AGRICULTURAL INFLUENCES ON LOW-ORDER STREAMS

EFFECTS OF AGRICULTURAL PRACTICE ON THE WATER QUALITY OF LOW-ORDER STREAMS IN THE BEAVER VALLEY WATERSHED

By

CATHERINE DIELEMAN, B.Sc.

A Thesis

Submitted to the School of Graduate Studies

for the Partial Fulfilment of the Requirements for

the Master of Science

McMaster University

MASTERS OF SCIENCE (2012) McMaster University

(Biology) Hamilton, Ontario

TITLE: Effects of agricultural practice on the water quality of low-order streams in the Beaver Valley watershed

AUTHOR: Catherine Dieleman, B.Sc. Hons. (McMaster University)

SUPERVISOR: Professor P. CHOW-FRASER

NUMBER OF PAGES: xix, 106

GENERAL ABSRACT

Eutrophication from agricultural runoff is a global issue, and can often result in degradation and loss of aquatic habitat. The overall objective of this study is to gain a better understanding of the factors that influence variation in water chemistry of low-order streams in an agricultural watershed. I focused on first-order streams because improved best management practices are implemented at this scale. The first chapter finds significant differences between the effects of livestock- vs and crop-based operations on water chemistry while modeling the relationship between independent landscape variables and major water-quality parameters in an agroecosystem. I also determine significant differences exist in dependent variables among seasons and are best described by the agriculturally relevant calendar (ARC). In Chapter 2, I compared the effectiveness of discrete and continuous sampling programs for monitoring the impacts of cattle disturbances on water quality. I found that daily total phosphorus (TP) concentrations (integrated sample taken every 6 hours) were not significantly correlated with precipitation and were significantly lower than discrete water samples. Turbidity readings (recorded every half hour) showed spikes that corresponded with cattle hydration events and increased levels of nutrients through backwash. These influences were greatest for TP concentrations when cattle were given direct access to streams during periods of low rainfall. We also found significant differences for pH, temperature, conductivity, dissolved oxygen and chlorophyll across the ARC seasons. In Chapter 3, I find a significant relationship between periphyton growth (grown on acrylic rods for 14 days) and the level of primary nutrients (TP, soluble reactive phosphorus,

total-ammonia nitrogen). Thus, for low-order streams influenced by small family farms, acrylic rods may be an inexpensive indicator of excess limiting nutrients. In such environments stream length may be a stronger measure of streams than stream order since total nitrogen, TP and pH were significantly correlated with stream length.

PREFACE

The following master thesis is composed of three chapters which have been prepared as stand-alone manuscripts for publication in scientific journals. Some duplication of information is unavoidable because of their stand-alone nature. The main body of the text and all of the manuscripts have been formatted according to requirements of the target journals.

My supervisor Dr. Patricia Chow-Fraser and I designed all the experiments conducted in all three chapters. I led the collection and analyses of all samples. I also completed all GIS analyses except for the delineation of watersheds for each of the study sites; these were completed by staff at the Ontario Ministry of Agriculture, Food and Rural Affairs under the direction of Dr. Stewart Sweeney and made available for our use. Below are the proper citations for each paper.

Dieleman, C. & Chow-Fraser, P. (2012). Water chemistry of first-order streams in relation to agricultural practice, landform features, storm events and season in an agriculturally dominant watershed.

Dieleman, C.& Chow-Fraser, P. (2012). Importance of monitoring continuously during three seasons of an agriculturally relevant calendar to determine impacts of livestock farming on a first-order stream.

Dieleman, C. & Chow-Fraser, P. (2012). The effect of agricultural practice on periphyton growth and the water chemistry of first- and second-order streams in the Beaver Valley watershed, Ontario, Canada.

.

ACKNOWLEDGEMENTS

There are many people to acknowledge who aided in the completion of this thesis. First I would like to thank my supervisor Pat. Her creativity and imagination in the field of scientific research is limitless and is always an inspiration. Her natural eye for fleshing out 'the story' is a Godsend, particular in times of high pressure. Your guidance will last a life time, my most sincere thank you for everything you have done. I also thank Mike Waddington for helpful comments during committee meetings, and Susan Dudley for sitting on my examining committee. I also give a hat tip to my field teams as well as all members of the Pat Chow-Fraser lab. Particularly those, such as Amanda, Chris, Ashley and Maria, who battled through storm after storm so I could have strong precipitation data. The hours Margaret and Leslie spent being introduced to electric fences, trekking through less than ideal terrain and, of course, acid washing were something few lab assists could handle. They have my many thanks for toughing it out with me. Rachel deCatanzaro gets a particular thanks for being my water chemistry mentor. I am sure my masters would not be what it is today without you.

The never ending support from the Beaver Valley community, particularly my friends and family, is of particular note. From driving four hours on the road to install my ISCO autosampler, to sampling first-order streams in a Blue Mountain winter storm, their participation in every study was almost palpable. My mother, Darlene Dieleman, deserves special recognition for her activities as my field 'lab manager'. Besides recording all of my data in the field during the winter season, she was a spring of encouragement in all of my endeavours. Those 7 am wake ups in January would have been much harder all by myself. My father, Rick Dieleman, must be thanked for his guidance, as it was critical in finding almost all of my study sites. His understanding of the local first-order streams in the Beaver Valley watershed is incomparable, one of his many talents I am forever grateful for. Both my brother Daniel Dieleman and cousin Douglas Collins's generous natures need also to be mentioned. Doug and Daniel took hours out of their personal time to help with the acid washing of ISCO containers and resetting the autosampler, often at dusk. For those who have worked with acid in less than ideal lighting you know the tribulations they faced week after week. Markus, Colleen and Laura Wolski (my youngest assistant at 5 months old) were all critical to data collection. Markus for practicing his yoga moves during my pilot study and Laura and Colleen for pulling me out of site 5 in March. My waterproof hikers are only so good. Of course we cannot forget the much needed and appreciated cookie supply and moral support provided by Carolynne and Ian Jewett. As well as the one night we ran out of light and Matt Jewett was there to the rescue us. Michael Brookfield must also be appreciated for his unwavering steadfast confidence in my skills and abilities. There was more than one dark day made bright by a few choice words that he always had at the ready.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIAIONS

ARC	Agriculturally Relevant Calendar
Chl	Chlorophyll *a*
CON	Conventional Calendar
COND	Conductivity
DO	Dissolved Oxygen
N	Nitrogen
P	Phosphorus
TEMP	Temperature
TAN	Total Ammonia-Nitrogen
TN	Total Nitrogen
TNN	Total Nitrate-Nitrogen
TP	Total Phosphorus
TSS	Total Suspended Solids
TURB	Turbidity
SRP	Soluble Reactive Phosphorus

GENERAL INTRODUCTION

Limiting Nutrients, Sediment and Eutrophication

The concentration of limiting nutrients in any given ecosystem determines its overall productivity (Smith, Tilman, & Nekola, 1999). Aquatic primary producers, including those of low-order streams, are limited by both nitrogen (N) and phosphorus (P) concentrations (Hecky & Kilham, 1988). As an aquatic ecosystem ages, it will naturally become more and more eutrophic (see Table i.1 for range of nutrients in various systems) (Sharpley, et al., 2003), but anthropogenic activities have accelerated this process and have increased the number of eutrophic systems globally to a crisis level (Fraters, Boumans, van Leeuwen, & de Hoop, 2001). One of the major negative impacts of eutrophication is the loss of biodiversity and ecological integrity, as a result of algal blooms and growth of nuisance aquatic plants (Carpenter, et al., 1998). Algal blooms reduce the amount of solar radiation reaching the bottom of lakes and rivers, and once they senesce, bacterial decomposition lowers the available dissolved oxygen and releases the P and N back into the water column, forming a positive feedback loop (Carpenter, et al., 1998). With lowered oxygen and light levels, many sensitive species are unable to survive, and this seriously disrupts natural community dynamics (Tilman, et al., 2001).

Phosphorus occurs in three main forms in streams: inorganic P, particulate organic P and dissolved P, with only soluble forms of inorganic P being available for aquatic-plant use (Correll, et al., 1999). Forms of phosphorus found in rural waterways can come from many sources including rainwater, plant biomass, fertilizers, livestock wastes and soil; however, rainwater is not a significant source in most freshwater systems (Nash & Halliwell, 1999). In an agricultural setting, soluble reactive phosphorus (SRP) tends to be the dominant form of P where no-till is practised, since soil erosion is greatly reduced (Cooke & Prepas, 1998; Harmel, et al., 2006; Sharpley, et al., 1994). No-till also prevents active mixing of soil and crop residues, thus inhibiting the sorption of excess P onto soil particles (Sharpley, et al., 1994). SRP, in particular, is then readily available for transport via surface runoff from fields to neighboring water ways. Even soils that are conventionally tilled can become saturated with P, and the excess phosphorus enters water bodies via runoff and erosion (Nash & Halliwell, 1999, Sharpley, et al., 2003). Carpenter, et al., (1998) estimate that between 3-20% of P applied to croplands is leached into waterways in this manner.

Nitrogen is also leached from agricultural lands and enters into aquatic ecosystems in various forms. A study by Goolsby, et al. (2000) showed that in some watersheds, total N levels have increased 2-5 times over natural levels. The elevated presence of this nutrient is attributed to fertilization, human sewage, livestock wastes, fossil fuel combustion and the decomposition of legumes, with many studies identifying fertilization and animal wastes as the main sources (Frediflder, et al., 1998; Peterson, et al., 2001). In such aquatic agroecosystems, the main forms of N are NH_4^+ and NO_3^-. NH_4^+ is generally associated with livestock excrement (Petersen, Roslev, & Bol, 2004) and decomposing organic matter (Wetzel, 1983), although it can be found in some fertilizers as well. NH_4^+ is generally found in lower concentration in headwater streams than is NO_3^- since it has lower nutrient loading and is quickly adsorbed to sediment or taken up by biota (Peterson, et al., 2001). Conversely, NO_3^- is strongly associated with fertilization (Fraters, et al., 2001) and, while it can be sorbed by both sediments and biota, it is not taken up as quickly as NH_4^+ (Peterson, et al., 2001). Like phosphorus, the soil has a fixed capacity to bond forms of nitrogen; once this capacity is surpassed, the excess N is mobile and can travel to adjacent waterways, particularly during storm events (McDiffett, Beidler, Dominick, & McCrea., 1989, Peterson, et al., 2001). In such a scenario, between 10 to 80% of applied N to one field can be leached out (Carpenter et al, 1998).

Agricultural practices such as conventional tilling and livestock pasturing also increases soil erosion, (Caux, et al., 1997) leading to three times the sediment pollution of deforestation (Waters, 1995). In crop lands the removal of complex root systems during harvest and the soil rotation during planting degrades the soil matrix leaving it prone to sediment loss, particularly during storm events (McConkey, Nicholaichuk, Steppuhn, & Reimer, 1997). At livestock sites, excessive grazing as well as the weight and hoof structure of cattle kill off important vegetation and compact soils, again leaving the land prone to sediment loss (Dunne, Western, & Dietrich, 2011). The environmental impacts of increased turbidity and sediments have also been well documented (CCME, 2002). Among other impacts, high turbidity and sediments can alter streambed composition, reduce stream productivity, clog gills, reduce fish growth, alter behavioral patterns of aquatic life, and decrease fish resistance to disease (Waters, 1995).

Agriculture

Humans, originally hunter and gathering societies, started to develop agricultural practices between 5 and 10 thousand years ago (Mazoyer, Roudart, & Membrez, 2006). At this time Neolithic societies around the globe started to plant crops and keep fauna in captivity for food. Since this humble origin, agriculture has undergone many advances in technology, often referred to as a revolution. The most recent of these are the two modern revolutions, the first occurring between 16th to the 19th century and the last starting in the 1960s and is still arguably ongoing (Mazoyer, et al., 2006; Sharpley, Gburek, Folmar, & Pionke, 1999). The first modern revolution introduced the concept of livestock and crop rotation cycles, which is still used today on small-scale farms. Previously, agriculturalists rotated their croplands, leaving one field fallow every year and pastured livestock in wild meadows (Mazoyer, et al., 2006). In the new scheme, the fallow lands are instead sown with grasses, such as legumes, which require very little nutrients from the soil (Tilman, 1998). The livestock would graze on this field for the season, fertilizing the land with their excrement while the grasses fix nitrogen into the land. During the winter season, cereal crops, such as winter wheat, were grown and this would be followed by a fodder crop to increase livestock and their manure outputs. As a result farmers were able to get approximately 50% greater yields with 50% less human labour (Mazoyer, et al., 2006). The excess manpower was then employed in mines and factories, stimulating the industrial revolution and prompting the second modern agricultural revolution.

The second revolution or the 'Green Revolution' occurred just after the Second World War. New advances in technology discovered during the war as well as in the 20th and 21st century were and still are being applied to farms the world over. Increasingly complex machines and chemicals are continuously being introduced to the agricultural environment to reduce human labor while increasing yields (Reaman, 1970). New species which have been heavily selectively bred or genetically modified are being utilized to increase outputs and profits. Farmers can now purchase much of the goods required to run their operation (chemical fertilizers, seeds, tools, fodder, breeding livestock) and this has led to crop specializations and the evolution of mono-cultivation (Reaman, 1970). Regions can specialize in the same product (e.g. row crops, livestock, or fruit). Increases in yields from this revolution have been massive, with a 100% increase in the outputs from a single farmer (Mazoyer, et al., 2006). As a result, < 5% of any given population is required to produce food to feed the entire country (Mazoyer, et al., 2006).

The environmental impact from this 'Green Revolution' has been well documented in the past 30 years with leading researchers calling for a '*Greener* Revolution' (Tilman, 1998). This research has identified modern intensive farming as a leading cause of anthropogenic eutrophication and erosion, events which can lead to loss of habitat quality and biodiversity in aquatic ecosystems (Frediflder et al, 1998, Nash & Halliwell, 1999). Tilman, et al. (2001) argues that agriculturally mediated degradation may surpass the impacts of climate change on the environment. Globally, humans already use more than a third of the terrestrial primary production and half of the available freshwater, while doubling the amount of both N and P in terrestrial and aquatic systems (Tilman, 2001). Agriculturalists alone, currently use over half of the productive terrestrial land (defined as lands not dominated by rock, desert, tundra, or boreal) with the most fruitful areas for farming already in use (Tilman, Cassman, Matson, Naylor & Polasky, 2002). In the next 50 years the global population is predicted to grow by 50%, doubling its demand for grains and straining an agricultural system already approaching the maximum yield and plagued with sustainability issues (Tilman, et al., 2002). Tilman, et al. (2002) suggest that advances in both technology and research will be vital to prevent further degradation by farming for both aquatic and terrestrial environments while meeting the needs of the growing populace.

Harmel, et al. (2006) argued that such studies should be completed at the scale of individual farms to produce results that can be used by farmers and environmental agencies to develop conservation strategies. Working at a local scale also encourages a healthy dialogue between researchers and agriculturalists. Owners of test sites often require water-chemistry reports in return for use of their lands. This allows farmers and scientists to have informal discussions regarding their own water quality as it relates to current trends. This will also allow researchers to produce realistic and achievable recommendations for agriculture as they will have a better perspective on the challenges of modern agriculturalists.

Low-Order Streams

The term ‘low-order’ is commonly used in literature to describe first- and second-order streams as determined by Stahler (1952) (Figure i.1). These streams form the ‘fingertips’ of the tributaries draining up the upper reaches of the watersheds (Horton, 1945) These streams can be perennial (running year round) or intermittent and ephemeral (running only seasonally and during major thaw and storm events) (Trenhaile, 2004). The perennial and intermittent streams both have groundwater sources, whereas ephemeral streams only carry runoff. Regardless of the source water, all three categories of streams have important functional roles within the watershed (Horton, 1945) and are all included in the Stahler stream order (Strahler, 1952).

These low-order streams are the ideal waterway to monitor and understand agricultural influences on a single farm. These systems have very small sub-watersheds where anthropogenic activities can easily be monitored (Harmel, Qian, Reckhow, & Casebolt, 2008). Many studies use large watersheds and sample the main river channels. Conducting studies at this scale makes it very difficult to separate out the multitude of human influences impacting the water. Working with such high-order rivers may indicate the general region within the watershed that has the problem, but may not indicate the source of the problem. With low-order streams, the observed water chemistry can be linked with confidence to the anthropogenic activities within its small sub-watershed. Once a causal relationship is established, then appropriate remediation and mitigation can be implemented.

Low-order streams are also hydrologically distinct from other water courses. These channels tend to have uniquely high ratios of sediment surface area to water volume, and thus provide ample opportunity for sediment-water interactions (Peterson, et al., 2001). This is important as these interactions allow for the sorption and desorption of limiting nutrients such as

N and P, which ultimately influences downstream water chemistry (Ensign & Doyle, 2006). These small streams also comprise 85% of most watersheds and are the source of over 50% of limiting nutrients that exit a basin (Peterson, et al., 2001).

Despite the obvious need for studies on agricultural impacts on headwater streams, few have been documented. Historically, it was assumed that the abiotic features of streams would render this habitat immune to eutrophication events (Smith, et al., 1999). Common features such as high stream velocities, high shading, low temperatures and in-stream grazing were thought to prevent prolific algae growth (Smith, et al., 1999). More recent research has falsified these beliefs, demonstrating that channelized aquatic habitats are quite susceptible to nutrient enrichment (Peterson, et al., 1993). As a result of all of these factors, it is critical to study these low-order streams in order to understand the influences of nutrient and sediment enrichment on water quality.

Thesis Objectives

As the human population continues to grow, demands for food and space will also multiply. Farmers are aware that in order to be profitable, they must reduce the loss of nutrients from their farms; this is not only good for the environment, but also makes economic sense since the cost of fertilizers is high, and topsoil is a limited and a non-renewable resource. Farmers and conservationalists alike require a greater understanding of agricultural influences on the health of aquatic ecosystems. The research presented here is my contribution to the body of knowledge that aims to promote sustainable agriculture for current and future generations.

Specifically, my first chapter examines the differences in water chemistry associated with crop and livestock agricultural practices. This research questions the appropriateness of treating all agricultural land use as a homogenous category of environmental impact, ignoring differences between farming practices. We also examine the predictive nature of different abiotic factors on water chemistry in an agricultural ecosystem to describe the main determinants of water quality over four seasons of the year. My second chapter builds on the first, and compares the effectiveness of continuous- and discrete sampling programs for monitoring the impacts of cattle disturbance on water quality of a first-order stream. The final chapter examines periphyton growth in relationship to water chemistry moving between first- to a second-order systems. My results should be useful for agriculturalists, environmental managers and ecologists who are interested in controlling nonpoint source nutrient and sediment loss.

REFERNCES

Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., & Smith, V. H. (1998).Nonpoint pollution of surface waters with phosphorus and nitrogen *Ecological Applications, 8*(3), 559-568.

Caux, P. Y., Moore,D.R.J., MacDonald, D. (1997). Ambient water quality guidelines (criteria) for turbidity, suspended and benthic sediments. Technical Appendix. Prepared for BC Ministry of Environment, Land and Parks.

CCME (Canadian Council of Ministers of the Environment). (2002). *Canadian water quality guidelines for the protection of aquatic life: total particulate matter In: Canadian environmental quality guidelines*, *1999*. Winnipeg; Canadian Council of Ministers of the Environment

Correll, D. L., Jordan, T. E., & Weller, D. E. (1999). Transport of nitrogen and phosphorus from Rhode river watersheds during storm events. *Water Resources Research*, *35*(8), 2513-2521.

Cooke, S. E., & Prepas, E. E. (1998). Stream phosphorus and nitrogen export from agricultural and forested watersheds on the Boreal Plain. *Canadian Journal of Fisheries and Aquatic Sciences*, *55*(10), 2292-2299.

Dunne, T., Western, D., & Dietrich, W. E. (2011). Effects of cattle trampling on vegetation, infiltration, and erosion in a tropical rangeland. *Journal of Arid Environments, 75*(1), 58-69.

Ensign, S. H., & Doyle, M. W. (2006). Nutrient spiraling in streams and river networks. *Journal of Geophysical Research.*, *111*(G4),1-13.

Fraters, D., Boumans, L. J. M., van Leeuwen, T. C., & de Hoop, W. D. (2001). Monitoring nitrogen leaching for the evaluation of the Dutch minerals policy for agriculture in clay regions. *The Scientific World Journal, 1*(1), 758-766.

Freifelder, R. R., Smith, S. V., & Bennett, R. H. (1998). Cows, humans and hydrology in the nitrogen dynamics of a grazed rural watershed. *Journal of Environmental Management*, *52*(2), 99-111.

Goolsby, D.A., Battaglin, W.A., Aulenbach, B.T., Hooper, R.P. (2000). Nitrogen flux and sources in the Mississippi River Basin. *The Science of the Total Environment*, 248(2-3),75-86.

Harmel, D., Potter, S., Casebolt, P., Reckhow, K., Green, C., & Haney, R. (2006). Compilation of measured nutrient load data for agricultural land uses in the United States. *Journal of the American Water Resources Association, 42*(5), 1163-1178.

Harmel, D., Qian, S., Reckhow, K., & Casebolt, P. (2008). The MANAGE Database: Nutrient Load and Site Characteristic Updates and Runoff Concentration Data. *Journal of Environmental Quality, 37*(6), 2403-2406.

Hecky, R. E., & Kilham, P. (1988). Nutrient limitation of phytoplankton in freshwater and marine environments: a review of recent evidence on the effects of enrichment. *Limnology and Oceanography, 33*(4), 796-822.

Horton, R.E. (1945). Erosional development of streams and their drainage basins; hydrophysical apporach to quantitative morphology. *Geological Society of America Bulletin*, *56*(3), 275-370.

Mazoyer, M., Roudart, L., & Membrez, J. H. (2006). *A History of World Agriculture*. London: Earthscan.

McConkey, B. G., Nicholaichuk, W., Steppuhn, H., & Reimer, C. D. (1997). Sediment yield and seasonal soil erodibility for semiarid cropland in western Canada. *Canadian Journal of Soil Science, 77*(1), 33-40.

McDiffett, W., Beidler, A., Dominick, T., & McCrea, K. (1989). Nutrient concentration-stream discharge relationships during storm events in a first-order stream. *Hydrobiologia, 179*(2), 97-102.

Nash, D. M., & Halliwell, D. J. (2000). Tracing phosphorous transferred from grazing land to water. *Water Research, 34*(7), 1975-1985.

Petersen, S. O., Roslev, P., & Bol, R. (2004). Dynamics of a pasture soil microbial community after deposition of cattle urine amended with [13C]urea. *Applied and Environmental Microbiology, 70*(11), 6363-6369.

Peterson, B. J., Deegan, L., Helfrich, J., Hobbie, J. E., Hullar, M., Moller, B., et al. (1993). Biological responses of a tundra river to fertilization. *Ecology, 74*(3), 653-672.

Peterson, B. J., Wollheim, W. M., Mulholland, P. J., Webster, J. R., Meyer, J. L., Tank, J. L., et al. (2001). Control of nitrogen export from watersheds by headwater streams. *Science, 292*(5514), 86-90.

Reaman, G. E. (1970). *A history of agriculture in Ontario* (Vol. 2). Aylesbury: Hazell Watson & Viney Ltd.

Sharpley, A. N., Chapra, S. C., Wedepohl, R., Sims, J. T., Daniel, T. C., & Reddy, K. R. (1994). Managing Agricultural Phosphorus for Protection of Surface Waters: Issues and Options. *Journal of Environmental Quality, 23*(3), 437-451.

Sharpley, A.N., T. Daniel, T. Sims, J. Lemunyon, R. Stevens, and R. Parry. (2003). *Agricultural Phosphorus and Eutrophication, 2nd ed*. U.S. Departmentof Agriculture, Agricultural Research Service, ARS–149, 44 pp

Sharpley, A.N., Gburek, W. J., Folmar, G., & Pionke, H. B. (1999). Sources of phosphorus exported from an agricultural watershed in Pennsylvania. *Agricultural Water Management, 41*(2), 77-89.

Strahler, A.N. (1952). Hypsometric (area-altitudue) analysis of erodional topography *Geological Society of America Bulletin, 63*(11), 1117-1142.

Strahler, A. N. (1957). Quantitative analysis of watershed geomorphology. *Transactions of the American Geophysical Union, 33*(6), 913-920.

Smith, V. H., Tilman, G. D., & Nekola, J. C. (1999). Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environmental Pollution, 100*(1–3), 179-196.

Tilman, D. (1998). The greening of the green revolution *Nature, 396*(6708), 211-212.

Tilman, D., Cassman, K. G., Matson, P. A., Naylor, R., & Polasky, S. (2002). Agricultural sustainability and intensive production practices. *Nature, 418*(6898), 671-677.

Tilman, D., Fargione, J., Wolff, B., D'Antonio, C., Dobson, A., Howarth, R., et al. (2001). Forecasting agriculturally driven global environmental change. *Science, 292*(5515), 281-284.

Trenhaile, A. S. (2004). *Geomorphology: a Canadian Perspective* (2 ed.). Don Mills: Oxford.

Waters, T., F. (1995). *Sediments in streams: sources, biological effects and control*. Bethesda: American Fisheries Society.

Wetzel, R., G.,. (1983). *Liminology* (2 ed.). Orlando: Holt, Rinehart & Winston, Inc.

Table i.1: Summary of nutrient levels for different aquatic environments and different trophic statuses. Modified from Smith, et al. (1999).

	Trophic state	TN ($mg\ m^{-3}$)	TP ($mg\ m^{-3}$)	chl *a* ($mg\ m^{-3}$)	SD (m)
Lakes	Oligotrophic	< 350	< 10	< 3.5	> 4
	Mesotrophic	350–650	10–30	3.5–9	2–4
	Eutrophic	650–1200	30–100	9–25	1–2
	Hypertrophic	> 1200	> 100	> 25	< 1
				Suspended chl *a* ($mg\ m^{-3}$)	Benthic chl *a* ($mg\ m^{-2}$)
Streams	Oligotrophic	< 700	< 25	< 10	< 20
	Mesotrophic	700–1500	25–75	10–30	20–70
	Eutrophic	> 1500	> 75	> 30	> 70
				chl *a* ($mg\ m^{-3}$)	SD (m)
Marine	Oligotrophic	< 260	< 10	< 1	> 6
	Mesotrophic	260–350	10–30	1–3	3–6
	Eutrophic	350–400	30–40	3–5	1.5–3
	Hypertrophic	> 400	> 40	> 5	< 1.5

[a] The terms oligotrophic, mesotrophic, and eutrophic correspond to systems receiving low, intermediate, and high inputs of nutrients. Hypertrophic is the term used for systems receiving greatly excessive nutrient inputs. TN, total nitrogen; TP, total phosphorus; TIN, total inorganic nitrogen; chl *a*, chlorophyll *a*; SD, Secchi disk transparency.

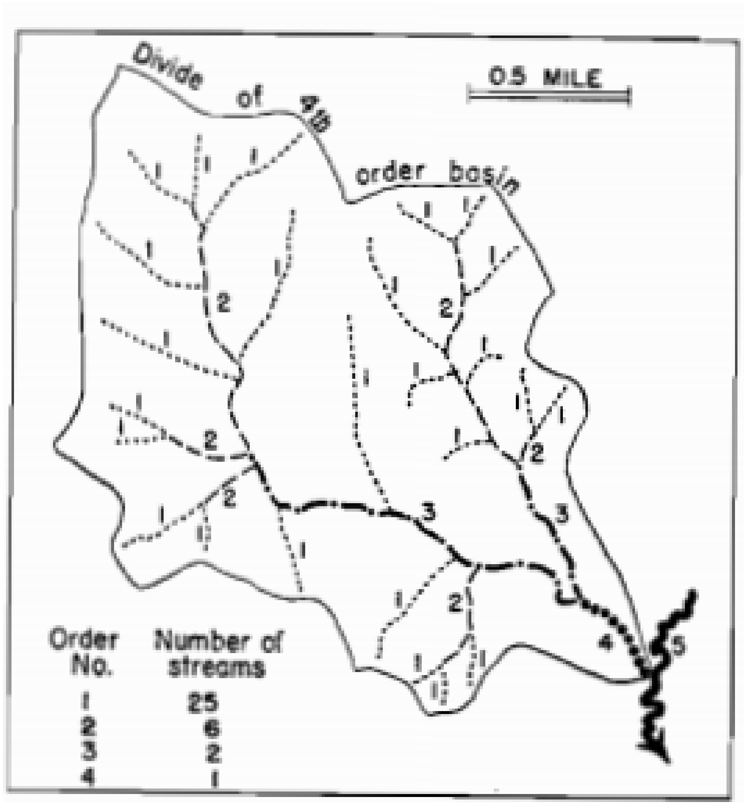


Figure i.1: Demonstration of Stahler stream order. Modified from Stahler (1957)

Water chemistry of first-order streams in relation to agricultural practice, landform features, storm events and season in an agriculturally dominant watershed

Catherine Dieleman

(Corresponding author: catherine.dieleman@gmail.com)

Patricia Chow-Fraser

(chowfras@mcmaster.ca)

McMaster University
Department of Biology
1280 Main Street West
Hamilton, ON L8S 4K1

Abstract

Elevated nutrient and sediment levels in agricultural runoff can degrade water quality and result in loss of stream habitat. Past studies have been conducted at the scale of watersheds and focused on higher-order streams; few have been conducted at the scale of individual family farms, where negative impacts of agricultural practices on first-order streams can be studied and for which best-management practices can be developed. In this study, we identify factors that influence the water chemistry of eight first-order streams in south central Ontario, Canada. Biweekly samples during the growing season (May to September) and monthly samples during the dormant period (November to April) were collected to compare temporal variation in total phosphorus (TP), total nitrogen (TN), total nitrate nitrogen (TNN), total ammonia nitrogen (TAN), total suspended solids (TSS), turbidity (TURB) and pH across sites. TP, TSS, TNN and pH all varied significantly across the four seasons of the 'agriculturally relevant calendar' (ARC; ANOVA; d.f.=3; $P<0.05$). When data were pooled for the entire year, TP, TAN, TURB, and TSS were significantly higher at the four livestock sites compared with the four crop-based sites. Elevated levels of TAN, TN, TP, TURB and TSS were associated with rainfall events throughout the year, while all water-chemistry parameters were significantly related to the combined effects of rainfall amount and agricultural practice (two-way ANOVA; d.f=3;$P<0.05$). Regardless of agricultural practice, pH, TAN, TSS, TURB and TP were positively related to the slope of the terrain while pH alone was positively related to watershed size. Stepwise regressions indicated that for first-order streams, rainfall, ARC season and slope had a greater effect on variation in water quality than did agricultural practice. Results also indicated that the dominant drivers of water chemistry in first-order streams change significantly according to ARC season.

Introduction

First-order streams account for up to 85% of tributaries and are a major source of nutrients and sediment into aquatic environments (Peterson, et al., 2001). The high ratio of surface area to volume for these small streams make them arguably the most influential aspect of an aquatic system in terms of water chemistry regulation; >50% of biologically limiting nutrients, such as nitrogen and phosphorus (Peterson, et al., 2001), and 75% of sediment (Petts, 1984) released from watersheds enter systems via low-order streams. Thus, the anthropogenic treatment of headwater streams governs the quality of downstream ecosystems and drinking water sources.

Farming has been a widespread component of the landscape for hundreds of years; however, with the advent of the Green Revolution, agriculture has intensified leading to more severe impacts on water quality and ecosystem health (Bennett, Carpenter, & Caraco, 2001; Matson, Parton, Power, & Swift, 1997). The problem has become so grave that countries around the globe have listed agriculture as the number one threat to water quality and have started many government-led initiatives to reduce or eliminate these effects (Fraters, et al., 2001; Sharpley, et al., 1999). The runoff from agriculture is a non-point source pollutant rich in nitrogen (N), phosphorus (P) and sediments, which in high concentrations have been shown to lead to eutrophication (Sharpley, Smith, & Naney, 1987). These contaminants originate from both crop-based and livestock-based agricultural practices through excessive application and storage of fertilizers and livestock feces on fields, pasture land and farm yards (Beaulac & Reckhow, 1982). It is estimated that approximately 5 to 20% of N is lost when applied as fertilizer and manure respectively; however, when infiltration as well as leaching to ground and surface waters is also considered, then up to 80% of applied N can be washed off crop land

(Carpenter, et al., 1998).

The use of heavy machinery and pasturing of cattle in agriculture also changes soil structure, destroying macropores and increasing erosion rates through detachment of soil particles (Dunne, et al., 2011; Fullen, 1985; Lal, 2001). Globally, conventional tilling methods elevate erosion rates from 10 to 100 times that of natural background levels, routinely surpassing average soil production rates of agricultural lands (Montgomery, 2007). The modern technique of no-tilling has been shown to reduce soil loss by 488 times that of conventional practices; despite this, only 16% of North American and 5% of global farmers employ this practice (Lal, Griffin, Apt, Lave, & Morgan, 2004). Overall, tilling can has negative impacts for both farmers and the ecosystem, decreasing soil productivity, increasing crop costs, while reducing stream productivity and limiting biodiversity (CCME, 2002).

Precipitation events as well as landform features (slope of the terrain, watershed area, stream length, elevation, soil class) in the watershed have been shown to exacerbate the effects of farming, facilitating the movement of both nutrients and sediment into aquatic systems (Beaulac & Reckhow, 1982; McDiffett, Beidler, Dominick, & McCrea, 1989; Salvia-Castellvi, Iffly, Vander Borght, & Hoffman, 2005). Over 90% of the phosphorus exported from a watershed comes from less than 10% of the area during a few intense storms during the year (Carpenter, et al., 1998). Studies have shown that during intense storm events, regions prone to leaching and erosion tend to have higher average slope and impermeable soils (Lal, 2001; Sharpley, McDowell, Weld, & Kleinman, 2001). Given that the Intergovernmental Panel on Climate Change has predicted an increase in the frequency and intensity of storm events (IPCC, 2007) and that agricultural impacts are known to be amplified by precipitation, it is important to study how these factors (landform features, different agricultural practices) interact and affect stream quality so that effective best management practices and nutrient management legislation can be developed.

A proper study of agricultural influences on water chemistry should be done over four seasons (Harmel, et al., 2008). Farming activities vary greatly through the year and from year to year depending on the agricultural practice and specific weather conditions. For example, even though the onset of the four seasons in the conventional calendar are fixed and defined by the position of the earth relative to the sun, for farmers, spring is marked by beginning of planting, which varies annually depending on prevailing weather patterns. Seasons of the 'agriculturally relevant calendar' (ARC) are determined by actions of farmers themselves, and may be more appropriate than the conventional calendar for interpreting impacts of specific practice types through the year.

Beaulac and Reckhow (1982) were one of the first to study the influences of particular agricultural practices on N and P loading, using a meta-analysis of over 40 published articles. They found higher rates of nutrient export from crop land compared with pasture land, while manure storage sites and feed lots had the greatest impact of all three practices. In a subsequent paper, Harmel, et al. (2006) pointed out that the original study did not account for site-to-site differences in landform features, which could have confounded their results. To date, no study has been published that compares the environmental impacts of different agricultural practices on the quality of low-order streams, while accounting for variation in physical land form features.

This is the first paper that compares the impact of both livestock and crop-based farming on the water quality of first-order streams. It is also one of only a few studies that simultaneously considers the major determinants of water-quality variation, including precipitation events and various landform features in the watershed, conducted over four consecutive seasons of the agriculturally relevant calendar. This is done so that we can determine the differential impact of the two agricultural practices with seasonal variation on water quality in headwater streams. We predict that water quality in streams that drain livestock practices will be more degraded than those that drain crop-based practices. We also predict that precipitation events will increase impacts across both types of agriculture, and that the relative importance of various independent variables will vary across the seasons for both agricultural practices. Our results will help farmers and environmental managers understand the type, amount and timing of pollutants associated with different farm practices, and advance the development of best management practices to protect the aquatic health of streams at the level of individual farms.

Methods

Watershed Description

The Beaver River drainage basin (618 km^2) is a quaternary watershed of Lake Huron that drains into Nottawasaga Bay and ultimately into Georgian Bay (Figure 1.1). The basin contains rural portions of the Grey Highland and the Towns of the Blue Mountains municipalities. Over 10% of the resident adult population is employed as agriculturists, compared to 3% of Ontario's population overall (Statistics Canada, 2006a, Statistics Canada, 2006b) and explains why majority of the watershed has been developed for agriculture. Farm operations in the Beaver Valley are non-industrial and low intensity, with a mixture of row and cereal crop as well as livestock-based practices. The karst topography of the region, in conjunction with its vast agricultural production, provides a plethora of agriculturally influenced first-order streams as potential study sties. By restricting the study region to a single watershed, we ensure that the streams examined have uniform hydrology and similar background water chemistry and overall weather conditions.

Study Site Selection

We used ArcInfo 9.3 (ESRI Inc., Redlands, California) to initially identify the first-order streams in geographic imaging system (GIS) and ensured they have easy road access for sampling purposes and drain only one type of agricultural practice. For each of the original 52 candidate streams identified, we obtained air photos to further delineate the potential sampling sites. Sites with more than minimal riparian buffering were omitted as this would confound the impact of agriculture on water quality (Schultz, et al., 1995). In total, 4 crop-based and 4 livestock-based sites met all of our criteria for selection (Table 1.1). We ascertained that the croplands had all been recently cultivated for row and cereal crops such as corn, soybean or grains and that all livestock-based sites had a stream in the vicinity of a barn, a manure pile, along with pasture land. These conditions ensured that the streams were constantly exposed to agricultural impacts and are representative of most small farm operations. We could not find any appropriate reference sites for this study because the entire Beaver River watershed had been clear cut and continuously cultivated since the first settlers entered the region in the 19th century (Euphrasia Historical Society, 2000).

Sampling Procedures

Grab samples were collected for determination of total phosphorus (TP), total nitrogen (TN), total nitrate-nitrogen (TNN), total ammonium-nitrogen (TAN) and total suspended solids (TSS). We used a LaMotte™ 2020e Turbidimeter to measure turbidity (TURB) in fresh samples collected in the field. Temperature (TEMP) and pH of the samples were also measured with an Orion Smart Check™ 020000A pH/temperature meter. Samples for TP, TN, TNN and TAN were collected in acid-washed 110 mL and 200mL Snap'N'Seal™ containers (Crosbie & Chow-Fraser, 1999). TSS samples were collected in acid-washed Nalgene™ bottles (1000-mL capacity) rinsed with the source water as indicated by Lind (1974). TP and TN samples were then put on ice in a cooler until they could be stored in a freezer prior to analysis (Crosbie & Chow-Fraser, 1999). TAN, TNN and TSS samples were placed on ice before they were processed shortly after collection. Snow depth and rainfall data were obtained from the Environment Canada weather station in Thornbury, Ontario.

Over the 15 months of this study, water samples were collected every two weeks in the growing season (28 May to 14 October in 2010 and 4, May to 29 July in 2011) as done by Domagalski, et al. (2008); samples were collected only monthly during the dormant season (10 Nov 2010 to 14 April 2011) as recommended by Gardner & McGlynn, (2009). TN samples were collected monthly throughout the study. Measurements of pH, TURB and TAN began on June 22nd 2010. Active perusal of storm events occurred on June 8th and July 29th in the 2011 growing season to ensure we obtained conditions other than base-flow for that year. All other storm events were sampled opportunistically. We could not collect samples when water levels in streams fell below 5cm and when snowfall accumulation exceeded 2m.

Sample Processing

The TP samples were digested for 45 minutes with potassium persulfate in an autoclave at 15 psi and 120 °C. The presence of phosphorus was determined according to the molybdenum blue method (Murphy & Riley, 1962) with a Genesys 10 UV Spectrophotometer. Water samples collected for TSS were filtered in the field through preweighed GC filters

(0.45μm pore size) and stored in the freezer until processing; filters were dried in an oven at 100°C for one hour, placed in a dessicator for another hour and then weighed. The TN, TNN and TAN samples were analyzed with HACH™ techniques and a HACH™ DR 890 colorimeter.

GIS Analysis of Watershed Features

All physical land form features were determined in GIS with ARCMap 10 (ESRI inc., Redlands, California, 2010; Table 1.1). Watersheds of the first-order streams were used to clip out relevant features for each site and used to determine elevation and slope of the surrounding terrain. Soil classes which represented ≥10% of the watershed area were included as watershed soil type. Soil class indicated permeability as defined by Chisholm, et al. (1984) and were obtained from the Ontario Ministry of Agriculture, Food and Rural Affairs. We calculated stream length occurring above the sampling location to account for the degree of exposure of each stream to agricultural impacts.

Statistical Analyses

Statistical tests were performed in SAS JMP version 7.0.1 (SAS Institute Inc., Cary, North Carolina). The water chemistry parameters were first either $\log_e$ or Box-Cox transformed to minimize hetroscedasticity (TP and TURB reported λ values of 0 and -0.2 respectively; Table 1.2). Slope of the terrain and watershed area were $\log_e$ transformed to normalize the data. When analyzing the data, we first screened all water-quality data and removed outliers. Pearson correlation coefficients and Spearman's p values were then calculated for all independent variables to test for and reduce significant multicollinearity (Table 1.3). Regression analysis was completed to compare stream length and watershed by for each agricultural practice type. Forward step-wise regressions were conducted for each water-chemistry variable for year-round data as well as for each ARC season. Watershed land forms, precipitation amount, and type of agricultural land use were entered into each model, as was ARC for the year-round models. We also compared the means of water-quality parameters across ARC seasons and between land-use practices (ANOVA and t-tests, respectively). We used a two-way ANCOVA to determine significant and interactive effects of agricultural practice (crop vs livestock) and levels of precipitation on water-quality variables.

Results

We found differences between agricultural practices with respect to slope and elevation of the surrounding terrain, watershed size, stream sample length and soil class (Table 1.1). Slopes corresponding to crop sites (3.03 to 3.79) tended to be lower than those for livestock sites (3.65 to 6.37), which are located at the base of the Niagara Escarpment ridge, a dominant feature of the Beaver Valley watershed. Although site 3 had the highest relief among crop-based farms, it was site 410 which had the majority of its cultivated fields on sloped land. Due to their association with the escarpment and valley walls, livestock sites had higher mean elevations compared with crop sites (mean of 375 vs 313 m above sea level, respectively). Watersheds associated with livestock farms were often twice as large as those associated with crop sites (mean of 101.3 vs 48.8 ha, respectively), presumably because of differences in slope and elevation between the two land uses. Even though in general, stream lengths increased with watershed size (see Figure 1.2), those corresponding to crop sites in this study were on average 190 m longer than those draining livestock sites (1150 vs 960 m). It is important to note that unlike livestock sites, watershed size of crop sites was not a significant predictor of stream length.

The two agricultural practices examined in this study generated different amounts of pollutants at different times of the years, reflecting specific activities associated with each practice. The source of nutrients and sediments from livestock operations, for example, are primarily associated with cattle grazing and the storage of manure; hence, the level of ammonia, phosphorus, and sediment tends to be very high for these sites (see Table 1.4). On the other hand, activities on croplands include tilling, fertilization, planting and harvesting; consequently, concentration of TN and TNN from cropland consistently surpass that from livestock farms, especially during the spring when planting takes place (Table 1.4). These trends were supported by the statistically significant differences in water-quality parameters between agricultural practice for both the annual data and the data grouped by ARC season. In general, we found significantly higher levels of TAN, TP, TSS and TURB in streams that drained livestock sites (Table 1.4; $P<0.05$) whereas, we found significantly higher levels of TNN and numerically higher levels of TN in streams draining crop sites than those draining livestock operations. By examining the data for each ARC season, we were able to resolve TNN spikes in streams that drain the crop sites during spring and winter. We also found that pH was significantly lower in crop-based compared with livestock-based sites during all four seasons (Table 1.4).

Next, we examined the separate and interactive effects of agricultural practice and rainfall amount on the water quality of these first-order streams (see Table. 1.5). Except for TNN and TN, levels of nutrients, suspended particles and pH were significantly higher in livestock than in crop sites ($P<0.05$); by contrast, TNN and TN concentrations were consistently elevated at crop sites compared with livestock streams. Regardless of land use, mean TP, TAN, TN, TSS and

TURB concentrations all increased significantly with increased rainfall, whereas TNN levels decreased. The TN response to rain was strongest at livestock sites during large rainfall events (>35mm), causing TN levels to surpass those at crop sites during these storms. Since we found no significant interaction between agricultural practice and rainfall, effects of precipitation on pollutant loading in first-order streams is the same for both livestock- and crop-based sites (Table 1.5).

Traditionally, the shift in season is defined by the conventional calendar; however, when our forward step-wise regression models were run, we found that accounting for differences in season according to the conventional calendar did not significantly ($P<0.05$) explain variation in water chemistry for any of the parameters except for pH (Table 1.6). On the other hand, when we used the season defined by the agriculturally relevant calendar, we were able to explain variations in TAN, TNN, TP and pH by as much as 23% (see results for TNN in Table 1.6). In these stepwise regression models, rainfall and agricultural practice (explaining up to 22% and 29% of the total variance, respectively) were consistently identified as two of the four major factors that controlled the water quality of first order streams. Slope was an important predictor of all forms of nitrogen in these regression models (up to 10% of the variance for TNN). Snow depth and watershed area individually explained up to 6% of the variance for any parameter. Only in the case of snow depth did we actually see the conventional calendar performing better than the ARC for explaining variance in TP (14% vs 5% variation, respectively).

All water-quality variables exhibited a strong seasonal pattern defined by ARC even when we ignored differences in land use practices and variation in rainfall (see Figure 1.3). Both pH and TNN concentrations (Figure 1.3a and d) were significantly higher in the spring and winter than in either summer or fall, whereas TP (Figure 1.3b) was highest in the spring and continued to decline through the remaining seasons. TSS was significantly lower in winter than in the other three seasons (Figure 1.3c).

Next, we examined the relationship between water quality and rainfall while ignoring differences in land use practices and ARC season. Despite the large unexplained variance (r^2-values ranged from 0.03 to 0.22), all water-quality parameters except pH were significantly related to rainfall amount (Figure 1.4 a-f); in most cases, the pollutant increased with rainfall, whereas TNN decreased (Figure 1.4b). Snow depth was another important predictor of water quality in streams; both TP (Figure 1.5a) and TURB (Figure 1.5c) decreased with snow depth, whereas pH increased (Figure 1.5b). While TAN and TURB levels increased as a function of slope (Figure 1.5e and f, respectively) TNN decreased (Figure 1.5d). Unlike all the other independent variables, watershed area only explained variation in pH, and the positive relationship for the year-round data (Figure 1.6a) appeared to be driven primarily by the spring data (Figure 1.6b).

Given the strong influence of season in the ARC, we conducted further stepwise regression analyses (Table 1.7). The data collected in spring were heavily influenced by rainfall amount, which emerged as the sole significant predictor for most of the parameters. Agricultural practice type was also an important predictor during this season particularly for pH and TNN (up to 60% of variance for pH). By comparison, trends in the summer are more difficult to generalize. Rainfall amount, agricultural practice, and slope were significant predictors in most regression models. The best relationship in terms of amount of variance explained was agricultural practice and pH but the r^2-value was relatively low (< 0.35). Rainfall amount and agricultural practice were again important predictors for parameters measured during the fall. Soil class explained 75% of the variance in TN, but this relationship was only observed for the fall data.

For the data collected in winter, land use and slope described majority of the variation in water chemistry, with slope alone describing 50% of the variance in TNN. Data collected during this one season were significantly influenced by watershed area and snow depth, which together explained almost 40% of the variation in TP.

Discussion

Our findings are generally consistent with those in the seminal study conducted by Beaulac and Reckhow (1982), who originally noted that on an annual basis P and N levels released by crop-based agriculture were greater than that exported from pasture-based agriculture, but less than that from feedlot/manure storage sites. Since the livestock operations in this study experience impacts from both pasture and manure storage, we were not surprised to find that first-order streams draining our livestock sites had significantly higher levels of pollutants than those draining cropland. What has been revealed by this study, and which we had not initially expected to find, was a divergence in the response of P and N associated with the two agricultural practices. We believe that these differences are due to the nature of farm activities associated with each season of the agriculturally relevant calendar for the two land uses (Table 1.4).

At the livestock sites, the high TP, TURB and TSS are a direct result of phosphorus and sediments being released from manure piles. Any precipitation that comes into contact with the excrement will readily transport the pollutants to streams that drain the farms. The amount of this pollutant load will depend on the intensity of the storm event and the proximity of the manure pile to the stream. The cattle also continuously disturbs the soil and make it prone to translocation during a storm event (Dunne, et al., 2011). By comparison, soil erosion also occurs on cultivated croplands during storms, especially when the root systems are not well developed or viable, but even at those vulnerable times, the levels of TSS and TURB tend to be lower than those at livestock sites (see Table 1.4). The similar trends in TP, TSS and TURB were expected as phosphate is easily adsorbed onto soil particles and become particulate phosphorus (McDowell 2003). Therefore, all variables that reflect the amount of suspended particles in the water will share similar trends when regressed against independent variables, particularly land use, slope and precipitation

There are several sources of ammonia in an agricultural setting. In livestock operations, the main source of ammonia is urea, which is excreted by cattle; and then hydrolyzed to ammonium, which is rapidly converted to ammonia (Kirchmann & Witter, 1992; O'Toole, Morgan, & McAleese, 1982). Ammonia can also be applied as an inorganic fertilizer. Therefore, as expected, we found elevated TAN levels in the runoff from both types of agricultural practices with higher TAN concentrations at livestock sites (Table 1.4) These finding are consistent with Petersen, et al. (2004) which concluded that the urine of livestock is the dominant supplier of ammonia in an agricultural setting.

Compared to ammonia, which is highly volatile, nitrate is a stable form of nitrogen that is not readily transformed into other chemical species or adsorbed onto soil particles (Peterson, et al., 2001) but it is highly soluble and easily leached from soils (Cooke and Prepas 1998). As a result nitrate is more likely be to found in streams draining fertilized lands than ammonia, although both forms of N can be applied as fertilizer (Cooke & Prepas, 1998). Thus the elevated levels of TN and TNN at our crop sites (Table 1.4) are due the use of inorganic fertilizers (Fraters et al, 2001), while the level of nitrogen is directly linked to the type of crops cultivated. In our case, the corn and cereal grains that were grown are known to require heavy N fertilization, while soybeans naturally fix nitrogen, a process which can also lead to N leaching (Peterson, et al., 2001). As a result, the total amount of nitrogen at crop sites are higher than those of livestock during baseflow conditions; however, during large storm events (>35mm) TN levels at livestock sites can exceed those at the crop sites. The generally elevated concentrations of nitrate at these crop sites may also be the reason that the pH is significantly lower at crop sites since chemical species of nitrogen are known acidification agents (Bolan, Hedley, & White, 1991).

Most of the water-quality (TAN, TN, TP, TURB and TSS) parameters responded predictably to large storm events by increasing their concentrations with rainfall (Arreghini, et al., 2005; Correll, Jordan, & Weller, 1999; McDiffett, et al., 1989; Sharpley, et al., 2008). TNN, however, decreased with higher volumes of rain, an inverse relationship which has also been reported by Borah, et al. (2003) and Fraters, et al. (2001). Since nitrate is an anion it does not readily bind to soil particles, and thus is easily transported to the stream regardless of the storm intensity. Larger volumes of rain merely dilutes the nitrate, leading to lower concentrations (McDiffett, et al., 1989). By comparison, pH is not significantly affected by rainfall amounts. In the Beaver Valley watershed, the dominant bedrock is limestone (Euphrasia Historical Society, 2000) which gives the water a high buffering capacity against changes in pH.

The seasonal differences in nutrients and suspended solids in first-order streams are related to activities specific to the two agricultural practices (Table 1.4). It is clear, however, that the four seasons should be defined by the agriculturally relevant calendar rather than the conventional calendar. It is also clear that data must be collected over four full seasons in order to fully represent the maxima and minima for these water-quality variables. For example, without sampling through the winter months, annual TP levels would have been overestimated for the livestock sites; this is presumably because cattle are kept indoors during the winter, and the soil is generally snow covered. By contrast, the TNN levels would have been underestimated, as nitrate concentrations was highest during the winter months due to decreased biotic uptake and increased decomposition (Gardner & McGlynn, 2009).

Regardless of how the seasons are defined, rainfall amount is the dominant driver of most water-chemistry parameters. For year round data, snow depth, like watershed area, was rarely a significant predictor of variation in water quality. Despite this, snow depth is key to understanding nutrient and sediment movement during thaws, and may become more important under climate-change scenarios. The comparatively minor influence of watershed size on water chemistry has also observed by Saliva-Castellvi (2005) for small watersheds.

In this study, slope emerged as an important factor for predicting the movement of nitrogen and sediment into streams. We found significantly higher TNN and TN concentrations in streams draining the land with low relief, and significantly higher TAN and TSS concentrations in streams draining more sloping land (Table 1.1). These trends reflect the deliberate choice of farmers to cultivate crops on flat land, and to reserve more sloping land for livestock grazing (Table 1.1). Even though the relationship between nutrients and slope is confounded by the choice of agricultural practice, similar results have been reported in the literature for sites in Europe and N. America. Heathwaite & Johnes (1996) and Fraters et al (2001) found that waters draining crop sites routinely have high NO_3^- exports, while runoff from highly grazed lands had >90% of its nitrogen as NH_4^+.

In hydrologically unaltered catchments, stream length varies directly with watershed size, and can be used as a surrogate to describe the amount of exposure to terrestrial land use

(Fitzpatrick, Scudder, Lenz, & Sullivan, 2001). This relationship is generally applicable to our livestock sites but not to the crop sites (see Figure 1.2). The lack of a significant relationship between catchment size and stream length is likely because streams in crop sites are routinely altered (channelized or lengthened) to enhance soil drainage, and thus, despite their smaller watershed size are significantly longer than those in livestock sites.

When we ran the stepwise regression models on data sorted by ARC season, we were able to confirm the importance of rainfall amount and agricultural practice as independent variables (Table 1.6). In spring, we observed elevated levels of nutrients and sediment that were presumably the direct consequence of inorganic fertilizers being added at the crop sites, and livestock grazing during storm events. While pH at crop sites decreased because of the addition of fertilizers, it increased at livestock sites in the spring because of a saturated watershed (figure 1.6) which enabled the loading of carbonates and bicarbonates from the escarpment during storms. Nutrient dynamics in streams are too complex in the summer for us to determine the key factors driving water quality at that time, and we suggest that all of the independent variables are important during this season. In addition, there are other confounding factors including the growth of periphytic algae and vascular plants that interfere with nutrient cycling in the streams during the summer months (Gardner & McGlynn, 2009). The fall season is generally punctuated by large intense rainfall events occurring over croplands in the midst of the harvest, while livestock are gradually removed from the now wet and unproductive pasture lands. These differences in land use and intensity of storms are the main drivers of water quality for this season. In the winter, when the cropland is frozen and livestock are confined to the barnyard, the amount of nutrients and sediment in streams are basically a function of the slope and agricultural practice. Slope is the main predictor of TNN and TN, nutrients associated with crop practices.

During the winter months, residual vegetation on cropland slowly degrades and release nutrients back into the stream (Alexander, Boyer, Smith, Schwarz, & Moore, 2007; Thomsen & Christensen, 1998).

Given the large seasonal variation in water quality, it is clear that data should not be compared across the seasons. The pre-eminence of agricultural practice, rainfall amount and slope as predictors of water quality in the stepwise regression models (Table 1.7) suggests they are important factors and should be considered when developing best management plans, nutrient management legislation, and remediation efforts. For the year-round data, agricultural practice corresponded with low r^2 values and entered many regression models in the fourth or fifth position (except for pH); in these cases, ARC season, rainfall and slope often over-rode differences caused by practice type alone. Despite this, agricultural practice was a significant predictor of many parameters when examined by ARC season. Our findings also indicate that precipitation does indeed amplify the negative impacts of both livestock-based and crop-based agricultural land uses on water quality with L sites having a greater effect on water chemistry than C sites. Thus, if the predictions of increased storm frequency and intensity in the future for the Great Lakes region are realized, agricultural land use may pose an even greater threat to the integrity of first-order streams and the downstream aquatic ecosystems.

Conclusion

The importance of understanding agricultural influences on the health of aquatic systems has never been so paramount. There is an ever increasing global demand for food and clean water as the human population continues to grow. While the advent of the Green Revolution has enabled farmers to grow enough food to feed the planet, the associated intensification of agricultural practices poses a major threat to clean water supplies and aquatic ecosystem health. Now agriculturalists are faced with the added challenge of a rapidly changing climate that can significantly alter how their land use practices influence the environment.

Even though the increased frequency and intensity of storm events will have huge impacts on first-order streams that drain both types of agricultural practices, degradation from livestock-based agriculture is expected to be significantly worse. Appropriate legislation and best management practices should be developed that properly account for these differences in land uses. It is no longer acceptable to treat agricultural land as homogeneous non-point source of aquatic degradation. We have also shown that season (as defined by ARC), precipitation amounts and slope can override effects of land use and lead to more accurate predictions of water quality variation of first-order streams. Further refinement of the type of agricultural practice (e.g. type of crops grown, till vs. no-till) should provide further insight into the relationship between agricultural activities and the resultant water chemistry in runoff. It is also beneficial to study how in-stream biota influence nutrient cycling during the growing season. Understanding the influence of physical features, land use and climate on nutrient and sediment movement in an agricultural setting will advance the development of suitable strategies for watershed management and conservation.

Acknowledgements

We are indebted to Stewart Sweeney, Ontario Ministry of Agriculture, Food and Rural Affairs, for supplying us with GIS and air photo data as well as delineating the watersheds for our eight study sites. He also provided encouragement and invaluable advice in the early stages of the project. Funding for this project has been provided by grants to PC-F from Georgian Bay Forever and Sierra Club Canada, and an OGS Scholarship to CD.

References

Alexander, R. B., Boyer, E. W., Smith, R. A., Schwarz, G. E., & Moore, R. B. (2007). The role of headwater streams in downstream water quality. *Journal of American Water Resources Association, 43*(1), 41-49.

Arreghini, S., Cabo, L. d., Seoane, R., Tomazin, R., Serafíni, R., & Iorio, A. F. d. (2005). Influence of rainfall on the discharge, nutrient concentrations and loads of a stream of the "Pampa Ondulada" (Buenos Aires, Argentina). *Limnetica*, *24*(3-4), 225-236.

Beaulac, M. N., & Reckhow, K. H. (1982). An examination of land use- nutrient export relationships. *Journal of the American Water Resources Association, 18*(6), 1013-1024.

Bennett, E. M., Carpenter, S. R., & Caraco, N. F. (2001). Human Impact on Erodable Phosphorus and Eutrophication: A Global Perspective. *BioScience*, *51*(3), 227-234.

Bolan, N., Hedley, M., & White, R. (1991). Processes of soil acidification during nitrogen cycling with emphasis on legume based pastures. *Plant and Soil, 134*(1), 53-63.

Borah, D. K., Bera, M., & Shaw, S. (2003). Water, sediment, nutrient, and pesticide measurements in an agricultural watershed in Illinois during storm events. *Transactions of the American Society of Agricultural Engineers, 46*(3), 18.

Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., & Smith, V. H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen *Ecological Applications, 8*(3), 559-568.

CCME (Canadian Council of Ministers of the Environment). (2002). *Canadian water quality guidelines for the protection of aquatic life: total particulate matter In: Canadian environmental quality guidelines, 1999*. Winnipeg; Canadian Council of Ministers of the Environment.

Chisholm, P.S. (1981). Hydrologic classification Ontario soils. Proceedings of the 13th Drainage Engineers Conference. Engineering Technical Publication 126-58, School of Engineering, University of Guelph, Guelph, Ont. pp.52-60.

Cooke, S. E., & Prepas, E. E. (1998). Stream phosphorus and nitrogen export from agricultural and forested watersheds on the Boreal Plain. *Canadian Journal of Fisheries and Aquatic Sciences, 55*(10), 2292-2299.

Correll, D. L., Jordan, T. E., & Weller, D. E. (1999). Transport of nitrogen and phosphorus from Rhode river watersheds during storm events. *Water Resources Research., 35*(8), 2513-2521.

Crosbie, B., & Chow-Fraser, P. (1999). Percentage land use in the watershed determines the water and sediment quality of 22 marshes in the Great Lakes basin. *Canadian Journal of Fisheries and Aquatic Sciences, 56*(10).

Domagalski, J. L., Ator, S., Coupe, R., McCarthy, K., Lampe, D., Sandstorm, M., et al. (2008). Comparative study of transport processes of nitrogen, phosphorus, and herbicides to streams in five agricultural basins, USA. *Journal of Environmental Quality, 37*(3), 12.

Dunne, T., Western, D., & Dietrich, W. E. (2011). Effects of cattle trampling on vegetation, infiltration, and erosion in a tropical rangeland. *Journal of Arid Environments, 75*(1), 58-69.

Euphrasia Historical Society. (2000). *Euphrasia.* Collingwood: Conestoga Press.

Fraters, D., Boumans, L. J. M., van Leeuwen, T. C., & de Hoop, W. D. (2001). Monitoring nitrogen leaching for the evaluation of the dutch minerals policy for agriculture in clay regions. *The Scientific World Journal, 1*(1), 758-766.

Fitzpatrick, F. A., Scudder, B. C., Lenz, B. N., & Sullivan, D. J. (2001). Effects of multi-scale environmental characteristics on agricultural steam biota in eastern Wisconsin. *Journal of the American Water Resources Association, 37*(6), 1489-1507.

Fullen, M. A. (1985). Compaction, hydrological processes and soil erosion on loamy sands in east Shropshire, England. *Soil and Tillage Research, 6*(1), 17-29.

Gardner, K. K., & McGlynn, B. L. (2009). Seasonality in spatial variability and influence of land use/land cover and watershed characteristics on stream water nitrate concentrations in a developing watershed in the Rocky Mountain West. *Water Resources Research., 45*(8), 1-14.

Harmel, D., Potter, S., Casebolt, P., Reckhow, K., Green, C., & Haney, R. (2006). Compilation of measured nutrient load data for agricultural land uses in the United States. *Journal of the American Water Resources Association, 42*(5), 1163-1178.

Harmel, D., Qian, S., Reckhow, K., & Casebolt, P. (2008). The MANAGE Database: Nutrient Load and Site Characteristic Updates and Runoff Concentration Data. *Journal of Environmental Quality., 37*(6), 2403-2406

Heathwaite, A. L., & Johnes, P. J. (1996). Contribution of nitrogen species and phosphorus fractions to stream water quality in agricultural catchments . *Hydrological Processes, 10*(7), 971-983.

IPCC (Intergovernmental Panel on Climate Change). 2007. *Climate Change 2007 – The Physical Science Basis: Contribution of Working Group I to the Fourth Assessment Report of the IPCC.* Cambridge: Cambridge University Press.

Kirchmann, H., & Witter, E. (1992). Composition of fresh, aerobic and anaerobic farm animal dungs. *Bioresource Technology, 40*(2), 137-142.

Lal, R. (2001). Soil degradation by erosion. *Land Degradation & Development, 12*(6), 519-539.

Lal, R., Griffin, M., Apt, J., Lave, L., & Morgan, M. G. (2004). Managing Soil Carbon. *Science, 304*(5669), 393-393.

Lind, O.T. (1974). *Handbook of Common Methods in Limnology, 2nd edition*. Iowa; Kendall/Hunt Publishing Company.

Matson, P. A., Parton, W. J., Power, A. G., & Swift, M. J. (1997). Agricultural intensification and ecosystem properties. *Science, 277*(5325), 504-509.

McDiffett, W., Beidler, A., Dominick, T., & McCrea, K. (1989). Nutrient concentration-stream discharge relationships during storm events in a first-order stream. *Hydrobiologia, 179*(2), 97-102.

McDowell, R., Sharpley, A., & Folmar, G. (2001). Phosphorus export from an agricultural watershed : Linking source and transport mechanisms. *Journal of Environmental Quality 30*(5), 1587-1595

McDowell, R.W., & Sharpley, A.N. (2003). Uptake and release of phosphorus from overland flow in a stream environment. *Journal of Environmental Quality, 32*(3), 937-948.

Montgomery, D. R. (2007). Soil erosion and agricultural sustainability. *Proceedings of the National Academy of Sciences, 104*(33), 13268-13272.

Murphy, J. & Riley, J. 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta, *27*, 31-36.

O'Toole, P., Morgan, M. A., & McAleese, D. M. (1982). The effects of soil properties, temperature and urea concentration on patterns and rates of urea hydrolysis in some Irish soils. *Irish Journal of Agricultural Research, 21*(2/3), 185-197.

Petersen, S. O., Roslev, P., & Bol, R. (2004). Dynamics of a pasture soil microbial community after deposition of cattle urine amended with [13C] urea. *Applied and Environmental Microbiology, 70*(11), 6363-6369.

Peterson, B. J., Wollheim, W. M., Mulholland, P. J., Webster, J. R., Meyer, J. L., Tank, J. L., et al. (2001). Control of nitrogen export from watersheds by headwater streams. *Science, 292*(5514), 86-90.

Petts, G. E. (1984). *Impounded Rivers. Perspectives for Ecological Management*. Chichester: John Wiley.

Salvia-Castellvi, M., Iffly, J. F., Vander Borght, P., & Hoffman, L. (2005). Dissolved and particulate nutrient export from rural catchments : A case study from Luxembourg. *The Science of the Total Environment, 344*(1-3), 15.

Schultz, R., Collettil, J., Isenhart, T., Simpkins, W., Mize, C., & Thompson, M. (1995). Design and placement of a multi-species riparian buffer strip system. *Agroforestry Systems, 29*(3), 201-226-226.

Sharpley, A. N., Gburek, W. J., Folmar, G., & Pionke, H. B. (1999). Sources of phosphorus exported from an agricultural watershed in Pennsylvania. *Agricultural Water Management, 41*(2), 77-89.

Sharpley, A. N., Kleinman, P. J. A., Heathwaite, A. L., Gburek, W. J., Folmar, G. J., & Schmidt, J. P. (2008). Phosphorus Loss from an Agricultural Watershed as a Function of Storm Size. *Journal of environmental quality, 37*(2), 7.

Sharpley, A. N., McDowell, R. W., Weld, J. L., & Kleinman, P. J. A. (2001). Assessing Site Vulnerability to Phosphorus Loss in an Agricultural Watershed. *Journal of Environmental Quality., 30*(6), 2026-2036.

Sharpley, A. N., Smith, S. J., & Naney, J. W. (1987). Environmental impact of agricultural nitrogen and phosphorus use. *Journal of Agricultural and Food Chemistry, 35*(5), 812-817.

Statistics Canada. 2006a. Community Profiles: Grey Highland, Municipality. http://www12.statcan.ca/census-recensement/2006 Retrieved Oct 1, 2009

Statistics Canada. 2006b. Community Profiles: The Town of the Blue Mountains. http://www12.statcan.ca/census-recensement/2006 Retrieved Oct 1, 2009

Thomsen, I. K., & Christensen, B. T. (1998). Cropping system and residue management effects on nitrate leaching and crop yields. *Agriculture, Ecosystems & Environment, 68*(1–2), 73-84

Table 1.1: Summary of landform features for sites in this study. Crop sites included row and cereal crops while livestock-based included manure storage and pasture land.

Site Code	Practice Type	Soil Class	Watershed Area (ha)	Slope of Terrain (%)	Elevation (m)	Stream Length (m)
3	Crop	C	95.44	3.79	429.78	2038
41N	Crop	C	51.12	3.26	363.38	1157
410	Crop	C	25.7	3.65	179.21	342
38	Crop	C	23.07	3.03	285.78	1061
24	Livestock	C	145.65	4.06	345.88	1638
13	Livestock	C	71.81	6.37	296.21	361
5	Livestock	C	110.82	3.65	457.72	1057
42	Livestock	CB	77.05	4.82	416.7	784

Table 1.2: List of water chemistry parameter transformations and abbreviations. Total phosphorus and turbidity had lamba values of 0 and -0.2 respectively.

Parameter	Abbreviation	Transformation
Total Nitrogen	TN	LOG_e
Total Nitrate-Nitrogen	TNN	LOG_e
Total Ammonia-Nitrogen	TAN	LOG_e
Total Phosphorus	TP	BOX-COX + 0.002
Total Suspended Solids	TSS	LOG_e
Turbidity	TURB	BOX-COX
pH	pH	N/A

Table 1.3: Matrix of Pearson's correlation coefficients for independent variables. Significant correlations are shown in bold.

	Snow Depth (cm)	Rainfall (mm)	Watershed area (m^2)	Slope (%)	Elevation (m)	Stream Sample Length (m)
Snow Depth (mm)	1.0000					
Rainfall (mm)	**-0.1983**	1.0000				
Watershed area (m^2)	-0.0022	-0.0119	1.0000			
Slope (%)	-0.0029	0.0003	**0.2079**	1.0000		
Elevation (m)	0.0007	-0.0149	**0.6302**	-0.0179	1.0000	
Stream Sample Length (m)	0.0007	-0.0287	**0.5575**	**-0.4281**	**0.5836**	1.0000

Table 1.4: Summary of mean water chemistry parameters sorted by season in the agriculturally relevant calendar (ARC) and agricultural practice. Transition from season to season within ARC is determined by activities of the agriculturalists. Values in bold indicate a significant difference (P<0.05; t-test) between livestock and crop-based practices for variable of interest.

	ARC season									
	Spring		Summer		Fall		Winter		Year-round	
Parameter	Livestock	Crop	Livestock	Crop	Livestock	Crop	Livestock	Crop	Livestock	Crop
TN (mg/L)	1.98 ± 0.81	2.81 ± 0.93	2.66 ± 0.61	3.24 ± 0.56	1.73 ± 0.36	1.86 ± 0.36	1.52 ± 0.26	2.50 ± 0.26	1.95 ± 2.09	2.74 ± 2.34
TNN (mg/L)	**0.11 ± 0.06**	**0.40 ± 0.06**	0.06 ± 0.02	0.08 ± 0.02	0.06 ± 0.05	0.14 ± 0.05	**0.16 ± 0.07**	**0.47 ± 0.07**	**0.10 ± 0.13**	**0.27 ± 0.38**
TAN (mg/L)	0.10 ± 0.03	0.09 ± 0.03	0.08 ± 0.02	0.05 ± 0.01	0.16 ± 0.16	0.11 ± 0.04	0.08 ± 0.02	0.04 ± 0.02	**0.10 ± 0.01**	**0.06 ± 0.01**
TP (mg/L)	0.45 ± 0.14	0.28 ± 0.14	**0.28 ± 0.06**	**0.10 ± 0.05**	**0.19 ± 0.05**	**0.03 ± 0.05**	**0.08 ± 0.02**	**0.05 ± 0.02**	**0.25 ± 0.51**	**0.12 ± 0.24**
TSS (mg/L)	17.20 ± 6.06	16.54 ± 6.32	35.04 ± 8.03	8.75 ± 7.07	**56.40 ± 16.78**	**7.64 ± 17.94**	**16.29 ± 6.63**	**2.43 ± 6.91**	**28.80 ± 57.55**	**8.87 ± 17.93**
TURB (NTU)	12.97 ± 0.03	9.65 ± 3.81	7.90 ± 2.36	6.23 ± 2.03	24.50 ± 12.01	16.51 ± 12.01	**19.86 ± 7.80**	**4.18 ± 7.95**	**16.00 ± 39.57**	**7.98 ± 21.05**
pH	**8.18 ± 0.06**	**7.66 ± 0.05**	**7.89 ± 0.07**	**7.36 ± 0.07**	**7.75 ± 0.09**	**7.29 ± 0.09**	**7.78 ± 0.06**	**7.47 ± 0.06**	**7.88 ± 0.36**	**7.43 ± 0.35**

Table 1.5: Results of a two-way ANCOVA testing the effects of agricultural practice (AGR) and rainfall amount (RAIN) on water-quality variables. Significant effects are shown in bold.

Parameter	n	P value		
		AGR	**RAIN**	**AGR*RAIN**
TNN	162	**0.0007**	**0.0145**	0.8895
TAN	136	**0.0015**	**<0.0001**	0.9333
TSS	175	**<0.0001**	**<0.0001**	0.7228
TURB	167	**0.0016**	**<0.0001**	0.4366
TN	121	**0.0385**	**0.0026**	0.2864
pH	173	**<0.0001**	0.9441	0.7358
TP	186	**0.0006**	**<0.0001**	0.7869

Table 1.6: Summary of significant (P<0.05) forward regression models for each parameter using year-round data. SLOPE=slope of surrounding terrain; RAIN=rainfall amount; WATAREA=watershed area; AGR=agricultural practice; SOIL=soil class; SNOW=snow depth. Models were run with the inclusion of season according to the agriculturally relevant calendar (ARC) or conventional calendar (CON). Number in bracket is the sample size. Predictors are shown in the order they entered each model. Only significant (P<0.05) predictors are shown.

	ARC				CON			
Parameter	AIC Value	r^{2adj}	Cumulative (r^2)		AIC Value	r^{2adj}	Cumulative (r^2)	
TN (120)	-66.02	0.19	SLOPE	0.09	-66.02	0.19	SLOPE	0.09
			RAIN	0.16			RAIN	0.16
			WATAREA	0.18			WATAREA	0.18
			AGR	0.19			AGR	0.19
			SOIL	0.22			SOIL	0.22
TNN (161)	30.23	0.33	ARC	0.23	70.61	0.19	SLOPE	0.10
			SLOPE	0.33			SNOW	0.16
TAN (136)	-16.8	0.22	RAIN	0.12	-13	0.14	RAIN	0.03
			SLOPE	0.20			SLOPE	0.14
			ARC	0.24				
TP (186)	-985.81	0.30	ARC	0.15	-992.91	0.33	SNOW	0.14
			RAIN	0.21			RAIN	0.20
			SNOW	0.26			WATAREA	0.21
			AGR	0.32			AGR	0.35
TSS (176)	79.64	0.29	RAIN	0.14	79.64	0.29	RAIN	0.14
			AGR	0.23			AGR	0.23
			WATAREA	0.28			WATAREA	0.28
			SNOW	0.30			SNOW	0.30
TURB (167)	450.24	0.30	RAIN	0.22	450.24	0.30	RAIN	0.22
			SLOPE	0.30			SLOPE	0.30
			SNOW	0.32			SNOW	0.32
pH (173)	-381.59	0.4	AGR	0.29	-392.66	0.44	AGR	0.29
			ARC	0.38			CON	0.41
			SOIL	0.39			SNOW	0.42
			WATAREA	0.41			SOIL	0.44
							WATAREA	0.46

Table 1.7: Summary of forward stepwise regression models for data sorted by agriculturally relevant calendar (ARC) season. Only significant (P<0.05) model and predictors are shown. See Table 1.6 for explanation of abbreviations for predictors.

ARC Season	Parameter	*n*	Predictor	r^2	Cumulative r^2	Adj r^2
Spring	TN	21	RAIN	0.19	0.19	0.15
	TNN	38	AGR	0.27	0.27	0.25
	TAN	26	RAIN	0.21	0.21	0.18
	TP	45	RAIN	0.13	0.13	0.11
	TSS	44	RAIN	0.34	0.53	0.50
			WATAREA	0.06		
			AGR	0.13		
	TURB	30	RAIN	0.75	0.80	0.78
			SLOPE	0.04		
	pH	32	AGR	0.60	0.76	0.73
			RAIN	0.12		
			WATAREA	0.04		
Summer	TN	38	WATAREA	0.05	0.12	0.04
			AGR	0.03		
			SOIL	0.03		
	TAN	39	SLOPE	0.13	0.13	0.11
	TP	56	SLOPE	0.18	0.26	0.21
			RAIN	0.03		
			WATAREA	0.04		
	TSS	53	AGR	0.11	0.11	0.09
	TURB	54	RAIN	0.20	0.25	0.22
			SLOPE	0.05		
	pH	56	AGR	0.34	0.46	0.43
			SOIL	0.07		
			WATAREA	0.05		
Fall	TN	12	SOIL	0.75	0.91	0.86
			SLOPE	0.04		
			AGR	0.08		
			WATAREA	0.03		
	TAN	33	RAIN	0.42	0.53	0.50
			SLOPE	0.11		
	TP	32	AGR	0.37	0.66	0.63
			RAIN	0.24		
			SLOPE	0.05		
	TSS	30	RAIN	0.18	0.18	0.15
	TURB	30	RAIN	0.26	0.38	0.33
			SLOPE	0.11		
	pH	32	AGR	0.31	0.31	0.28
Winter	TN	50	SLOPE	0.10	0.10	0.08
	TNN	52	SLOPE	0.51	0.51	0.50
	TAN	38	AGR	0.13	0.13	0.11
	TP	53	SNOW	0.18	0.54	0.49
			AGR	0.10		
			WATAREA	0.21		
			RAIN	0.05		
	TSS	48	AGR	0.18	0.18	0.16
	TURB	53	AGR	0.13	0.23	0.20
			WATAREA	0.09		
	pH	53	AGR	0.19	0.19	0.17

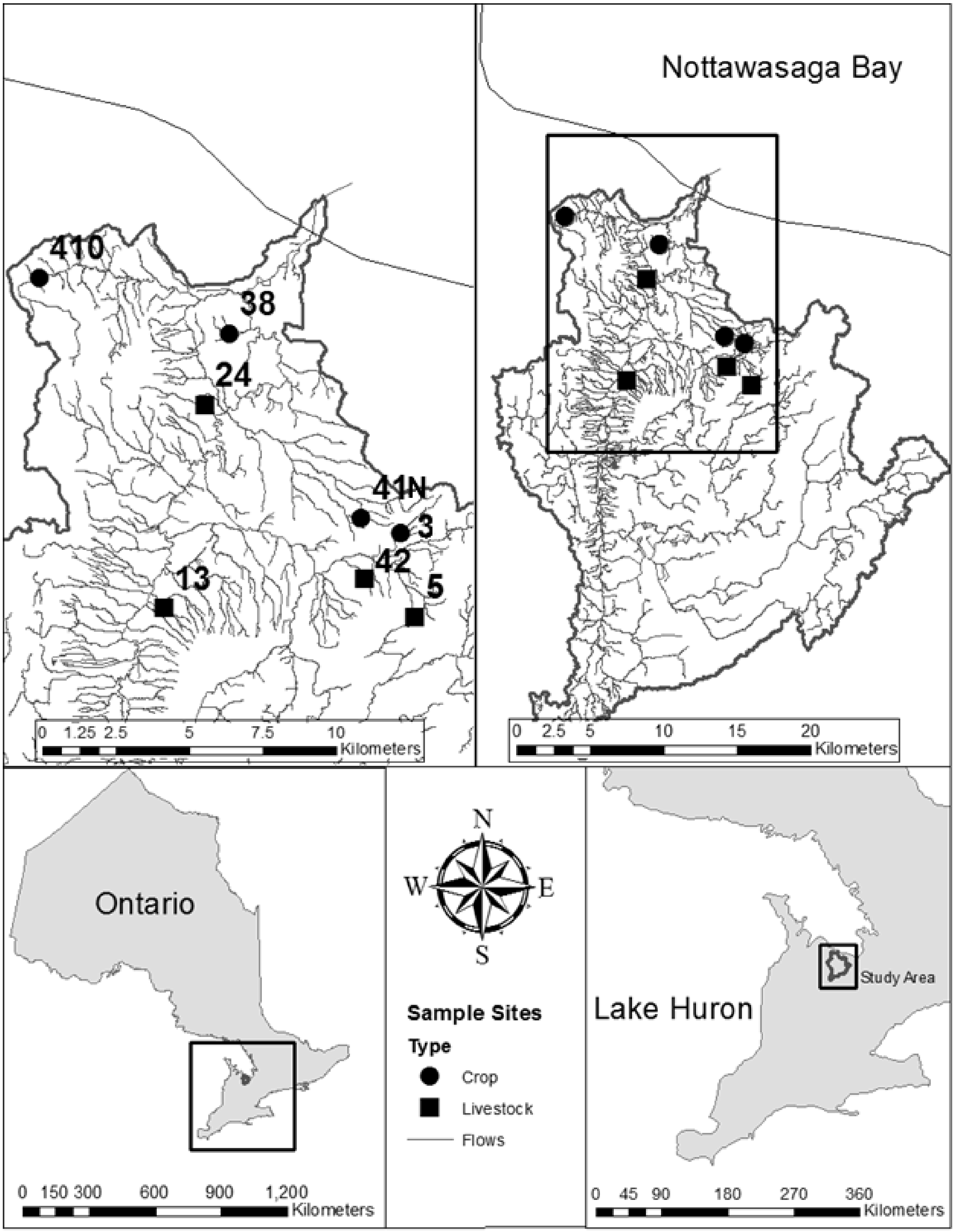


Figure1.1: Map of the study region and the eight sample sites in the Beaver Valley watershed. Dark circles indicate crop sites, while livestock sites are indicated by dark squares.

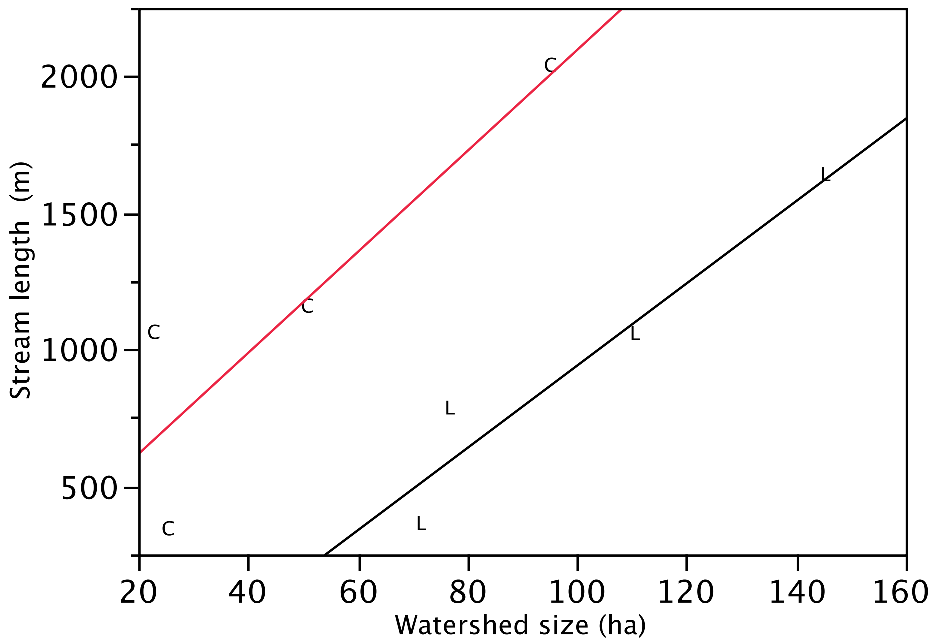


Figure 1.2: Relationship between stream length and watershed size for this study. "C" refers to crop sites; "L" refer to livestock sites. Linear regression lines were fitted separately for each agricultural practice. Only the regression coefficient associated with "L" sites was statistically significant. Stream length = -566.4009 + 15.065 * Watershed size; r^2 =0.93; P=0.0368).

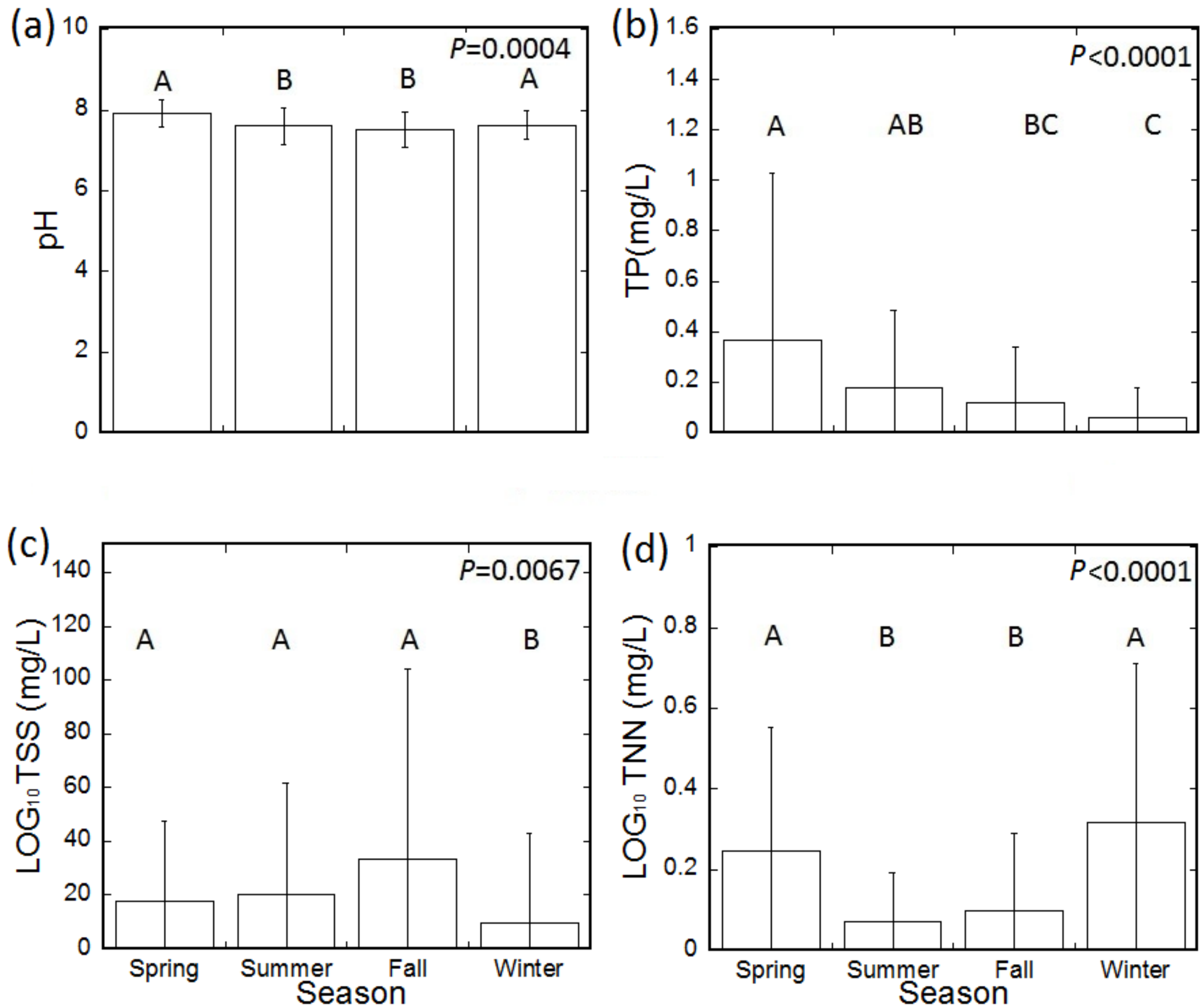


Figure 1.3: Comparison of mean a) pH b) TP (mg/L) c) TSS (mg/L) and d) TNN (mg/L) corresponding to each season of the agriculturally relevant calendar. Different letters indicate that means are significantly different (ANOVA; P<0.05) as indicated by a post-hoc test

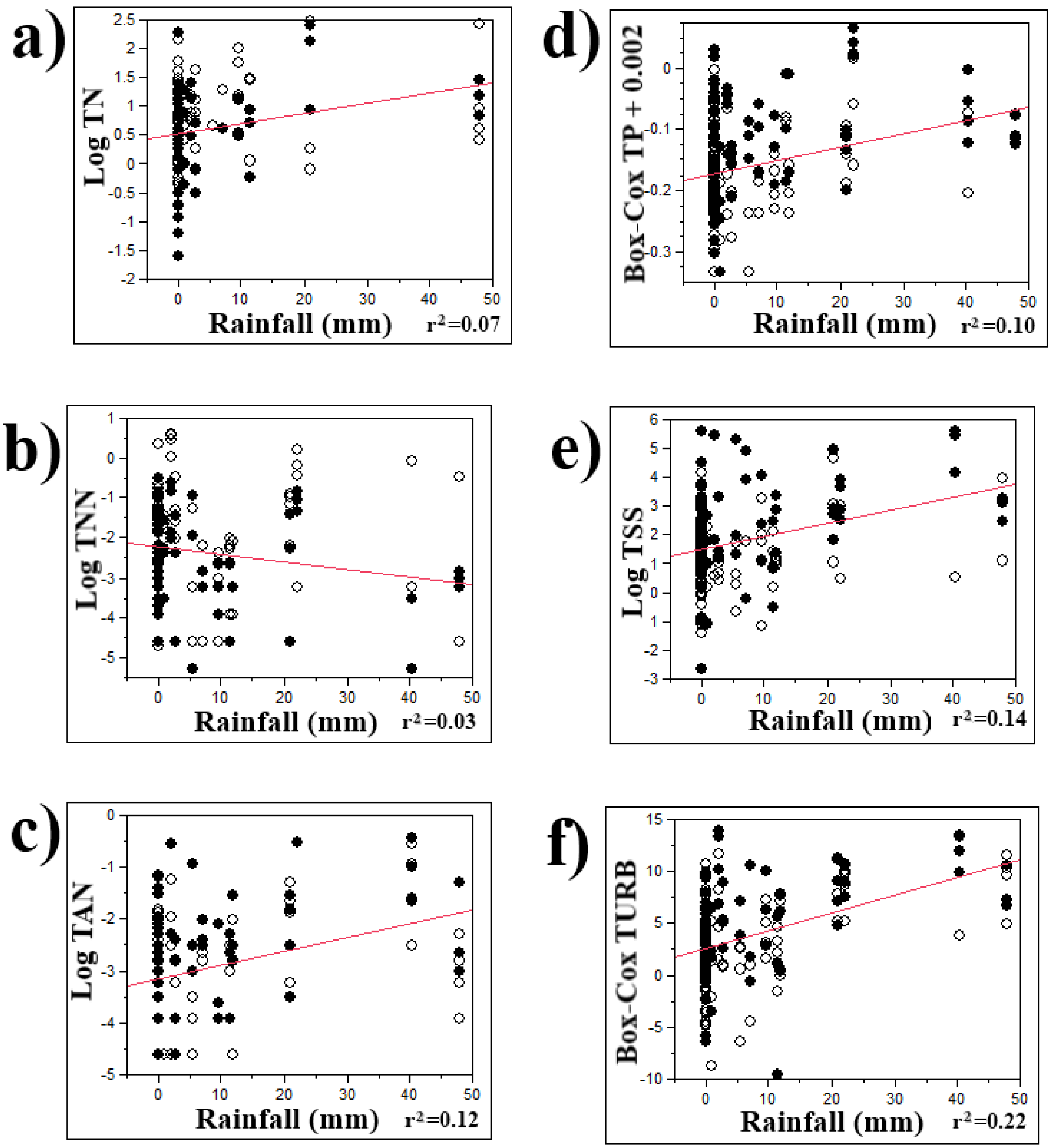


Figure 1.4: Linear regression of a) TN (mg/L) b) TNN (mg/L) c) TAN (mg/L) d) TP (mg/L) e) TSS (mg/L) and f) TURB (NTU) against rainfall amount for year-round data. Open and solid symbols correspond to crop-based and livestock sites, respectively. All regression coefficients were significantly different from zero ($P<0.05$).

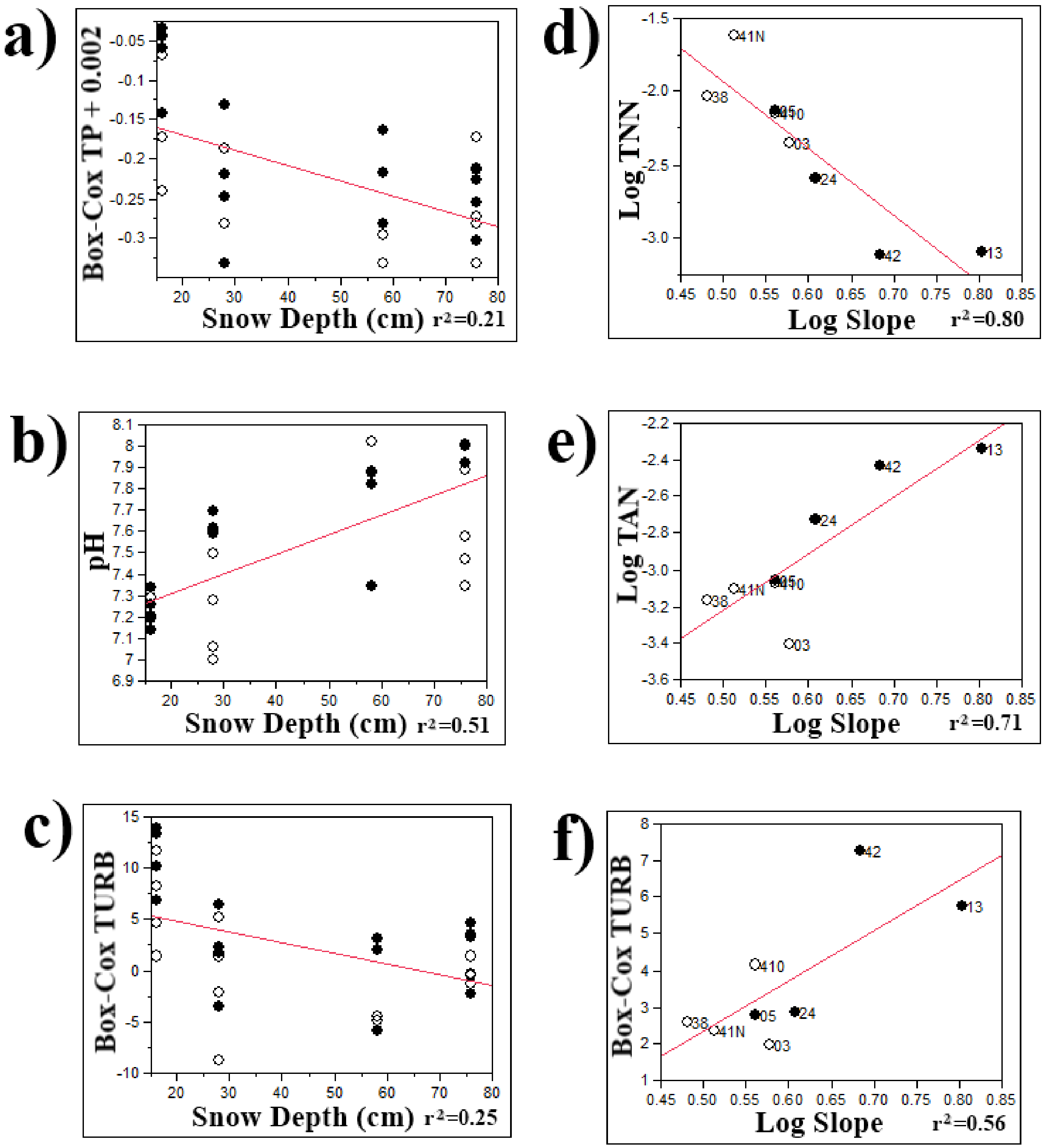
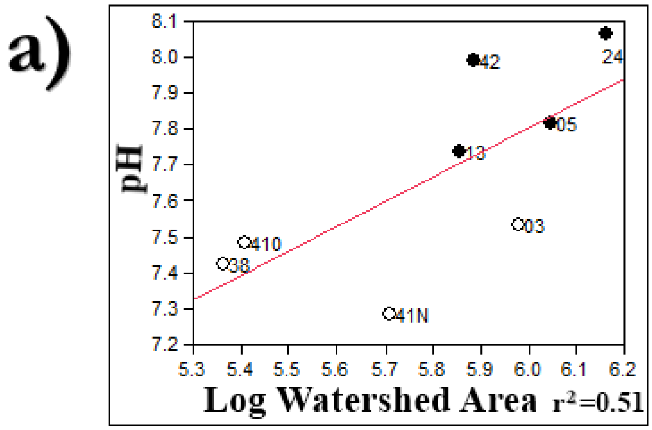


Figure 1.5: Linear regression of a) TP (mg/L) b) pH and c) TURB (mg/L) against snow depth and d) TNN (mg/L) e) TAN (mg/L) and f) TURB (NTU) against slope for year-round data. Open and solid symbols correspond to crop-based and livestock sites, respectively.



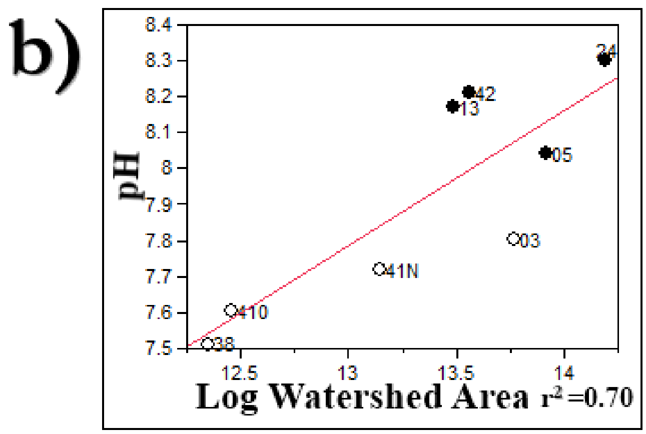


Figure 1.6: Linear regression of pH against watershed size (ha) for a) year-round data and b) data corresponding to spring of the agriculturally relevant calendar. Open and solid symbols correspond to crop-based and livestock sites, respectively.

Importance of monitoring continuously during three seasons of an agriculturally relevant calendar to determine impacts of livestock farming on a first-order stream

Catherine Dieleman

(Corresponding Author: catherine.dieleman@gmail.com)

Patricia Chow-Fraser

(chowfras@mcmaster.ca)

McMaster University
Department of Biology
1280 Main Street West
Hamilton, ON L8S 4K1

Abstract

Input of primary nutrients and sediments from agricultural runoff is a major pollutant in aquatic ecosystems and must be monitored effectively. For logistical reasons, many investigators use a discrete regime, sampling at weekly, biweekly or monthly intervals during only daytime hours. Such a regime could miss important activities that occur in the evenings or during storm events that may be critical for understanding variability in water chemistry of first-order streams. In this study, we compare data collected in a biweekly sampling program with those from a continuous sampling (using an automatic water sampler) program over a 5-month period (late May to mid-November). We chose a first-order stream that drains a livestock farm since this type of practice usually yields significantly higher inputs of nutrients and sediment than does crop land. We found that daily total phosphorus (TP) concentrations (integrated sample of water taken every 6 hours throughout the day) were not significantly correlated with storm events and were significantly lower than those associated with discrete water samples (t-test; $P<0.05$). Turbidity readings taken every half hour throughout the day showed spikes during the evening hours that corresponded with times when cattle drank water from the stream and increased the level of nutrients through backwash. These influences were greatest for TP concentrations when cattle were given direct access to streams during periods of low rainfall. We found significant differences for pH, temperature, conductivity, dissolved oxygen and chlorophyll (ANOVA; df=2; $P<0.05$) across three seasons (spring, summer and fall) as defined by an agriculturally relevant calendar. We confirm that seasonal changes in agricultural practices can significantly describe the water chemistry of first-order streams, and must be considered when developing best-management practices.

Introduction

The eutrophication of aquatic ecosystems is a global issue, and results from the excessive loading of primary nutrients and sediment from human activities (Sharpley, et al., 2003). Agricultural runoff is one of the major sources of these pollutants in streams and can lead to deterioration in water quality and aquatic habitat (Correll, 1998; Sharpley, Gburek, Folmar, & Pionke, 1999). If current trends continue, a 2.7-fold global increase in phosphorus-driven eutrophication of aquatic ecosystems is projected to occur in the next 20 to 50 years (Tilman, et al., 2001). Livestock operations which have manure storage or feed-lot aspects are of particular concern, with phosphorus loadings 1,000 times that of forested environments and 119 times that of row-crop watersheds (Beaulac & Reckhow, 1982). As a result, understanding the influence of livestock on first-order streams is of great importance. Since small streams compose approximately 85% of tributaries and are responsible for >50% of the limiting nutrients (Peterson, et al., 2001) and up to 75% of sediment exiting a watershed (Petts, 1984), effective monitoring of water quality in streams of agriculturally dominated landscapes is crucial if we are to implement successful remediation in affected areas.

For logistical reasons, many investigators use a discrete regime, sampling at weekly, biweekly or monthly intervals during only daytime hours. Studies have shown that such sampling regimes can either over- or under-represent the chemical properties of water in streams, especially during storm events (King & Harmel, 2003; Stevens & Smith, 1978). Grab samples in a discrete sampling program can only represent characteristics of the water quality at the time the water is collected, whereas water collected in a continuous sampling program comes from auto-samplers that integrate water collected at various times throughout the day. The difference between these two methods become particularly apparent during storm events when flushing of the stream causes spikes in water chemistry. There are similar effects on water-quality parameters due to cattle disturbance of streams. Davies-Colley, et al. (2004) concluded that when cattle access a stream, there is a temporary but intense spike in nutrients and sediment in the water column, not unlike a storm event. They also found that such events significantly affected water chemistry and had the potential for cumulative effects downstream. Unfortunately, most discrete sampling regimes are not able to capture the impacts of cattle disturbance due to lack of overlap in timing of the sampling and the disturbance.

The dominant activities on a farm shift throughout the year depending on local weather conditions; because of year-to-year variation in temperature and rainfall, the timing of spring activities such as feeding, pasturing and housing the cattle also tend to vary each year. Consequently, it makes little sense to examine the impact of farm activities in a given year based on the solar cycle. Instead, it is more meaningful to examine farm activities based on seasons of an agriculturally relevant calendar (ARC) that are defined by prevailing weather patterns in a particular year. Dieleman & Chow-Fraser (Chapter 1) showed that variations in water chemistry were better explained by seasons in the ARC than by those in the conventional calendar.

In a previous study, Dieleman & Chow-Fraser (Chapter 1) found that first-order streams draining farms that support livestock were associated with significantly higher concentrations of nutrients (phosphorus and nitrogen) and suspended sediment (total suspended solids and water turbidity) than those supporting crops. They also found significant variation in nutrient and sediment concentrations that were associated with the four seasons of ARC. Like many other investigators, Dieleman & Chow-Fraser used a discrete sampling program that took grab samples during daylight hours once every two weeks. While this sampling regime was adequate for comparing water-quality conditions between land use practices, it was insensitive to localized and temporary impacts associated with disturbance when cattle are given access to streams to rehydrate during the evenings.

In this paper, we examine how water-quality data obtained from a discrete sampling program differs from that of a continuous sampling program for a headwater stream that drains a livestock farm. In choosing a livestock as opposed to a crop-based farm, we expect to find significant differences between these sampling programs with respect to their ability to capture spikes in nutrients and sediments associated with cattle disturbance. We predict that data collected continuously will reveal impacts of rehydration events that cannot be reflected in discrete data. We will also relate differences in nutrient and sediment levels to ARC seasons and storm events throughout the sampling period. This is one of the first studies conducted on first-order streams that examines the effect of storms, cattle hydration events and sampling regimes on water quality, and will be important for understanding seasonal changes in the impacts of livestock farms on the quality of headwater streams.

Methods

Study Site Description

Our study was conducted in the northeastern portion of the Beaver Valley watershed ($618 km^2$) in Ontario, Canada (Figure 1). Located on the shores of Nottawasaga Bay, this watershed ultimately feeds into both Georgian Bay and Lake Huron. The area was settled in the mid 1800s as an agricultural community and has remained so over the years (Euphrasia Historical Society, 2000). The watershed contains chiefly small family farms which still employ crop and livestock rotation techniques. The farmers predominately cultivate row and cereal crops, such as canola, soybeans, corn and mixed grains, as well as livestock including both beef and dairy operations. The Beaver Valley is composed mainly of Vincent silty clay loam and Dunedin clay soils, creating a high runoff potential for water during storm events. The limestone-shale base creates naturally basic waters across the basin. This phenomenon is particularly noticeable near the Niagara Escarpment, a prominent land formation in the Beaver Valley watershed.

Our study site is located at the base of the escarpment and has a relatively large watershed area (0.77 km^2) as a result. Like majority of the basin, the soils in this first-order watershed are chiefly clay, although it does have a large portion of loam sediments. The proximity of this site to the escarpment creates a watershed with an average slope of 4.82%. As a result, the basin is used only for pasturing and housing beef livestock. The study stream itself is permanent and first-order, originating in the escarpment above the pasture land. Our sample site was approximately 200 m downhill of a manure storage area and a barn while surrounded by pasture land (a common arrangement for small farms). Throughout the pasture area and barn yard, the stream was often unfenced and commonly used as a hydration source for the cattle. The permanent nature of the stream and the large potential for influence from the livestock farm created an ideal site to continuously monitor cattle-mediated impacts on the water quality of the stream.

Data Collection and Processing

Between May 27th and November 10th, both discrete and continuous samples were collected to encompass the entire growing season. Continuous data were captured via the concurrent deployment of an ISCO™6720 automatic water sampler and a YSI™ 6600 multiprobe. The automatic water sampler collected daily composites for total phosphorus (TP) analysis, combining four 250-mL samples which were collected individually every six hours.

Roughly every 14 to 24 days, 250-mL subsamples were withdrawn from each 1-L bottle that contained a daily composite. Subsamples were held in acid-washed 200 mL Snap'N'Seal™ containers and placed on ice in a cooler until they could be stored in a freezer for transportation back to the lab for further processing. The multiprobe collected instantaneous readings in-situ every half an hour for turbidity (TURB), pH, temperature (TEMP), conductivity (COND), dissolved oxygen (DO), and chlorophyll (Chl). We calculated daily means for each parameter. Due to equipment failure, there were periods of time when TURB, pH and CHL data were not collected with the multiprobe. Since we did not have our own rain gauge, we had to use rain data recorded at a weather station in Thornbury, Ontario (operated by Environment Canada), a town that is approximately 10 km away from our site. We used total rainfall measured in Thornbury in the preceding 48-hour to account for the time lag between onset of precipitation event in Thornbury and when it would reach our site. Initial observations were also made prior to water collection to determine routine movements by the herd of cattle. During each sampling occasion, we observed the cattle for an hour to confirm their movement patterns and to record rotation of pasture land.

Data for the discrete sampling program came from a parallel study (Dieleman & Chow-Fraser; Chapter 1) that had been carried out over the same time period. All water samples were collected following protocols outlined by Lind (1974). TEMP, pH, and TURB readings were taken in-situ with an Orion Smart Check™ 020000A pH/temperature meter, and LaMotte™ 2020e Turbidimeter respectively. TP samples were collected in acid-washed 200ml Snap'N'Seal™ containers and placed on ice until they could be frozen for further processing. Once back in the lab both continuous and discrete TP samples were digested with potassium persulfate and autoclaved at 15 psi and 120°C. The molybdenum blue method (Murphy & Riley,

1962) was used to quantify phosphorus in the water samples.

Statistics

All statistical tests were completed in SAS JMP version 7.0.1 (SAS Institute Inc., Cary, North Carolina). All transformations used on the variables to produce normality and equal variance are outlined in Table 2.1. Parametric tests (ANOVA and t-test) were only used if the data met the assumptions of equal variance and normality; otherwise non-parametric tests were used (Kruskal-Wallis rank sum test and Wilcoxon rank sum tests).

Results

Before we compare the data between discrete and continuous regimes, we will first examine seasonal trends in the water-quality variables. Storm events occurred throughout the sampling period, but particularly during spring and fall seasons in the agriculturally relevant calendar (ARC; indicated in Figure 2.1). Since rain events cause soil erosion on farms, particularly those that support livestock, we expected to find close correspondence between levels of suspended particles and rainfall amounts. In fact, peaks in TP and TURB did coincide with the largest precipitation events during that year (maxima for these variables through the season are aligned for easy visual comparison in Figure 2.1). However, it is important to note that there were many peaks in TP and TURB during August and September that did not correspond with timing of rain events. COND also responded with the timing of storm events, but the relationship was not as simple. Immediately following the onset of the storm, COND levels plummeted, but then increased sharply within 24 to 48 hours. We did not see any obvious patterns in DO, TEMP and pH with rain events--only occasional spike which coincided with the onset of precipitation.

To further examine the effects of rainfall on the water-quality variables, we regressed the dependent variables against total rainfall amount measured 48 hours prior to sampling (Figure 2.3). Only TURB, COND and CHL varied significantly with rainfall amount. The relationship between TP and rainfall was not statistically significant (P=0.0624) but suggests a positive trend. Overall, however, all regressions were associated with a great deal of unexplained variation, indicating that rainfall was not a very good predictor of water-quality conditions for the continuous data.

We took a closer look at the continuous TURB and TP data during the period between large rain events, noting there were large fluctuations in both parameters that were unrelated to rain events (Figure 2.2). Based on field observations, we suspected that some of this fluctuation may have been due to disturbance by cattle when they were given access to the stream for regular hydration (Figure 2.2). Using TURB data that had been collected half hourly on July 17, 2010, we confirm that this is in fact the case (Figure 2.3). Throughout most of the day, TURB remained below 32 NTU, and towards dusk, when the cattle began to drink from the stream, TURB readings rose sharply at 6:00 pm and reached almost 800 NTU at 8:00 pm before returning to pre-dusk levels after 9:00 pm (Figure 2.4). This daily ritual occurred in both the morning and evenings and continued throughout the period when cattle had open access to the streams. On several occasions, we observed the entire herd drinking from the stream simultaneously. From late July to mid August, however, the cattle were no longer permitted to roam freely into the stream to drink as they were rotated onto the pasture land. During this time, TP readings were erratic, but were significantly lower than those measured the rest of the study period (Figure 2.5d). We found similarly elevated concentrations of COND and CHL following the cattle rotation (Figure 2.5c and e, respectively).

There were statistically significant seasonal differences in water-chemistry variables (Figure 2.6). Mean pH and COND values were highest during spring and lowest during the summer months (Figure 2.6a and c Kruskal-Wallis rank sum test; $P<0.05$). Not surprisingly, TEMP was warmest and DO was lowest during summer (Figure 2.6b and d). CHL followed similar patterns to that exhibited by COND and pH (Figure 2.6e).

The continuous sampling was able to capture the effects of numerous storms (several that were major, i.e. >40 mm) during the sampling period, and this offered many more opportunities to study their impacts of rain events than would have been possible with only a biweekly schedule of sampling. When we compared the two regimes directly, we found no significant differences in TEMP and pH data (Figure 2.7a and b, respectively; t-test). There was also no significant effect of sampling method on TURB data, even though data collected by the YSI™ 6600 tended to be much higher than those measured by the LaMotte™ 2020e Turbidimeter (Figure 2.7c). It is our experience that the YSI tends to yield spurious information and the data need to be checked for quality before they can be used. For this analysis, we routinely removed values that were > 1000 and any that were negative.

Mean TP values were significantly different between methods, with the mean associated with the continuous sampling regime being significantly lower than that associated with the discrete sampling regime (Figure 2.7d). This discrepancy is due to the instantaneous nature of grab samples that only show what happens at a single point during the rain event (see Figure 2.8). By contrast, the continuous sampling program integrates information through a 24 hour period, and captures peak concentrations as well as much lower concentrations leading up to and following the daily maximum. The graph shown in Figure 2.8 illustrates how during a large storm event, grab samples can overestimate TURB associated with the entire storm simply because it cannot account for the rest of the time before and after peak conditions when values were much lower. In this study, 6 of the 12 discrete samples collected had been taken on days with >5mm of precipitation and collected during the storm event as a result of random chance.

Discussion

The strong positive relationship between TP and precipitation amount is well documented for different aquatic environments and in different geographic locations in the world (Borah, Bera, & Shaw, 2003; Bowes, House, Hodgkinson, & Leach, 2005; Correll, Jordan, & Weller, 1999; McDiffett, Beidler, Dominick, & McCrea, 1989). In most cases, however, conclusions have been drawn from studies in which rain events are actively pursued, and in high-order stream systems. In this study, we report a weak relationship between TP and rain events because of the confounding effects of cattle disturbance. For headwater streams, these hydration events produced spikes in phosphorus concentrations that matched the magnitude of a medium-sized storm event and should therefore be monitored as a contributing factor.

Unfortunately, the resolution of our monitoring program for TP was not sufficient to bear out hourly variation through the day; however, TURB, like TSS, is well correlated with TP concentrations (Grayson, Finlayson, Gippel, & Hart, 1996) and was measured every half an hour during the study period. By examining trends in TP and TURB, we were able to confirm that both parameters fluctuated in accordance with cattle activity. The half-hourly TURB readings were able to closely track the hydration events by the herd, and were confirmed by our observations in the field. With some variation, the general patterns of disturbance in the morning (not shown) and/or evenings were consistent. Work by Davies-Colley, et al. (2004)

indicates that such cattle events may be large enough to significantly impact downstream water quality, suggesting these events could overshadow the effects of precipitation on TP levels. Once the pasture land was depleted of grass, the cattle were rotated into fields located further away from the stream, and from which they were fenced off (between late-July and August). During this period, the fluctuations in TP concentrations decreased and mean values were significantly lower than when livestock had access to the stream.

The mechanism by which the hydration events resulted in TP spikes in the stream is worth discussing because the cattle do not physically enter the stream. This is because the stream bed contains large pebbles and rocks that can cause the cloven hooves of the cattle to become bruised and damaged, and therefore, cows tend to avoid stepping into stony environments (Harris, et al., 1988). Instead, the animals will lean over the stream's edge to slurp up the water (see Figure 2.9). This technique still causes slumping of the streams banks from the weight of the livestock, but would not produce as dramatic an effect as if the entire herd entered the waterway. The loading of phosphorus results from the animals 'backwashing' into the stream, contaminating the stream with nutrients and bacteria from inside their mouths; when an entire herd drinks simultaneously, the backwashing could cause a spike in TP levels. Farmers know well that such backwashing by cattle routinely leads to algal blooms in watering troughs (15,000 L container), especially in the summer when there is plenty of light to stimulate the growth.

TP and TURB were the only two parameters that were not significantly related to ARC seasons. The other water chemistry variables appeared to be responding to changes in agricultural practices over the growing seasons. COND and pH were both elevated in the spring and fall, presumably because the watershed was saturated at these times and allowed greater rates of leaching of calcium, carbonate and bicarbonate ions from the limestone bedrock. When the watershed is saturated, the farmers keep the cattle indoors to avoid them sinking into the waterlogged soil and thus, there tends to be less impact directly associated with the cattle farming. Further research is required to determine the factors that lead to a seasonal shift in water chemistry for low-order streams that drain livestock operations. Nonetheless, the ARC effectively describes the seasonality in water chemistry and confirms the observation made by Dieleman & Chow-Fraser (Chapter 1) that data should not be compared across studies without accounting for differences in ARC seasons.

Studies that have examined nutrient loadings in various environments have found that discrete samples consistently both over- and under-estimated nutrient and sediment concentrations, particularly during storm events (Borah, et al., 2003; King & Harmel, 2003; Stevens & Smith, 1978; Swistock, Edwards, Wood, & Dewalle, 1997). This occurs as grab samples can only accurately describe the nutrient and sediment content of a stream at the exact time the sample was collected. Often that sample is used to represent the stream over numerous days or weeks; the longer the time span the larger the potential for bias (King & Harmel, 2003). An autosampler, however, can be programmed to take an integrated sample over a day (as in this study) or at regular intervals through a day (Swistock, et al., 1997). Such an intensive sampling program is necessary to capture highly variable and unpredictable events such as a storm or cattle disturbance. In the case of a livestock site, it is important for researchers to understand the movement patterns of the herd they are studying or to deploy a monitoring device as done by Davies-Colley, et al. (2004). Our study joins a growing body of literature that points out the limitation of grab samples because they only give a coarse estimate of variation in water chemistry (Robertson & Roerish, 1999). It is important to note that these results do not suggest that all discrete sampling regimes are inappropriate, instead it reminds us that models and conclusions drawn on such data will have a larger potential for error than those completed with continuously sampled data and should not be perceived as equal. The increased costs associated with a continuous sampling program, both in terms of equipment and labour, are impediment to most environmental agencies and investigators.

Our continuous dataset indicates that current discrete sampling methods may be underestimating or possibly completely missing the influence of cattle disturbance in first-order streams. Hydration events and other cattle-stream interactions tend to occur at similar times each day. Not unlike a storm event, these interactions can cause a large nutrient and sediment spike above background levels. Just as investigators now routinely chase after storm events to incorporate their influences, we urge others to monitor for livestock activities where appropriate. It is also important to account for the time lag in the response of some variables (e.g. CHL and COND) to rain events; such a lag is indicative of the first flush that results in the sediment or nutrient arriving predictably 24 to 48 hours following onset of summer storms. The concentration of COND at baseflow was initially diluted with the large volume of precipitation falling directly on the stream and in adjacent areas, but then increased a day later, reflecting the surface erosion from the watershed brought in by first flush--similar to what happens in urban setting (Seiheimer, Wei, Chow-Fraser, & Eyles, 2007).

Conclusions

Monitoring agricultural influences effectively has global importance. Large-scale water systems around the world have been degraded by the cumulative impacts of agricultural runoff.

Livestock sites are of particular concern as they have been shown to release significant levels of nutrients and sediment into the water column. Our study suggests that variation in water chemistry of first-order streams cannot be adequately captured with a program of regular grab samples, and this is consistent with findings for studies involving higher-order streams. Although grab samples can be used to gather coarse data at non-livestock sites, they are likely to under-represent the influence of cattle on a stream. Sampling programs should be designed to capture effects of hydration events as well as storm events. This is particularly important for describing TP during periods of low rain fall. Agriculturalists can also use this knowledge to avoid rotating cattle to areas where they can gain access to first-order streams, particularly during periods of low rain fall. We recommend that future studies focus on low-order streams and make interpretations that reflect agriculturally relevant seasons because only information collected at this spatial and temporal scale will be useful for devising effective best-management practices for family farms, which are arguably the only sustainable form of agriculture.

Acknowledgements

Funding for this project have been provided by grants to PC-F from Georgian Bay Forever and Sierra Club Canada, and an OGS Scholarship to CD

References

Beaulac, M. N., & Reckhow, K. H. (1982). An examination of land use- nutrient export relationships. *Journal of the American Water Resources Association, 18*(6), 1013-1024.

Borah, D. K., Bera, M., & Shaw, S. (2003). Water, sediment, nutrient, and pesticide measurements in an agricultural watershed in Illinois during storm events. *Transactions of the American Society of Agricultural Engineers, 46*(3), 18.

Bowes, M. J., House, W. A., Hodgkinson, R. A., & Leach, D. V. (2005). Phosphorus–discharge hysteresis during storm events along a river catchment: the River Swale, UK. *Water Research, 39*(5), 751-762.

Clary, W., P., & Webster, B., F. (1990). Riparian grazing guidelines for the intermountain region. *Rangelands, 12*(4), 209-212.

Correll, D. L. (1998). The Role of Phosphorus in the Eutrophication of Receiving Waters: A Review. *Journal of Environmental Quality, 27*(2), 261-266.

Correll, D. L., Jordan, T. E., & Weller, D. E. (1999). Transport of nitrogen and phosphorus from Rhode river watersheds during storm events. *Water Resources Research, 35*(8), 2513-2521.

Davies-Colley, R., J.,, Nagels, J., W.,, Smith, R., A.,, Young, R., G.,, & Phillips, C. J. (2004). Water quality impact of a dairy cow herd crossing a stream. *New Zealand Journal of Marine and Freshwater Research, 38*(4), 8.

Dieleman, C. & Chow-Fraser, P. (2012) Variation in water chemistry of first-order streams in relation to agricultural practice, landform features, storm events and season in an agriculturally dominant watershed of central Ontario, Canada

Euphrasia Historical Society. (2000). *Euphrasia.* Collingwood: Conestoga Press.

Grayson, R. B., Finlayson, B. L., Gippel, C. J., & Hart, B. T. (1996). The potential of field turbidity measurements for the computation of total phosphorus and suspended solids loads. *Journal of Environmental Management, 47*(3), 257-267.

Harris, D. J., Hibburt, C. D., Anderson, G. A., Younis, P. J., Fitspatrick, D. H., Dunn, A. C., et al. (1988). The incidence, cost and factors associated with foot lameness in dairy cattle in south-western Victoria. *Australian Veterinary Journal, 65*(6), 171-176.

King, K. W., & Harmel, R. D. (2003). Considerations in selecting a water quality sampling strategy. *Transactions of the American Society of Agricultural Engineers, 46*(1), 11.

Lind, O.T. (1974). *Handbook of Common Methods in Limnology, 2nd edition*. Iowa; Kendall/Hunt Publishing Company.

McDiffett, W., Beidler, A., Dominick, T., & McCrea, K. (1989). Nutrient concentration-stream discharge relationships during storm events in a first-order stream. *Hydrobiologia, 179*(2), 97-102.

Murphy, J. & Riley, J. 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta, *27*, 31-36

Peterson, B. J., Wollheim, W. M., Mulholland, P. J., Webster, J. R., Meyer, J. L., Tank, J. L., et al. (2001). Control of nitrogen export from watersheds by headwater streams. *Science, 292*(5514), 86-90.

Petts, G. E. (1984). *Impounded Rivers. Perspectives for Ecological Management*. Chichester: John Wiley.

Robertson, D. M., & Roerish, E. D. (1999). Influence of various water quality sampling strategies on load estimates for small streams. *Water Resources. Research., 35*(12), 3747-3759.

Seiheimer, T., Wei, A., Chow-Fraser, P., & Eyles, N. (2007). Impact of urbanization on the water quality, fish habitat, and fish community of a Lake Ontario marsh, Frenchman's Bay. *Urban Ecosystems, 10*, 299-319.

Sharpley, A.N., T. Daniel, T. Sims, J. Lemunyon, R. Stevens, and R. Parry. (2003). *Agricultural Phosphorus and Eutrophication, 2nd ed*. U.S. Department of Agriculture, Agricultural Research Service, ARS–149, 44 pp

Sharpley, A. N., Gburek, W. J., Folmar, G., & Pionke, H. B. (1999). Sources of phosphorus exported from an agricultural watershed in Pennsylvania. *Agricultural Water Management, 41*(2), 77-89.

Stevens, R. J., & Smith, R. V. (1978). A comparison of discrete and intensive sampling for measuring the loads of nitrogen and phosphorus in the river main, County Antrim. *Water Research, 12*(10), 823-830.

Swistock, B. R., Edwards, P. J., Wood, F., & Dewalle, D. R. (1997). Comparison of methods for calculating annual solute exports from six forested appalachian watersheds. *Hydrological Processes, 11*(7), 655-669.

Tilman, D., Fargione, J., Wolff, B., D'Antonio, C., Dobson, A., Howarth, R., et al. (2001). Forecasting agriculturally driven global environmental change. *Science, 292*(5515), 281-284.

Table 2.1: Summary of abbreviations for water chemistry parameters and associated transformations used prior to statistical analyses. Transformations varied, depending on the purpose of the comparisons..

Parameter	Abbreviation	Transformation for seasonal comparison	Transformation for sampling methodology comparison
Total Phosphorus	TP	LOG_e	LOG_e
Turbidity	TURB	LOG_e	LOG_e
pH	pH	EXP	N/A
Temperature	TEMP	N/A	LOG_e
Conductivity	COND	N/A	
Dissolved Oxygen	DO	N/A	
Chlorophyll	Chl	Box-Cox*	

* λ value of 0.8

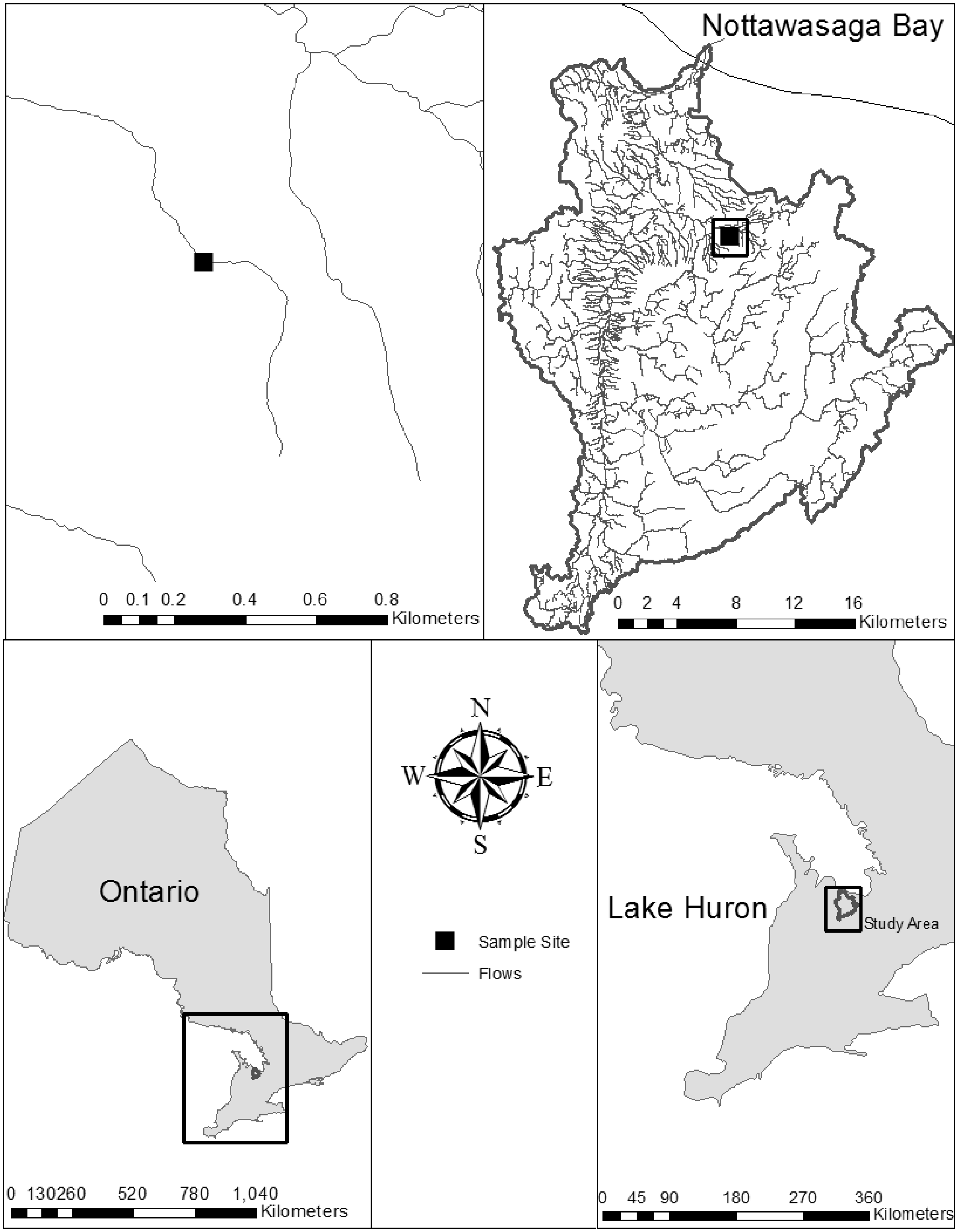


Figure 2.1: Map of the study region and sample site in the Beaver River watershed. The sample site (black square) was continuously sampled due to its high water flow and consistent agricultural influence.

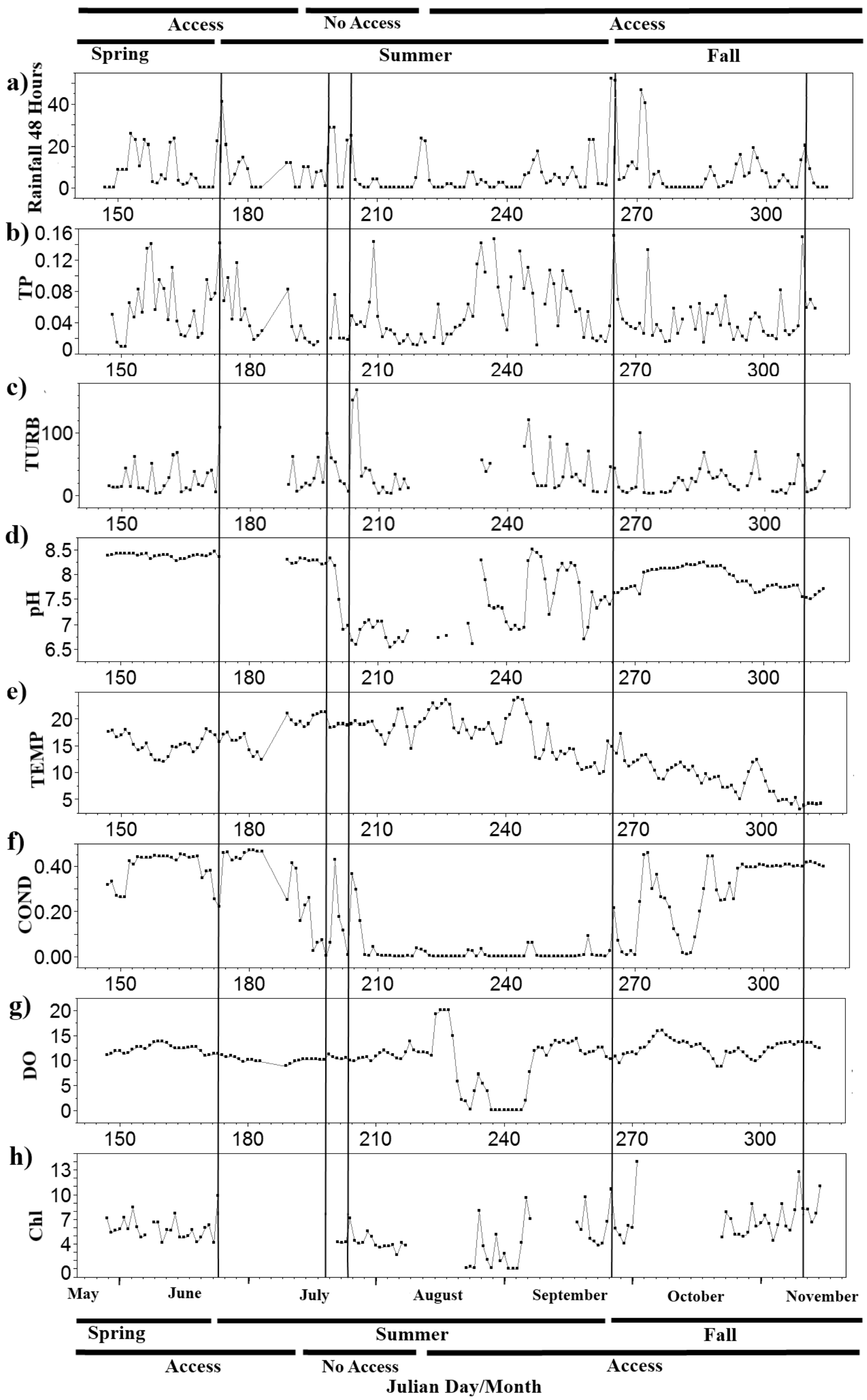


Figure 2.2: Plot of a) rainfall in the previous 48 hours (mm), b) TP (mg/L), c) TURB (NTU), d) pH, e) TEMP (Degrees C), f) COND (mS/cm), g) DO (mg/L) and h) CHL (ug/L) against time. Timing of the three seasons was determined by the agriculturally relevant calendar. "Access" and "No access" refers to the period when livestock had either direct or no access to the stream. Vertical lines mark the occurrence of peak rainfall during five rain events.

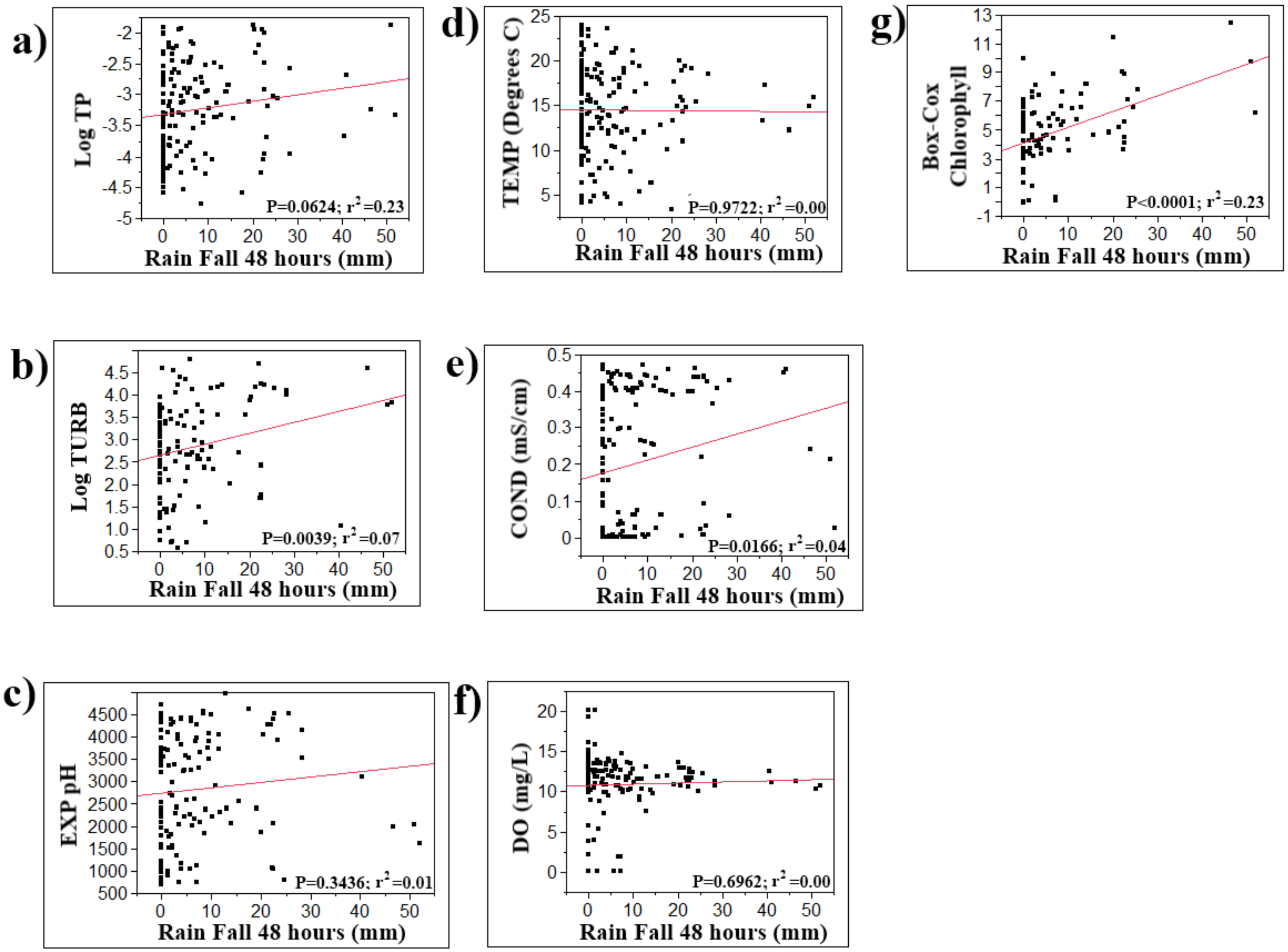


Figure 2.3: Regression relationship between a) TP (mg/L) b) TURB (NTU) c) pH d) TEMP (Degrees C) e) COND (mS/cm) f) DO (mg/L) and g) CHL (ug/L) versus rainfall over the previous 48 hours (mm).

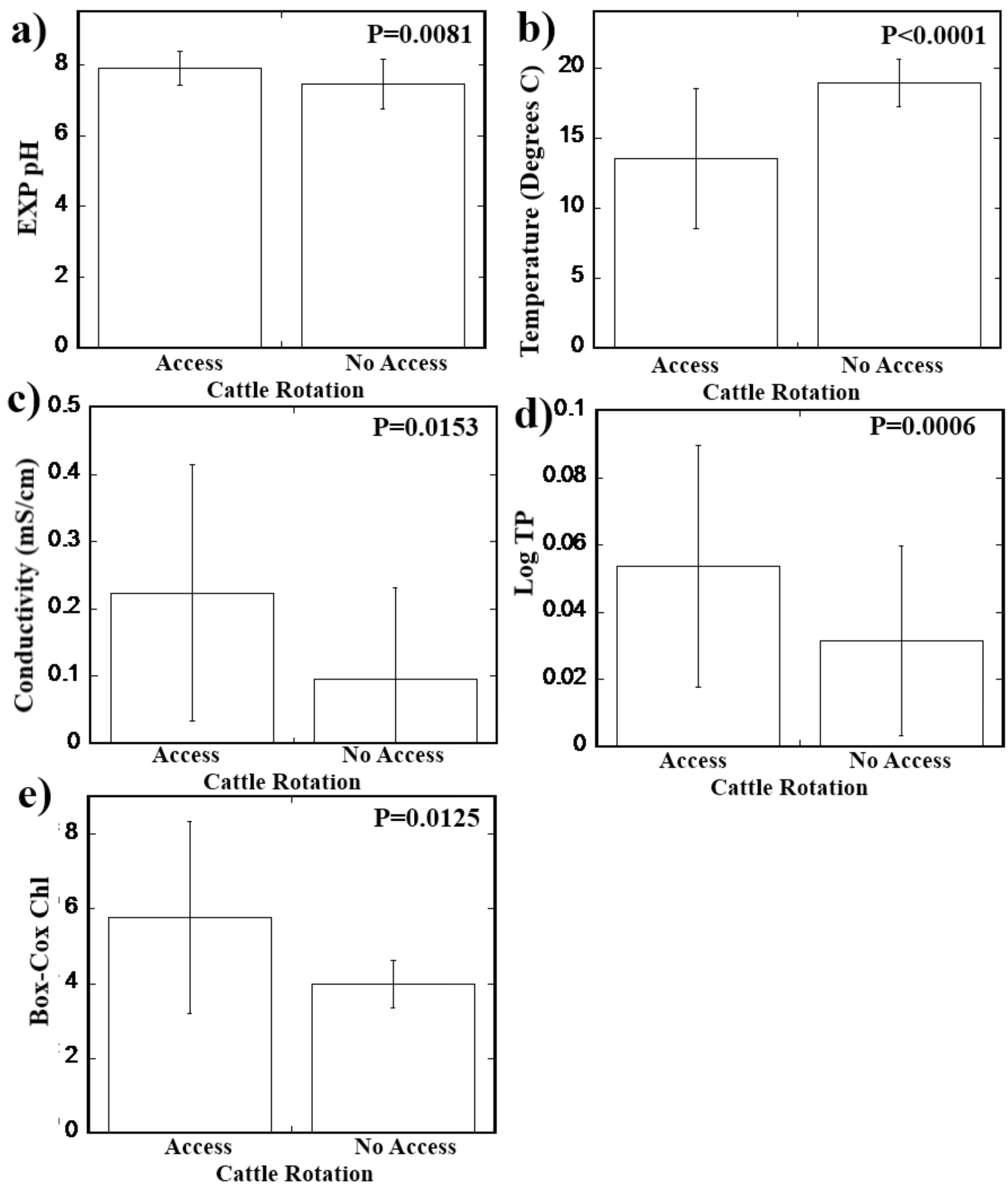


Figure 2.4: Comparison of mean a) pH b) TEMP (Degrees C) c) COND (mS/cm) d) TP (mg/L) and e) Chl (ug/L) during different cattle rotations. ‘Access’ and ‘No access’ refers to the period when livestock could or could not physically enter the stream. P-values correspond to comparison of means via a Wilcoxon rank sum test (pH, COND) or a t-test (all other variables).

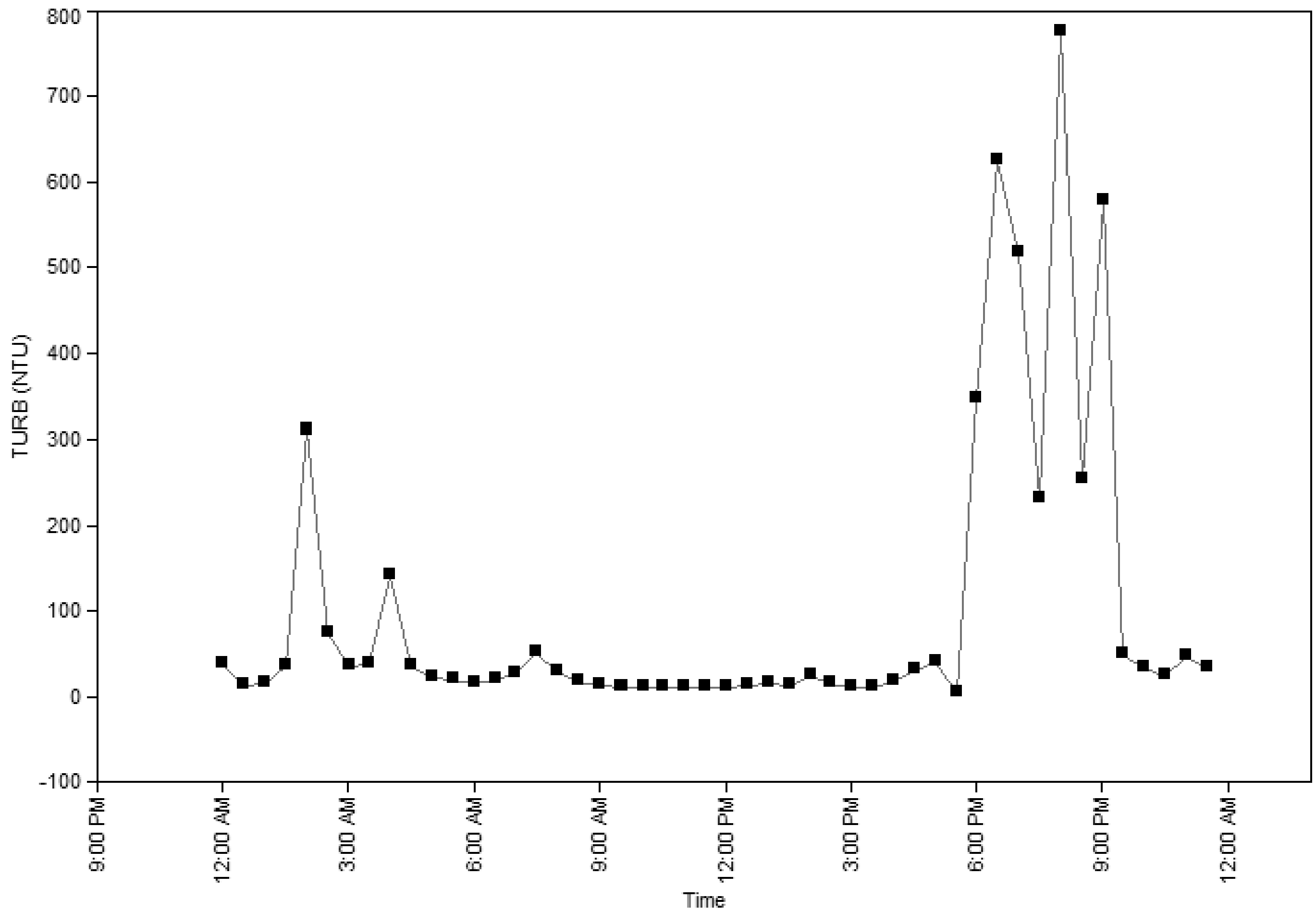


Figure 2.5: Changes in turbidity readings taken every 30 minutes on July 17, 2010. During this sampling period, there had been no significant rainfall in the area for the previous 72 hours. The peaks recorded between 7-9 pm coincide with a routine hydration event for the cattle.

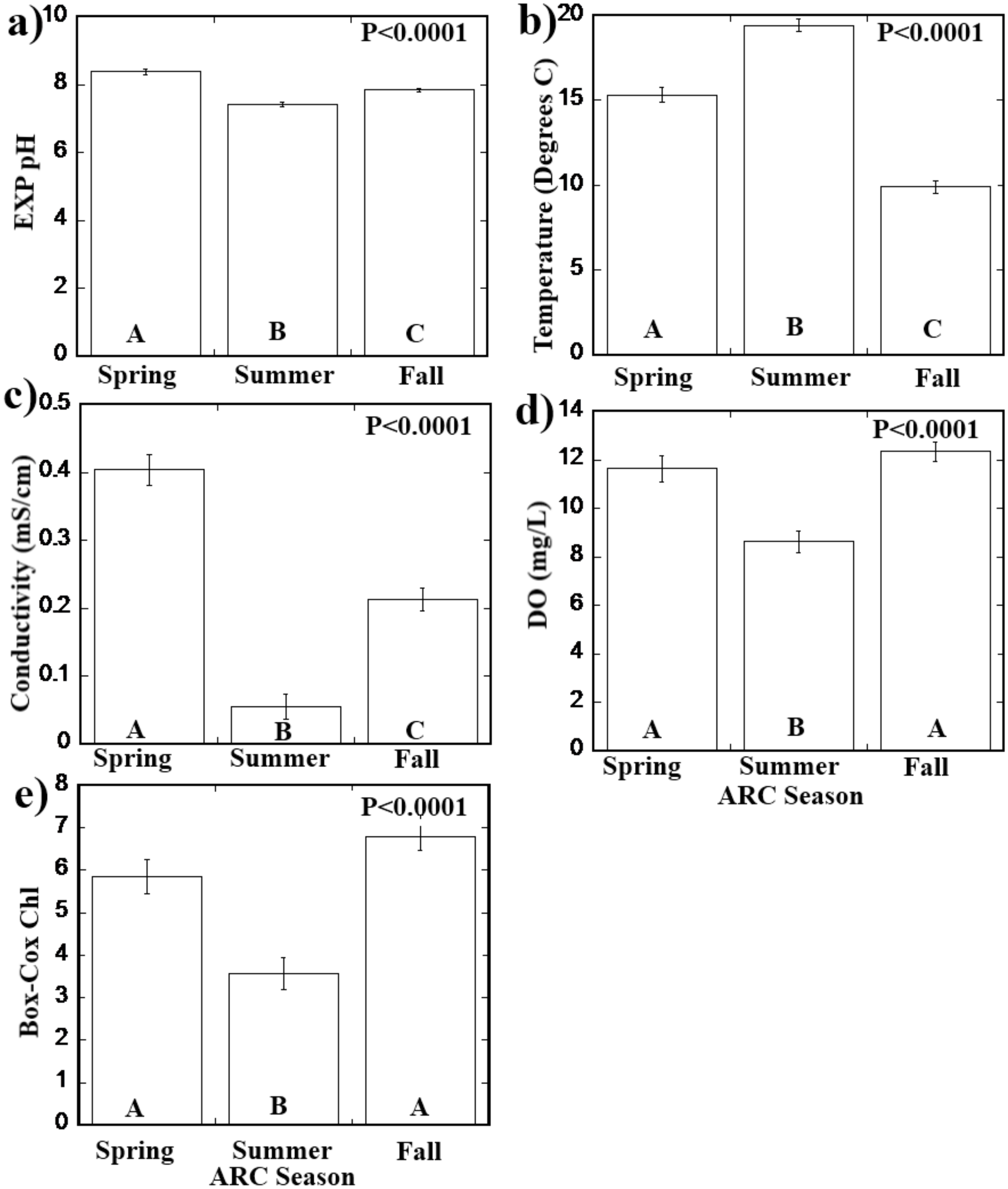


Figure 2.6: Comparison of mean a) pH b) TEMP (Degrees C) c) COND (mS/cm), d) DO (mg/L) and e) Chl (ug/L) calculated for spring, summer and fall in the agriculturally relevant calendar (ARC). Significant differences among means (ANOVA) are indicated by different letters calculated by a post hoc test.

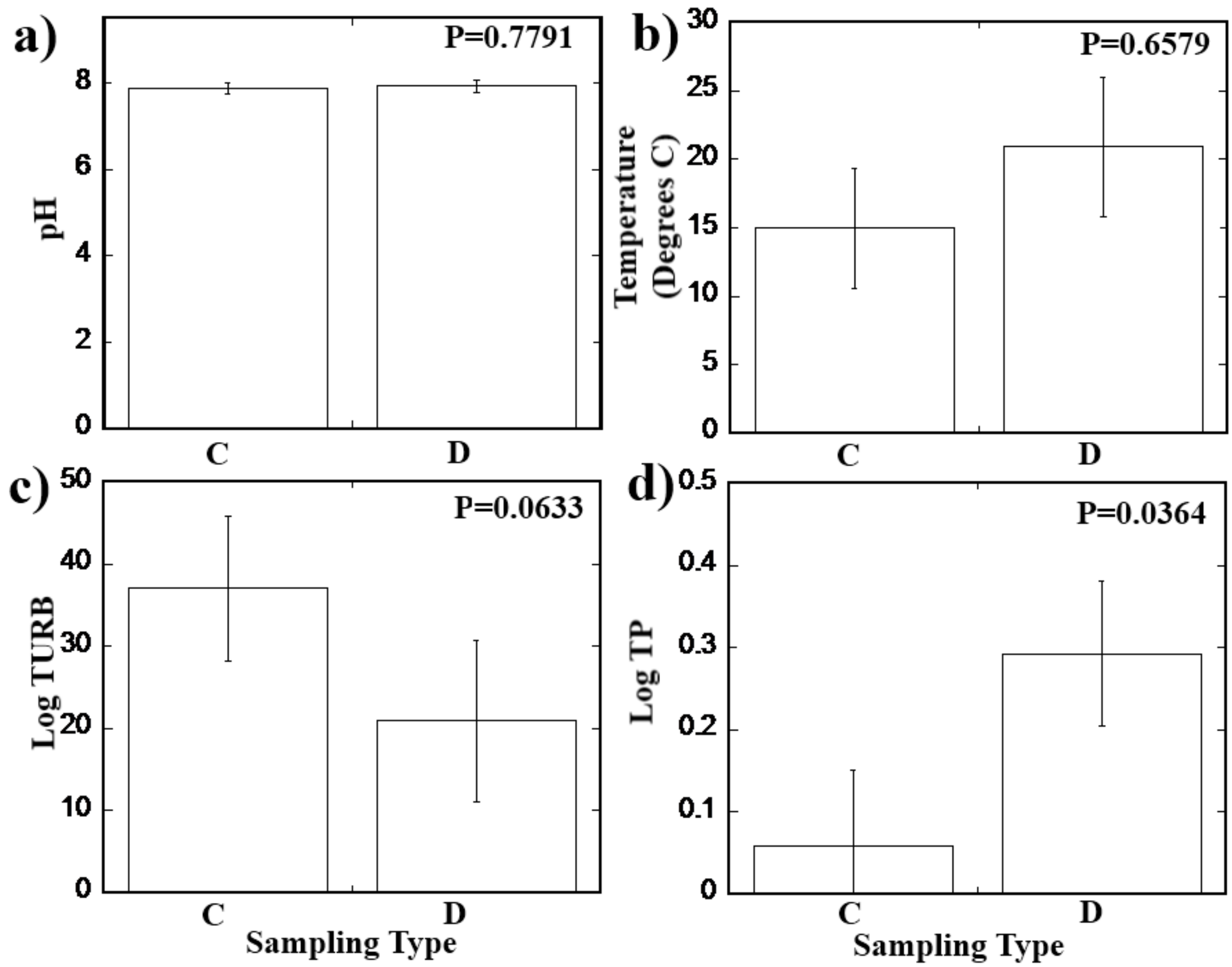


Figure 2.7 : Comparison of a) pH b) TEMP (Degrees C) c) TURB (NTU) and d) TP (mg/L) sampled continuously (C) and discretely (D). P-values correspond to t-tests comparing sampling types.

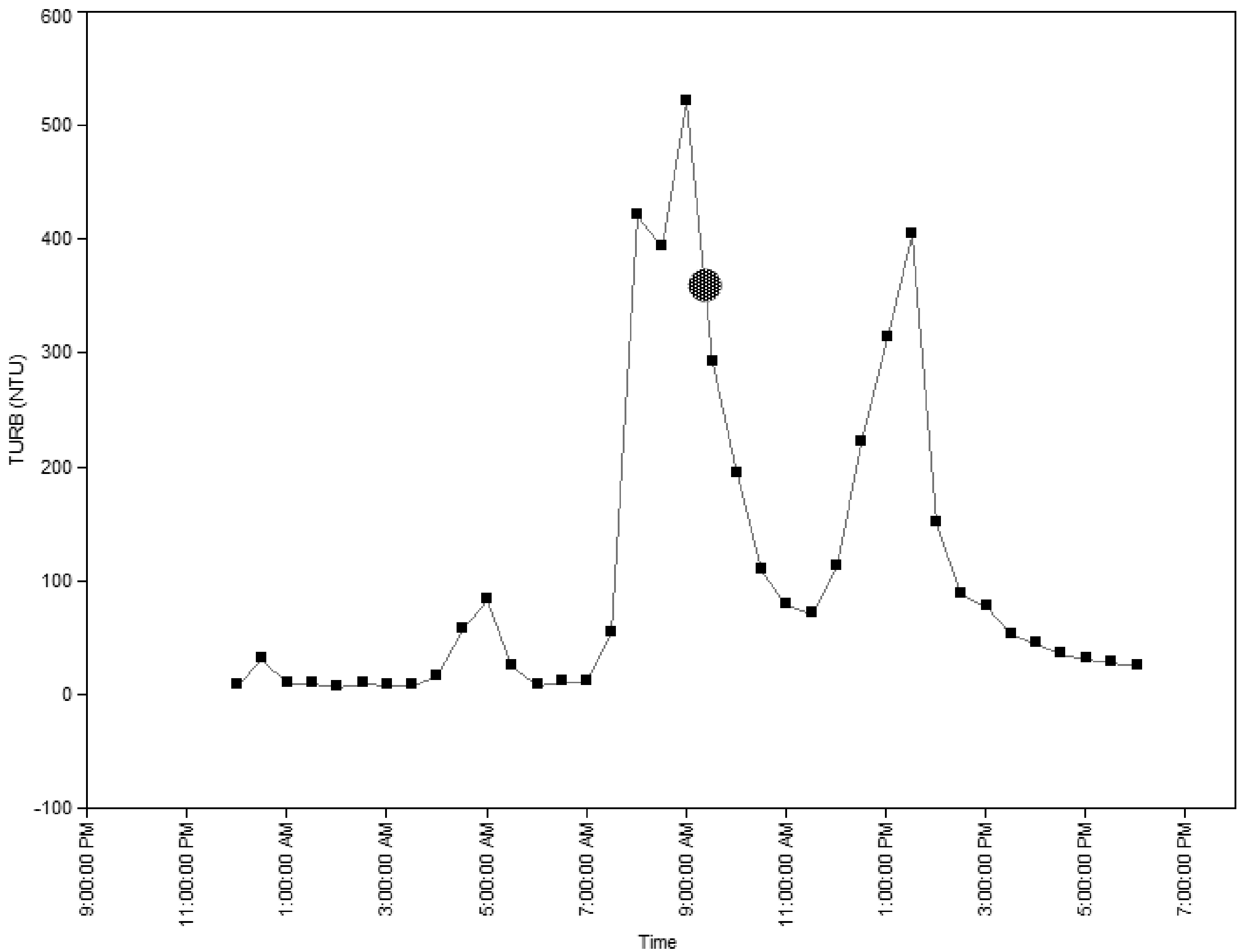


Figure 2.8: Changes in turbidity readings taken every 30 minutes during a storm event on June 22, 2010. The circle indicates the approximate time when the discrete samples were collected.

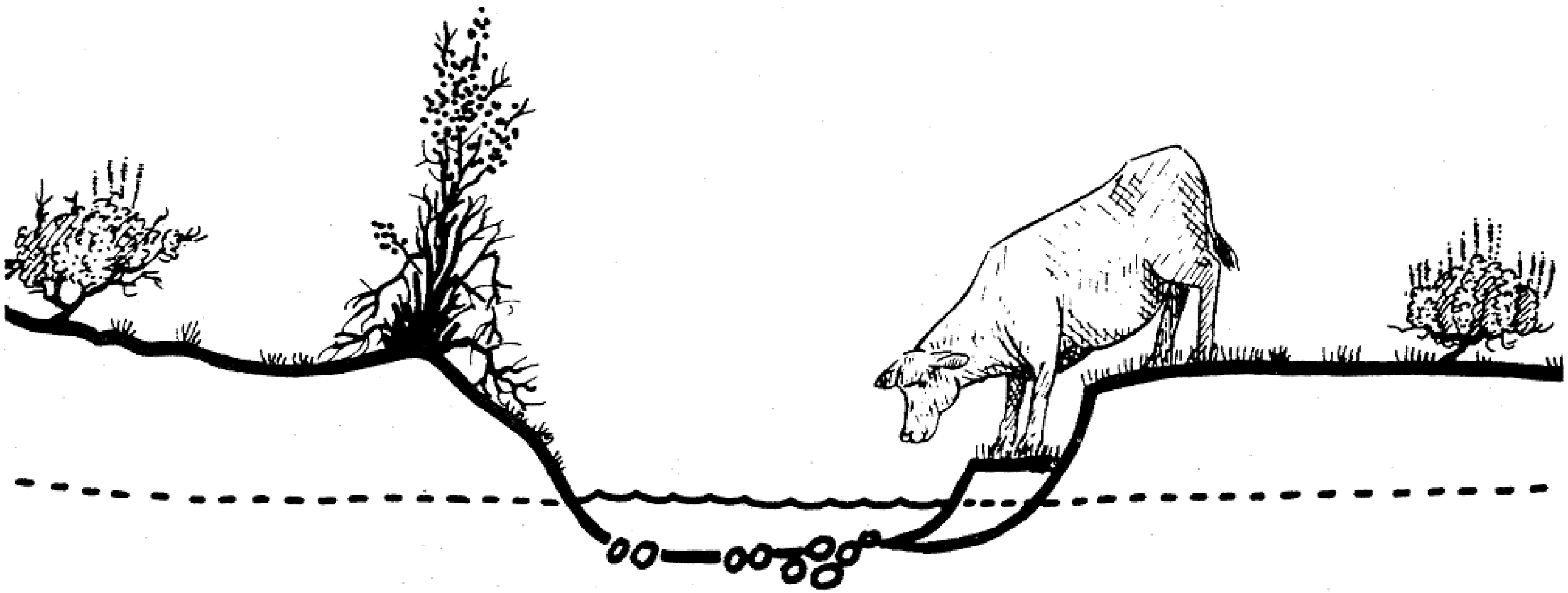


Figure 2.9: Drawing depicting common cattle hydration techniques at a stream with rocky substrate. As shown, livestock avoid damaging their cloven hooves on the rocks by leaning over the stream's banks to access the water. Image modified from Clary & Webster (1990).

The effect of agricultural practice on periphyton growth and the water chemistry of first- and second-order streams in the Beaver Valley watershed, Ontario, Canada.

Catherine Dieleman
(Corresponding Author: catherine.dieleman@gmail.com)

Patricia Chow-Fraser
(chowfras@mcmaster.ca)

McMaster University
Department of Biology
1280 Main Street West

Abstract

Agricultural runoff is rich in nitrogen, phosphorus, and sediments, which are pollutants that can accumulate in rivers and lakes and, in high concentrations, can lead to eutrophication and ultimately habitat loss and degradation. To protect downstream ecosystems from agricultural impacts it is paramount that farmers have an effective and inexpensive method to monitor nutrient runoff into their streams. Agriculturalists can then modify their nutrient application and storage methods to reduce nutrient losses for their own economic benefit and environmental gain. It is also important to understand how these impacts can move through an aquatic system to influence the water chemistry of higher-order streams. In this study we relate periphyton growth to routinely measured parameters of water quality in a farmed region of Ontario, Canada. Eighteen sites were sampled between June and July, nine of which were crop-based (soybeans, hay) and nine were livestock-based (beef) sites; twelve were first-order and six second-order streams. Clear acrylic rods were colonized with periphyton over a two-week incubation period. Periphyton growth increased with higher concentrations of total phosphorus (TP), soluble reactive phosphorus (SRP) and total-ammonia-nitrogen (TAN), but we did not find any significant difference between water-chemistry variables of first- and second-order streams. For low-order streams influenced by small family farms, acrylic rods may be an inexpensive indicator of TP concentrations, especially in a karst valley. In such environments stream length may be a stronger measure of streams than stream order since TN, TP and pH were significantly correlated with stream length.

Introduction

Runoff from agricultural practices are rich in nutrients and sediment, which in excess can to lead to eutrophication of aquatic environments and ultimately habitat loss and degradation. High levels of contamination occur when these non-point source pollutants accumulate throughout river complexes and are concentrated in high order river and lake systems. Once accrued, these limiting nutrients enable algal blooms to proliferate, and this reduces light penetration and, after senescence, can cause anoxia and mortality in aquatic life (Sharpley, et al., 1994). The impacts of this phenomenon are noted by government agencies globally, (Fraters, Boumans, van Leeuwen, & de Hoop, 2001; Sharpley, Gburek, Folmar, & Pionke, 1999) many of which have listed agriculture as the number one threat to water quality. Consequently, understanding the movement of agricultural impacts on water chemistry and effectively monitoring them is of paramount concern.

To confidently link agricultural activities with the resultant water chemistry, investigators must conduct studies on low-order streams. In these lotic environments periphyton, rather than planktonic algae dominate (Nijboer & Verdonschot, 2004). Periphyton is a polysaccharide matrix of bacteria, algae and fungi which commonly forms on aquatic substrates, such as marcophytes and rocks (Freeman & Lock, 1995). These masses easily take up nutrients from the water column, and function as the gateway between dissolved nutrients and biota in the upper trophic levels (Pringle, et al., 1988). In smaller streams, which have high volume to surface area ratios, these matrixes have the potential to greatly influence nutrient movement and function as a major nutrient reservoir (Nijboer & Verdonschot, 2004). This occurs due to characteristics, such as cell permeability and enzyme excretion, which renders periphyton sensitive to surfeit amounts of limiting nutrients such as nitrogen or phosphorus (Pringle, et al., 1988).

Due to the nature and importance of periphyton as a bioindicator, McNair & Chow-Fraser (2003) used clear acrylic rods to collect and monitor biofilms in 24 Great Lakes wetlands. Their work indicated that these rods are an excellent measure of nutrient conditions in marsh habitats. These rods have yet to be tested in agriculturally influenced lotic environments. These agroecosystems are distinct from wetlands, confounded by significant stream velocities (Ghosh & Gaur, 1998) and greater temperature and light variability, all determinants of periphyton growth (Munn, Osborne, & Wiley, 1989). We need to develop a more complete understanding of how periphyton grows in streams (Nijboer & Verdonschot, 2004), particularly in agricultural environments (Delong & Brusven, 1992) to help protect downstream water quality. .

Understanding how agricultural impacts change between low-order streams is also of great importance. Large bodied waters such as the Gulf of Mexico and Lake Erie have annually reoccurring dead zones due to presence of excessive nutrients which originate from low-order streams in agricultural lands (Matisoff, 2005; National Research Council, 2000). Up to 75% of sediment (Petts, 1984) and 50% of nutrients, such as nitrogen (Peterson, et al., 2001), which exit a watershed originate from headwater streams. As these nutrients move through entire watersheds, they accumulate, but little is known about nutrient concentrations as they move from first- to second- order streams. Alexander, et al. (2007), using a meta-analysis and modelling techniques, concluded that theoretically 65% of nitrogen in second-order streams originated from first-order waters, but to date, none of these observations have been field validated.

Here for the first time, we use acrylic rods to quantify the amount of periphyton growth in headwater streams in agriculturally dominant region of Ontario. We also present novel findings regarding the change in agriculturally mediated pollutants between first- to second-order streams. Past research leads us to predict that i) agricultural impacts will increase from first to second-order streams and ii) that periphyton growth will increase with higher concentrations of limiting nutrients.

Methods

Watershed Description

The Beaver Valley drainage basin ($618km^2$) is a quaternary watershed located in south western Ontario on the shores of Georgian Bay and thus Lake Huron (Figure 3.1). Although a slow conversion to recreational use has started in the last ten years the dominant land use remains agricultural, as it has been since it was settled in the mid 1800s (Euphrasia Historical Society, 2000). The operations in the region are small scale family farms with generally less than 100 cattle. Crop and livestock rotations are still a common practice, predominantly growing row crops such as corn and as well as cereal crops such as grains. The primarily clay based soils in an area in combination with the heavy rainfalls requires that the majority of the watershed's farm land to be tile drained. This is true as well for land found on the valley walls and near the Niagara Escarpment, a prominent natural feature in the watershed. The limestone and shale base of the region gives the water its naturally basic characteristics (Euphrasia Historical Society, 2000). Combined with the dominant agricultural land use and the karst topography in the region, rendering first and second order streams commonplace, the watershed provides a plethora of potential study sites. The utilization of a single watershed ensures that all study sites are exposed to similar background water chemistry, agricultural practices and weather conditions.

Study Site Selection

We used ArcMap 10.0 (ESRI Inc., Redlands, California) to select all of our streams. A multi-criteria analysis was employed to select sites which have been previously identified as 1) permanently flowing 2) either first- or second-order streams according to Strahler (1952) 3) draining only one type of agricultural practice (livestock or crop), and 4) had minimal buffer strips. A combination of air photos and geographic information system (GIS) files were utilized to complete this task. These features ensured that we were only working with headwater streams, which were not confounded by multiple agricultural activities nor had nutrient inputs too low to monitor. From the 62 potential study sites, 18 were selected after ground-truthing. Nine livestock sites were defined by a combination of pasture land, manure storage and a barn to represent practices common in Ontario and nine crop sites were selected that were associated with evidence of current crop activities, such as tillage and planting. Twelve of these were first-order streams, while 6 were second-order (Table 3.1).

Data Collection

Sampling occurred between June 14th and July 27th 2011; we sampled for periphyton and water chemistry every 14 days. All water samples were collected following protocols outlined by Lind (1974). We were unable to sample various sites during the study period due to prolonged low water levels. Total nitrogen (TN), total nitrate-nitrogen (TNN), total ammonia-nitrogen (TAN) and total phosphorus (TP) samples were collected in clean, acid washed 110ml and 200ml Snap'N'Seal™ containers and placed on ice, and either processed in field (TNN, TAN) or stored in a freezer (-4◦C) for further processing in-lab (TN,TP). Total suspended solids (TSS) and soluble reactive phosphorus (SRP) water samples were gathered in freshly acid washed 1 litre Nalgene™ bottles and promptly put on ice until they could be filtered in the field. Temperature (TEMP) and pH, turbidity (TURB) and conductivity (COND) were collected in-situ via Orion Smart Check™ 020000A pH/temperature meter, LaMotte™ 2020e Turbidimeter and YSI™ 6600 multiprobe respectively.

Periphyton samples were grown on clear acrylic rods 0.6cm in diameter which were scored every 5cm following the procedure described by McNair & Chow-Fraser (2003). The length of the rods depended on stream depth, ranging between 10 and 25cm. Each rod was first wiped with 90% isopropyl alcohol to remove any oils from handling, before they were inserted in the stream as a set of 3 to 6 in a latin-square pattern. Before placing the rods, a $1m^2$-area around each sample site had to be cleared of macrophytes and sedges to standardize light exposure. Two-week and four-week incubation periods were used, after which rods were removed and samples were collected in aluminum foil, placed on ice and finally stored in a freezer for later processing.

At the time when water and periphyton samples were collected, we also collected information on flow rate, stream width and average depth (Table 3.1). Flow rates were approximated by measuring the average time it took an orange peel to travel 10 to 30 cm in the centre of the stream, while stream width was measured from each edge of the water. Average depth was taken from values collected with a ruler at the edge, quarterly and halfway across the stream. Stream length was measured ex-situ via ArcMap 10.0 (ESRI Inc., Redlands, California).

Sample Processing

In the field, TSS was filtered through pre-weighed GC filters (0.45µm pore size), which were frozen for later processing in-lab. Once in the laboratory filters were thawed, heated for an hour at 100◦C, desiccated for another hour and finally weighed. In the field SRP samples were collected from TSS filtrate and stored in acid washed, 110ml Snap’N’Seal™ containers and frozen. In the lab TP and SRP samples were processed using the molybdenum blue method (Murphy & Riley, 1962) with a Genesys 10 UV Spectrophotometer to determine the presence of phosphorus. Total phosphorus was digested with potassium persulfate and autoclaved at 15 psi and 120°C to release phosphorus from any organic bonds. TN, TNN and TAN samples were all processed using a HACH™ DR 890 colorimeter following HACH™ methods. Periphyton growth was represented by chlorophyll *a* values and was analyzed by placing the 5cm segments into 10ml of 90% acetone for 24-96 hours for extraction (McNair & Chow-Fraser, 2003). The chlorophyll *a* absorbance was measured by a Fluorometer TD-700 before and after acidification to account for phaeophytin pigments. Values are reported as ug/cm^2/day to account for the amount of the substrate the periphyton growth covered and growth period.

Statistics

All statistical tests were completed in SAS JMP version 7.0.1 (SAS Institute Inc., Cary, North Carolina). All water chemistry parameters, periphyton, stream depth, stream width and discharge data were $\log_e$ transformed to minimize hetroscedasticity, except for COND, TEMP, TAN, TNN, TURB and flow data which were Box-Cox transformed with λ values of -1.2, -0.6,-0.4,-0.4, -0.2 and 0.2 respectively. T-tests and linear regression analyses were run as appropriate.

Results

Due to an uncharacteristically wet spring followed by a very dry summer, the water levels in many first- and even second-order streams dropped below 5cm in depth. Collecting uncontaminated water samples under such conditions proved to be a challenge as the sediment was easily disturbed. As a result, many of the water-chemistry variables collected at depths < 5cm were contaminated and had to be omitted from further analyses (Figure 3.2).

Stream Order

We found no significant differences between first- and second-order streams for most of the dependent variables and physical features of the streams (t-test; $P>0.05$). The only exception was stream discharge, for which second-order streams had significantly lower rates compared to first-order streams (Table 3.2). Given these findings, we compared water chemistry values to stream length, another method which has been used to characterize streams, as demonstrated by Fitzpatrick, et al. (2001). TN, TP and pH all were all significantly related to stream length (Figure 3.3). TN and pH both increased in magnitude for longer streams, while TP decreased. TSS and COND did not have significant relationships with stream length, although their trends support those of TP and pH respectively.

Periphyton Growth

Because of contamination problems in shallow water, we had to eliminate all data associated with the 28 days of incubation. Despite the small sample size, there was a significant relationship between periphyton growth (14 days) and TP, SRP and TAN (Figure 3.4).

Discussion

Stream Order

Stream order is a common indicator of the physical features of streams such as discharge, flow, width and depth, all of which increase predictably downstream (Wollheim, et al., 2001). The river continuum concept and nutrient spiralling are built upon this idea, as with greater discharge rates higher concentrations of nutrients are present (Wollheim, et al., 2001). The nutrient levels are then either suppressed or amplified by interactions with the biota (Newbold, Elwood, O'Neill, & Winkle, 1981). Standford & Ward's (1983, 1995) serial discontinuity concept points out problems in the aforementioned theories, which are caused by both human-made dams and beaver impoundments. Although impacts caused by dams are different from those described here, the same natural discontinuity which defies the present understanding of stream order and related nutrient movement are apparent.

During the dry summer months, evaporation in these agriculturally influenced first-order streams can cause the flow to be depleted before it reaches the second-order stream. Thus, while second order streams still have water, they are no longer directly connected to their own headwaters. Karst topography, such as that found in the Beaver Valley, can also interfere with the direct movement of waters from first-order to second-order streams. Finally, the length of the first order streams in the Beaver Valley can often surpass those of the second order, as they can drain valley walls and the Niagara Escarpment itself (Table 3.1; Figure 3.1). This discontinuity and difference in stream length can result in second-order streams having significantly lower discharge rates than those of first order. The lack of difference in flow, width and depth can result in nutrient concentrations that are similar between the two orders.

Due to this confounding problem with stream order, we used stream length instead of stream order as a predictor of trends in water chemistry. As was found by Alexander, et al. (2007), our TN as well as pH levels increased with stream length, likely because water of longer streams have a greater opportunity to interact with the limestone and shale and nitrogen in porewater. The limestone bedrock would release Ca^{2+} ions that makes the water naturally alkaline, with a higher pH. Unlike the other parameters, however, TP levels tended to be lower at sites with longer stream lengths, most likely because inorganic phosphorus becomes bound to sediment and settle out or are taken up by biota. Phosphorus is often limiting in aquatic environments with much shorter uptake times than nitrogen in both undeveloped (Davis &

Minshall, 1999) and agriculturally influenced streams (Bernot, Tank, Royer, & David, 2006). The average N:P ratio at all our sites was approximately 74. Thus, it is likely that local flora and fauna were able to absorb both the agriculturally mediated and the naturally occurring phosphorus, decreasing its concentration as it travelled downstream. TSS levels also decreased, albeit not significantly, with increasing stream length. It is also possible that over the longer lengths associated phosphorus settled out with the sediment. These findings suggest that in a karst valley, such as the Beaver Valley, defining streams by stream length may be more effective than using stream order.

Periphyton Growth

Numerous studies have examined the relationship between nutrient and periphyton growth (Delong & Brusven, 1992; Munn, et al., 1989; Nijboer & Verdonschot, 2004; Wollheim, et al., 2001). These studies have acknowledged that the bacterial masses appear to be limited by phosphorus (Freeman et al., 1995), while the algae depends on nitrogen inputs, of either NH_4^+ or NO_3^- (Nijboer & Verdonschot, 2004). Our results from an agroecosystem are consistent with the other publications that first used acrylic rods to measure periphyton in lotic (Lowe and Pan, 1996) and lentic systems (McNair & Chow-Fraser, 2003), demonstrating a significant relationship between periphyton biomass and concentrations of N and P. The limited availability of phosphorus may explain why periphyton biomass was significantly related to both TP and SRP, whereas McNair & Chow-Fraser (2003) only observed a relationship with TP. The trends associated with TAN may reflect the preference of bacteria for ammonia over other forms of nitrogen.

The significant relationship between nutrients and periphyton biomass renders the inexpensive acrylic rods an attractive method to monitor stream quality. Rods can be placed in lotic systems which are suspected to be impacted and if dramatic periphyton growth is observed after two-weeks, an excess of limiting nutrients can be assumed. Farmers in particular could place the rods in drainage ditches throughout the growing season to assess if they are losing expensive fertilizers to runoff due to over application. This simple procedure may actually allow farmers to evaluate the effectiveness of best-management practices and lead to improvements in soil and nutrient conservation programs. Four-week incubation periods are not recommended as the rods are prone to falling over in the clay-based streams whenever there are large storm events.

Conclusion

Understanding the movement and monitoring agricultural impacts is key to protecting downstream habitats from major eutrophication events like those of the Gulf of Mexico and Lake Erie. Acknowledging the discontinuity which can occur naturally in karst environments as well as during the dry periods is important when modelling nutrient movement from headwaters to river mouths. This is particularly true for head waters as they are the source of >75% of sediment (Petts, 1984) and limiting nutrients which exit a watershed. Under these conditions low-order streams do not follow theories outlined in the river continuum concept nor long-term nutrient spiralling for baseline flows. Although stream order can be a good indicator of stream activity, in a karst valley environment, stream length may be a superior measure.

Clear acrylic rods have a great potential to be used as an inexpensive bioindicator of excess limiting nutrients for agriculturalists and conservationalists alike. Their application in drainage ditches and headwater streams could provide information which saves agriculturalists financially and further enables conservationalists to better protect watershed quality. Future research which examines nutrient and periphyton growth on acrylic rods on higher order streams or longer stream lengths could increase the range of conditions that would be suitable for this technology. Only by working with farmers and helping them to understand the problems associated with nonpoint pollution can we solve issues such as that currently experienced in the Gulf of Mexico and in Lake Erie.

Acknowledgements

Funding for this project have been provided by grants to PC-F from Georgian Bay Forever and Sierra Club Canada, and an OGS Scholarship to CD

References

Alexander, R. B., Boyer, E. W., Smith, R. A., Schwarz, G. E., & Moore, R. B. (2007). The role of headwater streams in downstream water quality. *Journal of American Water Resources Association*, *43*(1), 41-49.

Bernot, M. J., Tank, J. L., Royer, T. V., & David, M. B. (2006). Nutrient uptake in streams draining agricultural catchments of the midwestern United States. *Freshwater Biology, 51*(3), 499-509.

Davis, J. C., & Minshall, G. W. (1999). Nitrogen and phosphorus uptake in two Idaho (USA) headwater wilderness streams. *Oecologia, 119*(2), 247-255.

Delong, M. D., & Brusven, M. A. (1992). Patterns of periphyton chlorophyll α in an agricultural nonpoint source impacted stream *Journal of the American Water Resources Association,* *28*(4), 731-741.

Euphrasia Historical Society. (2000). *Euphrasia.* Collingwood: Conestoga Press.

Fitzpatrick, F. A., Scudder, B. C., Lenz, B. N., & Sullivan, D. J. (2001). Effects of multi-scale environmental characteristics on agricultural steam biota in eastern Wisconsin. *Journal of the American Water Resources Association, 37*(6), 1489-1507.

Fraters, D., Boumans, L. J. M., van Leeuwen, T. C., & de Hoop, W. D. (2001). Monitoring nitrogen leaching for the evaluation of the dutch minerals policy for agriculture in clay regions. *The scientific world journal, 1*(1), 758-766.

Freeman, C., Chapman, P. J., Gilman, K., Lock, M. A., Reynolds, B., & Wheater, H. S. (1995). Ion exchange mechanisms and the entrapment of nutrients by river biofilms. *Hydrobiologia, 297*(1), 61-65.

Freeman, C., & Lock, M. A. (1995). The biofilm polysaccharide matrix: A buffer against changing organic substrate supply? *Limnology and Oceanography, 40*(2), 272-279.

Ghosh, M., & Gaur, J. P. (1998). Current velocity and the establishment of stream algal periphyton communities. *Aquatic Botany, 60*(1), 1-10.

Lind, O.T. (1974). *Handbook of Common Methods in Limnology, 2nd edition*. Iowa; Kendall/Hunt Publishing Company.

Lowe, R.L., and Pan, Y. (1996). Benthic algal communities as bio-logical monitors. In Stevenson, R.J., Bothwell, M.L., Lowe, R.L (ed) .(1996). *Algal ecology: freshwater benthic ecosystems* (pp. 705-739). New York, Academic Press.

Matisoff, G. (2005). Lake Erie trophic status collaborative study. *Journal of Great Lakes Research, 31*(1), 1-10.

McNair, S. A., & Chow-Fraser, P. (2003). Change in biomass of benthic and planktonic algae along a disturbance gradient for 24 Great Lakes coastal wetlands. *Canadian Journal of Fisheries and Aquatic Sciences, 60*, 676-689.

Munn, M., Osborne, L., & Wiley, M. (1989). Factors influencing periphyton growth in agricultural streams of central Illinois. *Hydrobiologia*, *174*(2), 89-97.

Murphy, J. & Riley, J. 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta, *27*, 31-36

National Research Council. (2000). *Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution*: The National Academies Press.

Newbold, J. D., Elwood, J. W., O'Neill, R. V., & Winkle, W. V. (1981). Measuring Nutrient Spiralling in Streams. *Canadian Journal of Fisheries and Aquatic Sciences, 38*(7), 860-863.

Nijboer, R. C., & Verdonschot, P. F. M. (2004). Variable selection for modelling effects of eutrophication on stream and river ecosystems. *Ecological Modelling, 177*(1–2), 17-39.

Peterson, B. J., Wollheim, W. M., Mulholland, P. J., Webster, J. R., Meyer, J. L., Tank, J. L., et al. (2001). Control of Nitrogen Export from Watersheds by Headwater Streams. *Science, 292*(5514), 86-90.

Petts, G. E. (1984). *Impounded Rivers. Perspectives for Ecological Management*. Chichester: John Wiley.

Pringle, C. M., Naiman, R. J., Bretschko, G., Karr, J. R., Oswood, M. W., Webster, J. R., et al. (1988). Patch Dynamics in Lotic Systems: The Stream as a Mosaic. *Journal of the North American Benthological Society, 7*(4), 503-524.

Sharpley, A. N., Chapra, S. C., Wedepohl, R., Sims, J. T., Daniel, T. C., & Reddy, K. R. (1994). Managing Agricultural Phosphorus for Protection of Surface Waters: Issues and Options. *Journal of Environmental Quality, 23*(3), 437-451.

Sharpley, A. N., Gburek, W. J., Folmar, G., & Pionke, H. B. (1999). Sources of phosphorus exported from an agricultural watershed in Pennsylvania. *Agricultural Water Management, 41*(2).

Strahler, A., N. (1952). Hypsometric (area-altitude) analysis of erodional topography *Geological Society of America Bulletin, 63*(11), 1117-1142.

Wollheim, W. M., Peterson, B. J., Deegan, L. A., Hobbie, J. E., Hooker, B., Bowden, W. B., et al. (2001). Influence of Stream Size on Ammonium and Suspended Particulate Nitrogen Processing. *Limnology and Oceanography, 46*(1), 1-13.

Ward, J.V. & Standord, J.A.(1983) Serial discontinuity concept of lotic ecosystems. In Fontaine, T.D., Bartell, S.M. (1983). *Dynamics of Lotic Systems* (pp. 29-42). Ann Arbor, Ann Arbor Science

Ward, J. V., & Stanford, J. A. (1995). The serial discontinuity concept: extending the model to floodplain rivers. *Regulated Rivers Research & Management, 10*(159-168), 159.

Table 3.1: Description of physical features of study sites.

Site	Agriculture Type	Stream Order	Stream Width (cm)	Stream Depth (cm)	Stream Flow Rate (cm/s)	Stream Discharge (m^3/s)	Stream Length (m)
CM 1	Crop	1	58.8 ± 7.09	2.0 ± 0.35	10.0 ± 1.76	0.001 ± 0.0002	1115
CM 2	Crop	1	66.0 ± 2.94	10.3 ± 1.30	179.5 ± 49.66	0.121 ± 0.0096	1117
CM 15	Crop	1	43.0 ± 0.00	7.6 ± 0.00	0.03 ± 0.00	0.000 ± 0.0000	183
CM 16	Crop	1	98.5 ± 8.50	3.9 ± 0.52	3.6 ± 0.97	0.001 ± 0.0003	826
CM 17	Crop	1	26.5 ± 5.50	2.8 ± 0.51	14.0 ± 14.00	0.001 ± 0.0007	399
CM 18	Crop	1	35.0 ± 8.19	1.6 ± 0.58	8.3 ± 8.34	0.001 ± 0.0012	203
LM19	Livestock	1	83.0 ± 15.00	5.8 ± 0.90	59.0 ± 0.00	0.038 ± 0.0000	1412
LM20	Livestock	1	64.0 ± 0.00	8.7 ± 0.00	0.0 ± 0.0	0.000 ± 0.0000	570
LM24	Livestock	1	161.3 ± 33.38	5.8 ± 0.84	394.0± 75.75	0.314 ± 0.2136	131
LM25	Livestock	1	200.0 ± 12.66	20.7 ± 1.35	42.8 ± 22.32	0.162 ± 0.0795	1119
LM26	Livestock	1	251.3 ± 13.63	10.4 ± 2.33	46.2 ± 11.51	0.139 ± 0.0675	126
LM30	Livestock	1	98.8 ± 15.75	5.6 ± 1.28	9.9 ± 3.60	0.006 ± 0.0024	203
CM 1/2	Crop	2	62.5 ± 5.97	2.6 ± 1.19	28.2 ± 15.49	0.001 ± 0.0006	2930
CM 15/16	Crop	2	91.0 ± 31.00	3.8 ± 0.62	2.3 ± 0.00	0.001 ± 0.0000	1332
CM 17/18	Crop	2	14.9 ± 4.05	1.4 ± 0.56	22.7 ± 17.87	0.000 ± 0.0001	601
LM19/20	Livestock	2	330.0 ± 20.00	9.8 ± 1.46	219.3 ± 0.00	0.861 ± 0.0000	2009
LM24/25	Livestock	2	139.0 ± 1.00	15.4 ± 1.14	5.7 ± 1.52	0.014 ± 0.0005	1275
LM26/30	Livestock	2	103.3 ± 9.39	6.3 ± 0.63	7.8 ± 4.10	0.466 ± 0.0022	375

Table 3.2: Comparison of average water chemistry parameter responses by stream order. Significant relationships are shown in bold. P-values are based on normalized transformations for each parameter.

Parameter	Mean by Stream Order		P-Value
	1	2	
TN (mg/L)	3.46 ± 5.00	2.86 ± 1.79	0.5979
TNN (mg/L)	0.12 ± 0.17	0.11 ± 0.17	0.5812
TAN (mg/L)	0.03 ± 0.03	0.10 ± 0.15	0.1513
TP (mg/L)	0.03 ± 0.03	0.04 ± 0.05	0.6839
SRP (mg/L)	0.02 ± 0.02	0.02 ± 0.01	0.9718
TSS (mg/L)	9.65 ± 9.86	4.29 ± 3.83	0.3577
TURB (NTU)	2.01 ± 1.27	2.57 ± 2.53	0.5910
COND (uS/cm)	347.00 ± 78.33	366.63 ± 122.75	0.9100
pH	7.93 ± 0.25	8.11 ± 0.19	0.0692
TEMP	15.25 ± 3.75	15.80 ± 4.09	0.7575
Width (cm)	113.57 ± 77.27	152.25 ± 128.85	0.1681
Depth (cm)	7.56 ± 6.01	6.01 ± 5.23	0.1561
Flow (cm/s)	80.90 ± 138.53	29.10 ± 55.91	0.2320
Discharge (m^3/s)	**877.44 ± 280.11**	**608.36 ± 415.47**	**0.0116**

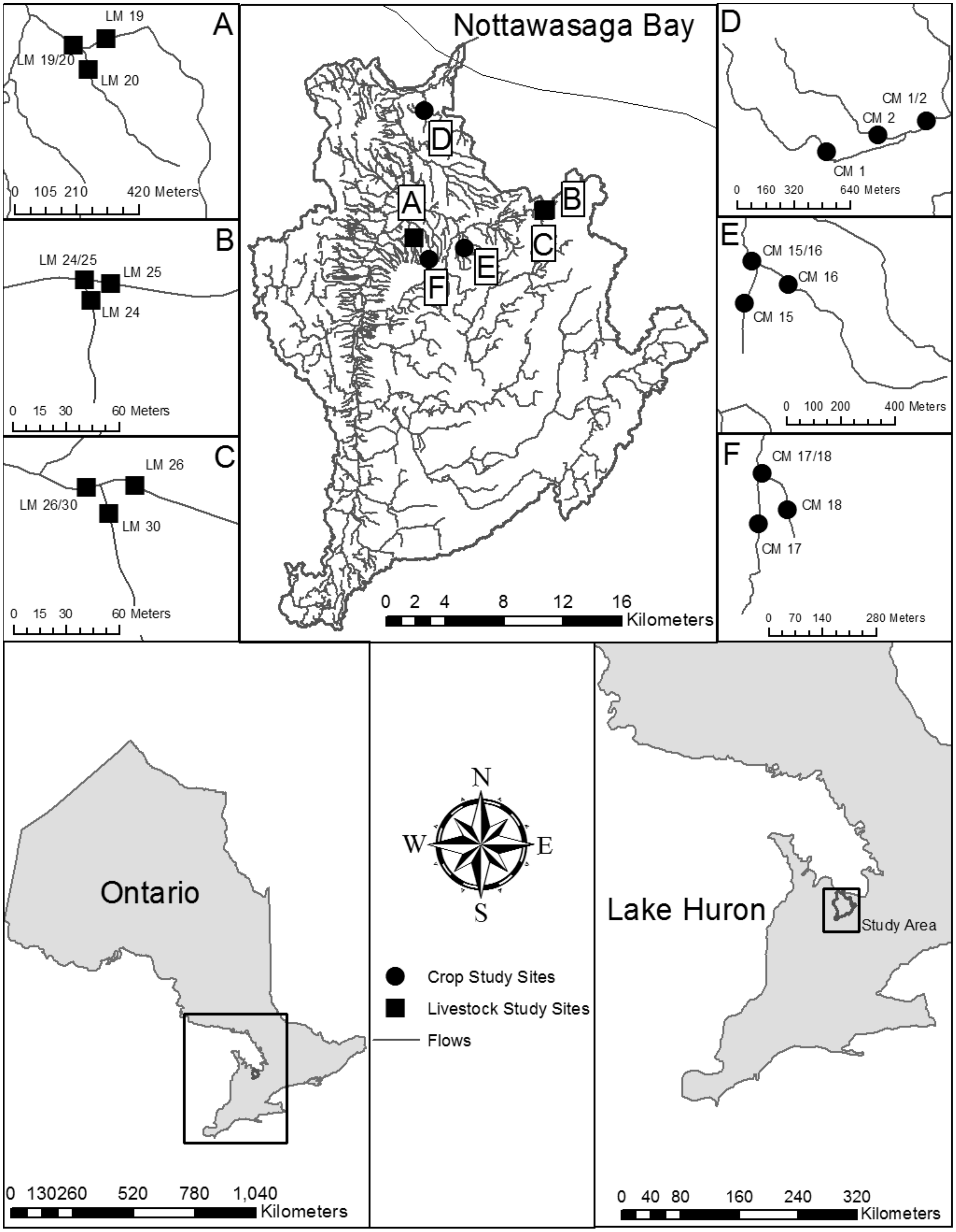


Figure 3.1: Study region and sample site map. Crop based agriculture sites are shown as black circles, while livestock are shown as black squares.

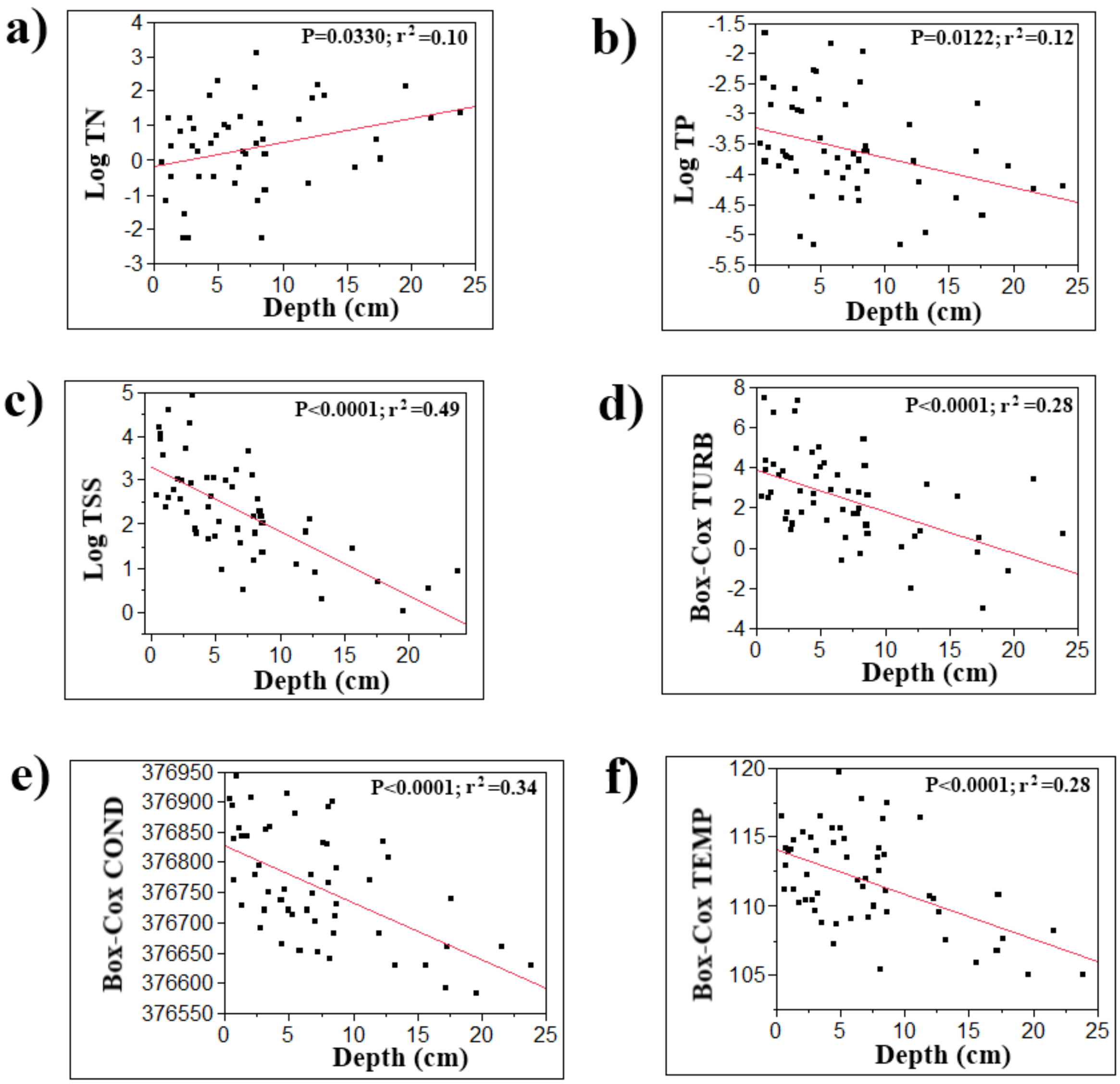


Figure 3.2: Relationship between a) TN (mg/L) b) TP (mg/L) c) TSS (mg/L) d) TURB (NTU) e) COND (uS/cm) and f) TEMP (Degrees C) and stream depth (cm).

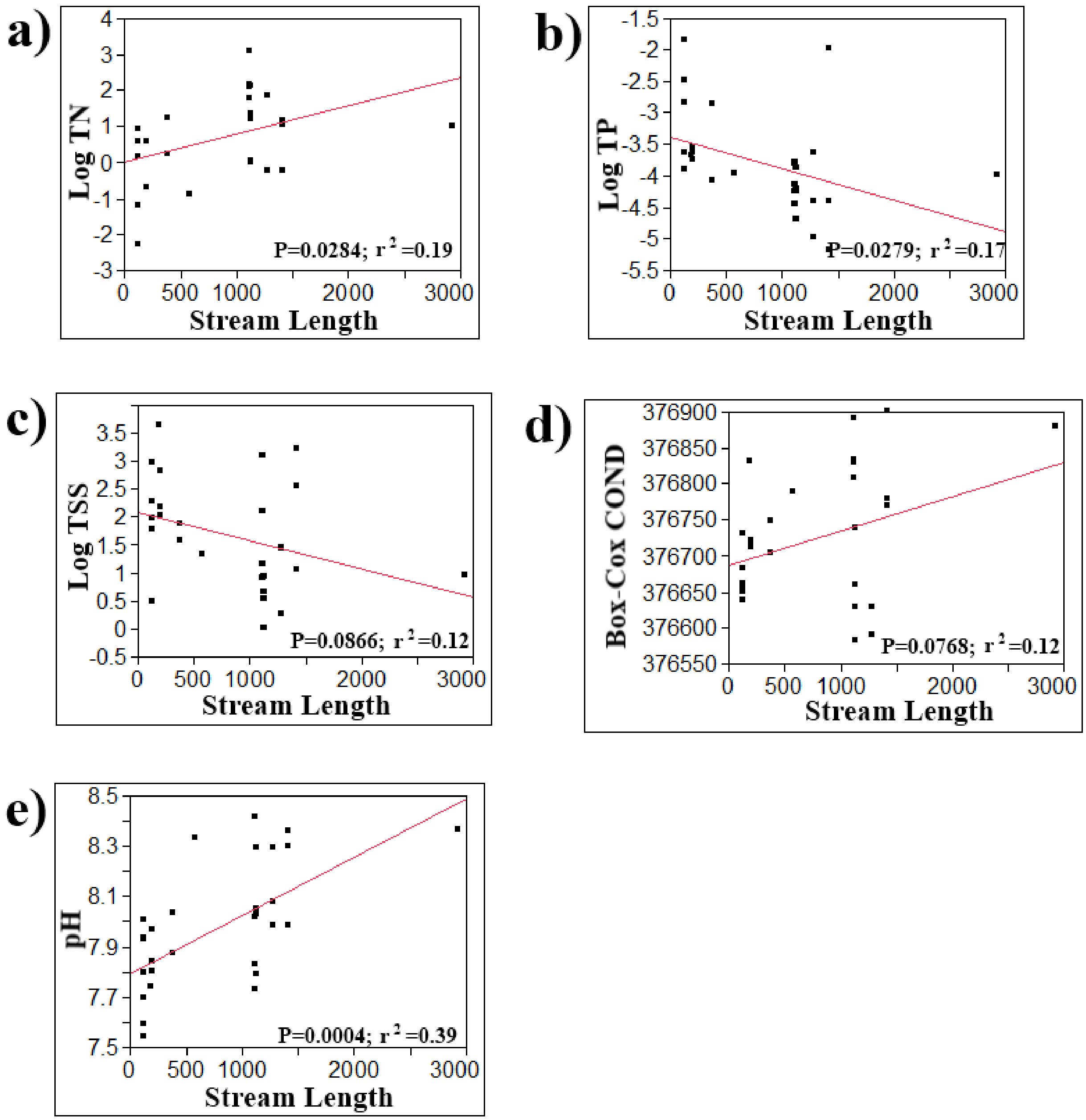


Figure 3.3: Summary of relationships between a) TN (mg/L) b) TP (mg/L) c) TSS (mg/L) d) COND (uS/cm), e) pH and stream length (m).

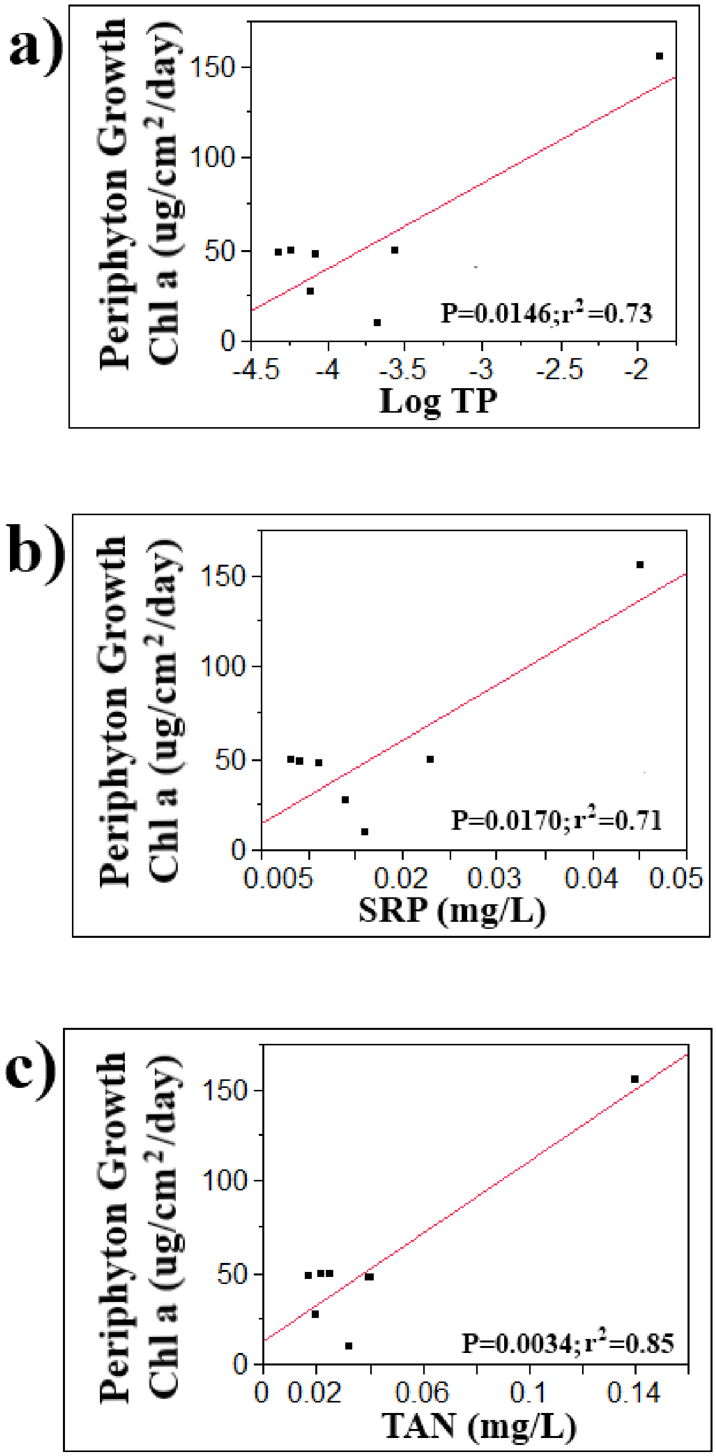


Figure 3.4: Relationship between periphyton growth (µg/cm^2/day) and a) TP (mg/L) b) SRP (mg/L) c) TAN (mg/L) in first and second-order streams.

GENERAL CONCLUSION

The goal of this thesis was to assist farmers, conservation authorities, fellow scientists and related governing bodies to find better ways to protect aquatic habitat from agricultural runoff, while helping farmers manage their nutrient use. It is clear that there are differential impacts on water courses based on the farming practices of livestock-based and crop-based operations. Tilman, et al. (2001) has predicted that eutrophication issues all over the world will be amplified because of increased quantity and severity of storms due to global climate change. Since streams draining livestock farms respond strongly to large precipitation events, efforts should be made to mitigate the impacts of nutrients and sediments in runoff during the more frequent and higher-intensity storm events that are predicted to occur in Ontario (IPCC 2000). Understanding the biotic and abiotic factors which influence this agricultural runoff will be critical in preventing degradation of aquatic ecosystems (Sharpley, et al., 1994). Our predictive models can be used for just that, aiding in determining important agricultural lands for restoration, remediation or prolonged fallowing.

One of the most encouraging finding in this thesis is that rotating cattle away from a stream can lead to a significant decrease in TP concentrations. These small headwater streams appear to quickly and positively respond to reduced cattle disturbance. These results suggest that at a minimum, cattle should not have access to these streams during dry periods when the stream is the most susceptible to cattle events. More importantly though, these results indicate that small-scale family farms may be a sustainable way to produce food. We also showed that traditional discrete sampling programs cannot be used to monitor the impacts of such cattle disturbances. Like storm events, these interactions must be actively pursued, to properly assess the influence of livestock with direct access to streams.

We also describe pollutant changes in an agricultural setting between first and second order streams. We were at first surprised to determine that there was no significant difference in the water chemistry between these stream orders. We later concluded that this is due to the physical nature of headwater streams in both a valley and karst environment. Except for stream discharge, there was no observable difference between first- and second-order streams. As a result, we proposed the use of stream length rather than stream order to reflect stream activities. This is due to the discontinuity in flow between first and second order streams which has many implications for Newbold, et al.'s (1981) nutrient spiraling concept. We were also able to deduce that periphyton rods may be an inexpensive indicator of excess limiting nutrients including total phosphorus, soluble reactive phosphorus and ammonia nitrogen.

Many aspects of this research has direct application to both the Beaver Valley and to other jurisdictions in N. America. For farmers in the Beaver Valley, something that could be implemented immediately is to avoid cattle gaining accessing to first-order streams directly and to provide drinking troughs whenever possible. Secondly, farmers can use acrylic rods to monitor periphyton growth as an inexpensive and effective bioindicator of excess nutrient in their streams. In much of the Great Lakes region, particularly areas influenced by the Niagara escarpment, many of the water-chemistry models derived here can be utilized to help identify areas which can sustainably support agriculture as well as areas that should not be farmed. The differences we found in this study regarding the impacts of the two common agricultural practices and changes associated with ARC seasons should have general relevance to most jurisdictions in N. America and elsewhere.

References

IPCC (Intergovernmental Panel on Climate Change). 2007. *Climate Change 2007 – The Physical Science Basis: Contribution of Working Group I to the Fourth Assessment Report of the IPCC.* Cambridge: Cambridge University Press.

Newbold, J. D., Elwood, J. W., O'Neill, R. V., & Winkle, W. V. (1981). Measuring Nutrient Spiralling in Streams. *Canadian Journal of Fisheries and Aquatic Sciences, 38*(7), 860-863.

Sharpley, A. N., Chapra, S. C., Wedepohl, R., Sims, J. T., Daniel, T. C., & Reddy, K. R. (1994). Managing Agricultural Phosphorus for Protection of Surface Waters: Issues and Options. *Journal of Environmental Quality, 23*(3), 437-451.

Tilman, D., Fargione, J., Wolff, B., D'Antonio, C., Dobson, A., Howarth, R., et al. (2001). Forecasting agriculturally driven global environmental change. *Science, 292*(5515), 281-284.