycling through the other processes, and volatilization of NH_3 from NH_4^+ salts to the atmosphere (Keeney 1982). NH_4^+ exchange is readily reversible and soils have finite sorption capacity, however, so these are not expected to be important NH_4^+ sinks at the CURC (Nommik 1965). Volatilization increases with temperature and water loss, and significant losses have been demonstrated in the alkaline surfaces of acid soils, flooded soils and pastures and have been shown to be greatest with urea (Du Plessis and Kroontje 1964; Denmead *et al.* 1974; Fenn and Kissel 1974). Volatilized ammonia is typically redeposited near its source, however, so this is not expected to be major loss pathway at the CURC.

The relatively high levels of NO_3^- observed at upland ground and surface water sites are likely the result of high rates of NH_4^+ volatilization in the farmed valley, local redeposition on the valley slope and high rates of denitrification rapidly converting NH_4^+ to NO_3^-.

Conversely, a suppressed denitrification is also likely the reason NH_4^+ is higher in grasslands in CURC-South. Grasslands in the south catchment are typically lower in the landscape than corn fields and animal sites, and even most wooded areas. Though valley soils generally are well drained, grassland groundwater sites tended to remain below the farm's water table most of the year during 2015-2016. Thus where one would expect the total transformation of NH_4^+ to NO_3^- in the warm, summer months, suppression of denitrification soils may result in higher NH_4^+ concentrations where soils remain anoxic.

The declining trend of NH_4^+ in CURC-North is curious. Carbonaceous organic matter with C:N ratios greater than 22 are associated with rapid net mineralization of organic N to NH_4^+, while proteinaceous organic matter with C:N ratios less than 22 are associated with net immobilization (Keeney 1982). Since cow manure has a C:N ratio of between 10-30, we could see either net mineralization or immobilization depending on manure nutrient quality, which declines with storage (Smil 2004). The data, unless contaminated early on, by ammonia-based cleaning agents or cigarette smoke prior to banning in or near buildings late in the 20th century, seem to indicate NH_4^+ is quickly cycled to other forms: either nitrified to NO_3^-, preferentially taken up by crops and immobilized, or volatilized (Broadbent 1968; Keeney 1982). Another possibility is that the application of anhydrous ammonia on the farm in the 1970s resulted in high, early concentrations and that levels fell once the practice was abandoned (Bouldin 2016).

Total Dissolved Phosphorus

P enters into a series of reactions when added to soils which can result in the release of soluble reactive P (SRP), some of which is biologically fixed and harvested with the crop. The balance is either sorbed to positively charged cation exchange sites as particulate P which can be transported to surface waters in runoff, remains in crop residues and is incorporated to SOM, or is lost in solution to surface and groundwaters (Bailey 1968; NRC 1993; Carpenter *et al.* 1998; Idris *et al.* 2012). Sorption to soil particles is pH dependent, increasing as soil pH decreases. Capacity is also related to the abundance of aluminum, making alumino-silicate clay soils highly sorptive (NRC 1993; Idris *et al.* 2012). While the transport of P to groundwater is generally harmless, the transport of P to surface waters through runoff is problematic, however, as Schindler (1977) found that many freshwater lakes are P limited and Vollenweider (1968) demonstrated that aquatic concentrations of PO_4-P of between 0.32-0.97 μM (10-30 μg/L) in lakes are sufficient to initiate the process of eutrophication. Carpenter *et al.* (1998) estimates that between 1950 and 1995 intensive application of fertilizers has resulted in the net addition of ~400 x 10^6 Mg P to croplands globally. Caraco (1995) further estimates that 3-20 percent of that amount, 12-80 x 10^6 Mg P, could be eroded or leached to surface waters globally. This is a troubling number given that Kerr et al. (1970) found concentrations as little as 0.03 μM P can support the production of one billion blue-green algae cells.

I hypothesized that concentrations of TDP would remain relatively stable over time unless the high sorption capacity of strongly acid soils in the valley floor was overwhelmed by P additions. In this case sorption sites would be saturated with P and result in significant export. Export to the SRB Basin would not be as troublesome as transport via Fall Creek to nearby Cayuga Lake which suffers from P pollution from sources within its watershed, of which the CURC is a part (Likens 1984; Georgakakos 2015). At groundwater sites where farming does occur, mean concentrations of 0.5 (μM) P are well within the range shown by Vollenweider (1968) where P may be sufficient to initiate eutrophication in P-limited lakes. Winter high concentrations when no crop is grown on corn fields could indicate differences in CURC-South indicate the massive P additions from manuring and the equally massive crop demand and soil sorption capacity to draw down P concentrations to levels commensurate with the less intensively farmed north during the growing season.

CONCLUSION

Every food production system affects the environment. Here, I have shown that agricultural activity on a single farm located on two small catchments with two markedly different allocations of land use can potentially have significantly different effects on water quality. Where land use distribution is nearly two-thirds unfarmed, concentrations remain low in "natural" areas such as forested sites and grasslands, indicating ability to cycle applied nutrients as they move across the landscape in ground and surface waters exceeds applied nutrients. Yet, where the opposite distribution is true, even where land is as little as 50 percent dedicated towards agricultural production, the influence of farming on nutrient levels in unfarmed areas is overwhelming, producing a seasonal convergence across all land use units to levels seen only in feedlots or manured corn fields.

When applied judiciously, manure can be of great benefit, improving both the chemical and physical properties of nearly all soil types and increase the soil's ability to hold water and resist compaction (Madison *et al.* 1986; NRC 1993). Yet, with sufficiently high animal densities, manure production can not only become financially burdensome for farmers but may be ecologically burdensome to the land they farm, overwhelming natural nutrient cycling and inducing plant stress in terrestrial ecosystems and eutrophication in aquatic systems.

Perhaps most concerning is the increasing trend in NO_3^- in the less intensively farmed CURC-North, at nearly two thirds the rate of the more intensively farmed CURC-South, which may yet result in elevated NO_3^- concentrations at wooded sites to levels only previously seen in corn fields and sites near the feedlot. Continued monitoring should be considered to collect samples from each of the land use category in both catchments, as resampling for this study unfortunately did not completely capture each land use unit in both small catchments. Further increases in sample size will better elucidate the impact of the CURC on water quality in the watersheds of which it is a part.

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